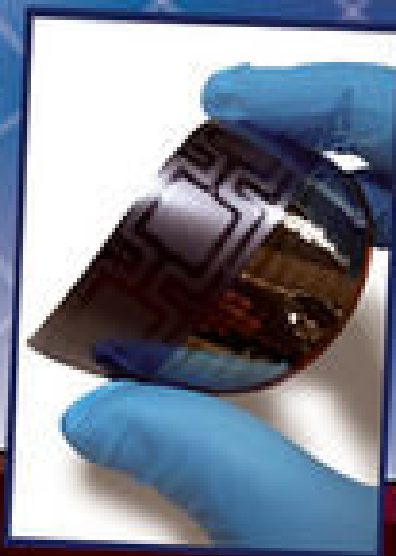


Advances in Solar Cell Materials and Storage

Printable Solar Cells



Edited by
Nurdan Demirci Sankir
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Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Advances in Solar Cell Materials and Storage

Series Editors: Nurdan Demirci Sankir and Mehmet Sankir

Scope: Because the use of solar energy as a primary source of energy will exponentially increase for the foreseeable future, this new series on Advances in Solar Cell Materials and Storage will focus on new and novel solar cell materials and their application for storage. The scope of this series deals with the solution-based manufacturing methods, nanomaterials, organic solar cells, flexible solar cells, batteries and supercapacitors for solar energy storage, and solar cells for space.

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Edited by
Nurdan Demirci Sankir
and Mehmet Sankir



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This edition first published 2017 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
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Library of Congress Cataloging-in-Publication Data

Names: Demirci Sankir, Nurdan, editor. | Sankir, Mehmet, editor.

Title: Printable solar cells / edited by Nurdan Demirci Sankir and Mehmet Sankir.

Description: Hoboken, NJ : John Wiley & Sons, Inc., 2017. | Includes index.

Identifiers: LCCN 2017005570 (print) | LCCN 2017010422 (ebook) |

ISBN 9781119283713 (cloth) | ISBN 9781119283737 (Adobe PDF) |

ISBN 9781119283744 (ePub)

Subjects: LCSH: Solar cells--Research. | Solar cells--Design and construction. | Photovoltaic cells. | Photovoltaic power generation. | Perovskite.

Classification: LCC TK2960 .P75 2017 (print) | LCC TK2960 (ebook) |

DDC 621.31/244--dc23

LC record available at <https://lcn.loc.gov/2017005570>

Cover image: Mehmet Sankir and Russell Richardson

Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Exeter Premedia Services Private Ltd., Chennai, India

Printed in

10 9 8 7 6 5 4 3 2 1

Contents

Preface	xv

Part I Hybrid Materials and Process Technologies for Printable Solar Cells

1 Organic and Inorganic Hybrid Solar Cells	3
<i>Serap Güneş and Niyazi Serdar Sariciftci</i>	
1.1 Introduction	4
1.2 Organic/Inorganic Hybrid Solar Cells	5
1.2.1 Introduction to Hybrid Solar Cells	5
1.2.2 Hybrid Solar Cells	5
1.2.2.1 Operational Principles of Bulk Heterojunction Hybrid Solar Cells	5
1.2.2.2 Bulk Heterojunction Hybrid Solar Cells	8
1.2.2.3 Bilayer Heterojunction Hybrid Solar Cells	12
1.2.2.4 Inverted-Type Hybrid Bulk Heterojunction Solar Cells	15
1.2.2.5 Dye-Sensitized Solar Cells	16
1.2.2.6 Perovskite Solar Cells	21
1.3 Conclusion	23
References	25
2 Solution Processing and Thin Film Formation of Hybrid Semiconductors for Energy Applications	37
<i>J. Ciro, J.F. Montoya, R. Betancur and F. Jaramillo</i>	
2.1 Physical Chemical Principles of Film Formation by Solution Processes: From Suspensions of Nanoparticles and Solutions to Nucleation, Growth, Coarsening and Microstructural Evolution of Films	38
2.2 Solution-Processing Techniques for Thin Film Deposition	40
2.2.1 Spin Coating	42
2.2.2 Doctor Blade	43

2.2.3	Slot-Die Coating	44
2.2.4	Spray Coating	46
2.3	Properties and Characterization of Thin Films: Transport, Active and Electrode Layers in Thin Film Solar Cells	46
2.4	Understanding the Crystallization Processes in Hybrid Semiconductor Films: Hybrid Perovskite as a Model	50
2.4.1	Thermal Transitions Revealed by DSC	50
2.4.2	Heat Transfer Processes in a Meso-Superstructured Perovskite Solar Cell	53
2.4.3	Effect of the Annealing Process on Morphology and Crystalline Properties of Perovskite Films	55
2.4.4	Role of Precursor Composition in the Crystallinity of Perovskite Films: Understanding the Role of Additives and Moisture in the Final Properties of Perovskite Layers	56
	References	57
3	Organic-Inorganic Hybrid Solar Cells Based on Quantum Dots	65
	<i>Wenjin Yue</i>	
3.1	Introduction	65
3.2	Polymer/QD Solar Cells	67
3.2.1	Working Principle	67
3.2.2	Device Parameters	68
3.2.2.1	Open-Circuit Voltage (V_{oc})	68
3.2.2.2	Short-Circuit Current (J_{sc})	68
3.2.2.3	Fill Factor (FF)	69
3.2.3	Device Structure	70
3.2.4	Progress of Polymer/QD Solar Cells	71
3.2.4.1	Device Based on Cd Compound	71
3.2.4.2	Device Based on Pb Compound	74
3.2.4.3	Device Based on $CuInS_2$	76
3.2.5	Strategy for Improved Device Performance	78
3.2.5.1	QDs Surface Treatment	78
3.2.5.2	<i>In-Situ</i> Synthesis of QDs	81
3.2.5.3	Polymer End-Group Functionalization	82
3.3	Outlooks and Conclusions	83
	Acknowledgment	83
	References	84

4	Hole Transporting Layers in Printable Solar Cells	93
	<i>David Curiel and Miriam Más-Montoya</i>	
4.1	Introduction	94
4.2	Hole Transporting Layers in Organic Solar Cells	97
4.2.1	Utility of Hole Transporting Layers	97
4.2.1.1	Energy Level Alignment at the Interfaces and Effect on the Open-Circuit Voltage	98
4.2.1.2	Definition of Device Polarity, Charge Transport and Use as Blocking Layer	102
4.2.1.3	Optical Spacer	103
4.2.1.4	Modulation of the Active Layer Morphology and Use as Protective Layer	103
4.2.2	Overview of Materials Used as Hole Transporting Layers	104
4.2.2.1	Polymers	104
4.2.2.2	Small Molecules	109
4.2.2.3	Metals	112
4.2.2.4	Metal Oxides	112
4.2.2.5	Metal Salts	116
4.2.2.6	Carbon Nanotubes	116
4.2.2.7	Graphene-Based Materials	116
4.2.2.8	Self-Assembled Monolayers	119
4.3	Hole Transporting Layers in Dye-Sensitized Solar Cells	121
4.3.1	Overview of Materials Used as Hole Transporting Layers	123
4.3.1.1	Small Molecules	123
4.3.1.2	Polymers	126
4.4	Hole Transporting Layers in Perovskite Solar Cells	127
4.4.1	Overview of Materials Used as Hole Transporting Layers	128
4.4.1.1	Small Molecules	128
4.4.1.2	Polymers	137
4.4.1.3	Metal Oxides	139
4.4.1.4	Metal Salts	140
4.4.1.5	Carbon Nanotubes	141
4.4.1.6	Graphene-Based Materials	142
4.5	Concluding Remarks	143
	References	143

5	Printable Solar Cells	163
	<i>Alexander Kovalenko and Michal Hrabal</i>	
5.1	Introduction	164
5.2	Printable Solar Cells Working Principles	165
5.2.1	CIGS Solar Cells	165
5.2.2	Perovskite Solar Cells	167
5.2.3	Organic Solar Cells	170
5.2.4	Printable Charge-Carrier Selective Layers	172
5.3	Solution-Based Deposition of Thin Film Layers	173
5.3.1	Coating Techniques	174
5.3.1.1	Casting	174
5.3.1.2	Spin Coating	174
5.3.1.3	Blade Coating	176
5.3.1.4	Slot-Die Coating	177
5.3.2	Printing Techniques	179
5.3.2.1	Screen Printing	180
5.3.2.2	Gravure Printing	182
5.3.2.3	Flexographic Printing	184
5.3.2.4	Inkjet Printing	185
5.4	Characterization Techniques	189
5.4.1	Characterization of Thin Layers	189
5.4.2	Electrical Characterization of Solar Cells	190
5.5	Conclusion	194
	References	197

Part II Organic Materials and Process Technologies for Printable Solar Cells

6	Spray-Coated Organic Solar Cells	205
	<i>Yifan Zheng and Junsheng Yu</i>	
6.1	Introduction	205
6.2	Introduction of Spray-Coating Method	206
6.2.1	History of Spray Coating	206
6.2.2	Spray-Coating Equipment	206
6.2.2.1	Airbrush Spray Deposition	206
6.2.2.2	Ultrasonic Spray Deposition	209
6.2.2.3	Electrospray Deposition	210
6.2.3	Spray-Coating Treatment	212
6.2.3.1	Thermal Annealing	213
6.2.3.2	Solvent Treatments	214

6.3	Materials for Spray Coating	216
6.3.1	Organic Materials	216
6.3.2	Metal Oxide and Nanoparticles	220
6.3.3	Perovskite	222
6.4	Application of Spray Coating	224
6.5	Conclusions	226
	Acknowledgment	226
	References	226
7	Interface Engineering: A Key Aspect for the Potential Commercialization of Printable Organic Photovoltaic Cells	235
	<i>Varun Vohra, Nur Tahirah Razali and Hideyuki Murata</i>	
7.1	Introduction	236
7.2	SD-PSCs Based on P3HT:PCBM Active Layers	240
7.2.1	Increase in Donor-Acceptor Interface through Nanostructuration of SD-PSCs	240
7.2.2	Generation of Vertical Concentration Gradient by Addition of Regiorandom P3HT in SD-PSCs	242
7.2.3	Generation of Vertical Concentration Gradient and Molecular Orientation by Rubbing P3HT in SD-PSCs	246
7.3	High Performance BHJ-PSCs with Favorable Molecular Orientation Resulting from Active Layer/Substrate Interactions	248
7.4	Strongly Bond Metal Leaves as Laminated Top Electrodes for Low-Cost PSC Fabrication	252
7.5	Conclusions	257
	References	258
8	Structural, Optical, Electrical and Electronic Properties of PEDOT: PSS Thin Films and Their Application in Solar Cells	263
	<i>Sheng Hsiung Chang, Cheng-Chiang Chen, Hsin-Ming Cheng and Sheng-Hui Chen</i>	
8.1	Introduction	264
8.2	Chemical Structure of PEDOT:PSS	265
8.3	Optical and Electrical Characteristics of PEDOT:PSS	267
8.4	Electronic Characteristics of PEDOT:PSS	270
8.5	Highly Conductive PEDOT:PSS Thin Films	271
8.6	Hole-Transporting Materials: PEDOT:PSS Thin Films	273
8.6.1	Effect of PEDOT/PSS Ratio	274
8.6.2	Effect of Spin Rate	275

8.6.3	Effect of Thermal Annealing Temperature	277
8.6.4	Effects of Viscosity of PEDOT:PSS Solutions	278
8.7	Directions for Future Development	281
8.8	Conclusion	282
	Reference	283

Part III Perovskites and Process Technologies for Printable Solar Cells

9	Organometal Trihalide Perovskite Absorbers: Optoelectronic Properties and Applications for Solar Cells	291
	<i>Timur Sh. Atabaev and Nguyen Hoa Hong</i>	
9.1	Introduction	291
9.2	Optical Properties of Organic-Inorganic Perovskite Materials	293
9.3	Charge Transport Properties	294
9.4	Electron Transporting Materials (ETM)	295
9.5	Hole-Transporting Materials (HTM)	295
9.6	Perovskite Solar Cells Architectures	296
9.7	Perovskite Deposition Methods	298
9.8	Photoexcited States	300
9.9	Hysteresis	300
9.10	Stability in Humid Environment	302
9.11	Stability Under UV Light Exposure	302
9.12	Stability at High Temperatures	303
9.13	Additives	304
9.14	Conclusions and Outlook	305
	Acknowledgment	306
	References	306
10	Organic-Inorganic Hybrid Perovskite Solar Cells with Scalable and Roll-to-Roll Compatible Printing/Coating Processes	313
	<i>Dechan Angmo, Mei Gao and Doojin Vak</i>	
10.1	Introduction	314
10.2	Optoelectronic Properties	316
10.3	History	317
10.4	Device Configurations	318
10.5	Functional Materials	321
10.5.1	The Organic-Inorganic Halide Perovskites	322
10.5.2	Electron-Selective Layer	324

10.5.3	Hole-Selective Layer	325
10.5.4	Transparent Electrode	325
10.5.5	Counter Electrode	326
10.6	Spin Coating	327
10.7	Roll-to-Roll Processing	331
10.8	Substrate Limitation	331
10.9	Printing and Coating Methods	333
10.9.1	Coating Methods	334
10.9.1.1	Slot-Die Coating	334
10.9.1.2	Spray Coating	339
10.9.1.3	Doctor Blade Coating	342
10.9.1.4	Knife Coating	344
10.9.1.5	Reverse Gravure Coating	345
10.9.2	Printing Methods	346
10.9.2.1	Gravure Printing	346
10.9.2.2	Flexographic Printing	347
10.9.2.3	Screen Printing	349
10.9.2.4	Inkjet Printing	350
10.10	Future Outlook	352
	References	352
11	Inkjet Printable Processes for Dye-Sensitized and Perovskite Solar Cells and Modules Based on Advanced Nanocomposite Materials	363
	<i>Theodoros Makris, Argyroula Mourtzikou, Andreas Rapsomanikis and Elias Stathatos</i>	
11.1	Introduction	364
11.1.1	Dye-Sensitized Solar Cells	364
11.1.2	Perovskite Solar Cells	367
11.2	Inkjet Printing Process	369
11.2.1	Inkjet Printing in DSSC Technology	370
11.2.1.1	Inkjet Printing of Transition Metal Oxides	372
11.2.1.2	Inkjet Printing of Dyes on Semiconducting Oxides	373
11.2.1.3	Inkjet Printing of Ionic Liquid-Based Electrolytes	374
11.2.2	Inkjet Printing in Perovskite Solar Cell Technology	377
11.2.2.1	Inkjet Printing of Perovskite Material	378
11.3	Conclusions	379
	References	379

Part IV Inorganic Materials and Process Technologies for Printable Solar Cells

12 Solution-Processed Kesterite Solar Cells	385
<i>Fangyang Liu</i>	
12.1 Introduction	385
12.2 Fundamental Aspects of Kesterite Solar Cells	386
12.2.1 Crystal Structure	386
12.2.2 Phase Space and Secondary Phases	388
12.2.3 Optical and Electrical Properties	390
12.2.4 Device Architecture	391
12.3 Kesterite Absorber Deposition Strategies	393
12.4 Electrodeposition	395
12.4.1 Stacked Elemental Layer (SEL) Electrodeposition	396
12.4.2 Metallic Alloy Co-electrodeposition	398
12.4.3 Chalcogenide Co-electrodeposition	399
12.5 Direct Solution Coating	400
12.5.1 Hydrazine Solution Coating	401
12.5.2 Particulate-Based Solution Coating	402
12.5.3 Molecular-Based Solution Coating	405
12.6 Conclusion	409
References	409
13 Inorganic Hole Contacts for Perovskite Solar Cells: Towards High-Performance Printable Solar Cells	423
<i>Xingtian Yin and Wenxiu Que</i>	
13.1 Introduction	424
13.2 Transition Metal Oxides	426
13.2.1 Molybdenum Oxide (MoO_x , $x < 3$)	426
13.2.2 Nickel Oxide (NiO)	428
13.2.2.1 Mesoscopic NiO Perovskite Solar Cells	428
13.2.2.2 Planar NiO Perovskite Solar Cells	429
13.2.3 Binary Copper Oxide (CuO and Cu_2O)	439
13.2.4 Other Transition Metal Oxides	440
13.3 Non-Oxide Copper Compounds	440
13.3.1 Cuprous Iodide (CuI)	441
13.3.2 Cuprous Rhodanide (CuSCN)	441
13.3.3 Copper Sulfide (CuS)	442
13.3.4 CuAlO_2	443
13.3.5 CuInS_2 and $\text{Cu}_2\text{ZnSnS}_4$	444

13.4	Other Inorganic HTMs	444
13.4.1	PdS Quantum Dots (QDs)	444
13.4.2	Two-Dimensional (2D) Materials	445
13.5	Towards Printable Solar Cells	446
13.6	Conclusions and Perspectives	449
	Acknowledgment	450
	References	450
14	Electrode Materials for Printable Solar Cells	457
	<i>Lijun Hu, Ke Yang, Wei Chen, Falin Wu, Jiehao Fu, Wenbo Sun, Hongyan Huang, Baomin Zhao, Kuan Sun and Jianyong Ouyang</i>	
14.1	Introduction	458
14.2	Transparent Conjugated Polymers	459
14.2.1	Solvent Additive Method	460
14.2.2	Post-Treatment of PEDOT:PSS Films	461
14.2.3	Printing PEDOT:PSS Inks	463
14.3	Carbon-Based Nanomaterials	463
14.3.1	Graphene	466
14.3.2	Carbon Nanotubes	472
14.4	Metallic Nanostructures	476
14.4.1	Metal Nanomeshes	476
14.4.2	Metal Nanowire Networks	480
14.4.3	Ultrathin Metal Films	482
14.5	Multilayer Thin Films	486
14.6	Printable Metal Back Electrodes	491
14.7	Carbon-Based Back Electrodes	494
14.8	Summary and Outlook	497
	Acknowledgment	498
	References	498
15	Photonic Crystals for Photon Management in Solar Cells	513
	<i>Shuai Zhang, Zhongze Gu and Jian-Ning Ding</i>	
15.1	Introduction	513
15.2	Fundamentals of PCs	515
15.3	Fabrication Strategies of PCs for Photovoltaics	518
15.3.1	1D Multilayer PCs	519
15.3.2	2D PCs	524
15.3.3	3D PCs	527
15.4	Different Functionalities of PCs in Solar Cells	530
15.4.1	PC Reflectors	531
15.4.2	PC Absorbers	535

15.4.3	Front-Side PCs	538
15.4.4	PCs for Other Functionalities	540
15.5	Summary and Outlook	540
	Acknowledgment	542
	References	542
	Index	549

Preface

The sun provides energy for the immense diversity of life forms found on earth. Conversion of this energy into electricity by means of photoelectric effect with an acceptable efficiency and price may provide all the energy needs for humankind. New materials and manufacturing techniques are key issues for increasing the efficiency and reducing the cost of photovoltaic devices. Hence, this book series focuses on materials and manufacturing techniques as well as the storage applications for solar cells. The first volume of the series, *Printable Solar Cells*, compiles the objectives related to the new materials from solution processing and manufacturing techniques for solar cell applications. The chapters are written by distinguished authors who have extensive experience in their fields. A broader point of view and coverage of the topic are provided due to the multidisciplinary contributor profile, including physics, chemistry, materials science, biochemical engineering, optoelectronic information, photovoltaic and renewable energy engineering, electrical engineering, mechanical and manufacturing engineering. Therefore, readers will absolutely have a chance to learn about not only the fundamentals but also the various aspects of materials science and manufacturing technologies for printable solar cells. The book contains information which could be presented in energy and materials science-related courses at both undergraduate and graduate levels.

This book is organized into four parts. Part I (Chapters 1–5) covers the organic and inorganic hybrid materials and solar cell manufacturing techniques. In this section, descriptions of the operational principles and types of hybrid solar cells, physical and chemical principles of film formation by solution processes, polymer/quantum dot hybrid solar cells, hole transporting layers and solution processing techniques are described. Part II (Chapters 6–8) is devoted to organic materials and processing technologies. Details of the spray-coating technologies and the organic materials used in these methods are given in this section. Part II also demonstrates the key features of interface engineering for printable organic solar cells. This phenomenon is very important to increase the device performance and decrease the production cost of printable solar cells. Finally, structural,

optical, electrical and electronic properties are presented as well as the fabrication parameters of thin films of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), which is one of the most commonly used organic polymers for photovoltaic applications. The main focus of Part III (Chapters 9–11) is perovskite solar cells, which is a new and promising family for photovoltaic applications. Working principle, device architectures, deposition methods and stability of the perovskite solar cells are given in this section. In addition, the optical properties and photovoltaic performance of organometal trihalide perovskite absorbers are also addressed. Finally, information on dye-sensitized solar cells, the inkjet printing process and modules based on advanced nanocomposite materials are described.

This book concludes with Part IV (Chapters 12–15), inorganic materials and process technologies for printable solar cells. Structural, optical and electrical properties of kesterites, device architecture and deposition strategies are extensively summarized in this part. As described in Part III, tremendous progress has been made in perovskite solar cells over the last few years and the efficiency of these devices has exceeded 20%. Inorganic hole transport materials for transition metal-oxide perovskite solar cells, including Cu_2O , CuSCN , CuInS_2 and $\text{Cu}_2\text{ZnSnS}_4$, are discussed in Part IV. These materials inevitably affect the device performance and stability. Electrode materials and photonic crystals for solar cell applications are the last two topics covered in this book. Top and bottom electrodes used in thin film solar cells implement the transmission of sunlight through the absorber layer and the electron collection. In other words, optical, electrical and mechanical properties of the electrode materials are important to ensure good photovoltaic performance as well as compatibility with substrate materials and printing techniques. In this respect, transparent conjugated polymers, carbon-based nanomaterials, metallic nanostructures and ultrathin metal films are summarized in Part IV. Finally, new and promising developments of photon management in solar cells based on photonic crystals are given. Fundamentals of photonic crystals, fabrication strategies and utilization of these materials in photovoltaic devices as reflector and absorber layers are summarized in the last section.

In conclusion, we would like to emphasize that the first volume of the *Advances in Solar Cell Materials and Storage* series provides an overall view of new and highly promising materials and their fabrication technologies for printable solar cell applications. In addition, the materials property–manufacturing method–photovoltaic performance relationship of the organic, inorganic and hybrid structures have been extensively discussed in this book. Therefore, readers from diverse fields, such as chemistry,

physics, materials science and engineering, and mechanical and chemical engineering, will definitely take advantage of this book to comprehend the impacts of the new materials and solution-based manufacturing on the inevitable rise of solar power.

Series Editors

Nurdan Demirci Sankır, PhD and Nurdan Mehmet Sankır, PhD
Department of Materials Science and Nanotechnology Engineering,
TOBB University of Economics and Technology
January 2017

Part I

HYBRID MATERIALS AND PROCESS TECHNOLOGIES FOR PRINTABLE SOLAR CELLS

Organic and Inorganic Hybrid Solar Cells

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Abstract

The dream of conversion of sunlight into electricity via cheap and cost-effective routes has led researchers to develop the so-called third generation organic and hybrid solar cells in the last two decades. The hybrid solar cells combine the advantages of the organic semiconductors, such as easy tuning of the chemical and physical properties and desirable thin film-forming properties, with that of the inorganic semiconductors such as well-defined electronic structure, high charge mobilities and thermal stabilities. Many research studies have been performed to find the ideal organic/inorganic hybrid material combinations and device architectures, which has resulted in significant progress being achieved. During the last three years a new family of photovoltaic compounds called “perovskites” have been the focus of attention. Such organic/inorganic hybrid solar cells based on ionic salts of organic compounds with lead halides show efficiencies up to 22%. In this chapter, we will analyze the progress of research in hybrid solar cells, and the limitations and routes to be followed for their further improvement will be discussed.

Keywords: Organic solar cells, hybrid solar cells, polymer solar cells, conjugated polymers, inorganic nanoparticles, third generation photovoltaics, bulk hetero-junction solar cells, conducting polymers

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1.1 Introduction

The need for the supply of clean energy is one of the challenges of our decade since the conventional routes used until recently as a source of energy, such as coal and oil, are limited and will run out [1]. Environmentally friendly, cost-effective, efficient solutions are of great interest to solve the clean energy supply problem. Solar cells which convert sunlight into electricity are foreseen as a viable tool to produce electricity from the sun. Solar energy is clean, abundant and cost-free.

Solar cell technologies are traditionally divided into three main categories which are called generations. The first generation solar cell technology involves techniques which are cost and energy intensive [2]. They include single- and multi-crystal silicon solar cells which are produced on a wafer bearing either only one crystal or crystal grains. The recent power conversion efficiency (PCE) of a single crystal silicon solar cell is 25% whereas a multicrystal silicon solar cell exhibits a PCE of 21% [3].

Second generation solar cells consist of a-Si thin films, mc-Si, CdTe, CIS and CIGS. The PCEs of CIGS (minimodule) is 18% whereas for CdTe (cell) PCE is recorded as 21% [3]. For a-Si and mc-Si thin-film solar cells, PCEs are 10% and 11% respectively [3]. Although the second generation solar cells are less efficient than the first generation solar cells, their costs are lower; on the other hand, they are more likely applicable to the building integrations and are more compatible with flexible substrates [2].

Third generation solar cells include nanocrystal solar cells, organic/hybrid solar cells and dye-sensitized solar cells and perovskite solar cells. Third generation solar cells are novel technologies which are cost and energy effective, suitable for flexible substrates and can be easily integrated. Despite many advantages, their comparably lower efficiencies and stability issues stand as major drawbacks towards their commercialization. However, a new family of photovoltaic compounds called “perovskites” have been the focus of attention and if the stability issues of these new types of photovoltaics can be addressed and solved they will be candidates to compete with the other PV technologies which have already taken their place in the PV market.

In this chapter, among the three different generations of solar cells, we will mostly focus on the organic/inorganic hybrid solar cells which belong to the third generation group and will analyze the progress of research, their limitations and will discuss the routes to be followed for their further improvement.

1.2 Organic/Inorganic Hybrid Solar Cells

1.2.1 Introduction to Hybrid Solar Cells

Although first and second generation solar cells have received considerable attention due to their high power conversion efficiencies, the high production costs and availability problems related to the materials, such as indium (In), continue to be the main issues to be overcome to meet the recent demand [4]. The advantages such as the low cost, flexibility, easy production and scalability offered by organic solar cells put this field somewhere between applied science and engineering research [5]. There has been a tremendous increase in the power conversion efficiency of solution-processed organic solar cells from 2.5% [6] to ca. 11% [7] within only 14 years. However, stability issues due to the sensitivity of organic materials to oxygen and moisture still remain to be solved. Inorganic semiconductors have high charge carrier mobilities and also good chemical stabilities. The idea of combining the advantages of both organic and inorganic semiconductors has led to the birth of the concept of hybrid solar cells. A hybrid solar cell consists of both organic and inorganic semiconductors in which the advantages, such as high solubility, good film formation, flexibility and low cost, offered by organic semiconductors are combined with the advantages, such as high charge carrier mobility and good stability, offered by inorganic semiconductors. Many different concepts have been realized to fabricate hybrid solar cells. Their power conversion efficiencies are still lower than their inorganic counterparts. However, the parameter space to choose from is large and only a fraction of possible combinations have been realized [8]. Further research and development strategies for optimization of different types of hybrid solar cells will be discussed below.

1.2.2 Hybrid Solar Cells

1.2.2.1 *Operational Principles of Bulk Heterojunction Hybrid Solar Cells*

Hybrid solar cells consist of blend films of inorganic semiconductors and conjugated polymers sandwiched between two metal electrodes (see Figure 1.1). The difference in the organic solar cells is the use of inorganic semiconductors in the device configuration. Therefore, the operational principles of hybrid solar cells is very close to organic solar cells and consists of the following consequent steps [4]:

- i. Absorption of photons;
- ii. Generation of excitons within the active layer;

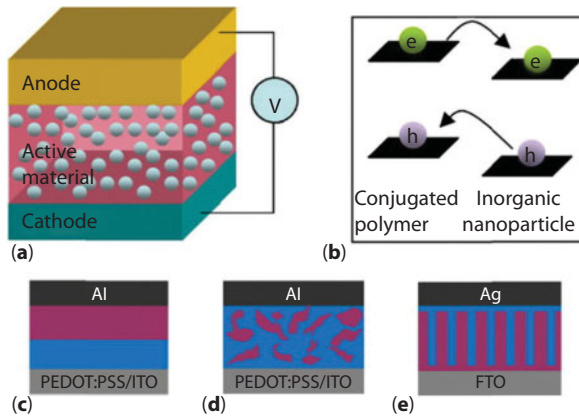


Figure 1.1 General structure of a hybrid solar cell: (a) representation for working principle of polymer/nanoparticles, (b) energy level diagram and charge transfer process, (c) bilayer, (d) bulk, and (e) ordered heterojunction. (Reprinted with permission from [4]; Copyright 2014 © Elsevier)

- iii. Diffusion of excitons;
- iv. Dissociation of excitons;
- v. Transport of charges to the appropriate electrodes;
- vi. Collection of holes and electrons at the electrodes.

The photoactive layer of the bulk heterojunction hybrid solar cells consists of inorganic semiconductor nanoparticles and conjugated polymers. Inorganic semiconductors have been widely used to transport the electrons (as acceptors) whereas conjugated polymers have been used to transport the holes (as donors). Organic materials may have a donor or an acceptor character. Molecular materials that have a low ionization potential and thus can easily donate an electron are denoted as electron donors. Materials that have a high electron affinity and thus can easily take up an electron are denoted as electron acceptors. They can be efficient electron or hole transporters, which is determined by intermolecular orbital overlap in the solid state [9]. They can also be both hole and electron transporters. Recently, [6,6]-phenyl- C_{61} -butyric acid methylester (PCBM) has been demonstrated to have a similar hole mobility to its electron mobility. An ideal donor should permit efficient hole transport, that is, *p* type, whereas an ideal acceptor should permit efficient electron transport, that is, *n* type. In the case of organics, the *n*- and *p*-type definitions refer to the fact that *n*-type semiconductors are good electron conductors, whereas *p*-type ones are good hole conductors. Therefore, an

alternative definition for organic semiconductors is donor for the p type and acceptor for the n type. In organic and hybrid solar cell terminology, the donor gives electrons to the acceptor [9]. In the case of inorganic semiconductors, for example, n -type silicon is achieved by introducing donor impurities. Doping mechanisms in organic and inorganic semiconductors are totally different. Most semiconducting polymers are hole conductors as donor polymers. However, they can also be electron conductors.

For a favorable charge transfer the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the inorganic nanoparticles and the conjugated polymers should be chosen properly. The LUMO and the HOMO of the conjugated polymers should lie above the conduction and valence band edges of the inorganic nanoparticles, respectively, for an efficient charge transfer. In this case, the electrons are transferred from the LUMO level of the conjugated polymer to the conduction band of the inorganic semiconductor whereas the holes are transferred from the valence band of the inorganic semiconductor to the HOMO level of the conjugated polymer [4]. The photoexcitations in organic materials lead to bound electron-hole pairs, which are called excitons. Excitons have to be separated into free charge carriers within their lifetime. Otherwise, they may recombine, which is not a preferential step for the solar cell operation. Exciton diffusion length for the organic materials is within the range of 5–10 nm. A p - n junction is used to separate the excitons into free charge carriers. In the bulk heterojunction concept, by blending the p - and n -type semiconductors, p - n junction is distributed throughout the bulk of the film so that each exciton reaching the junction can be separated into free charge carriers, which is called exciton dissociation. Distributing the p - n junction throughout the film increases the probability of exciton dissociation within the lifetime of the excitons and also within the distance of exciton diffusion length. This is one of the reasons why the short circuit current density, and thereby the power conversion efficiencies of bulk heterojunction solar cells, is higher than that of bilayer heterojunction solar cells which consist of individual bilayer films of n - and p -type semiconductors sandwiched between two metal electrodes.

As previously mentioned, blend films of inorganic semiconductors and conjugated polymers are sandwiched between two metal electrodes. As substrates, conducting electrodes (for example, glass or plastic covered with ITO) are used. As a transparent conductive electrode, ITO (indium tin oxide) allows light to pass through the cell. On the transparent conducting substrate, PEDOT:PSS, poly(3,4-ethylene-dioxythiophene) doped

with polystyrene-sulphonic acid, is commonly coated from an aqueous solution. This PEDOT:PSS layer improves the surface quality of the ITO electrode (reducing the probability of shorts) and facilitates hole injection/extraction. Furthermore, the work function of this electrode can be changed by chemical/electrochemical manipulation of the PEDOT layer [10]. A photoactive layer consisting of blends of conjugated polymer and inorganic nanoparticles is cast on top of the PEDOT:PSS coated ITO substrates from solution. The choices for the second metal electrode have been aluminum (Al), silver (Ag), gold (Au), etc. The choice of the metal should ensure that an ohmic contact is formed between the metal and the semiconductor.

1.2.2.2 Bulk Heterojunction Hybrid Solar Cells

Initial efforts to fabricate hybrid solar cells started with mimicking the bulk heterojunction concept studied in organic solar cell research. The bulk heterojunction concept in organic solar cells has been realized by blending two organic semiconductors, one of which is an electron donor and the other an electron acceptor. The same concept has been applied to hybrid solar cells by blending inorganic semiconductors as nanoparticles with conjugated polymers.

The advantages of this concept can be summarized as following:

1. Inorganic semiconductors may have high absorption coefficients and high charge carrier mobilities [11].
2. Band gap of the inorganic materials can easily be tuned via synthetic routes using the size quantization effect. Therefore, inorganic nanoparticles absorbing at different wavelengths can be available [11].
3. The availability problem of acceptor materials, as is the case in organic solar cells, may be overcome by controlling the *n*- and *p*-type doping levels of inorganic nanoparticles via synthetic routes.

In the initial studies of hybrid solar cells, inorganic nanoparticles took the place of the fullerene-based acceptors which have been widely used in organic solar cells. The synthesis of fullerenes is rather energy intensive and difficult. On the other hand, the colloidal synthesis of inorganic nanoparticles is comparably easier. Also, the absorption range of inorganic nanoparticles is wider than that of fullerenes, which in turn means that thinner devices can be fabricated.

The CdSe nanocrystals were the first nanocrystals studied in hybrid solar cells. They have absorption at a spectral range between 300 nm to 650 nm [12].

One of the first studies on hybrid bulk heterojunction solar cells using CdSe nanoparticles was published by Huynh *et al.* [13]. They demonstrated that hybrid solar cells could be fabricated using semiconductor nanorods together with polymers. The control of the nanorod length enabled efficient electron transport through the device and also the tunability of the nanorod radius led the authors to tune the bandgap, which in turn helped the overlapping between the absorption of the nanorods and the solar emission spectrum. They achieved a PCE of almost 2% under air mass (AM) 1.5 global solar conditions [13].

The main success behind the efficient hybrid bulk heterojunction solar cells using nanocomposites is the ability of the dispersion of the nanoparticles into the polymer matrix to create a high interfacial area between two materials for a better charge transport [14]. Organic ligands are adsorbed onto the surface of the nanoparticles which passivate the surface for stability and make them soluble. Although organic ligands are indispensable for the nanoparticles, dispersion of nanoparticles into the polymer matrix is highly affected by the existence of these ligands and effective dispersion of the nanoparticles is highly necessary. It has been demonstrated by Huynh *et al.* that the use of binary solvents is effective in helping the dispersion of nanoparticles within the polymer matrix [14]. It has also been demonstrated that the heat treatment furthers the removal of the ligand and increases the photocurrent and thereby the power conversion efficiency.

Later studies revealed that the choice of the morphology of the CdSe, whether being either nanoparticle, nanorod or tetrapod, played a role in the overall efficiency of the hybrid solar cells. Greenham *et al.* demonstrated that hybrid bulk heterojunction solar cells using blends of branched CdSe nanoparticles and polymers gave a better photovoltaic performance as compared to the hybrid solar cells fabricated from nanorod/polymer blends. They achieved a PCE of almost 2% under AM 1.5 illumination [15]. They have shown that the electron extraction in the devices employing 3D CdSe tetrapods is more efficient as compared to the devices employing 1D nanorods and added that the control of the nanoparticle shape in 3D CdSe tetrapods helps to control the morphology and the efficiency of the devices comprising nanoparticle/polymer blends.

Besides the morphology of the CdSe nanoparticles the choice of the polymer is also important for the overall performance of hybrid solar cells. The use of a low band gap polymer (PCPDTBT) and CdSe tetrapod blend in the hybrid bulk heterojunction devices led to a PCE over 3%. The

PCPDTBT, which is a low band gap polymer offering a broad absorption spectrum, was helpful for efficient photon harvesting. Therefore, the idea of making use of the better overlap of the polymer absorption and the solar emission spectrum led to a better performance [16].

Another choice of inorganic semiconductor used in hybrid solar cells has been CdS nanorods. Devices comprising multiarmed CdS nanorods and MEH-PPV polymer exhibited a PCE over 1% under AM 1.5 illumination. The improved efficiency of the devices was attributed to the use of pyridine as a solvent instead of HDA. Pyridine, which was attached to the surface of CdS nanocrystals during refluxing, improved the solubility of CdS nanocrystals and also the dispersion in MEH-PPV film. As a result of an efficient charge transfer and exciton dissociation, power conversion efficiency was improved [17].

Most of the studies in the literature have focused on either the morphology of the nanoparticles or the choice of the polymer. However, interface between the nanoparticles/nanorods and the polymer is also an important issue. It has been demonstrated that interface modification of CdS nanorod surface can improve the efficiency of hybrid bulk heterojunction devices. Chen *et al.* used aromatic acids as interface modifiers. They achieved a better efficiency upon addition of an aromatic acid. This better performance was attributed to the reduced surface trap and defects of CdS nanorods, rearrangement of the surface energy level via dipole formation and prevention of the back charge transfer, and finally the improved compatibility between CdS nanorods and P3HT [18].

Although the use of CdSe and CdS nanoparticles in hybrid solar cells has attracted considerable attention, the limited power conversion efficiencies as compared to organic and inorganic solar cells have led researchers to search for other inorganic semiconductor nanoparticles to investigate in hybrid solar cells. CuInS₂ (CIS) and CuInSe₂ have been other choices of materials investigated in hybrid solar cells. CIS has a high absorption coefficient ($\alpha = 10^5 \text{ cm}^{-1}$) and photoconductivity and also its type of conductivity (n or p type) can be tuned via controlling the stoichiometry [19]. On the other hand, CISE has a low band gap and good radiation stability [20, 21]. Although these have been the first studies to focus on evaluating the synthesis and use of organic ligand-capped CIS and CISE in hybrid solar cells, the PCE of hybrid solar cells using these nanocrystals was rather limited. Morphology problems due to the limited dispersion of the inorganic nanocrystals and the conjugated polymer because of the existence of the organic ligand and the high serial resistances can be counted as the reasons for the poor device performance.

Although the hybrid solar cells consisting of blends of CdSe, CdS, CuInS₂, CuInSe₂ and conjugated polymers have been widely investigated,

poor device performance, high temperature synthesis of inorganic nanoparticles and the toxicity of the Cd-containing materials have motivated researchers to search for alternative materials [22]. The use of precursor $\text{Ti}(\text{i-PrO})_4$ for TiO_2 , which was added to the solution containing MDMO-PPV prior to spin casting, has been an alternative material [23]. This $\text{Ti}(\text{i-PrO})_4$ precursor was converted *in situ* into TiO_2 [23] by exposure of the cast film to moisture and a consecutive high vacuum treatment. Such devices exhibited a PCE of 0.2% [23, 24]. TiO_2 crystallization requires high temperatures ($>350^\circ\text{C}$ [25]) and such high temperatures may lead to the deformation of the polymer because conjugated polymers cannot stand high temperatures. Crystallinity of the network of TiO_2 limits the charge transport in these hybrid devices.

A new approach employing ZnO through a precursor route has been applied by Beek *et al.* [26]. The authors fabricated precursor-ZnO:polymer hybrid bulk heterojunction solar cells by spin coating a solution containing an organozinc compound and a conjugated polymer followed by thermal annealing at moderate temperature. Hence, a crystalline ZnO network was formed in the polymer phase which led to a higher PCE as compared to the hybrid bulk heterojunction solar cells employing amorphous precursor- TiO_2 :polymer hybrid solar cells. Hybrid solar cells using this concept exhibited a PCE of over 1% [26].

Although various combinations of inorganic nanoparticles and semiconducting polymers have been widely investigated in hybrid bulk heterojunction solar cells, their PCE still remains limited. The reasons behind the limited PCE can be summarized as following [8]:

- i. The synthesis of the inorganic nanoparticles may require high temperatures;
- ii. The organic ligand surrounding the nanoparticles may prevent the dispersion of nanoparticles in polymer matrix;
- iii. The synthesis routes may lead to nanoparticles with different properties which affect the reproducibility of the nanoparticles;
- iv. The organic ligand itself is an insulator which blocks the electron transport between the particles;
- v. The toxicity of the materials, such as Cd, used in the synthesis of inorganic nanoparticles.

Despite the problems mentioned above, bulk heterojunction hybrid solar cells are an interesting device concept that is worth studying further to improve upon these problems since the choice of parameter space is

large and only a small fraction of possible combinations have been realized. The addition of inorganic nanoparticles and quantum dots into the P3HT:PCBM blends as a third component may be an alternative way to fabricate more efficient hybrid bulk heterojunction solar cells [27].

1.2.2.3 Bilayer Heterojunction Hybrid Solar Cells

Bilayer heterojunction hybrid solar cells consist of bilayer films of an inorganic semiconductor and a conjugated polymer cast on top of each other sandwiched between two metal electrodes. Figure 1.1 shows the device structure of the hybrid bilayer solar cells. Contrary to the bulk heterojunction hybrid solar cells mentioned above, bilayer heterojunction solar cells consist of only one p-n junction, which is defined within the geometrical interface between the *p*- and the *n*-type semiconductors. Excitons which can only reach this interface within their lifetime can be separated. Therefore, exciton dissociation is rather limited to one interface [4]. This is counted as one of the most important limitations of bilayer heterojunction hybrid solar cells.

An alternative attractive approach in bilayer heterojunction solar cells has been the combination of the conducting polymers as the hole conducting layer and the crystalline silicon. Chemical structures of conducting polymers can be easily tailored and thereby the chemical and physical properties of their thin films can be tuned. On the other hand, a thin film of conducting polymer can be easily formed on Si substrates via cost-effective and easy methods.

Polyaniline (PANI) has been one of the earliest choice of materials investigated as a hole transport layer in organic/Si heterojunction devices. Doped PANI is a very good hole collector and exhibits an almost metallic conductivity which makes it an interesting material to be investigated [28, 29]. Early studies focused on electrochemically deposited polyaniline (PANI)/Si heterojunctions [30, 31]. However, these devices showed rather low rectification ratios which employed rather thick films. Rectification ratios were further improved in a study where polyaniline/Si heterojunctions were prepared by spin coating polyaniline films on top of n-Si substrates. These devices exhibited a higher rectification ratio and were recommended for use as gas sensors [32]. The dependence of the open circuit voltage of PANI/Si heterojunctions under illumination has been studied by Wang and Schiff [33]. The largest V_{oc} obtained in this study was 0.51 V. However, extrapolating the results to higher conductivity films, they suggested V_{oc} s of 0.7 V could be achievable.

Another choice of conducting polymer has been poly(3-hexyl)thiophene (P3HT). P3HT exhibits a high hole mobility [34]. On the other

hand, HOMO and LUMO levels of P3HT are compatible with the valence (VB) and conduction (CB) bands of Si, which favors a charge transfer between P3HT and Si [35, 36]. Si/P3HT heterojunction has been demonstrated to be a viable way for photovoltaic applications as a cheap and low temperature alternative to traditional silicon solar cells [35]. The crucial parameters for efficient solar cells on Si wafers have been addressed by Avasthi *et al.* [35]. A low offset between the VB of Si and the HOMO of the organic semiconductor is necessary for a high photocurrent whereas a large offset between the CB of Si and the LUMO of the organic semiconductor is necessary for a high open circuit voltage [35]. It has been demonstrated by the authors that Si/P3HT satisfies these conditions. Hence, they achieved a PCE of over 10%.

Investigations on P3HT/n-Si heterojunction using surface photovoltage spectroscopy revealed that there is a high interaction between the P3HT molecules and the surface states of n-Si [37]. According to this study, as compared to bare Si, the band bending in the silicon substrate and the density of interface states of the P3HT/n-Si heterojunction increase significantly. The charge separation and transport in the P3HT layer are much slower than that in silicon [37].

It has also been shown that interface treatments in P3HT/n-Si heterojunctions can improve the forward current density drastically due to the prevention of oxide layer formation [38]. The thickness of the oxide layer also plays an important role in the ideality factor. Thinner oxide layers give a better performance such as an enhanced forward current density and lower ideality factor [38].

Besides PANI and P3HT, PEDOT:PSS has also been widely used as a hole transport layer in organic/n-Si heterojunction devices. Hybrid solar cells fabricated by coating PEDOT on n-SiNW arrays have been studied by He *et al.* [39]. They achieved a PCE of 9%. They demonstrated that the thickness of the SiNW array plays a role in the overall PCE. PCE of 9% was achieved with a SiNW thickness of 0.9 μm . They added that the performance of the solar cells is limited with the thickness of the SiNW by severe recombination as a result of increased SiNW aggregation. It has also been demonstrated that the Si substrate contributes to the photocurrent generation [39].

In another study based on PEDOT:PSS/n-Si hybrid devices, it has been shown that the Si surface termination conditions play an important role in the overall PCE [40]. He *et al.* studied the solar cell performance of the hydrogen-terminated H-Si and oxide-terminated (SiO_x -Si) Si surfaces [40]. They obtained a maximum PCE of over 10% with a SiO_x -Si surface. They attributed this high performance to the favorable band alignment and

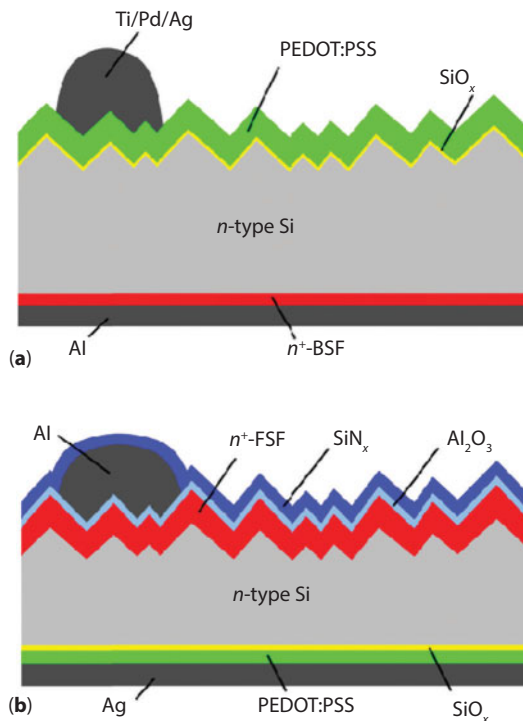


Figure 1.2 Schematics of (a) a front-junction organic-silicon heterojunction cell and (b) a back-junction (“BackPEDOT”) solar cell on *n*-type silicon. (Reprinted with permission from [41]; Copyright 2014 © Elsevier)

internal electric field at the junction interface that results in an efficient charge separation [40].

The efficiency of PEDOT/*n*-Si heterojunction devices was further improved by using the BackPEDOT cell concept, which was introduced by Zielke *et al.* (see Figure 1.2) [41]. They achieved a PCE of 17%. Both front junction and back junction (BackPEDOT) cells were fabricated on *n*-type crystalline silicon with random-pyramid (RP) textured front. The PEDOT:PSS layer was deposited either on the front surface, creating a front junction, or on the rear surface, creating a back junction solar cell [41]. They have concluded that the efficiency of this type of solar cell is highly limited with the series resistance losses and added that if these losses are neglected an efficiency of 21% can be extracted for their best BackPEDOT cell.

The efficiency of PEDOT/*n*-Si heterojunction devices has been reviewed by Zielke *et al.* in detail in ref. [42].

1.2.2.4 *Inverted-Type Hybrid Bulk Heterojunction Solar Cells*

Over the last decade, as mentioned above, many studies have been performed for the improvement of bulk heterojunction-type solar cells since these types of devices offer many advantages such as low cost, chemical tailoring of organic materials and flexibility. Most of the studies in the literature have focused on the improvement of the power conversion efficiency. However, stability is an important issue which has to be equally taken into account. The degradation in organic solar cells is divided into two groups, one of which is intrinsic and the other extrinsic [43]. Recent progress and stabilization of organic solar cells are reviewed in ref. [43] in detail. The intrinsic degradation includes phase separation at the organic/cathode interface [44], phase segregation at semiconductor interfaces [45], interdiffusion at interfaces [46] and morphological degradation [47, 48]. Extrinsic degradation is caused by oxygen and water. Oxygen is the dominant extrinsic degradation [43, 49–51]. The conventional bulk heterojunction device structure is in the form of ITO/PEDOT:PSS/photoactive layer (polymer:fullerene)/Al. The back metal contact Al is sensitive to air [52]. On the other hand, the acidic nature of the PEDOT:PSS leads to the deterioration of the active layer and the bottom electrode [53, 54]. To solve these problems in conventional bulk heterojunction solar cells, non-corrosive metals, such as silver (Ag) and gold (Au), are used as alternatives to Al. This type of geometry is called inverted-type geometry.

Inverted-type solar cells have been studied by several groups. TiO_2 and ZnO have been widely used as electron transport layers in the inverted geometry [55–58].

As electron transport layers, TiO_2 and ZnO films have several advantages such as high electron mobility, optical transparency in the region where the photoactive layer absorbs light and practical synthesis. Initial efficiencies of inverted solar cells employing TiO_2 as electron transport layers were limited to 3 to almost 4% [55, 56]. There are several critical parameters which affect the efficiency of inverted-type solar cells. One of the important parameters is the structure of the electron transport films. There are several techniques to synthesize electron transport layers mostly for TiO_2 and ZnO in the literature. Most of them focus on the synthesis via sol-gel procedure [59]. The thin film formation, especially for TiO_2 films, depends on the method of film preparation. It has been demonstrated that the homogeneous and well-defined TiO_2 morphology is necessary for excitation dissociation and charge separation [59]. Another important parameter for the improvement of inverted-type solar cells is the use of a buffer layer as hole transporting layer between the photoactive layer and the Ag/

Au electrode. Buffer layers such as vanadium pentoxide (V_2O_5), molybdenum trioxide (MoO_3), nickel oxide and tungsten trioxide (WO_3) have been demonstrated to improve the PCE of inverted-type solar cells [60–63]. Their roles have been addressed as the modification of the interface, hole extraction and the suppression of the electrons from the active layer and thereby prevention of recombination at the interface [63].

Besides metal oxides, CdS, ZnS and In_2S_3 have also been studied as electron transport layers in inverted-type solar cells [64–70]. Using these semiconductors as hole transport layers, PCEs in the range of 0.3% to 3% have been achieved.

The biggest jump in PCEs of inverted-type solar cells from moderate (0.3 to 3%) to pretentious (almost 10%) values have been achieved by an intrusion of a polymer interlayer [71]. By inserting a neutral polymer interlayer of poly(2-ethyl-2-oxazoline) (PEOZ) between ZnO layer and the photoactive layer, the authors achieved a certified PCE of almost 10%, which has been the highest PCE for inverted-type hybrid solar cells reported up to now [71]. This substantial increase upon addition of PEOZ layer was attributed to the significant reduction in work function and the improved morphology.

The use of nonconjugated zwitterions has also been an important step in the development of hybrid inverted-type solar cells. Metal oxide and inorganic semiconductor free electron transport layers were prepared by blending zwitterions with polyethylene glycol (PEG).

Different kinds of small molecule zwitterions have been employed in the device and PCE of almost 8% was achieved [72]. The V_{oc} and FF have been improved significantly due to zwitterions. Also, the uniform morphology of zwitterion/PEG blends suppressed the recombination at the active layer/metal electrode interface.

1.2.2.5 Dye-Sensitized Solar Cells

A dye-sensitized solar cell consists of a wide band gap semiconductor with nanocrystalline morphology associated with a sensitizer dye as light-absorbing material and a liquid electrolyte (see Figure 1.3). Dye-sensitized solar cells (DSSC) have been one of the most popular and investigated types of solar cells during the last decade. A wide band gap, mesoporous oxide semiconductor with nanometer-sized particles is one of the most critical parts of a dye-sensitized solar cell. The nanocrystalline film is sintered to ensure the electrical contact between the particles. A dye is adsorbed onto the surface of the nanocrystalline film by immersing the nanocrystalline film into dye solution. Upon photoexcitation an electron is injected into

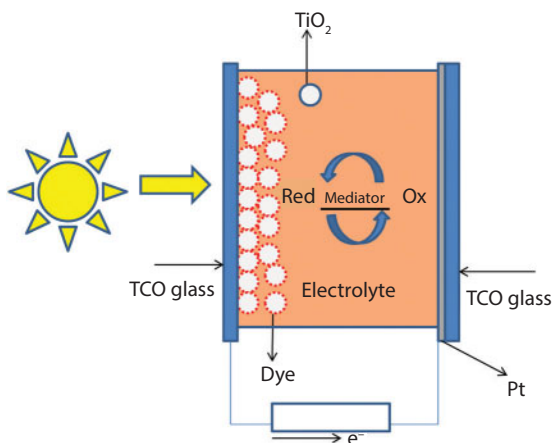


Figure 1.3 Schematic of a dye-sensitized solar cell.

the conduction band of the semiconductor. The state of the dye is preserved by an electron donation from the electrolyte. The electrolyte is usually an organic solvent containing redox system such as iodide/triiodide. The reduction of the triiodide leads to the regeneration of the iodide [73].

There are three important critical components in the DSSCs: (i) nano-structured electrodes which generally consist of a wide band gap semiconductor; (ii) dyes which are used as photosensitizers and; (iii) electrolytes which can be either liquid redox electrolytes or gel or polymer electrolytes. For an efficient dye-sensitized solar cell all three components should fulfill some requirements. These requirements and the studies to fulfill these requirements are summarized below.

i. Semiconductor Oxide

TiO₂, ZnO and SnO₂ have been widely investigated in DSSCs [74–86]. Among all these semiconductors, TiO₂ has been the choice of material. TiO₂ is a wide band gap semiconductor which is stable and nontoxic. TiO₂ possesses three crystal forms of anatase, rutile and brookite. The morphology of TiO₂ plays an important role in the overall efficiency of DSSCs. The preparation methods of TiO₂, for example, lead to different crystal forms and therefore different morphologies and efficiencies [59]. On the other hand, depending on the preparation methods, the surface area of TiO₂ may change. Large surface area is required for the proper adsorption of dye onto the TiO₂ surface and also for a better electron transport. Coating the top of the mesoporous TiO₂ layer with a porous layer of large size of TiO₂ particles can affect the light scattering of TiO₂ [81].

ii. Dye

Metal complexes [87–94], porphyrins [95–99], phthalocyanines [99–107] and organic dyes [108–112] have been widely investigated in DSSCs.

The strong binding of the dye onto the TiO_2 surface has to be ensured. Metal complex dyes contain anchoring ends which make the dyes adsorb and bind onto the semiconductor surface.

The absorption range of a dye is substantial. Its absorption spectrum should cover the visible range and/or may extend to the near infrared (NIR) for photon harvesting purposes.

The dye should possess photo, electrochemical and thermal stability.

The dye and the redox couple should potentially match each other, which means that the potential of the redox couple has to be chosen closer to that of the dye, but a driving force is necessary to ensure efficient dye regeneration by the redox mediator [113].

Another issue related to dye is the aggregation, which is an undesired phenomenon in DSSCs. An appropriate molecular design and the use of an antiaggregation coadsorbent can prevent the dye aggregation on the TiO_2 surface [114]. Although dye aggregation is an undesired process for DSSCs, in some limited cases, a controlled aggregation may enhance the photocurrent generation [115].

iii. Electrolyte

Electrolyte is one of the most crucial parts of a DSSC since it is responsible for both the carrier transport between the electrodes and also dye regeneration. Liquid electrolytes have been more widely investigated in DSSCs.

The liquid electrolytes should be chemically stable. Also, they should be easily prepared, and should have a high conductivity, low viscosity and good interfacial wetting between electrolytes and electrodes [116]. They should also possess a good solubility. However, they should not dissolve the dye or the semiconductor layer. On the other hand, the solvent should not have leakage or evaporation to prevent the loss of the liquid electrolyte [116].

The redox potential and the regeneration of the dye should be considered to choose the electrolyte properly. After the injection of an electron into the conduction band of the TiO_2 , the oxidized dye must be reduced to its ground state very fast [116].

The electrolyte should not have an absorption in the visible range. Redox couple ions can interact with the injected electrons which in turn increases the dark current [116].

Although liquid electrolytes have been widely used in the most efficient DSSCs, they have some practical problems such as leakage and evaporation

of solvent, photodegradation and dissolving of the dye from the semiconductor surface, and corrosion of the counter electrode. Quasi-solid-state electrodes and ionic liquids have been investigated as alternatives to liquid electrolytes to solve these problems. The quasi-solid-state electrolyte system is a molecular or nanomolecular aggregate system which possesses high ionic conductivity whereas ionic liquids are salts in liquid state [117].

As is the case in many photovoltaic research fields, DSSC research has mostly focused on increasing the PCE of DSSCs by taking into account the requirements mentioned above, and also on improving the device stability and reducing the device costs. Investigations of the nanoscale morphology of the metal oxide and/or other semiconductor electrodes, synthesis and use of new dyes, the nature of the kinetics of the electrolyte, and the search for alternatives to liquid electrolytes, such as gel or polymer electrolytes, have been ways of overcoming the problems of efficiency, stability and costs.

The initial efforts focused on fabricating DSSCs using a compact semiconductor film as electrode [40]. Since the initial work by O'Reagan *et al.* there has been a tremendous effort to improve the efficiency of DSSCs. The breakthrough was achieved by introducing a mesoporous semiconductor with a high interfacial area [118]. In this study, it was demonstrated that mesoporous TiO_2 is necessary to increase the interfacial area, which would increase the dye adsorption. Ruthenium (Ru)-based dyes with a broad optical absorption have been introduced. Another milestone was achieved by the TiCl_4 surface treatment on the TiO_2 electrodes [119]. The development of dyes led to a further improvement in DSSCs. A PCE of 12% has been achieved using the black dye (N749) as photosensitizer [120]. Recently, PCE of DSSCs has been increased to 13% using a molecularly engineered porphyrin dye, coded as SM315, which features the prototypical structure of a donor- π -bridge-acceptor, which both maximizes electrolyte compatibility and improves light-harvesting properties [121].

1.2.2.5.1 Solid-State Dye-Sensitized Solar Cells

Although dye-sensitized solar cells based on liquid electrolytes reached high efficiencies, the liquid electrolyte seems to cause problems, such as evaporation or leakage of electrolyte due to improper sealing, which may limit the device performance. Diffusion of oxygen and moisture through the improper sealing may lead to the reaction of the electrolyte with oxygen and water molecules. One of the ways to overcome this problem is the replacement of the liquid electrolyte with a solid or quasi-solid hole transporter.

In a solid-state dye-sensitized solar cell, the mesoporous metal oxide electrode is in intimate contact with a solid-state hole transporter.

A monolayer of photosensitizer dye is attached onto the surface of this electrode. Upon photoexcitation an electron is injected into the conduction band of the semiconductor oxide. The state of the dye is preserved by an electron donation from the hole conductor. The upper edge of the valence band of *p*-type semiconductors must be located above the ground state level of the dye so that the hole conductor will be able to transfer holes from the sensitizing dye after the dye has injected electrons into the semiconductor electrode.

The most common approach to fabricate solid-state DSSCs is by using *p*-type semiconductors. These *p*-type semiconductors should fulfill the following requirements [122]:

- i. They must penetrate into the pores of semiconductor electrode;
- ii. They should be deposited without dissolving the dye layer;
- iii. They must be transparent in the region where the dye absorbs light and if they absorb light they must be as efficient as electron injection of the dye.

The main difference between solid-state and liquid electrolyte DSSCs is the properties of the charge transport. In the solid-state cell, the charge transport is electronic whereas when using liquid or polymer electrolyte, ionic transport takes place [123].

Initially inorganic *p*-type semiconductors such as CuI and CuSCN were used as hole transporters in dye-sensitized solar cells [124, 125]. However, the difficulty of proper filling of the pores with these hole transporters leads to rather moderate efficiencies as compared to that of liquid electrolyte-based DSSCs.

Electrochemical polymerization has been investigated to overcome the pore filling problem. Polyprole was electrochemically polymerized directly on the pores of semiconductor oxides [126, 127].

A major breakthrough was reported by Grätzel's group using an organic *p*-type molecule (2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene or spiro-OMeTAD) together with a ruthenium complex (N3) [128]. The increase in the PCE was attributed to the infiltration of spiro-OMETAD into the pores of TiO₂. By adding salt additives into the spiro-OMETAD, the efficiency was increased over 3% by Krüger *et al.* [129]. Later, Grätzel *et al.* demonstrated that efficiency can be further increased by adding silver ions into the dye solution and performing dye uptake in the presence of silver ions [130]. The efficiency has been increased to 4%. Recently, PCE over 7% was achieved by using a high molar extinction

coefficient organic D- π -A sensitizer and *p*-doped spiro-MeOTAD as hole conductor. This has been the highest power conversion efficiency for solid-state DSSCs achieved up to now [131].

Conjugated polymers have also been used in solid-state DSSCs. Poly(3-alkylthiophenes) were the material of choice [132–134]. The highest efficiency was achieved for the devices employing P3HT. A PCE over 3% was reported [135]. A new dye coded as D35 was used and this high PCE was attributed to the high hole conductivity of the dye. It was concluded that the dye hole conduction is a significant parameter in the TiO_2 /dye/polymer systems [135]. A PCE of almost 7% was achieved for the DSSCs employing poly(2,5-dibromo-3,4-ethylenedioxythiophene) (PEDOT). Highly transparent organized mesoporous TiO_2 (OM- TiO_2) was used. OM- TiO_2 was prepared via sol-gel synthesis of TiO_2 using a template of an amphiphilic graft copolymer that consisted of a poly(vinyl chloride) (PVC) backbone and poly(oxyethylene methacrylate) (POEM) side chains (PVC-g-POEM). This high efficiency was attributed to the high conductivity of PEDOT and also to the improved hole transporter-OM- TiO_2 interface [136].

Polymeric gel electrolytes have also been applied in solid-state DSSCs [137–140]. However, the PCEs were rather moderate as compared to liquid electrolyte-based DSSCs.

1.2.2.6 Perovskite Solar Cells

Although organic, hybrid and dye-sensitized solar cells have been widely investigated, their commercialization still stands as an issue since the maximum achieved PCE of these devices are still lower than that of their inorganic counterparts. Besides PCEs, the stability problems of the organic/hybrid solar cells due to the sensitivity of organic materials to oxygen and moisture have not been solved yet. Also, high-temperature processing required for electrode preparation in DSSCs, leakage and evaporation problems of the liquid electrolyte and the stability of the hole transporting materials are the issues which still need to be resolved for DSSCs.

During the last three years a new family of photovoltaic compounds called “perovskites” have been the focus of attention. Such organic/inorganic hybrid solar cells based on ionic salts of organic compounds with lead halides show high efficiencies.

Perovskite ABX_3 ($X = \frac{1}{4}$ halogens) structure consists of organic components in cuboctahedral A site and inorganic components in octahedral B site and the chemistry of the organic and inorganic components can be tailored to tune the optical, electronic, magnetic, and mechanical properties of hybrid materials [141].

One of the first studies on perovskite solar cells was based on the use of 2–3 nm-sized perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ nanocrystal. By electrochemical junction with iodide/iodine-based redox electrolyte a PCE of almost 7% was achieved [141].

Later, the PCE was increased to almost 10% for solid-state devices in which spiro-OMETAD was employed. Femto second laser studies combined with photoinduced absorption measurements showed charge separation to proceed via hole injection from the excited $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ NPs into the spiro-MeOTAD followed by electron transfer to the mesoscopic TiO_2 film. It has been demonstrated that the use of a solid hole conductor dramatically improved the device stability compared to $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ -sensitized liquid junction cells [142].

Chung *et al.* demonstrated that the solution-processable *p*-type direct band gap semiconductor CsSnI_3 can be used for hole conduction instead of a liquid electrolyte. The resulting solid-state dye-sensitized solar cells consist of $\text{CsSnI}_{2.95}\text{F}_{0.05}$ doped with SnF_2 , nanoporous TiO_2 and the dye N719, exhibited a PCE over 10% (almost 9% with a mask). It has been shown that with a band gap of 1.3 electron volts, CsSnI_3 enhances visible light absorption on the red side of the spectrum to outperform the typical dye-sensitized solar cells in this spectral region [143].

Snaith *et al.* employed a crystalline perovskite absorber (a mixed Halide perovskite absorber, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) with intense visible to near-infrared absorptivity, that has a PCE of almost 11% in a single junction device under simulated full sunlight [144]. They achieved V_{oc} s of more than 1.1 volts, despite the relatively narrow absorber band gap of 1.55 eV.

High-performance $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite solar cells with a PCE of almost 17% using chemically tailored new conjugated copolymers have been realized by Xue *et al.* [145]. It has been demonstrated that the new hole selective layers with well wetting and electronic properties improve the device performance.

Adam *et al.* fabricated perovskite solar cells on highly conductive PEDOT:PSS substrates. PEDOT:PSS was deposited with dimethyl sulfoxide (DMSO) and Zonyl as additives. This process enables the fabrication of perovskite solar cells using [6,6]-phenyl-C61-butyric acid methylester (PCBM) as electron transport layer with PCEs higher than 12%, low hysteresis and excellent operational stability [146].

Recently, PCEs over 20% have been achieved by replacing the perovskite of methylammonium lead iodide (MAPbI_3) with formamidinium lead iodide (FAPbI_3) [147]. The band gap of the latter allows broader absorption of the solar spectrum relative to the former. They reported a method for depositing high-quality FAPbI_3 films involving FAPbI_3 crystallization

by the direct intramolecular exchange of dimethylsulfoxide (DMSO) molecules intercalated in PbI_2 with formamidinium iodide. This process produces FAPbI_3 films with (111)-preferred crystallographic orientation, large-grained dense microstructures, and flat surfaces without residual PbI_2 , which in turn leads to PCEs over 20%.

As summarized above, organolead halide perovskites constitute a highly promising class of materials, but suffer limited stability under ambient conditions without heavy and costly encapsulation [148]. Recently, Kaltenbrunner *et al.* reported on ultrathin ($3\ \mu\text{m}$), highly flexible perovskite solar cells (see Figure 1.4) with stabilized PCE of 12% and a power-per-weight as high as $23\ \text{Wg}^{-1}$. To facilitate air-stable operation, they introduced a chromium oxide–chromium interlayer that effectively protected the metal top contacts from reactions with the perovskite [148].

1.3 Conclusion

Since the first report on solar cells there has been a tremendous effort to develop solar cells with high performance and stability. Three different routes were followed to achieve this goal which led to the so-called “first, second and third generation” solar cells. In this chapter, we reviewed the recent progress in organic/inorganic hybrid solar cells which are counted among the third generation solar cells. Hybrid solar cells consisting of both organic and inorganic semiconductors have been widely studied during the last decade. The three main approaches to producing hybrid solar cells were bulk heterojunction hybrid solar cells, dye/solid-state dye-sensitized solar cells and perovskite solar cells. Although their efficiencies are still low as compared to first and second generation type solar cells, intensive research all over the world has led to an understanding of their limitations and also the ways to overcome these limitations. This is really an important step since both the problem and the solution are well defined. The main goal is the commercialization of these solar cells. Besides efficiencies, lifetime-stability and production costs are also crucial and have to be taken into account equally. In almost 25 years, the moderate values of efficiencies have been increased to ambitious values so that we are talking about a further possible commercialization step. There is intense interest in the field and it is growing fast. On the other hand, the parameter space to choose from is large and simple and low-cost processability attracts much attention. In this competition between the different types of hybrid solar cells, perovskite solar cells seem to breast the tape since in only three years there has been a noticeable improvement in both their efficiency and stability.

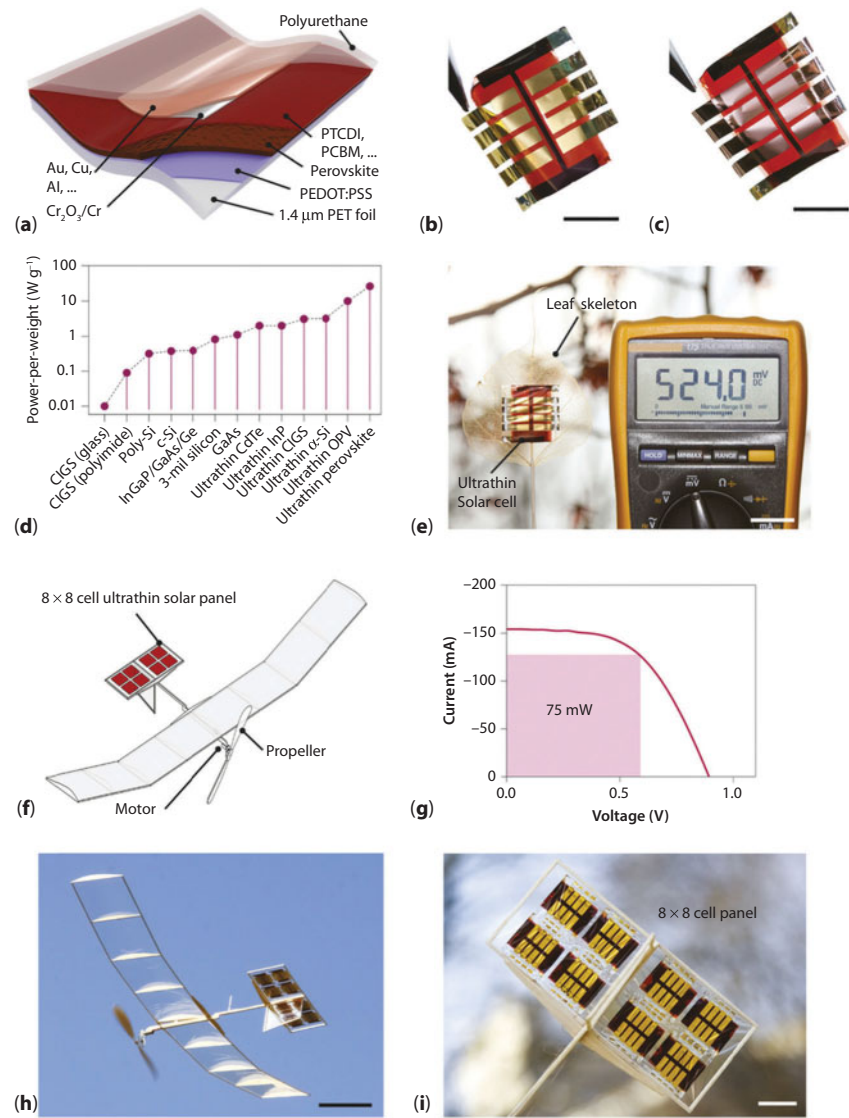


Figure 1.4 (a) Schematic of the solar cell stack; (b) Freestanding 3-m-thick solar cells with gold top metal; (c) Perovskite solar foil with low-cost copper back contacts; (d) Power-per-weight of ultrathin perovskite solar cells is more than double the nearest competing photovoltaic technology; (e) Dried leaf skeleton covered with a solar array of eight cells; (f) Schematic drawing of the solar-powered model airplane; (g) Power output of the 64-cell solar panel; (h) Snapshot of the model plane during solar-powered outdoor flight; (i) Close-up photograph of the horizontal stabilizer with integrated solar panel. (Reprinted with permission from [148]; Copyright © 2015 Macmillan Publishers Ltd.)

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Solution Processing and Thin Film Formation of Hybrid Semiconductors for Energy Applications

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Abstract

Finding an abundant, renewable and carbon-free source of energy is a primary global necessity. In this context, electricity production from solar cell devices has been a matter of intensive research in the last three decades. Currently, the best solar cell technologies are based on inorganic semiconductors that require relatively expensive manufacturing techniques. Alternatively, solution processing offers a strategy to reach low cost mass production of solar devices. In this approach, the main components of the device are processed in the form of colloidal or precursor inks. This chapter first discusses the main physical phenomena driving film formation by solution processing. Then, the basic features of some relevant techniques used for film deposition are presented. In the third section, the main characterization methods of semiconductor films are presented. Finally, the crystallization process of semiconductor thin films is discussed using hybrid organic-inorganic perovskites as a model material. Overall, this chapter presents relevant aspects about film formation of hybrid semiconductor materials. Rather than the presentation of an exhaustive list of materials used as semiconductor films, representative cases of materials recently used for the fabrication of solution-processed solar cells are closely analyzed.

Keywords: Solution process, hybrid-semiconductor film formation, perovskite crystallization, film deposition and characterization techniques

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2.1 Physical Chemical Principles of Film Formation by Solution Processes: From Suspensions of Nanoparticles and Solutions to Nucleation, Growth, Coarsening and Microstructural Evolution of Films

Fabrication of printable optoelectronic devices and especially solar cells requires the formation of several layers on a substrate starting from different precursor solutions. Hence, the initial concentration and chemical composition of the precursor solution as well as its interaction with the substrate play a fundamental role in the formation of films with specific functionality. Optimal morphological and microstructural film properties such as high coverage, uniformity, small roughness, big grain size, and absence of voids or pinholes are required for the fabrication of highly efficient optoelectronic devices [1]. Materials science provides the framework for understanding the fundamental phenomena involved in the formation of solution-processed thin films.

The formation of a film typically starts with the deposition of a precursor solution on a substrate and continues with the removal of the solvent, causing supersaturation of the film. The solvent can be removed by heating [2, 3], addition of an antisolvent [4–6] or application of vacuum [7] in order to induce solvent evaporation, as shown schematically in Figure 2.1a. The supersaturation of the precursor causes the appearance of species which cluster together into single crystal nuclei [8]. These nuclei form at the solution-substrate interface and within the precursor solution, leading to heterogeneous or homogeneous nucleation, respectively. There are some equations that allow calculation of the nucleation rate as a function of the supersaturation ratio (S) defined as $S = C/C_s$; C being the solute concentration and C_s the solubility limit [9]. Figure 2.1b shows the dependence of the nucleation rate on S . At low S values, the heterogeneous nucleation prevails while the homogeneous nucleation is dominant at high S . For the formation of a uniform film, it is necessary to promote the heterogeneous nucleation at the solution-substrate interface rather than the homogeneous because in this way a higher amount of nuclei is formed on the substrate, leading to higher surface coverage of the film. Some practical strategies have been developed to control the nucleation rate of hybrid semiconductor films such as the controlled evaporation of the solvent by gradual annealing [10, 11] or vacuum treatment [7], modification of the solvent properties by additives [12] or the tuning of the wettability of the precursor on the substrate [13]. As we will

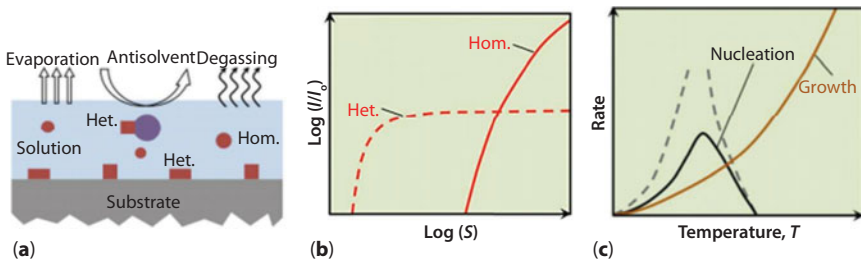


Figure 2.1 (a) Schematic illustration of nucleation during supersaturation of a wet film solution. (b) Normalized nucleation rate as a function of supersaturation ratio S . (c) Nucleation and growth rate as a function of temperature. Hom. denotes homogeneous and Het. heterogeneous (adapted from [8]).

show in the following sections, the use of these strategies for controlled nucleation process leads to films with optimal morphological and crystalline properties. After nucleation the next step in the formation of a film is the growth and coarsening of crystals. The rate of these processes is dependent on the temperature, as shown in Figure 2.1c. The growth rate increases steadily as a function of the temperature while the nucleation rate has a maxima at some specific temperature. As we mentioned before, to achieve a film with high surface coverage it is necessary to promote a high rate of heterogeneous nucleation at the substrate-solution interface, but also to keep a low growth rate, especially at the initial stage of the thermal treatment. As we will show later, inadequate thermal annealing protocols lead to films with poor coverage, probably because of a high growth rate combined with a slow or homogeneous nucleation rate. The final step of the film formation is the coarsening of the crystals. At this stage a film with a particular distribution of grain size and boundaries is formed. Here, it is also important to control the variables of thermal treatment in order to achieve films with desired microstructural properties such as high grain size, absence of voids, and a controlled amount of grain boundaries.

The basic concepts discussed here are the conceptual framework of the solution processing of thin films. In the following sections we will show the application of some of these concepts to the solution processing of hybrid semiconductor films. In particular, we will discuss the role of the deposition techniques on the final properties of the films as well as the strategies used to tune the crystallization processes such as control of the thermal treatment and the use of additives to adjust the properties of the precursor solution.

2.2 Solution-Processing Techniques for Thin Film Deposition

The development of photovoltaic technology has closely followed the advancements in microelectronics, inheriting both their advantages and limitations. In fact, the transistor realization in the mid-50s at Bell Labs motivated shifting the research in selenium as active photovoltaic material towards silicon. Since then, all concepts related to the development of microelectronics, such as p-n junctions, doping and, of course, the fabrication techniques, were replicated in the solar cells field. For instance, the growing of high purity silicon relied on the Czochralski process [14] which, although it enabled a high quality material, also prompted a slow high-cost processing method, since it involved high temperature and long crystallization times. First and second generation of solar cells nurtured from manufacturing techniques developed for the microelectronics industry [15], such as evaporative methods (e.g., molecular beam epitaxy), glow-discharge methods (e.g., sputtering), gas-phase chemical processed (e.g., chemical vapor deposition) and liquid-phase chemical techniques (e.g., electroplating, mechanical), as summarized in Table 2.1.

Table 2.1 Classification of semiconductor fabrication techniques (reprinted from [15]).

Classification	Processes	Examples
Evaporative methods	Vacuum evaporation	Conventional vacuum, electron-beam, molecular beam epitaxy (MBE) ...
Glow-discharge processes	Sputtering	Diode, reactive, magnetron ...
	Plasma processes	Plasma oxidation, plasma anodization, polymerization ...
Gas-phase chemical processes	Chemical vapor deposition (CVD)	Epitaxy, atmospheric-pressure, laser-induced ...
	Thermal-forming processes	Oxidation, nitridation, ion implantation, ...
Liquid-phase chemical techniques	Electro processes	Electroplating, electrophoretic ...
	Mechanical techniques	Spray pyrolysis, spin-on, liquid phase epitaxy...

The techniques have evolved around the production and processing of wafers. At this moment the wafer industrial standard size is 300 mm. Since microelectronics have evolved towards miniaturization, this area constraint does not represent a drawback. However, when considering large-area electronics, such as displays and solar cells, the area limitation is a serious difficulty to mass production.

Implementing a full methodology based on solution processing constitutes the current trend towards reaching the industrial massification of solar cells. The main motivation for this effort is reaching deposition techniques compatible with the high throughput and mature paper and plastic printing industry. Recent efforts have been addressed to transfer the achievements of lab-scale spin coating processing in third generation hybrid solar cells towards industrially compatible solution processing techniques such as blade coating, spray coating and printing techniques (screen, flexographic, inkjet, etc.). Furthermore, the relevance of solution processing has stimulated some research teams to reconsider even the fabrication of second generation solar devices [16–18], as shown in Table 2.2.

A complete list of solution processing methods correlated to their film formation properties can be found elsewhere [23, 24]. In general, solution processing methods can be classified into four groups: drop casting, spin coating, meniscus-guided and printing [25]. In this section, we will analyze spin coating due to its relevance at lab-scale. On the other hand, we will consider doctor blade and slot-die as reference meniscus-guided methods and finally spray coating as printing method. The basic dynamics and relevant solar cells results are presented for all the mentioned techniques.

Table 2.2 Summary of devices partially developed using solution-based methods.

Solar technology	Efficiency (%)	Ref.
Perovskite	21.1%	[19]
CIGS	13.6%	[16]
Organic	11.3%	[20]
CdTe	10.3%	[18]
Kesterite	9.6%	[21]
Small molecule	6.7%	[22]
a-Si	0.7%	[17]

2.2.1 Spin Coating

Spin coating is by far the most commonly used solution-based fabrication technique. The basics steps for the film formation are illustrated in Figure 2.2. Initially, the solution or dispersion of the material is dispensed on the substrate. The substrate is accelerated until reaching a constant angular speed. During this stage, most of the solution or dispersion (95–98%) [26] is centrifuged out of the substrate and a uniform wet film is formed. Finally, the fluid dynamics mainly relate to the solvents evaporation and thinning down to reach the final film. The dynamics of the spin coating process can be assessed from the balance between viscous and centrifugal forces and evaporation. The thickness $h(t)$ of the wet film can be obtained from the equations:

$$\text{Analytical [26–28]: } h(t) = \int \left[-\frac{2\rho\omega^2}{3\eta} h^3 - k_g (C_v^i - C_v^o) \right] dt \quad (2.1)$$

where ω , ρ , η , k_g , C_v^i and C_v^o correspond to the radial velocity, density, viscosity, mass transfer coefficient, concentration of solvent at the interface and concentration of solvent in the bulk vapor phase, respectively.

$$\text{Empirical [23]: } h = k\omega^\alpha \quad (2.2)$$

where ω corresponds to the angular velocity, and k and α to empirical constants.

Early stages of the process are flow dominated while final stages are evaporation dominated [26, 27]. One of the key advantages of spin coating is that achieving a uniform wet film guarantees a final uniform solid film [26]. Interestingly, interference colors [26] can be observed during the consolidation of the wet film because of the coherent interaction of thin films and white light. In that sense, those interference colors are a mark certifying the uniformity of the final film.

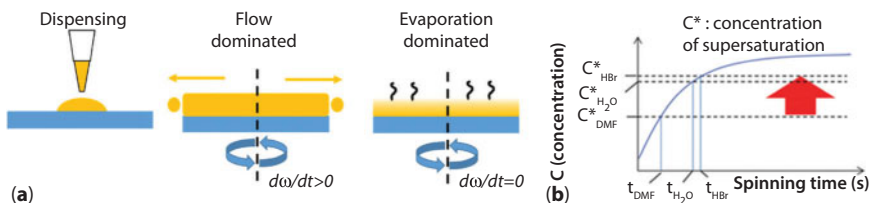


Figure 2.2 (a) Basic stages during a spin coating process. (b) Supersaturation shifting depending on the ink composition (reprinted from [27]).

Besides uniformity, films need to achieve full surface coverage to prevent pinholes which can potentially generate in shunting paths. Reaching those dense films requires controlling the crystallization of the deposited material. As mentioned in the previous section, crystallization involves nucleation and growth stages. The nucleation starts after a supersaturation status is realized and dense films are favored by beginning nucleation with highly concentrated wet films [27]. Accordingly, modifying the ink properties for reaching a high supersaturation concentration of the wet film is crucial to reach full coverage films, as shown in Figure 2.2b.

The popularity of this method relies on its simplicity and high repeatability. In fact, the current best power conversion efficiencies for perovskite solar cells surpassing 20% have been realized implementing spin coating as deposition method [7, 19]. However, the method is limited to lab-scale use since just 2–5% of the initial ink is effectively deposited on the substrate [26]. This situation has motivated the research of alternative and more scalable solution processing methods.

2.2.2 Doctor Blade

As mentioned before, the scaling up of photovoltaic technology has been guided by the experience in paper printing evolved during decades. Interestingly, the “doctor blade” technique arose from a cleaning procedure where a blade was employed to wipe the excess ink in *doctor* rolls from letterpress equipment [29]. To date, doctor blade has been employed in developing organic solar cells [30], CIGS [16] and perovskite solar cells [31, 32] and has inspired the development of more sophisticated techniques such as slot-die coating and curtain coating [24, 30].

The flow dynamics of the ink/paste to deposit depends on the geometrical setup, as shown in Figure 2.3a. An analytical approximation for the dry film thickness h can be obtained from the Navier-Stokes equation:

$$\text{Analytical [33, 34]: } h = \frac{\alpha\beta}{2} \frac{\rho_{slurry}}{\rho_{dry}} H_o \left(1 + \frac{\Delta P \cdot H_o^2}{6\eta LU} \right) \quad (2.3)$$

where α and β are correction factors related to the side flow during drying and drying shrinkage, respectively. The rest of the variables, ρ_{slurry} , ρ_{dry} , H_o , ΔP , η , L and U , correspond to the ink/paste density, dry film density, gap

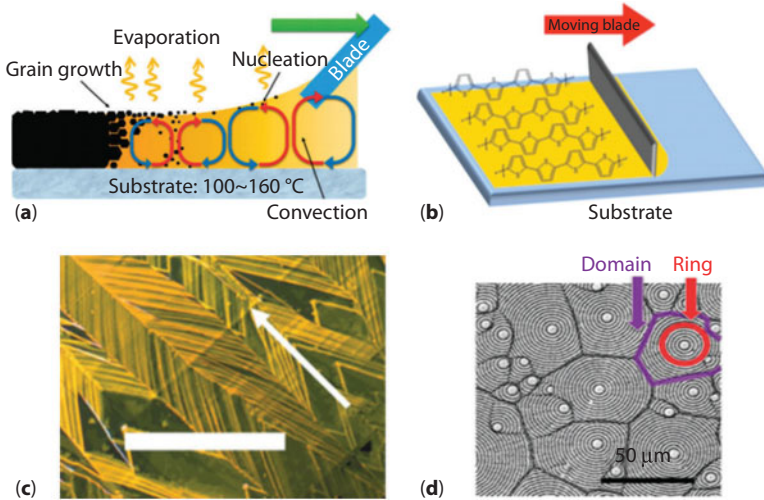


Figure 2.3 (a) Basic film formation processes during doctor blade (reprinted from [31]). Besides layer formation, the doctor blade can influence the layer crystallization leading to (b) molecular orientation in a Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b'] dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) film (reprinted from [35]), (c) crystal orientation in a 5,50-bis(4-butoxyphenyl)-2,20-bithiophene (dbo-P2TP) film (reprinted from [36]), and (d) perovskite crystal size enlargement (reprinted from [31]).

height, hydrostatic pressure, viscosity under the blade, length of the blade and blade relative velocity, respectively.

$$\text{Empirical [23]: } h = \frac{1}{2} \left(\frac{gc}{\rho} \right) \quad (2.4)$$

where g , c and ρ correspond to the substrate/blade gap, solid materials concentration in the ink and final film density, respectively.

Similarly to spin coating, films grown by doctor blade experience a process of nucleation, crystal growth and solvent evaporation (Figure 2.3a). However, unlike spin coating, the doctor blade itself can induce molecular [35] and crystal orientation [31, 36], as shown in Figure 2.3b–d.

2.2.3 Slot-Die Coating

In terms of film formation, uniformity and ink management, slot-die constitutes the most promising technique to scale up photovoltaic technology [37, 38]. Being that slot-die is a meniscus-guided method, its flow dynamics is similar to the one for doctor blade. The only difference arises

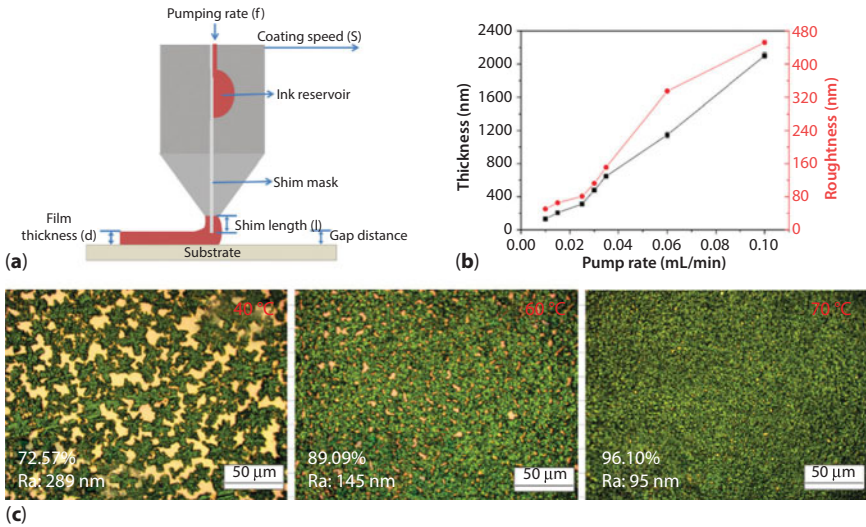


Figure 2.4 (a) Basic parameters governing the slot-die processing. (b) Example of the variation of thickness and roughness of a perovskite film with different solution pumping rates. (c) Resulting perovskite surface coverage percentage as a function of the processing temperature.

from the mechanical configuration where the meniscus is kept static while the substrate moves with a continuous ink supply, as shown in Figure 2.4a. The empirical equations for the resulting film thickness are given by:

$$\text{High viscosity regime [23]: } h = \frac{f}{Sw} \cdot \frac{c}{\rho} \quad (2.5)$$

where f , S , w , c and ρ correspond to the flow rate, web speed, coated width, solid concentration in the ink and the density of the dry film, respectively.

$$\text{Low viscosity regime (including shim) [39]: } h = k \frac{lfcS^{2/3}}{Tw\rho} \quad (2.6)$$

where l , k and T correspond to the shim length, a proportionality constant and the processing temperature.

Most of the inks employed in printable solar cells belong to the low viscosity regime (around 4 mPas) [39]. In such a case, a positive shim is implemented to ensure the uniformity of the deposited layer. As shown in Equation 2.6, there are several variables associated with the film formation. For instance, in the case of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, both the layer thickness and surface roughness are strongly increased after boosting the ink

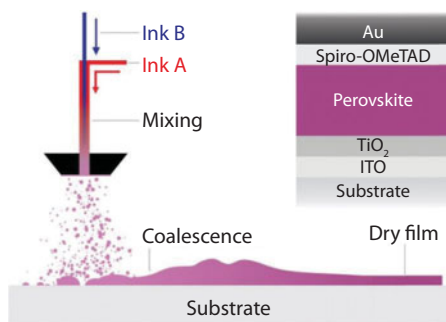


Figure 2.5 Basic process during spray coating enabling compositional studies of the resulting films (reprinted from [42]).

pump rate [40] (Figure 2.4b). On the other hand, the surface layer coverage closely depends on the selected processing temperature [40], as shown in Figure 2.4c. A proper tuning of all these processing variables has enabled solar devices with efficiency surpassing 15% [37].

2.2.4 Spray Coating

The spray coating process is considered a model printing technique. This technique has been widely explored in the painting industry and relies on the transformation of the ink into droplets using an inert carrier gas. The droplets are ejected from a nozzle and deposited on a surface, as illustrated in Figure 2.5. A variation called spray pyrolysis takes place when the surface is hot enough and the precursors are properly selected to induce a chemical reaction. This is the most commonly used technique to form compact TiO_2 films [41]. Reaching an ultra-smooth surface might be challenging using this technique [23], however, its implementation has enabled solar cells as efficient as 15% [42], facilitating film compositional studies.

2.3 Properties and Characterization of Thin Films: Transport, Active and Electrode Layers in Thin Film Solar Cells

Third generation solar devices are formed by single films whose thicknesses typically range from a few nanometers to microns. Each film forming the solar device is intended to have a specific optical and electronic function. Buffer layers are designed to have selective charge conductivity (either hole or electron preferential transport) and high optical band gap to

prevent parasitic absorption. On the other hand, photoactive layers are designed to absorb as much light as possible while having a high charge conductivity. Finally, electrodes must have a high electrical conductivity and at least one electrode must be designed to be semitransparent. The intrinsic morphological properties of each layer determine their resulting optoelectronic performance. Additionally, the surface properties must be properly tuned to allow an adequate interaction with neighboring layers. In this section, a summary of the most employed characterization techniques is presented in the framework of third generation solar cells.

Table 2.3 Thin film basic characterization techniques.

Electronic characterization			
<i>Technique</i>	<i>Abbreviation</i>	<i>Layer property</i>	<i>Ref.</i>
Space-charge limited current	SCLC	Mobility, permittivity	[43, 44]
Capacitance	C	Electrical permittivity	[45]
Capacitance-voltage	C-V	Flat band potential	[46]
		Carrier density	
Photo-thermal deflection spectroscopy	PDS	Urbach energy/Energetic disorder	[47]
Photoluminescence	Steady PL	Quenching	[47]
	Time-resolved PL	Charge-carrier lifetime	
Cyclic voltametry	CV	Energy levels	[48, 49]
Van der Pauw	VDP	Resistivity	[50]
Optical characterization			
<i>Technique</i>	<i>Abbreviation</i>	<i>Layer property</i>	<i>Ref.</i>
UV-VIS spectrometry	UV-VIS	Band gap	[51]
		Average visible transmission	[52]
		Reflectivity	[53]
Ellipsometry	----	Refractive index	[54]
		Extinction coefficient	
Optical microscopy	OM	Micrometric microscopy	[55]
Surface and morphological characterization			
<i>Technique</i>	<i>Abbreviation</i>	<i>Layer property</i>	<i>Ref.</i>
Profilometry	----	Thickness	[56]
		Roughness	

(Continued)

Table 2.3 Cont.

Scanning electron microscopy	SEM	Nanoscale microscopy	[57]
Transmission electron microscopy	TEM	Nanoscale microscopy	[58]
Atomic force microscopy: Conductive and photoconductive	AFM	Nanoscale surfaces	[59]
	c-AFM, pc-AFM		
Kelvin probe microscopy	KPFM	Work function	[47]
X-ray photoelectron spectroscopy	XPS	Surface chemistry	[60, 61]
Ultraviolet photoelectron spectroscopy	UPS		
Contact angle	CA	Wettability	[13]
Compositional characterization			
<i>Technique</i>	<i>Abbreviation</i>	<i>Layer property</i>	<i>Ref.</i>
X-Ray diffraction	XRD	Crystalline phase	[4, 47]
Energy dispersive X-ray spectroscopy	EDS/EDX	Elemental composition	[62]
Grazing-incidence small-angle X-ray scattering.	GISAXS	Nanoscale organization	[63]
Grazing-incidence wide-angle scattering	GIWAXS	Nanoscale organization	
Raman spectroscopy	Raman	Vibrational and rotational modes	[64]
Fourier transform infrared spectroscopy	FTIR	Atomic vibrations	[4]
Differential scanning calorimetry	DSC	Thermal transitions	[11, 62]
Thermo-gravimetric analysis	TGA		[65]
Mechanical characterization			
<i>Technique</i>	<i>Abbreviation</i>	<i>Layer property</i>	<i>Ref.</i>
Cohesion energy	----	Layer cohesion	[66]
Fracture test	----	Adherence	
Flexibility	----	Stretching cycles	[56]

In addition, a thin hybrid perovskite layer ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is characterized as an example.

There are multiple approaches to characterize thin films. At the end, each layer must accomplish specific optoelectronic properties resulting from their intrinsic characteristics and the interface must be engineered to allow a proper interaction with neighboring functional layers. Table 2.3 presents a list of the most common thin film characterization techniques in the context of hybrid solar cells. Although non-exhaustive, the table intends to collect representative works for future reference.

A set of measurements towards the characterization of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer are presented as an example in Figure 2.6. The perovskite precursor was prepared as reported elsewhere [67]. Initially, the uniformity and density of the perovskite film was validated by optical microscopy (OM). The resulting surface coverage was strongly dependent on the perovskite precursor composition and the selected crystallization method. Remarkably, the solvent engineering process yielded the higher surface coverage perovskite layers [67]. The morphology of the layer was further revealed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) and a grain size of around 300 nm was found. X-ray diffraction (XRD) analysis allowed confirming the characteristic tetragonal phase of the perovskite. On the other hand, the perovskite ink precursor exhibited a 17° low contact angle (CA) with the underlying nickel oxide hole transporting layer. Such a low angle relates to the capacity of the perovskite

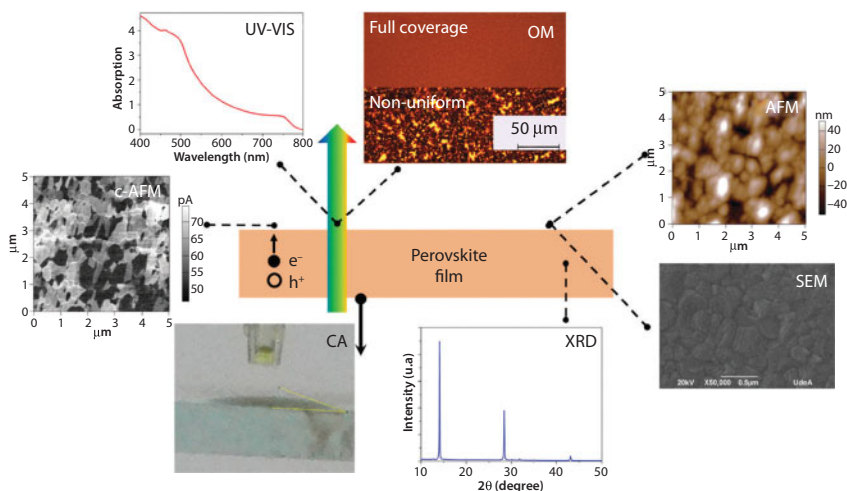


Figure 2.6 Approach used to characterize a hybrid perovskite thin film.

precursor to present fast nucleation yielding to small crystals [13, 68]. Additionally, the perovskite showed a moderate surface roughness below 10 nm which also favors the nucleation of the top transport buffer layer. Finally, the resulting optical and electronic properties of the perovskite layer were evaluated using ultraviolet-visible spectroscopy (UV-VIS) and conductive AFM (c-AFM), respectively. In the first case, a broad band absorption spreading along the visible spectrum was obtained. In addition, the c-AFM map demonstrated the capacity of the formed layer to allow the extraction of the photogenerated charge.

2.4 Understanding the Crystallization Processes in Hybrid Semiconductor Films: Hybrid Perovskite as a Model

Besides the influence of the deposition techniques on the morphology and the opto-electronic properties of semiconductor films, there are other subsequent processes that determine the final properties of the material. In particular, most of the semiconductor layers are submitted to thermal annealing after the initial stage of film formation. This step is necessary for the nucleation, growth and coarsening of the grains, as well as to promote phase transformations that lead to a specific morphology, crystalline structure and orientation in the material of interest. In this section, we apply the concepts of film formation, characterization and deposition techniques mentioned above to prepare high-quality hybrid perovskites layers. Especially, we illustrate the influence of the thermal annealing process on the final properties of a semiconductor layer by presenting the study of thermal transformations in hybrid perovskites as a model in planar and mesoporous configurations.

2.4.1 Thermal Transitions Revealed by DSC

Hybrid lead-halide perovskites have emerged in the last years as promising materials for photovoltaic applications [69, 70]. Perovskite solar cells (PSC) with a photovoltaic conversion efficiency (PCE) as high as 22.1% have been recently reported [71]. Such high efficiencies have been reached through the optimization of morphology [72–74] as well as the microstructure of the perovskite [13, 75] because these factors have a direct influence on the photovoltaic performance of PCEs. In terms of morphology, it is crucial to achieve a perovskite layer with high surface coverage, relative

small roughness and uniformity across the entire film [7]. With respect to microstructure, it is important to optimize the grain size, distribution and texture [76–78]. The optimal control of the above-mentioned factors leads to a perovskite layer with a minimal amount of defects, namely voids, pin-holes or grain boundaries. Several strategies has been deployed to achieve high-quality perovskite films such as solvent [4] and compositional engineering [79], additives in the perovskite precursor [80–82] or heuristic optimization of the annealing conditions [2, 3].

After the initial stage of film formation, perovskites need a thermal treatment to accomplish the full transformation of the precursors (lead halides and organic salts) into the desired perovskite absorber. Despite the enormous importance of the thermal processing in PSCs, there is no consensus in the literature about optimal parameters of thermal annealing. Therefore, annealing temperatures have been reported ranging from 90 to 150 °C as well as annealing times ranging from 2 up to 180 minutes [83–86]. Recently, it was demonstrated that differential scanning calorimetry (DSC) is a useful technique to guide the perovskite crystallization

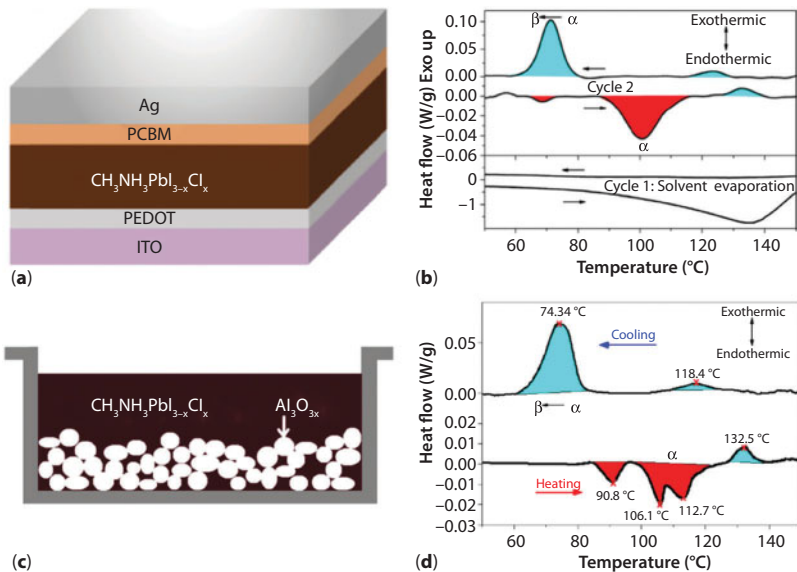


Figure 2.7 Calorimetric analysis of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite. (a) Typical planar solar cell architecture; (b) DSC analysis of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ prepared *in situ* from solution on the DSC pans; (c) Schematic illustration of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ embedded into mesoporous Al_2O_3 scaffold with a part of the perovskite forming a capping layer; (d) DSC analysis of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ in the presence of Al_2O_3 scaffold as shown in (c). (Adapted from [11, 62])

[11, 62]. Analysis of DSC thermograms of the mixed halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) allowed us to establish a rational thermal annealing protocol which only depends on the precursor composition and device architecture. Interestingly, DSC could be applied for the analysis of thermal transitions in PSC experiments in planar [11] as well as in mesoporous architectures [62]. Figure 2.7 shows the calorimetric analysis of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite when it is used in a planar architecture, where all the layers are compact films (see Figure 2.7a), or in a mesoscopic architecture, where the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite is embedded into a mesoporous scaffold, as schematized in Figure 2.7c.

In all cases, DSC revealed two exothermic and two endothermic peaks. The main endothermic peak corresponds to the formation of an α -phase perovskite. This peak is located at $T_{\text{onset}} = 85^\circ\text{C}$ for the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ without Al_2O_3 while it is shifted at higher temperature ($T_{\text{onset}} = 96.1^\circ\text{C}$) for the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ in the presence of the alumina scaffold. This is due to the insulator character of the mesoporous Al_2O_3 layer which retards the energy transfer and therefore the temperature of the thermal transition. Surprisingly, the main endothermic peak in Figure 2.7d is split into two peaks with maxima at 106.1 and 112.7°C . As shown in Figure 2.7c, some part of the perovskite is fully infiltrated into the alumina scaffold while the rest forms a capping layer. Hence, the peaks correspond to the formation of the α -phase perovskite in two different regions: the perovskite infiltrated into the mesoporous layer and the perovskite capping layer. On the other hand, DSC showed two exothermic peaks which correspond to the reorganization of the perovskite material. The small peak corresponds to a recrystallization while the main peak is assigned to the transformation from the α - to the β -phase perovskite.

Based on the features observed in the DSC thermograms, the optimal annealing protocol of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ could be envisaged. In particular, DSC enabled us to determine the optimal plateau annealing temperature, which is the most relevant variable to control. In particular, we found a close correlation between the thermal transitions revealed by DSC and the photovoltaic performance of PSC. To demonstrate this point, several devices were fabricated under different annealing protocols, as shown in Figure 2.8a.

From Figure 2.8b it is evident that the PCE of the device depends on the crystallization conditions of the perovskite layer. The best performing device was the one annealed at a plateau temperature of 130°C , reaching an average PCE of 8.7%. This result can be explained in the framework of the DSC thermogram. At 130°C the formation of the α -phase perovskite is fully accomplished and this temperature also corresponds to

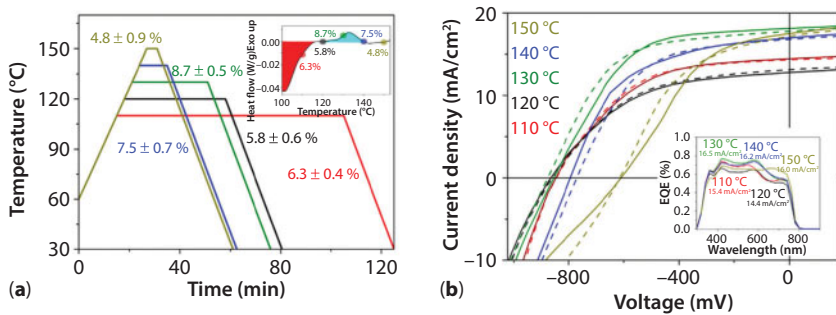


Figure 2.8 Pin planar perovskite solar cells developed under different crystallization processes. (a) Thermal processing protocol of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layer. Inset: average PCE correlated in the DSC thermogram. (b) Average J-V curves for the different devices. (Adapted from [11])

the onset of the exothermic recrystallization peak. Therefore, under these annealing conditions a highly ordered and fully crystallized perovskite is accomplished. Actually, XRD diffractogram corroborated this conclusion, as is shown later. In the next subsection, we demonstrate that the DSC technique is also applicable for optimizing the annealing process in meso-superstructured perovskite solar cells.

2.4.2 Heat Transfer Processes in a Meso-Superstructured Perovskite Solar Cell

As discussed above, the thermal transitions of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ material change in the presence of an Al_2O_3 scaffold. The mesoporous scaffold causes two effects: retards the energy transfer due to the insulator character of alumina and splits the formation process of the α -phase perovskite. These facts could be evidenced in Figure 2.7d where all the DSC peaks shifted to higher temperatures and the main endothermic peak was also split into the formation of the α -phase perovskite at the fully infiltrated and the capping layer zones. However, these are not the only effects of the Al_2O_3 scaffold.

In a meso-superstructured solar cell, the mesoporous alumina layer ($\text{m-Al}_2\text{O}_3$) has an average pore size of 26 nm [87] while the crystallite size of the perovskite is around 90 nm [62]. As a consequence, during the annealing process the perovskite infiltrated into the $\text{m-Al}_2\text{O}_3$ can suffer thermal stress. Actually, simulations of the mechanical behavior (Figure 2.9) show that the higher thermal stress values (lighter colors in Figure 2.9a) are

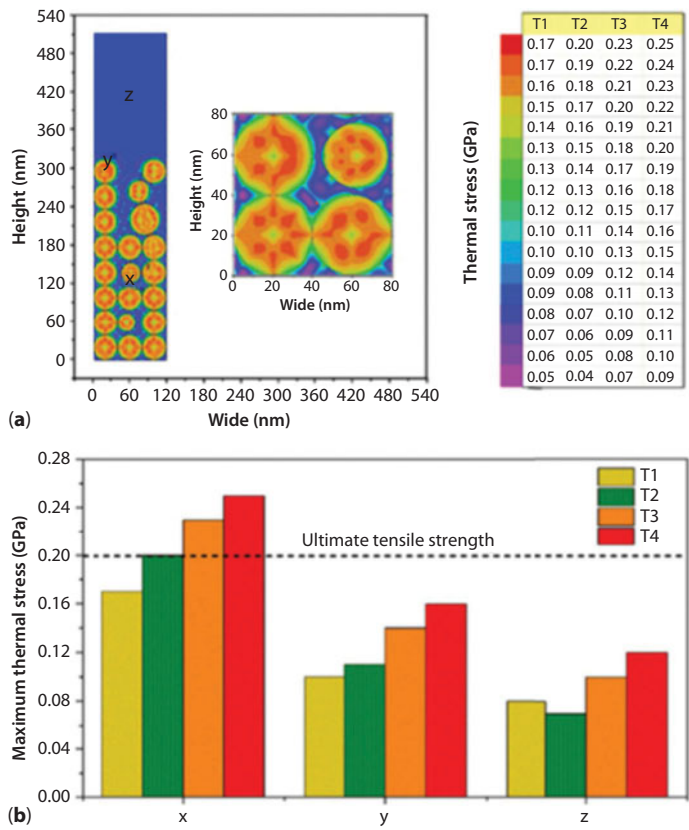


Figure 2.9 Thermal stress simulations at different annealing temperatures: (a) Stress distribution in the active layer (m-Al₂O₃ + perovskite); (b) Maximum thermal stress in the alumina scaffold (x), alumina/capping layer interface (y) and capping layer (z) at T1 = 90 °C, T2 = 100 °C, T3 = 110 °C and T4 = 120 °C. (Reprinted from [62])

located in the mesoporous layer due to the high thermal expansion experienced by the perovskite inside a confined space. Meanwhile, perovskite in the capping layer zone experiences lower thermal stress because the CH₃NH₃PbI_{3-x}Cl_x layer can grow and expand freely on the top of the capping layer.

For some annealing conditions (i.e., T ≥ 110 °C and t > 30 min) the perovskite can surpass its ultimate tensile strength, as shown in Figure 2.9b. In this case, the hybrid perovskite could mechanically break and the charge transport would be dramatically affected. As a result, the plateau step of the annealing process must be developed at T < 110 °C. However, DSC indicated that a temperature around 130 °C is necessary to reach

the recrystallization peak. This problem could be solved by applying an annealing treatment of 100 °C for 90 min followed by a “flash annealing” at 130 °C. In this way we achieve a slow crystallization without mechanical stress and reach the recrystallization temperature suggested by DSC for a short period of time. Under these conditions, meso-superstructured perovskite solar cells with efficiencies up to 10.89% could be developed [62]. In general, a careful analysis of the thermal transitions revealed by DSC as well as the study of the heat transfer process during thermal annealing allows the establishment of a rational thermal annealing protocol for highly efficient perovskite solar cells.

2.4.3 Effect of the Annealing Process on Morphology and Crystalline Properties of Perovskite Films

Thermal heating of the perovskite layers not only determines the PCE of solar cell devices, but also has a direct relationship with the crystalline and morphological properties of the perovskite films. Figure 2.10a shows the crystalline properties of perovskite films annealed at different plateau temperatures according to the annealing protocols depicted in Figure 2.8a. It can be seen that the crystallite size increases with the annealing temperature. Moreover, the degree of crystallinity of the film increases for temperatures from 110 up to 140 °C. For a temperature higher than 140 °C the crystallinity decreased due to induced thermal degradation [11, 65]. In general, from Figure 2.10a can be concluded that the optimal annealing temperature is 130 °C. At this temperature a high degree of crystallinity along with bigger crystallite size could be achieved without exposing the perovskite to the risk of induced thermal degradation that appears at

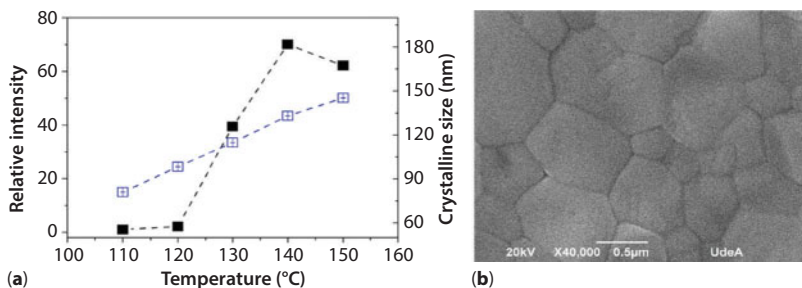


Figure 2.10 Crystallinity and morphology of perovskite films: (a) XRD study of perovskite films fabricated under different annealing conditions showing crystallinity of the films (reprinted from [11]); (b) SEM images of a perovskite film at the optimum annealing temperature of 130 °C.

temperatures close to 150 °C. This set of XRD results correlate well with the information provided by the DSC analysis.

At the optimal annealing temperature of 130 °C a perovskite films with optimal morphological characteristics can be achieved, as shown in Figure 2.10b. It can be seen from the SEM image that the perovskite films has large crystalline domains in the range of 0.5 to 1 μm and also has no voids or pinholes, forming a compact film ideal for application as absorber layer in a planar solar cell.

2.4.4 Role of Precursor Composition in the Crystallinity of Perovskite Films: Understanding the Role of Additives and Moisture in the Final Properties of Perovskite Layers

The formation of a thin film by solution processing techniques requires the induction of supersaturation in the precursor solution by removal of the solvent. Hence, the composition and concentration of the precursor solution has a large influence on the final properties of the film. Figure 2.11 shows the short-circuit current density of solar cell devices developed from perovskite precursors with different additives at concentration of 2 wt% [88]. It can be seen that water and DIO additives increase the photocurrent of the cells while DMSO has a negative impact. The higher photocurrent is related to an enhanced absorption of light by the active film. Therefore, the difference in the photocurrent values can be inferred from the morphology of the perovskite films. A SEM image of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film made from a precursor with water additive is shown in Figure 2.11b, while

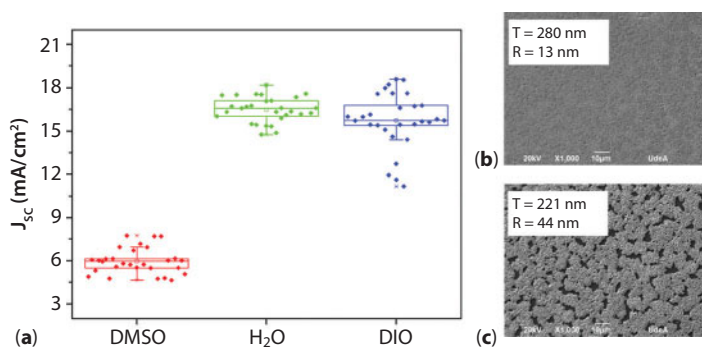


Figure 2.11 (a) Short-circuit current of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ solar cells fabricated from precursors with different additives. (b,c) Morphology of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film with water and DMSO added to the precursor solution, respectively. In Figures (b) and (c), “T” denotes thickness and “R” denotes roughness of the film.

Figure 2.11c shows the film made with DMSO. Despite both films have similar thickness (around 250 nm) they have enormous morphological differences. The $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film made with added water has no voids or pinholes and its surface roughness is relatively small (around 13 nm). In contrast, the film made with DMSO has pinholes and higher roughness (around 44 nm). The presence of pinholes decreases the capacity of adsorption of photons per unit area of film, leading to a poorer photocurrent in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layer. The better morphology of perovskite films with water additive can be explained by two facts [12]: the increased solubility of the precursor components and the lower boiling point of water which facilitate the solvent evaporation. As a consequence, the addition of water facilitates the nucleation and growth of the perovskite on the substrate. In contrast, DMSO has a higher boiling point and is difficult to remove when the film is forming.

Overall, the experimental results shown in Figure 2.11 demonstrate that small changes in the precursor composition have a large influence on the properties of the perovskite films and this is reflected in the performance of the solar cell devices.

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Organic-Inorganic Hybrid Solar Cells Based on Quantum Dots

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Abstract

In this chapter, we review the progress in the development of organic-inorganic hybrid solar cells consisting of conjugated polymer and semiconductor quantum dots (QDs). Topics covered include: work principle, device parameters, device structure, study process and improved strategy for polymer/QD solar cells. Finally, critical factors limiting the device performance are highlighted and strategies for further device improvement are demonstrated. The aim of this chapter is to show a comprehensive understanding of device performance related to material structure and surface treatment in organic-inorganic hybrid solar cells based on QDs in order to fabricate more efficient photovoltaic devices.

Keywords: Polymer/QD solar cells, surface treatment, device performance, charge transfer

3.1 Introduction

Polymer solar cells have received considerable attention over the past several decades due to their advantageous properties such as light weight, flexibility, and solution processability [1, 2]. However, the rather lower electron mobility than hole mobility in most conjugated polymers results

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Nurdan Demirci Sankir and Mehmet Sankir (eds.) Printable Solar Cells, (65–92)
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in the easy recombination of charge carrier in the photoactive layer and low device efficiency. In this regard, incorporating inorganic semiconductor nanocrystals as electron acceptors to form the hybrid solar cells either through simple mixing or through linking the components together via specific interactions such as covalent, coordination, ionic, or hydrogen bonds, affords a promising method for efficient solar cells.

In particular, a tiny material known as quantum dots (QDs) can excite two or multiple electron-hole pairs at a time when absorbing one photon [3], which is known as multiple exciton generation (MEG). Based on the particular properties, QD solar cells can exceed the S-Q limit with an efficiency at 66% and even higher to 80% [4]. Hybrid polymer/QD solar cells may offer a series of advantages over traditional polymer/fullerene systems. Firstly, QDs can also produce the photogenerating carriers, contributing to the greater light absorption than that of fullerene derivatives. Secondly, the quantum size effect leads to a tunable energy gap of QDs to allow energy level matching between the donor and acceptor in the solar cells [5, 6]. Moreover, the possibility of choosing the spectral window for the complementary absorption profile in relation to the polymer is also expected. For example, as QD size decreases, the absorption maximum is blue-shifted from the quantum confinement effect, resulting in a change in the band gap energy, thus offering a better coverage of solar spectrum. Thirdly, QDs are expected to provide ultrafast photoinduced charge carrier transfer to organic semiconductors, leading to efficient charge transfer between donor and acceptor. Finally, QDs have relatively high electron mobility and good photo- and chemical-stability.

However, device efficiencies currently achieved for polymer/QD solar cells are significantly lower than those achieved for polymer/fullerene devices. This is mainly related to the poor uncontrollable continuous percolation network, the inability to form a well-defined interface between QDs and the polymer matrix, the decreasing interfacial area originated from the phase separation of QDs and polymers, and the presence of surface traps in the QDs affecting charge generation and transport.

In this chapter, we provide a more comprehensive view of the background and the state-of-the-art of polymer/QD solar cells, critical factors limiting the device performance and strategies for further device improvement. The aim of this chapter is to show a comprehensive understanding of device performance related to material structure in organic-inorganic hybrid solar cells based on QDs, with affording the opportunity to go through previous reports.

3.2 Polymer/QD Solar Cells

3.2.1 Working Principle

Generally speaking, the working principles of the hybrid polymer/QD solar cells are similar to organic bulk heterojunction (BHJ) solar cells; typically, the conversion of light energy into electricity contains four main steps (shown in Figure 3.1): (i) light absorption; (ii) excitons diffusion; (iii) excitons dissociation and charge transfer; and (iv) charge transport and collection. In step 1, polymer mainly absorbs the photon to generate the excitons (bound electron-hole pairs). However, the inorganic QDs may contribute partially to the photon absorption although they mainly act as electron acceptors in polymer/QD solar cells. In step 2, the excitons must diffuse to the donor/acceptor interface for dissociation before recombination. The exciton diffusion length in most of the conjugated polymers is measured to be 4–20 nm [7, 8]. To reduce the possibility of exciton recombination, the BHJ structure is fabricated. The distance that excitons diffuse to the interface is reduced owing to the interpenetrating network of donors and acceptors less than 10 nm [9]. In step 3, the excitons will dissociate into negative and positive charges at the donor/acceptor interface if the energy offsets between the lowest unoccupied molecular orbital (LUMO) of the donor and acceptor is larger than the excitonic binding energy, which is typically 0.1–0.5 eV [10, 11]. In step 4, the separated holes and electrons are transported within the donor and acceptor, respectively. Then they migrate to their respective electrodes driven by an internal electric field resulting from the difference of the Fermi level of the electrodes, and consequently are collected by the electrodes, leading to the generation of the photocurrent and photovoltage.

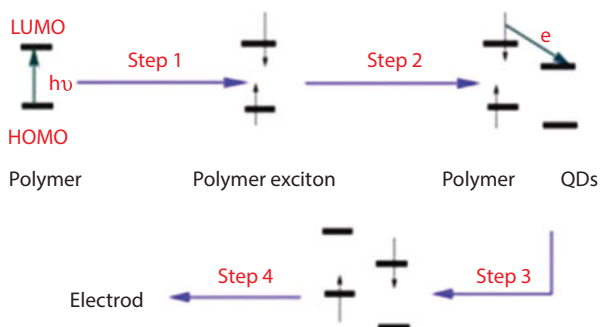


Figure 3.1 Work principle of polymer/QD solar cells.

3.2.2 Device Parameters

Photovoltaic devices are characterized by open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF) and ultimately the efficiency, in which the efficiency is determined by $V_{oc} \times J_{sc} \times FF$.

3.2.2.1 Open-Circuit Voltage (V_{oc})

When the cell is operated at open circuit, $I = 0$ and the voltage across the output terminals is defined as the open-circuit voltage (V_{oc}) (shown in Figure 3.2). The origin of V_{oc} in bulk heterojunction devices is still not well understood. Brabec considered the maximum of V_{oc} as being related to the energy difference between the highest occupied molecular orbital (HOMO) level of the donor and the LUMO level of the acceptor [12]. Scharber *et al.* reported a breakthrough on the relationship between the energy levels of the D-A blend and V_{oc} , using PCBM as the acceptor [13]. The simple relationship $V_{oc} = (|E^{\text{Donor}}\text{HOMO}| - |E^{\text{PCBM}}\text{LUMO}|)/e - 0.3$ suggests that V_{oc} is directly proportional to the diagonal band gap of the heterojunction; however, there exists an empirical loss factor related to the bulk heterojunction design. Vandewal [14] discovered a similar relationship by analyzing charge transfer absorption using Fourier transform photocurrent spectroscopy. The V_{oc} related to the effective band gap is typically $E_g/q - 0.43$. Moreover, he suggests that V_{oc} is related to the spectral position of the charge transfer band, which is determined mainly by the energetics of the HOMO level of the donor and the LUMO level of the acceptor [15].

3.2.2.2 Short-Circuit Current (J_{sc})

When the cell is operated at short circuit, $V = 0$ and the current through the terminals is defined as the short-circuit current (J_{sc}) (shown in

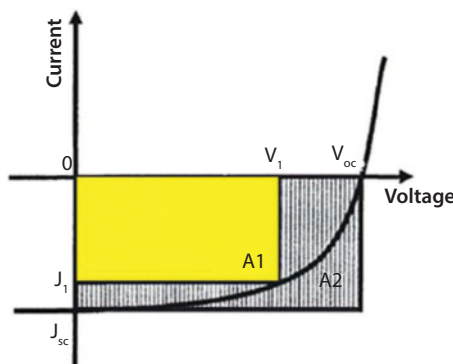


Figure 3.2 Current density–voltage (J – V) characteristics for polymer/QD solar cells.

Figure 3.2). J_{sc} is directly related to the light harvesting, exciton diffusion, charge separation, transport and collection. As a result, the efficiency of the above four steps would impact the J_{sc} . Firstly, the absorption yield of the device was characterized by η_{abs} , which is the most effective way to increase J_{sc} [16]. The absorption spectrum of the material is dependent on both the band gap and absorption coefficient of the material, as well as the thickness of the active layer [17]. As a result, low band gap polymers are chosen to increase the light-harvesting abilities [18–20]. It is noted that not only the organic semiconductor materials but also the inorganic QDs can absorb incident light to create excitons in hybrid solar cells. Secondly, excitons diffuse to the D-A interface, described as η_{diff} . This is dependent on both the excitonic diffusion length, which is determined by the polymer property, and the distance between excitation and the nearest interface, which is related to the nanoscale design of the photoactive layer. As the excitonic diffusion length in conjugated polymers is as low as 4–20 nm [8, 10, 21], as a result, controlling the D-A arrangement is crucial for successful exciton diffusion. Next, there is charge carrier transport throughout the device, which is described by the parameter η_{tr} . Normally, hole transport is through polymer, while electron transport is through QDs. Charge transport of inorganic QDs occurs via a process of hopping between energy states, which is affected by the traps and recombination sites in the photoactive film. The effective transport depends greatly on the mobility of the associated semiconductors [22]. Finally, chargers were collected by the electrodes, the parameter η_{cc} represents the collection efficiency. To inject the electron into cathode successfully, the energy level edge of the conduction band in the acceptor must be lower than the work function of the metal. Similarly, to inject the holes into anode successfully, the HOMO level of the donor must be higher than the work function of the transparent anode. A discrepancy between the work function of the anode and cathode is required to provide a direction for the photocurrent. Normally, intermediate layers between the photoactive layer and electrodes are introduced to make the injection of charge carriers more energetically favorable [23, 24]. The quality of the ohmic contact with the cathode, which is determined by the nature of the interface, also influences the charge collection efficiency.

3.2.2.3 Fill Factor (FF)

Fill factor is the ratio of the maximum power point to the product of V_{oc} and J_{sc} , which is typically $FF = A1/A2$, where $A1 = V_1 \times J_1$ and $A2 =$

$V_{oc} \times J_{sc}$ (shown in Figure 3.2). Bulk heterojunction solar cells generally display lower FF, which may originate from the parasitic loss of series and shunt resistance. The increased series resistance is a result of the poor conductivity through the active layer and reduced charge carrier injection into the electrodes, resulting in the difficulty in obtaining the ideal zero series resistance. Conversely, the ideal diode case demands infinite shunt resistance. Reduction in R_{sh} is caused by imperfections within the photoactive film or current leaks at the interface between layers in the device [25], which resulted from the nonideal nanomorphology, the active layer/cathode and the discrepancy between electron and hole mobility [26]. It is noted that the FF of BHJ devices degrade as the time increased, as a result of a non-stable nanomorphology, and incorporation of oxygen and water vapor leading to the interface recombination.

3.2.3 Device Structure

The polymer/QD solar cells contain a photoactive layer and two electrodes with different work functions (shown in Figure 3.3). The anode is normally a semitransparent oxide layer, such as indium tin oxide (ITO), which is covered with the PEDOT:PSS. The PEDOT:PSS normally acts as a hole transporter and exaction blocker. Moreover, it is also used as an anode buffer material for smoothening the surface, which enhances the adhesion of the upper light-absorbing layer, sealing the active layer from oxygen and keeping the anode material from diffusing into the active layer [27–29]. On the top of the PEDOT:PSS, the 100–200 nm photoactive layer which is formed using the mixture of QDs and polymer is deposited by the spin-coated method. The cathode, typically made of Al, Ca, Ag and Au, is vacuum deposited on top of the photoactive layer. With this device structure, the light is illuminated through the glass substrate.

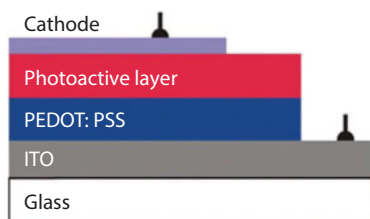


Figure 3.3 Device structure of polymer/QD solar cells.

3.2.4 Progress of Polymer/QD Solar Cells

3.2.4.1 Device Based on Cd Compound

Cadmium sulfide (CdS) and cadmium selenide (CdSe) are the two most studied QDs related to solar cell application. Greenham *et al.* were the first to study the photoluminescence and photoconductivity of the materials formed with mixtures of poly(1-methoxy-4-(2-ethylhexyloxy-2,5-phenylenevinylene)) (MEH-PPV) and either CdS or CdSe QDs [30]. The results showed that efficient photoconductivity could be attained at high QD concentrations, with the electrons and holes transporting through the QDs and polymer. Then Huynh *et al.* reported bulk heterojunction solar cells based on poly(3-hexylthiophene) (P3HT) and CdSe QD with 7 nm diameter, confirming that the electron transport is dominated by hopping in networks consisting of QDs [31]. Subsequent studies focused on the solvent selection to optimize the device performance. For example, the QDs dispersion in the polymer could be controlled by the use of binary solvent mixtures [32]. By varying the concentration of the pyridine/chloroform solvent mixture, phase separation was well tuned to the nanometer scale, achieving the higher efficiencies [33–35]. It is noted that Ren *et al.* used 4.0 nm CdS QDs capped with n-butylamine and P3HT nanowires, and adjusted the usage of solvents in the processing. For the so-called non-grafting process, 1,2-dichlorobenzene was the solvent used for both CdS QDs and P3HT nanowires, resulting in the minimum phase segregation of the maximum P3HT/CdS interface. Devices prepared with 80 wt% CdS QDs by a non-grafting procedure showed an average J_{sc} of 1.9 mA/cm², V_{oc} of 0.8 V, FF of 0.40 and power conversion efficiency (PCE) of 0.6%. Compared to this, in the so-called grafting process, P3HT and CdS were formed by first dissolving into 1,2-dichlorobenzene and octane, respectively, then mixing these two solutions together. Devices fabricated using the grafting method, followed by ligand exchange processes using ethanedithiol, obtained the maximum J_{sc} of 10.9 mA/cm², V_{oc} of 1.1 V, FF of 0.35, and obtained the current record efficiency of 4.1% for a hybrid polymer/QD device [36]. As another Cd compound, CdTe QDs have an absorption spectrum extending into the near infrared (NIR) range, however, the first hybrid solar cell based on CdTe QDs showed a very low efficiency of 0.05% [37]. Recently, Chou *et al.* reported a significantly improved efficiency of 3.2% for CdTe-based hybrid solar cells with a monoaniline-capped polymer as the donor [38].

The solar cells based on Cd compound displayed the low PCE, which is owe to the surface ligand covered on QDs forms an obstacle, resulting in the poor charge transfer. Han *et al.* used CdSe QDs with a 4.5 nm diameter crystallized in zinc blende structure, covered with 1-octadecene and

oleic acid and combined with MEH-PPV in solar cells, displaying a low device efficiency [35]. As a result, the formation of bicontinuous donor-acceptor phases and a well-defined interface in the photoactive layer are demanded. An important step in the design of various photovoltaic devices consists of the replacement of original surfactants by new surface ligands to shorten the distance among QDs to improve the charge transport properties. Greenham *et al.* investigated the effects of QD capping ligand on the charge transfer between polymer and CdSe QDs, indicating that the ligand-covered QDs created a barrier layer that prevented the QDs from approaching the polymer [30]. Normally, long-chain ligand-capped QDs could be exchanged with short-chain ligands to enhance the interface area. Carter and coworkers thoroughly investigated P3HT:CdSe blends with tributylamine or butylamine on QDs surfaces and the devices based on butylamine-treated CdSe QDs gave the highest efficiency [39]. Moreover, thiol treatment is an effective method [40, 41]. Wu and Zhang treated CdSe QDs using benzene-1,3-dithiol by a vapor annealing method. As a result, J_{sc} and PCE improved by 70% and achieved a record efficiency of 3.2% for CdSe-based hybrid PVs [42]. Ren *et al.* reported the hybrid PVs based on P3HT and CdS QDs treated with 1,2-ethanedithiol (EDT), displaying a 70% improvement in the efficiency [36]. Zhou *et al.* reported the efficiency of 2% for hybrid solar cells using a combination of P3HT and CdSe QDs treated with hexanoic acid [43, 44]. Fu *et al.* used acetic acid instead of n-butanethiol for the post-deposition treatment of P3HT:CdSe QDs hybrid, leading to an increase of PCE from 1.37% to 1.95% [45]. A different approach was recently demonstrated by Alberio *et al.*, who prepared CdSe QDs (3.0 nm) capped with C_{70} and observed that the chemical linkage between QDs and fullerenes is key for an efficient charge transfer from QD to fullerene. Three devices with the active layer as P3HT with CdSe capped with C_{70} (P3HT/ C_{70} -CdSe), with CdSe capped with pyridine (P3HT/py-CdSe) and a mixture of P3HT, PC₇₀BM and CdSe capped with pyridine (P3HT/PC₇₀BM/py-CdSe) were investigated. The results showed that P3HT/ C_{70} -CdSe device obtained the highest efficiency. The addition of C_{70} did not have a strong influence on the average carrier lifetime, but the polymer/QD interface modified by C_{70} produced an obstacle between polymer/ C_{70} [46]. To overcome the QDs aggregation after the surface treatment, Khan reported the *in-situ* synthesized CdTe QDs in P3HT, resulting in an increased J_{sc} and V_{oc} [93].

Additionally, Cd-based QDs were added in binary solar cell to increase light harvesting, forming the ternary solar cells. De Freitas systematically investigated a ternary system based on PFT, PCBM, and TOPO-coated CdSe QDs to fabricate polymer/PCBM/CdSe ternary solar cells [47]. The

concentration of CdSe QDs affected device performance, resulting in an enhancement of PCE from 0.5% (PFT/PCBM binary cell) to 0.8% (containing 20 wt% PFT, 40 wt% PCBM, 40 wt% 4.0 nm CdSe) after the incorporation of CdSe into the PFT/PCBM system. The CdSe QDs could contribute to light harvesting and charge generation, but the transport of electrons and holes to the electrodes was carried out by PCBM and the polymer, respectively [48]. Moreover, the size of CdSe QDs also affected J_{sc} , which was related to the different-sized QDs resulting in different light absorption and film morphology. The larger-sized QD resulted in the higher J_{sc} and efficiency [49]. Ternary systems based on P3HT/PCBM/CdSe were investigated by adding 2.5 nm CdSe QDs functionalized with methyl viologen. The addition of CdSe QDs promoted an increase in the J_{sc} , displaying the QDs absorption contribution in 560–600 nm. However, for a low ratio of CdSe, the photocurrent was accompanied by a space charge build up that limited device performance, which could be caused by deep trapping states localized either on QDs surfaces or at an interface between QDs and another component such as P3HT, LiF, PCBM or PEDOT [50]. Fu *et al.* investigated the device based on FTO/TiO₂/P3HT:PCBM:CdSe (10:10:1)/PEDOT:PSS/Ag, producing an efficiency of 3.05%. The CdSe QDs tend to aggregate and facilitate electron transport. The cell exhibited a high stability and retained the high efficiency after 21 days of exposure to air [51]. Alves *et al.* showed that the chemical structure of the polymer has a decisive influence on the efficiency of ternary systems based on QD/polymer/fullerene. By comparing the device containing different thiophene units in the polymer chain (PFT and P3HT), it was shown that polymers are easily coordinated with inorganic QDs and tended to aggregate, precluding electron transport through the fullerene phase [52]. Peterson *et al.* also confirmed that the presence of a strong interaction between S-containing 3-hexylthiophene units in P3HT with CdSe QDs is the reason for the space charge build up that limited device performance [50]. Khan *et al.* fabricated P3HT/PCBM/CdS QD solar cells; the PCE increased from 0.45% (no CdS) to 0.87%, mainly originating from the formation of a charge transfer complex between P3HT and CdS resulting in an increase in J_{sc} . Thermal annealing resulted in the further enhancement of PCE to 0.95% [53]. Obviously, in ternary systems, inorganic QDs mainly improve the charge transport but not the light absorption. Jotterand and Jobin reported a decreased device efficiency after the incorporation of hexadecylamine-capped CdSe QDs with diameters ranging from 2.2 nm to 6.3 nm into a P3HT/PCBM device. The authors intended to use CdSe as an additional photoabsorber but not the electron acceptor; however, the increased absorbance originating from CdSe QDs did not

contribute to the photocurrent. Moreover, the maximal efficiency generated by the photovoltaic cell was inversely proportional to the absorption. The decreased efficiency originated from the hexadecylamine coating, in which the charges were trapped after they were generated [54].

3.2.4.2 Device Based on Pb Compound

The Pb-based QDs have some exceptional properties including (i) efficient light-absorbing capacity from visible and near-IR regions, (ii) relatively long excitonic lifetime (200–800 ns), (iii) high quantum efficiency (80%), (iv) comparatively large Bohr radius (18 nm for PbS and 46 nm for PbSe), and (v) well water solubility. Sargent *et al.* prepared ITO/PETOT/MEH-PPV/PbS/Mg hybrid solar cells with the photoactive layer consisting of MEH-PPV and PbS QDs via simple blending approach. The device displayed tunable optical absorption by the quantum size effect, however, the EQE at 975 nm that originated from PbS contribution was extremely small (0.0008%) [55, 56]. Wang *et al.* synthesized PbS QDs using MDMO-PPV as a capping material and dispersed them into MDPO-PPV; however, the efficiency was still low [57]. Colbert *et al.* provided spectroscopic evidence that hole transfer produces long-lived charges in PbS/PDTPQx-HD (poly(2,3-bis(2-hexyldecyl) quinoxaline-5,8-diyl-alt-N-(2-hexyldecyl)dithieno[3,2-b:20,30-d]pyrrole)) films [58]. Watt *et al.* combined PbS QDs covered with short-chain amines with MEH-PPV, obtaining efficiencies of 0.7% and 1.1% under white light and single wavelength irradiation, respectively. Compared to the original oleate ligands covered PbS, the charge carriers are more efficient to tunnel through the ligand barrier, or to transfer directly from the conjugated polymer to QDs surface [59]. Seo *et al.* combined PDTPBT with oleic acid-capped PbS QDs treated with 1,2-ethanedithiol. The PDTPBT/PbS device (wt% = 10/90) exhibited an overall PCE of 2.07%, and the insertion of a TiO_2 layer between the active layer and metal electrode resulted in the improved PCE of 2.70% [60]. Zhang *et al.* employed two different-sized PbS QDs to fabricate a bilayer configuration solar cell with the structure of ITO/ZnO/PbS/polymer/MoOx/Ag. Small-sized QDs led to the increased V_{oc} in comparison to devices fabricated with larger QDs. The surface ligands on QDs were replaced with 1,3-benzenedithiol by post-deposition treatment, in combination with two polymers, PCDTBT and PCPDTTBT, respectively. Compared to the device without the polymer layer which displayed a PCE of 1.89% (V_{oc} of 0.41 V, J_{sc} of 10.35 mA/cm², FF of 0.44), the PCE reached 4.22% after inserting a 15 nm-thick PCPDTTBT layer, with overall improvement in all photovoltaic parameters (V_{oc} of 0.63 V, J_{sc} of 12.99 mA/cm², FF of 0.52). In contrast to PCPDTTBT, the

insertion of a 21 nm-thick PCDTBT layer reduced J_{sc} and FF to 2.54 mA/cm² and 0.11, respectively, resulting in a poor PCE of 0.20% [61]. Piliego *et al.* combined post-treated PbS QDs by 1,4-benzenedithiol and the narrow band gap polymer PDPPTPT, delivering an optimized performance with J_{sc} of 12.5 mA/cm², V_{oc} of 0.47 V, FF of 49% and PCE of 2.9% [62]. Moreover, low band gap polymers containing *N*-alkyldithienopyrrole moieties, such as poly(2,3-didecyl-quinoxaline-5,8-diyl-*alt*-*N*-octyldithieno[3,2-*b*:2',3'-*d*]pyrrole) (PDTPQx) [63] and poly[2,6-(*N*-(1-octylnonyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PDTPBT), were blended with PbS QDs and incorporated with a TiO₂ buffer layer to improve the maximum PCE up to 3.8% [60]. Photoinduced absorption spectroscopy provided evidence for long-lived, microseconds to milliseconds, positive polarons on the conjugated polymer, PDTPQx-HD, following selective photoexcitation of the PbS QDs [58, 64]. A device based on low band gap polymers compared to common conjugated polymers (i.e., P3HT, MDMO-PPV, etc.) indicates that the energy level alignment is the crucial parameter to achieve more efficient energy conversion in these systems. However, in spite of the significant improved efficiency in the device based on low band gap polymers and PbS QDs, the device efficiency is fairly low compared to PbS QDs based on all-inorganic thin-film solar cells, that PbS were combined with a metal oxide layer to fabricate solar cell [65, 66].

Jiang *et al.* were the first to report a hybrid solar cell that consisted of P3HT and PbSe QDs [67]. The device showed PCE of 0.04%, confirming an effective electron transfer between the polymer and PbSe QDs. Cui *et al.* prepared a P3HT/PbSe hybrid photovoltaic device using 6 nm diameter PbSe QDs stabilized with oleate as a capping layer. Although the PCE was only 0.14%, the infrared response (780–1600 nm) contributed to 33% of the overall photocurrent [68]. Jiang *et al.* prepared the device consisting of different-sized PbSe QDs with either MEH-PPV or P3HT, obtaining sizeable photovoltaic response from the ultraviolet to the infrared range [69]. Noone *et al.* used photoinduced absorption spectroscopy (PIA) to investigate mixtures of PbSe QDs with P3HT or MDMO-PPV, suggesting hardly the presence of charge transfer or energy transfer [70]. Nam *et al.* presented hybrid solar cells with high efficiency utilizing ternary composite consisting of poly[2,6-(4,40-bis-(2-ethylhexyl)dithieno[3,2-*b*:20,30-*d*]-silole)-*alt*-4,7(2,1,3-benzothiadiazole)] (PSBTBT), 4 nm PbS_xSe_{1-x} QDs and PbS_xSe_{1-x} nanorods with 4 nm diameter and an elongated length of 30–40 nm. With a ratio of PbS_{0.7}Se_{0.3} QD:nanorod = 0.3:0.7, a PCE of 3.4% was obtained, originating from the stronger light harvesting and charge separation ability, with efficient electron transport via straight nanorod pathways that are continuously interconnected by QDs [71].

3.2.4.3 Device Based on CuInS_2

Copper indium disulfide (CuInS_2) has a small direct band gap of 1.5 eV that is well matched to the solar spectrum, a large absorption coefficient ($\alpha = 5 \times 10^5 \text{ cm}^{-1}$) and a low toxicity, and is regarded to be a promising light-absorbing material for solar cells [72]. We studied hybrid solar cells based on CuInS_2 QDs systematically, fabricating solar cells with different structures, and observed the influence of QDs crystal phase and size on device performance. We synthesized 2–4 nm zinc blende CuInS_2 QDs and applied them in polymer/ CuInS_2 QDs solar cells. CuInS_2 QDs act as an effective electron acceptor for the hybrid solar cells with a wide spectral response extending from 300 to 900 nm, by allowing the efficient charge separation for neutral excited states produced either on the polymer or on the QDs. Moreover, surface treatment to the CuInS_2 QDs by removing the major part of capping agent on the QDs enhances the efficiency of the energy transfer from polymer to QDs and ultimately the solar cell performance [73]. Then we prepared different-sized chalcogenide CuInS_2 QDs and fabricated the solar cells. The solar cells exhibit size-dependent J_{sc} and V_{oc} with a wide spectral response extending from 300 to 900 nm. The increased V_{oc} for the smaller QDs is the result of the enlarged energy level difference between the polymer and CuInS_2 QDs due to the E_{c} of QDs shifted to the higher level, while the higher J_{sc} mainly correlates with the increased MEH-PPV/ CuInS_2 specific interfacial area for the more effective charge transfer from polymer to CuInS_2 resulting in the formation of more effective interpenetrating networks for charge transport [74]. Moreover, CuInS_2 QDs were incorporated into oriented polymer/oxide solar cells to fabricate ternary solar cells. Previously, Nam *et al.* reported P3HT/PCBM/ CuInS_2 solar cells where CuInS_2 QDs were incorporated into organic matrix at different weight ratios; the results showed that the CuInS_2 QDs at low weight ratios could improve device performance and mainly originated in the increased light harvesting for higher J_{sc} [75]. We prepared MEH-PPV- CuInS_2 hybrids as light harvester by blending chalcogenide CuInS_2 QDs with polymer MEH-PPV at equal weight ratio, which were filled into the interspaces between the TiO_2 nanorods (NA) in preparing MEH-PPV- $\text{CuInS}_2/\text{TiO}_2$ -NA solar cells. The MEH-PPV- $\text{CuInS}_2/\text{TiO}_2$ -NA devices exhibited a much higher J_{sc} than MEH-PPV/ TiO_2 -NA cells, due to the broad complementary absorption of organic and inorganic components for light harvesting, additional MEH-PPV/ CuInS_2 and $\text{CuInS}_2/\text{TiO}_2$ interfaces for exciton dissociation, and the formation of continuous and highly condensed interpenetrating CuInS_2 -QDs channels for effective charge transport [76]. In order to improve the device performance, surface

treatment of the chalcogenide CuInS_2 QDs was carried out and applied in polymer-based solar cells. As a result, MEH-PPV- $\text{CuInS}_2/\text{TiO}_2$ solar cells based on the treated CuInS_2 QDs obtained much higher device performance than that containing the pristine CuInS_2 QDs, achieving the efficiency of 2.02% under AM 1.5 illumination [77]. Furthermore, the change in electron acceptor leads to various device performances, we studied the device using ZnO as electron acceptor. Ternary MEH-PPV- $\text{CuInS}_2/\text{ZnO}$ solar cells fabricated by incorporating zincblende CuInS_2 QDs into pristine MEH-PPV as light harvester and vertically aligned ZnO nanorod array as electron acceptor. Results showed that MEH-PPV- $\text{CuInS}_2/\text{ZnO}$ solar cells exhibited increased photovoltaic performance compared to MEH-PPV/ZnO devices and the device properties were dependent on the weight ratio (R) between CuInS_2 and MEH-PPV. The results showed that a certain concentration of QDs would improve J_{sc} and V_{oc} ; however, the obviously decreased J_{sc} , V_{oc} at too high R value is attributed to the serious aggregations of CuInS_2 QDs, resulting in QDs not being well dispersed in the organic matrix [78]. Moreover, the effects of photoactive layer structure, such as the change of spinning rate, thermal annealing temperature, annealing order and annealing method, on device performance are observed to obtain the maximum device performance. Crystal phase of QDs is another important factor impacting device performance. We fabricated MEH-PPV- CuInS_2 /oxide nanoarrays hybrid polymer-based solar cells, using wurtzite (or chalcopyrite) CuInS_2 QDs and ZnO nanoarrays (or TiO_2 nanoarrays). The devices based on metal oxide and CuInS_2 that belong to the same crystal system contribute to the increased device performance, which possibly results from the more effective energy transfer and transport between metal oxide and CuInS_2 with the same crystal system [79]. Additionally, the inorganic composited material based on CuInS_2 was synthesized and applied in solar cells. Binary $\text{TiO}_2/\text{CuInS}_2$ -core/shell nanoarrays (TCIS-NAs) with polycrystalline film of zincblende CuInS_2 quantum dots as shell and single-crystalline TiO_2 nanorod as core are applied in polymer-based solar cells with MEH-PPV infiltrating into TCIS-NAs, producing a MEH-PPV/TCIS-NAs device with ternary photoactive layer. Devices exhibit a much better performance depending on the CuInS_2 shell thickness (L), and the similar L -dependences of J_{sc} , V_{oc} and electron lifetime (or charge recombination) in the MEH-PPV/TCIS-NA solar cells mainly correlated with the photon absorption by CuInS_2 [80]. Furthermore, we observed the influence of CuInS_2 with different depositing methods on the device performance of polymer-based solar cells consisting of TiO_2 - CuInS_2 composites. Results showed that TiO_2 - CuInS_2 composites prepared by the deposition of CuInS_2 on TiO_2 with one-step

method displayed much higher J_{sc} which correlated with the increased absorptivity and charge separation efficiency, and the higher V_{oc} originated from the presence of strong interaction between TiO_2 and $CuInS_2$, resulting in the effective modification of TiO_2 surface by $CuInS_2$ [81].

3.2.5 Strategy for Improved Device Performance

3.2.5.1 QDs Surface Treatment

The QDs synthesized by the colloidal method are capped with a protective layer of surfactant molecules with long hydrocarbon chains to prevent aggregation of QDs. However, the surfactant also prevents the effective charge transfer between QDs and polymer. As a result, good contact between organic and inorganic components should also be considered as a prerequisite due to the improvement in charge separation at the contact interface.

3.2.5.1.1 Pyridine Treatment

Greenham *et al.* first investigated the effects of capping ligand on the initial charge transfer process between polymer and CdSe QDs. The luminescence quenching of polymer was observed as a manifestation of the effective exciton dissociation. MEH-PPV could not be quenched effectively by 4 nm diameter CdSe QDs which were capped with a long alkyl chain such as trioctylphosphine oxide (TOPO); however, the PL quenching was efficient after TOPO was treated with pyridine. Obviously, the TOPO created a barrier layer which isolated QDs and polymer, preventing the charge transfer [30]. An effective method to overcome the problem is exchanging the long-chain ligand with short-chain ligands, which could enhance the interface area and ensure effective charge transfer. As a result, ligand exchange using pyridine has normally been used for improving the device performance of hybrid solar cells. We carried out the surface treatment on $CuInS_2$ QDs which covered the $-SPh$ capping groups by using 4-tert-butylpyridine (TBP) in an ethanol solution at 60–80 °C. The TBP treatment removes the major part of the $-SPh$ groups existing in the ligand 4-bromothiophenol (HSPh) on QDs, resulting in an increase by 23% in the PL quenching efficiency. As a result, the MEH-PPV/ $CuInS_2$ device based on TBP-treated $CuInS_2$ QDs displayed significantly improved V_{oc} , J_{sc} and IPCE values. However, some polymers (such as P3HT) are not soluble in pyridine, resulting in the effect of surface treatment not ideal. Alivisatos *et al.* removed the excess pyridine by pumping the device under low pressure ($<10^{-6}$ mbar) or thermal annealing and obtained a significantly improved device performance [32].

3.2.5.1.2 Amine Treatment

Sargent *et al.* produced a device based on MEH-PPV and PbS QDs treated with octylamine [82]. There was significant improvement compared with devices fabricated from OA-coated QDs, demonstrating the effectiveness of amine treatment. Later on, Carter *et al.* thoroughly investigated P3HT:CdSe blends with different short ligands (including tributylamine, butylamine, and pyridine) on the surface of QDs [39]. The devices based on butylamine-treated CdSe QDs gave the highest efficiency, therefore, butylamine was proved to be an effective surfactant for PbS QDs, with the polymer/PbS device demonstrating an efficiency of over 0.5% [63]. In addition to these direct treatments of long ligands with short amines, Prasad *et al.* developed an indirect method [83]. They replaced the bulky synthesized ligand with tert-butyl N-(2-mercaptoethyl) carbamate containing a tert-butoxycarbonyl (tBOC) group. The tBOC group releases isobutene and carbon dioxide during thermal annealing, leaving cysteamine covered on the QD surface. In addition to the amine treatment, hydrazine treatment is another effective method. The PbSe QDs capped with alkanedithiols having different-length hydrocarbon chains displayed an increase in the mobility of charge carriers with a decrease in the interparticle distance [84]. Moreover, treatment of PbSe QDs capped with oleic acid in hydrazine led to an increase in the conductivity of QD layers by ten orders of magnitude [85]. It should be noted that the conducting properties of QD layers depend on both the mobility and concentration of free charge carriers. Replacement of the ligands on QD surfaces can lead to the decreased interparticle distance contributing to the higher charge carrier mobility and an increased concentration of free charge carriers. Treatment of the QD surfaces with ligands as well as thermal annealing both lead to the changes in the defect number.

3.2.5.1.3 Thiol Treatment

Colloidal QDs have benefitted a lot from thiol treatment, resulting in the development of solar cells. Wu *et al.* managed to perform thiol treatment using a vapor annealing method. The blends consisting of P3HT and pyridine-treated CdSe QDs were spin-coated on the substrate, then the substrate was left for vapor annealing using benzene-1,3-dithiol. The benzene-1,3-dithiol was diffused into the blend film and replaced some of the original ligands during the vapor annealing process. As a comparison, the J_{sc} and PCE improved by 70%, achieving a record efficiency of 3.2% [42]. Prasad *et al.* employed a post-ligand exchange method to replace OA ligands with EDT. The blends of PDTPBT and OA-coated PbS QDs were firstly spin-coated, then EDT solution in acetonitrile was spin-coated

on the blend film to exchange OA. With a layer of TiO_2 QDs as the hole-blocking layer covering the cathode, the device exhibited a high efficiency of 3.78% [60], significantly higher than previous PbS-based hybrid PVs [63]. Ren *et al.* reported a high efficiency of 4.1% for the device based on P3HT and CdS QDs treated with EDT, displaying a 70% improvement in PCE [36]. In the experiment, CdS QDs were first treated with butylamine, then dipped in EDT solution in acetonitrile for 30 s, followed by solvent annealing overnight. More recently, Brutchey *et al.* demonstrated that tert-butylthiol-treated CdSe QDs displayed better solubility in tetramethylurea at high concentrations. The device based on P3HT and tert-butylthiol-treated CdSe QDs obtained an efficiency of 1.9% without any thermal annealing process [86]. Compared with an amine or pyridine, the thiol provides stronger binding with CdSe QDs. As a result, the ligand exchange with thiol obtained higher efficiency, thereby improving charge transfer efficiency. In addition, the different ligand treatments resulted in the changed LUMO and HOMO levels of the QDs. The tert-butylthiol-treated CdSe QDs resulted in a favorable band alignment between the HOMO of P3HT and the conduction band of CdSe, contributing to the increased V_{oc} to 0.8 V [86, 87]. Moreover, vacuum treatment or thermal annealing led to the changes in the conductivity type of the films. The n-butylamine-treated PbS QDs exhibited p-type conductivity because oxides covering the surface of QDs acted as p-type dopants. The subsequent treatment with ethanedithiol caused the surface concentration of oxides to decrease, which led to a decrease in the concentration of charge carriers. Piliago *et al.* fabricated PDPPTPT/PbS QD solar cells, in which the active layer (PDPPTPT/PbS) was soaked several times in an acetonitrile solution of 1,4-benzenedithiol to replace the oleic acid ligands. It is noted that this device was prepared without using poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) as the hole transporting layer [62].

3.2.5.1.4 Acid Treatment

The ligand covering the QDs surface could also be replaced by an acid. Prasad *et al.* used a post-chemical treatment to exchange long ligands with the acid [88]. The film that was spin-coated from a solution consisting of P3HT and OA-capped PbS QDs was immersed into an acetic acid solution for 30 min for ligand exchange. The photoluminescence (PL) decay confirmed that the charge transfer was enhanced for the acid-treated film. As a result, this post-chemical treatment resulted in a significant improvement in the device performance. Zhou *et al.* reported P3HT/CdSe solar cells with the efficiency of 2% by using CdSe QDs treated with hexanoic acid [43, 44]. The surface treatment of spherical CdSe QDs was carried out

by a novel post-synthetic treatment method, in which QDs were washed with hexanoic acid; the amine ligand was reduced during the washing process. The QDs improved their solubility after acid treatment, resulting in a high concentration of CdSe QDs in P3HT beneficial to the formation of efficient percolation networks and improved charge transfer processes [43]. Ulteriorly, Zhou *et al.* applied the same procedure to different ligand-capped CdSe QDs, then mixing the treated-QDs with the low band gap polymer PCPDTBT, obtaining a record efficiency of 2.7% (J_{sc} 8.2 mA/cm², V_{oc} 0.59 V and FF 55%). Moreover, the device based on PCPDTBT and 7.1 ± 0.4 nm CdSe QDs treated by hexanoic acid exhibited a further improvement of the PCE up to 3.1%, which originated from the improved connectivity of the interpenetrating network due to removing the ligand. Then, an alternative way for further improving QDs network connectivity was obtained by mixing QDs and nanorods together. The presence of nanorod is beneficial to the electron transport in the vertical direction, and the QDs could reduce nanorod nanorod horizontal aggregation. Devices based on the mixture of QD and nanorod exhibited a higher efficiency of 2.8% [89]. In addition, the size of QDs impacts the influence on the device performance. The device based on PCPDTBT and acid-treated large-sized CdSe QDs exhibited a PCE of 3.1% (J_{sc} 8.6 mA/cm², V_{oc} 0.63 V and FF 0.56), which was attributed to the formation of an improved connection of the inorganic network [89]. We carried out a solvothermal approach to remove the organic amine ligand with hexane acid on the surface of CuInS₂ QDs. Results showed that the decreased organic amine ligand on the surface of CuInS₂ QDs both promoted QDs aggregation and quenched the polymer fluorescence more effectively. As a result, MEH-PPV-CuInS₂/TiO₂ solar cells based on the treated CuInS₂ QDs obtained much higher device performance than that containing the pristine CuInS₂ QDs, achieving the efficiency of 2.02% under AM 1.5 illumination [77].

3.2.5.2 *In-Situ Synthesis of QDs*

In-situ synthesis of the QDs in a polymer film, which is performed by the deposition of films from polymer solutions containing a soluble precursor of the inorganic QDs, followed by the decomposition to form QDs in the pre-deposited film, is also an effective method for the better contact between QDs and polymer. Reynolds *et al.* reported *in-situ* growth of CdS QDs from the precursor in P3HT and prepared the solar cells; the device displayed much higher V_{oc} and J_{sc} than that from the blend of P3HT and CdS QDs capped by oleic acid or hexylamine. Different from the discrete, unaggregated QDs in the pre-synthesized QDs, *in-situ* grown CdS QDs

formed an interconnected layer, resulting in the different morphology interfaces. Clearly, the contact between the conducting polymer and QDs, as well as between QDs and QDs, is essential for the better photovoltaic performance, which is due to the interfacial contacts impacting charge separation and transport [90]. Dayal *et al.* employed dimethylcadmium and sulfur as precursors and a mixture of 1-octadecene and 1,2,4-trichlorobenzene as solvents; the growth of QDs was carried out at 230 °C in P3HT solution. Note that the use of high temperature and high boiling-point solvents yields more homogeneously dispersed CdSe QDs [91]. Peng *et al.* employed P3HT as the ligand to synthesize 5–10 nm sized P3HT-capped CdSe QDs in a mixed solution of 1,2,4-trichlorobenzene and dimethyl sulfoxide and produced P3HT/CdSe solar cells. The device exhibited V_{oc} of 0.54 V, J_{sc} of 4.25 mA/cm², FF of 57.5% and PCE of 1.32% [92]. Khan *et al.* used cadmium acetate dihydrate and tellurium powder in trioctylphosphine as precursors to synthesize CdTe QDs in P3HT. The ratio of P3HT to cadmium acetate precursor plays a significant role in controlling the size of QDs. After the P3HT/CdTe device is combined with PCBM, J_{sc} is increased [93]. Similarly, a polymer/CuInS₂ device was fabricated by *in-situ* synthesis of CuInS₂ to obtain 2.8% PCE, using copper and indium xanthates as precursors that would decompose in the polymer matrix during the thermal treatment [94].

3.2.5.3 Polymer End-Group Functionalization

End-group functionalization of polymer is useful for improving the QDs dispersion in the polymer matrix and providing intimate contact between polymer and QDs through covalent interactions to offset the defect originating from the short exciton diffusion distance of the polymer (<10 nm). The P3HT end-groups were functionalized using Br/allyl and H/(–SH) as terminating chemical groups and integrated with CdSe QDs, leading to device efficiency of 0.9% and 0.6%, respectively [95]. Dayal *et al.* synthesized CdSe QDs in P3HT solution without the surfactant and dispersed homogeneously in P3HT. The CdSe-P3HT composites displayed a longer photocarrier lifetime which resulted from the effective photoinduced charge separation without the phase separation [91]. Gradecak *et al.* prepared CdS QDs bounded P3HT nanowires with 10 nm diameter through solvent-assisted grafting and carried out the ligand exchange to enhance the interfacial interactions and contact area, realizing the highest exciton dissociation efficiency with J_{sc} of 10.9 mA/cm, V_{oc} of 1.1 V, FF of 0.35 and PCE of 4.1% [36]. Obviously, polymer functionalization is not only beneficial for controlling the morphology of the photoactive layer, but is also favorable to the charge carrier transport.

3.3 Outlooks and Conclusions

Polymer/QD solar cells have attracted increased interest because the devices offer complementary advantages in organic and inorganic components; however, the PCEs of these devices are currently low, obtaining 3–4% up to date. Device performance optimization may focus on the following aspects.

First, the energy-level alignment at the interface is critical. The weak excitonic absorption in a low band-gap semiconductor cannot provide sufficient light harvesting in the IR region. An optimal band gap of ~ 1.5 eV is suggested for polymers in the polymer/QD device, which is beneficial to obtain the maximum light-harvesting ability and V_{oc} as well. In addition, the LUMO of the polymer needs to be aligned with the conduction band of the QDs.

Second, the control of the polymer/QD interface remains vital because good contact between organic and inorganic components should be considered for the improvement in charge separation at the contact interface. The removal of the original ligands with long insulating alkyl chains can improve the efficiency of charge transfer and transport. However, ligand exchange rate could not be controlled precisely, and exchange effects are not well understood. Another effective approach to obtain better contacts between QDs and polymers is the *in-situ* growth of QDs directly in a polymer matrix. However, QD size, shape, and distribution within the polymer matrix are difficult to control, which would impact the dielectric, electronic, optical, and structural properties of the photoactive layer, and ultimately the device performance.

Third, ideal phase separation is necessary for the charge transportation and influences J_{sc} directly. A continuous network in the photoactive layer can greatly reduce the possibility for charge carriers to hop between QDs, which resulted in the charge recombination during their transportation to the electrode. Moreover, the mobility of holes in polymers is much lower than that of electrons in QDs, which resulted in the different transport rate and influenced the electron recombination. As a result, how to obtain the effective interpenetrate network structure and balance the electron and hole transfer rate to minimize the recombination loss is important to increase the device performance.

Acknowledgment

This chapter was supported by the International Cooperation Project of Anhui Province (1503062018), Visiting Research Scholar Project for

Young/Middle Excellent Talents of Anhui Province (gxfxZD2016110) and Preeminent Youth Foundation of Anhui Polytechnic University (2016JQ002).

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Hole Transporting Layers in Printable Solar Cells

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Abstract

The incessant evolution of organic and hybrid solar cells has demonstrated that a multilayer architecture is required for an optimum device functioning. Although more attention has been traditionally focused on the active layer materials, it is the interfacial materials, placed between the electrodes and the active region, which might play some of the most critical roles in the solar cell. In this regard, interfacial layers can modulate the compatibility between the electrodes and the active layers in terms of morphology, surface energy or energy level alignment. Furthermore, interfacial layers modulate the light absorption working as optical spacers, assist in the exciton confinement and preserve the active layer from damage or degradation. However, the most important role of interfacial layers concerns the charge transport, defining an energy gradient for the selective migration of free charge carriers from the active layer to the electrodes.

This chapter offers a comprehensive description of those materials specifically working as hole transporting layers in organic, dye-sensitized and perovskite solar cells. Conjugated polymers, small molecules, metals, metal oxides, self-assembled monolayers, carbon nanotubes and graphene-based materials will be discussed along with their influence on different aspects aimed at the optimization of the solar cell performance.

Keywords: Hole transporting materials, organic semiconductors, organic solar cells, dye-sensitized solar cells, perovskite solar cells

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4.1 Introduction

The evolution of the photovoltaic technology has experienced incessant progress in the search for more efficient solar cells to make solar energy a legitimate option to solve the present and future problems of world energy demand. Within this context, the last fifteen years have witnessed the emergence of many innovative approaches related to new types of devices targeting solar energy conversion. Among these new devices, the contribution coming from the application of materials of organic nature has been very significant. These novel organic materials have given shape to the topic of organic and hybrid solar cells, where materials with an organic and inorganic origin are combined in the photovoltaic device. Since the first report of the photovoltaic effect being observed for a device based on organic materials [1, 2], the research on organic and hybrid solar cells has always focused on the crucial objective of improving the comparatively lower efficiency of these devices compared to other types of solar cells, mainly based on the use of inorganic semiconductors. In this regard, several alternatives have been intensively studied with the aim of fabricating competitive devices. The most representative examples of these devices can be classified into three groups: organic solar cells (OSCs) [3, 4], dye-sensitized solar cells (DSSCs) [5] and perovskite solar cells [6]. In turn, these groups can be divided into different categories according to some typical characteristics of these devices such as the type of photoactive material, the internal architecture of the solar cell or the fabrication method, to mention a few. The intensive research on organic and hybrid photovoltaics has led to independently certified efficiency records for laboratory-scale results (solar cells with an area of 1 cm^2) as remarkable as 11.2% for OSCs, 11.9% for DSSCs and 19.7% for perovskite solar cells [7]. These great advances necessarily come from the interdisciplinary exploration of the physics, chemistry and engineering involved in these solar cells. The fabrication methods and device architecture have settled protocols for both laboratory and large-scale manufacturing. One of the most important aspects related to the industrial viability of this new generation of photovoltaic devices focuses on the reduction of the fabrication cost, which can be achieved by producing printable solar cells. Accordingly, a plethora of printing techniques have been adapted to implement continuous roll-to-roll fabrication [8]. Moreover, solution processing also implies the development of printing methods and inks to be applied on plastic substrates which confer on the final devices very attractive technical properties such as lightness and flexibility. Besides, the progress in organic photovoltaics is inherently associated with the synthesis and evaluation of innumerable materials whose properties can be tuned up to improve light harvesting, thin film morphology or charge transfer processes within the

solar cell. Studies about the principles that govern charge carrier generation and transport in individual organic materials, as well as in the interior of the solar cells [9], where several materials are combined, have enabled a better understanding of the photovoltaic device functioning and degradation [10].

Nevertheless, independently of the research discipline contributing to the optimization of the organic solar cells performance, what has been unequivocally demonstrated is that, as it has just been mentioned, this new generation of photovoltaic devices is inevitably based on a multilayer structure. The distinction of the specific roles that different materials must play to complete the working principles of organic solar cells (exciton generation, exciton diffusion, exciton dissociation, charge transport and charge collection) has led to a high degree of specialization in the investigation of different types of materials for the photoactive layer, the interfacial layers and the electrodes.

Although much research has focused on the active layer materials [11], it is the interfacial materials, placed between the electrodes and the photoactive region, which might play some of the most critical roles in solar cell performance [12, 13]. A very brief description of the different stages for the conversion of solar energy into electricity in organic solar cells can give an idea of the importance of interfacial layers (Figure 4.1). Thus, instantaneously after the sunlight absorption, mainly by the donor component of the active layer, an exciton is produced. A sequence of steps must rapidly occur in order to generate free charge carriers before that excited state relaxes back to its ground state. Differently from inorganic semiconductors, the exciton generated in organic molecules maintains the hole and the electron tightly bound due to the low dielectric constant typical of most organic materials. For this reason, a second material, with an appropriate energy level distribution, must intervene in the active layer to promote an electron transfer that enables the exciton dissociation (commonly an offset of around 0.3 eV

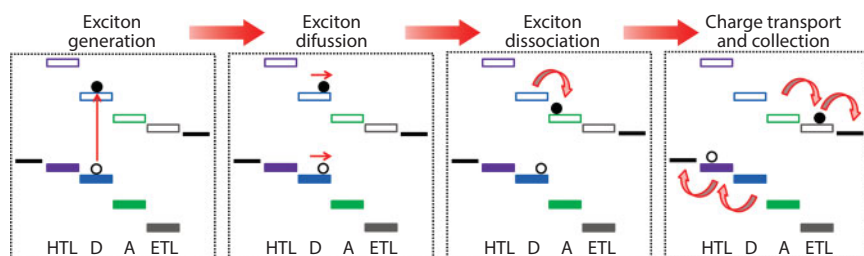


Figure 4.1 Schematic representation of the working principle in organic solar cells. HTL: Hole Transporting Layer; D: Donor material; A: Acceptor material; ETL: Electron Transporting Layer.

is required between the donor and acceptor energy levels to accomplish the exciton dissociation) [14]. Since this charge transfer process takes place at the interface between the donor and the acceptor material, the exciton, which can be generated anywhere within the layer corresponding to the photoactive material, must diffuse to reach that donor-acceptor interface. Nevertheless, the diffusion length of the exciton within the organic layer is normally limited to a few tens of nanometers, which implies that a compromise has to be reached to work with the optimum thickness for that layer to absorb as much as possible of the incident radiation, but also favoring that most of the produced excitons can shift towards the donor-acceptor interface [15]. Once the exciton has dissociated, the resulting free charge carriers have to travel to the electrodes so that an electrical current is produced. Accordingly, the electrons and holes percolating towards the electrodes have to go through another interface. Usually, the materials employed in the active layer and those used as electrodes do not have an ideal energy level correlation, making more difficult the free charge carrier collection at the contacts. Moreover, the electrons and holes leaving the active layer must selectively follow the right polarity pathway with electrons migrating to the cathode and holes moving to the anode. It is precisely at this stage of the photocurrent generation mechanism where interfacial layers become indispensable to overcome these difficulties and to obtain an efficient solar cell. Consequently, the insertion of additional layers between the photoactive region and the electrodes will improve the charge transport and charge collection processes and this will have a beneficial effect on the parameters that determine the solar cell efficiency (Power Conversion Efficiency, PCE), namely open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor (FF). Depending on the location of the interfacial layers, they can be classified as hole transporting layers (HTLs), placed between the active layer and the anode, or electron transporting layers (ETLs), placed between the active layer and the cathode.

It is worth highlighting that for a material to function as interfacial layer, it must fulfill certain requirements:

- i. Transparency to the solar radiation so as not to interfere with the light absorption by the active layer.
- ii. Energy level alignment with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the donor and acceptor materials in the active layer respectively. Correlation between HOMOs is required for hole transporting layers and correlation between LUMOs for electron transporting layers (Figure 4.1).

- iii. Energy level alignment with the electrode work function. Correlation with the anode work function is required for hole transporting layers and correlation with the cathode work function for electron transporting layers.
- iv. Charge mobility. Since the charge carriers have to be transported from the active layer to the electrodes, a balanced transport rate and good charge mobility will attenuate the possibility of charge accumulation and recombination.
- v. Large HOMO-LUMO energy gap. Depending on the internal morphology of the active layer (especially in the case of bulk heterojunctions), the possibility exists that some charge carriers shift towards the wrong electrode. The presence of HTLs with a high energy LUMO, or ETLs with a low energy HOMO, would work as a blocking barrier for the wrongly directed charge carriers, avoiding a possible short circuit (Figure 4.1).

Despite the number of conditions that should be found in any interfacial layer, their unquestionable utility in organic and hybrid solar cells has encouraged the search for materials which can contribute to the optimization of the device performance. An enormous variety of results have been reported for interfacial layers in solar cells with a single active layer. Besides, apart from the mentioned hole transporting layers and electron transporting layers, in the case of stacked or tandem solar cells an additional interfacial layer has to be inserted between the different subcells to enable the collection of holes and electrons and their subsequent recombination. This offers an idea of the broad area open for research within the topic of interfacial layers not only in solar cells but also in the field of organic electronics in general. Accordingly, increasingly specialized investigations have been developed throughout the last few years. For that reason, this chapter will present the fundamentals of the main roles played by interfacial layers as well as a wide view of the most recent advances regarding hole transporting materials in organic and hybrid solar cells.

4.2 Hole Transporting Layers in Organic Solar Cells

4.2.1 Utility of Hole Transporting Layers

The strategic location of charge transporting layers between the photoactive section and the external electrodes enables them to share two different interfaces with quite dissimilar features, namely organic-organic and

organic-inorganic (the inorganic side typically being a metal or a conducting oxide). Consequently, all the important functions of an interfacial layer could be summarized in the essential objective of softening any abrupt change, in the most ample sense, due to the differences in the physical and chemical properties at both sides of the interfaces. Among the main roles of any interfacial layer should be noted the modulation of energy level alignment, the influence on the morphology, the blocking effect and control of charge carrier transport, the adjustment of the optical field and the protection of the active layer.

4.2.1.1 Energy Level Alignment at the Interfaces and Effect on the Open-Circuit Voltage

The interaction at the interface between two materials will depend on the extent that their orbitals get to overlap, thereby producing a hybridization at the contact surface. Considering the interfaces formed by organic materials deposited on metals, metal oxides or other organic materials, the degree in the strength of surface interactions will depend on the adsorption process. When a weak physisorption occurs, as is typical for solution processed or evaporated thin films, it can be assumed that no hybridization takes places, or is negligible. Conversely, when the interface is produced by chemisorption and covalent bonds are formed, as is the case in the formation of self-assembled monolayers, a significant alteration of the molecular orbitals at the interface will complicate the description of the interfacial system. Nevertheless, it is well established that good correlation of the energy levels at both sides of the heterojunction is required to achieve efficient charge transport through it. However, the electronic structure at the surface of the solids is difficult to accurately characterize due to the number of causes that can affect it, thereby producing some modifications with respect to the properties in the bulk. The atomic or molecular order at the surface of the material, the presence of even minor impurities or the methodology followed for the buildup of the interface can influence the way in which interactions happen at the heterojunction.

In the case of metal electrodes, the atoms at the surface can release electrons through a tunnel effect which creates a negatively charged layer within a distance of angstroms from the surface, leaving positively charged ions at the outermost layer of the solid. This charged double layer creates a surface potential that alters the metal work function at its surface. Additionally, the distribution of the surface electron density can be modified by the adsorption of an organic material. In turn, this will change the surface dipole with a concomitant decrease in the metal work function. This process is known as the push-back effect or pillow effect [16].

As far as organic semiconductors are concerned, the weak noncovalent interactions governing the molecular arrangement in the solid state result in an electronic structure which does not allow the application of the band theory, but very much resembles that of the isolated molecules with localized energy levels. In this regard, the HOMO and LUMO orbitals could be interpreted as the higher limit of the valence band and the lower limit of the conduction band respectively, to establish an analogy between the organic semiconductors and their inorganic counterparts. In π -conjugated systems, such as those representative of organic semiconductors, when an electron is withdrawn from the HOMO or an electron is added to the LUMO a polaron is formed with the appearance of energy levels within the original HOMO-LUMO gap. These intragap energy levels correspond to the definition of SOMO (single occupied molecular orbital) and set the basis for the integer charge-transfer (ICT) model which has been extensively studied to explain the electrode/organic contacts with negligible hybridization at the interface (Figure 4.2) [17].

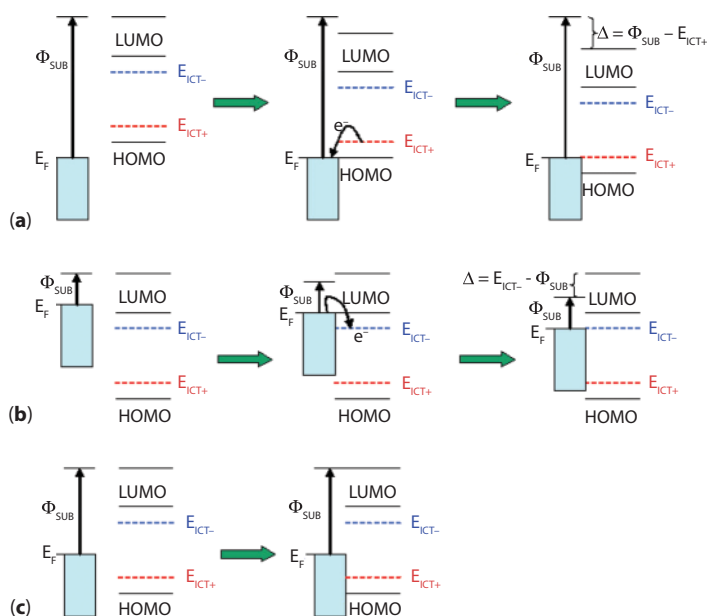


Figure 4.2 Evolution of the energy-level alignment at the substrate interface upon physisorption of a π -conjugated organic material (small molecule or polymer). (a) $\Phi_{\text{sub}} > E_{\text{ICT}+}$: Fermi-level pinning to a positive integer charge-transfer state; (b) $\Phi_{\text{sub}} < E_{\text{ICT}-}$: Fermi-level pinning to a negative integer charge-transfer state; (c) $E_{\text{ICT}-} < \Phi_{\text{sub}} < E_{\text{ICT}+}$: vacuum level alignment. The charge-transfer-induced shift in vacuum level, Δ , is shown where applicable. (Adapted with permission from [17]; Copyright © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

Despite the weak interaction at the interface formed by physisorbed organic molecules on the surface of an electrode, charge carriers can still be transferred via a tunneling mechanism through a distance of very few angstroms. The relative energy between the electrode work function ($\Phi_{\text{sub.}}$) and the polaronic energy levels ($E_{\text{ICT}+}$ or $E_{\text{ICT-}}$) will determine the direction of the charge transfer process. When the polaronic level is located below the LUMO, it is defined as a negative integer charge-transfer state, $E_{\text{ICT-}}$. Conversely, when the polaronic level is located above the HOMO, it is defined as a positive integer charge-transfer state, $E_{\text{ICT}+}$. Accordingly, three possible scenarios are set out:

- i. $\Phi_{\text{sub.}} > E_{\text{ICT}+}$: the work function of the electrode is larger (applying an absolute value criteria) than the $E_{\text{ICT}+}$. In this case, electrons will spontaneously be transferred from the organic molecules to the electrode. This leaves an interface section, a few angstroms thick, where a layer of positively charged molecules face a negatively charged layer on the electrode surface and an interfacial dipole comes up. The charge transfer and the potential associated with this dipole evolve until an equilibrium is reached. When this happens, the $E_{\text{ICT}+}$ from the organic molecules at the interface and the Fermi energy from the electrode have equalized, which is known as Fermi level pinning. This result, connected to the potential energy at the interface, produces a decrease of the vacuum level or, analogously, decreases the work function of the electrode.
- ii. $\Phi_{\text{sub.}} < E_{\text{ICT-}}$: the work function of the electrode is smaller than the $E_{\text{ICT-}}$. In this case, electrons will spontaneously be transferred from the electrode to the organic molecules. This leaves an interface section with a positively charged surface on the electrode and a negatively charged surface on the organic material. The corresponding dipole and its associated potential keep growing until an equilibrium is reached. When this happens, the $E_{\text{ICT-}}$ from the organic molecules at the interface has equalized the Fermi energy from the electrode, producing the Fermi level pinning with the concomitant up-shift of the vacuum level or, in other words, increases the work function of the electrode.
- iii. $E_{\text{ICT}+} > \Phi_{\text{sub.}} > E_{\text{ICT-}}$: the work function of the electrode is between $E_{\text{ICT}+}$ and $E_{\text{ICT-}}$. The formation of this contact displays an energy barrier that hinders the spontaneous charge

transfer at the interface. Under these circumstances, no interfacial dipole is created and the vacuum level remains aligned throughout the interface.

The Fermi level pinning can be interpreted as the formation of ohmic contacts. In this regard, several experiments combining a series of substrates, covering a wide range of work functions ($\Phi \approx 3.45\text{--}6.1$ eV), and a series of organic π -conjugated materials (polymers and small molecules), covering a wide range of HOMO energies (ionization potential $\approx 4.0\text{--}6.0$ eV), have been carried out to prove that the Fermi level is effectively pinned according to the principles described by the integer charge-transfer model [18, 19].

It is worth mentioning that this model has also been used to study organic/organic interfaces where weak noncovalent interactions adapt to the context where the ICT model is applicable [17]. Studies carried out on several organic/organic interfaces concluded that the interface dipole depends on: i) the subjacent substrate work function; ii) the deposition sequence of the multilayer stack.

Concerning the critical effect that energy level alignment has on the performance of organic solar cells, it has been demonstrated that the formation of ohmic contacts plays an important role in determining the open-circuit voltage of organic solar cells. When ohmic contacts are formed between the electrodes and the donor and acceptor material in the active layer (anode/donor:acceptor/cathode), the open-circuit voltage is defined by the difference between the E_{ICT^+} in the donor material and the E_{ICT^-} in the acceptor material. The same V_{oc} dependence is observed when ohmic contacts include Fermi level pinning through interfacial layers (anode/HTL/donor:acceptor/ETL/cathode). Accordingly, as previously mentioned for the organic/organic interfaces, the sequence of energy levels in the stacked materials can improve the formation of ohmic contacts, which highlights the important effect that hole transporting layers can have on the V_{oc} [20].

When non-ohmic contacts are present, the open-circuit voltage is determined by the difference between the work functions of the electrodes.

Different experiments have been reported where in order to maintain the architecture of a solar cell, only one of the electrodes has been changed to modify its work function. The results showed that in those cases where Fermi level pinning was confirmed and the ohmicity of the contacts was achieved, the V_{oc} was independent from the identity of the electrode and was determined by the energy levels of the components in the active layer. Conversely, in the presence of non-ohmic contacts the V_{oc} changed with the work function of the different tested electrodes [21].

Finally, molecular doping of organic semiconductors has been proved as a valid strategy to modulate the energy level alignment at the interfaces [22]. Nevertheless, the control of the doping ratio and its effect on the properties of the doped interfacial layer, as well as the availability of appropriate *p*- and *n*-dopants, make the development of this approach a bit more intricate.

4.2.1.2 *Definition of Device Polarity, Charge Transport and Use as Blocking Layer*

The basic structure of an organic solar cell (anode/donor:acceptor/cathode) necessarily involves the use of a transparent electrode and a metal back electrode. Moreover, two different architectures have been employed in the fabrication of these solar cells: conventional architecture, where the transparent electrode works as anode, and inverted architecture, where the transparent electrode works as cathode. Although many different materials and composites have been used as transparent electrodes, indium tin oxide (ITO) is the most common resource due to its high transmittance and low resistance. Besides, since the work function of ITO can form adequate contacts with many different interfacial materials, it could be used as transparent electrode both in conventional and inverted organic solar cells. Therefore, for solar cells including interfacial layers (anode/HTL/donor:acceptor/ETL/cathode) the polarity of the device for the appropriate collection of electrons and holes can be determined by the properties of those selective transport layers. Additionally, in those solar cells using an active layer based on a blended bulk heterojunction, the charge carriers might randomly migrate to any of the electrodes. The alignment of the E_{ICT^+} levels in the HTL and the donor material and the E_{ICT^-} levels in the ETL and the acceptor material will guide the charge carriers towards the right electrode. Furthermore, for those charge carries that could eventually shift in the wrong direction, the interfacial layers play the additional role of blocking layers. In this regard, HTLs with a high LUMO energy could block electrons trying to migrate to the anode and ETLs with a low HOMO energy would block holes migrating to the cathode.

The transport of the charge carriers from the active layer to the electrodes requires a low resistance so that recombination processes or charge accumulation within the device is reduced. In agreement with this, the interfacial materials also contribute to enhance the charge transport and to balance the conduction of electrons and holes. Consequently, this can decrease the series resistance, R_s , which intervenes in the optimization of the fill factor of the solar cell [23].

Additionally, the excitons generated within the active layer also have to diffuse to the donor/acceptor interface to dissociate. However, the direction for their diffusion is not predetermined. For that reason, the use of the interfacial layers with wide optical gaps will also enable the confinement of the exciton within the active layer.

4.2.1.3 *Optical Spacer*

The thickness of active layers in organic solar cells is limited by the inherent low charge transport of organic materials. Thus, sunlight absorption will require materials with very high extinction coefficients. When light enters the solar cell through the transparent electrode, it goes across the active layer and the fraction that has not been absorbed is reflected by the back electrode and passes again through the active layer, forming a standing wave. Accordingly, modulation of the optical field within the device and control of the interference processes, depending on the refractive index and thickness of the multilayer structure, can improve light absorption. Interfacial layers which are transparent to sunlight can be used as optical spacers. The optimization of the interfacial layer thickness will distribute the electric field of the incident radiation, positioning its maximum in the section where the active layer is located. Alternative approaches, such as diffraction gratings, curved solar cells or inclusion of plasmonic nanostructures, have also been used to engineer light trapping inside the solar cell [13].

4.2.1.4 *Modulation of the Active Layer Morphology and Use as Protective Layer*

Free charge carrier generation and the subsequent percolation within the active layer are highly conditioned by the microstructure of the organic materials. Considering the active layer as a mixture of at least two materials (polymers or small molecules with electron-donor or electron-acceptor character), the arrangement of each of them, the phase segregation into different domains and the size of these domains are features whose results are certainly difficult to control since many different aspects can intervene in their modification. As expected, the molecular structure is the most critical feature to control the morphology of the materials. The composition of the mixture is also a very important feature influencing the microstructure of the active layer. Besides, the method employed for the processing of the active layer includes many different factors: film deposition technique (vacuum or solution processing), solvents, additives and annealing (thermal or vapor), to mention a few.

All the above reasoning is related to the conditions that might affect the microstructure of the active layer itself. However, if we consider the active

layer as a certain section of the solar cell, the effect of other parts, such as the electrodes and the interfacial layers, on the morphology of the active layer should also be considered. For example, the roughness of the ITO surface can represent a problem when trying to achieve the right interpenetration of the materials mixed in the active layer. This difficulty can be solved by inserting an interfacial layer which softens the surface for the subsequent deposition of the active layer. Another important property to bear in mind is the correlation between the surface energy of the materials in the active layer and that of the underlying substrate. This will affect the phase segregation of the components blended in the active layer. Accordingly, depending on which material has a lower or higher surface energy, this will segregate to the air interface or the substrate interface, respectively. The substrate surface energy can be modified by changing the nature of the substrate itself or can be altered by coating with an interfacial layer. This strategy is especially useful in the case of interfacial materials attached as self-assembled monolayers.

Apart from the effect that interfacial layers have on the morphology of the photoactive materials, they can also preserve the stability of the active layer. A common protocol for the fabrication of organic solar cells implies the evaporation of the metal electrode. In the event that metal particles reach the active layer they could fatally damage the device. Also, a chemical reaction at the metal interface would have a detrimental effect on the solar cell functioning. Accordingly, the presence of interfacial layers could protect the active layer from these adverse scenarios.

Moreover, organic materials often experience degradation in the presence of environmental oxygen and water. For that reason, optoelectronic devices based on organic materials are normally encapsulated to extend their lifetime. Nevertheless, the development of interfacial materials with a high stability towards ambient conditions and certain hydrophobicity could also attenuate the degradation of organic solar cells.

4.2.2 Overview of Materials Used as Hole Transporting Layers

4.2.2.1 *Polymers*

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), 1, is by far the most employed polymeric anode interfacial material in organic photovoltaic devices (Figure 4.3). PEDOT:PSS is a water-soluble mixture of PEDOT doped with PSS. When deposited as thin film, the layer surface is mostly covered by PSS with the sulphate groups facing the surface. The success of PEDOT:PSS relies on its high conductivity, transparency in the visible range of the spectrum, insolubility in the most

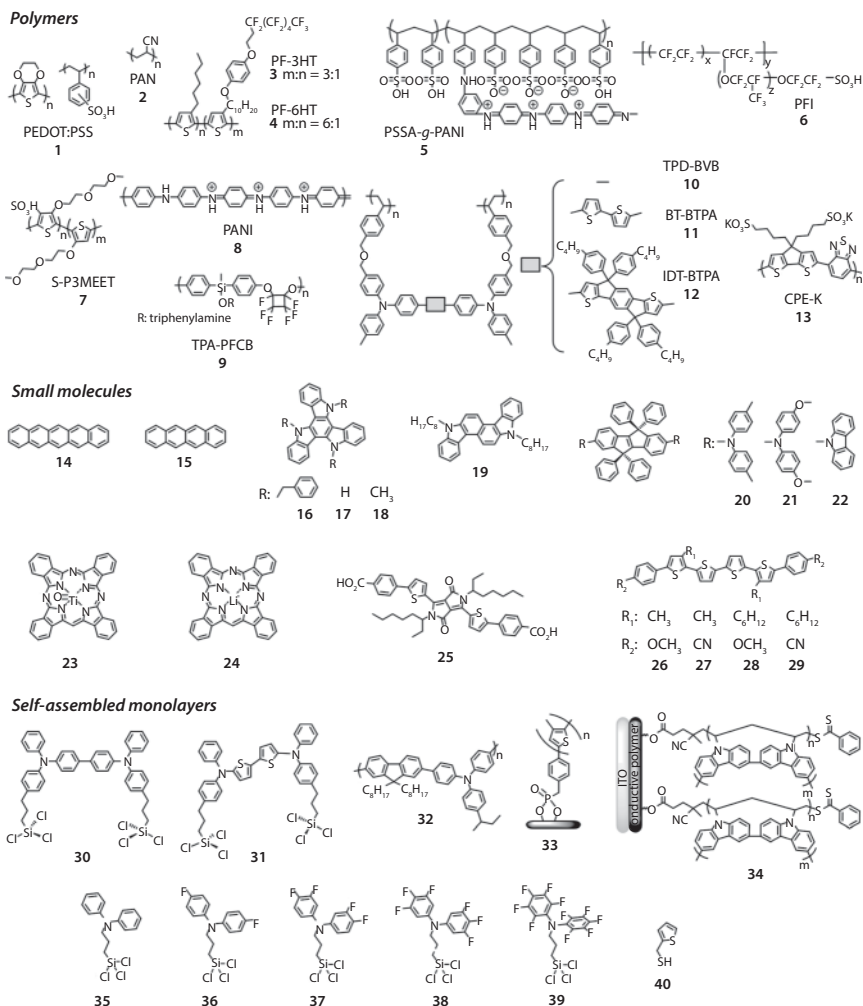


Figure 4.3 Chemical structures of polymer, small molecules and self-assembled monolayers used as hole transporting materials in organic solar cells.

frequently used organic solvents, easy processing conditions and suitable energy level alignment with the work function of the commonly used ITO electrode. Additionally, its presence softens the roughness of the ITO surface, reducing the occurrence of pinhole defects in the device. Besides its wide use in single junction solar cells, PEDOT:PSS combined with other electron transporting materials performs as a proficient intermediate layer and optical spacer in tandem solar cells [24]. However, despite the high efficiency reported for solar cells using PEDOT:PSS as

anode interfacial layer, its hygroscopicity and acidic nature can cause the device degradation and the reduction of its lifetime [25]. The etching of the ITO surface induced by the PEDOT:PSS acidity represents one of the most serious drawbacks of this material. Furthermore, these problems are accentuated at higher temperatures. Accordingly, it is necessary to explore alternative materials which equal or surpass the performance of PEDOT:PSS but emend its drawbacks. In this search, PEDOT:PSS still represents the reference HTM to assess the effectiveness of the novel materials.

As a strategy to partially overcome some of the PEDOT:PSS limitations, different kinds of additives have been added to its aqueous solution. The presence of additives can contribute to improve the homogeneity of the film morphology, increase the HTL conductivity and promote the phase segregation between PEDOT and PSS domains. Furthermore, in the case of devices with an inverted architecture, additives can reduce the surface tension of the hydrophilic PEDOT:PSS layer, improving its adhesion to the hydrophobic underlying active layer.

Surfactant additives, such as Triton X-100 [26], Zonyl FS-300 [27], Surfynol 104 [28], or Capstone Dupont FS-31 [29], have been explored to evaluate the above-mentioned features. Analogously, polar organic solvents with high boiling point, such as dimethyl sulfoxide [30], ethylene glycol [31], isopropanol [32], methanol and/or *ortho*-dichlorobenzene [33], can contribute to enhance the HTL conductivity by several orders of magnitude either upon blending with PEDOT:PSS or by a post-deposition treatment of the HTL. The high dielectric constant of the solvents promotes the shielding of the Coulombic interactions between the PEDOT and PSS moieties which induce their phase separation. Accordingly, the formation of PEDOT-enriched regions leads to better charge transport pathways. A similar effect was observed for silica nanodots (SND) functionalized with hydroxyl or amino groups [34]. In this case, the higher surface potential of the SND-NH₂ additives induced a stronger phase separation which led to smaller domains in the PEDOT:PSS films, outperforming the devices prepared with neat PEDOT:PSS.

Metal nanoparticles can improve the device operation when blended with PEDOT:PSS owing to both electrical and optical effects. In fact, the HTL conductivity can be adjusted by the variation of the nanoparticle concentration [35]. Besides, gold and silver nanoparticles exhibit localized surface plasmon resonance (LSPR) in the visible range of the spectrum, which enhances the absorption of the light-harvesting layer. Thus, the improved photon absorption, together with the increased electrical conductivity in

the PEDOT:PSS blend, results in higher J_{sc} and better PCE than pristine PEDOT:PSS interlayers [36].

Alternatively to the employment of additives, an evaporated thin layer of LiF (1 nm) on top of PEDOT:PSS can smooth the surface morphology and enhance the surface energy and the wettability of the active layer [37, 38]. It was observed that while the presence of LiF mainly contributed to the V_{oc} increase, PEDOT:PSS mostly improved the J_{sc} . So, the synergistic effect of its combination as a dual buffer layer resulted in the enhancement of both parameters, yielding better PCEs [39]. Similarly, V_2O_5 nanowires deposited onto PEDOT:PSS also formed dual HTL. This combination showed better electron blocking ability and also contributed to improve light absorption at the active layer due to the reflection and refraction of the incident light [40]. This finally resulted in the improved J_{sc} and PCE (3.56%) with respect to the single interlayers of V_2O_5 (3.12%) and PEDOT:PSS (3.08%).

Water-soluble phenol formaldehyde resin (BSPF), bearing alkyl sulfonic acid groups, was developed for the preparation of PEDOT:BSPF interlayers with the aim of replacing the acidic non-conducting PSS dopant of PEDOT [41]. After optimizing the PEDOT:BSPF ratio, both higher pH values and conductivities than PEDOT:PSS were obtained. As a result, PEDOT:BSPF-1:4 yielded identical PCE to PEDOT:PSS.

Among the alternative polymer materials to replace PEDOT:PSS as anode interfacial layer, polyacrylonitrile (PAN), **2**, is a cost-effective candidate [42]. Devices with 1 nm of PAN showed photovoltaic parameters that were quite comparable to those of the reference PEDOT:PSS-based device. Interestingly, PAN-based devices maintained 60% of their initial efficiency after more than nine days in contrast to the rapid degradation of the PEDOT:PSS-based devices.

A different strategy for HTLs involves the use of polythiophene block copolymers, where some of the thiophene comonomers had a fluorinated side chain substituent. Following this approach, two novel diblock copolymers (PF-3HT, **3**, and PF-6HT, **4**) were synthesized and evaluated in devices with inverted architecture [43]. When these copolymers were blended together with the active layer materials (P3HT:[60]PCBM) a spontaneous segregation occurred after spin coating. Whereas the P3HT segments in the HTL copolymer embedded into the P3HT regions of the active layer, the perfluorinated segments in the copolymer remained on the surface of the active layer, interacting with the anode metal. The resulting interfacial dipole shifted the anode work function, which improved the solar cell efficiency when compared to the PEDOT:PSS control device.

Water-soluble and self-doped conducting copolymers based on poly(styrenesulfonic acid) (PSSA) covalently grafted with polyaniline (PANI), PSSA-g-PANI, **5**, also represent an attractive alternative to PEDOT:PSS [44]. The electrical properties of PSSA-g-PANI can be adjusted by changing the molar ratio of the monomers (PSS and ANI) during the polymerization process. Unlike PEDOT:PSS, PSSA-g-PANI copolymers exhibited higher electrochemical stability, electrical conductivity and transparency, lower acidity and smoother film surfaces. Thus, the J_{sc} and V_{oc} were slightly increased but the FF remained almost unchanged, resulting in a higher PCE (3.99%) than PEDOT:PSS (3.31%).

Furthermore, the PSS-g-PANI work function can be further modified by the addition of a perfluorinated ionomer (PFI), **6**, improving the energy level alignment [45]. Due to the low surface energy of the fluorinated dopant, it can also self-segregate, producing PFI-enriched top surfaces. Interestingly, it was also observed that the presence of PFI enhanced the device lifetime. A related analysis concerning the effect of doping with PFI was performed by using self-doped (S-P3MEET), **7** [46]. The employment of the S-P3MEET/PFI HTLs increased the V_{oc} values up to ~1 V and improved the overall device functioning. Camphorsulfonic acid (CSA) has also been utilized as doping agent for PANI, **8**, allowing the HTL work function tuning through the extent of interlayer protonation [47]. Remarkably, devices having PANI:CSA films exhibited a superior long-term stability compared to those with PEDOT:PSS [48]. Only a 15% reduction of the initial efficiency values was observed for the PANI:CSA-based devices after one and a half years, in contrast to the faster complete degradation with PEDOT:PSS.

Dual polymer-based hole transporting layers frequently offer better results than HTLs based on a single component. This has been studied for different PEDOT:PSS combinations [49]. Interfacial *p*-doping has been observed for polymers having an ionization energy smaller than the PEDOT:PSS Fermi energy. In these cases PSS can work as a *p*-dopant. However, when the ionization energy was higher, as in the case of APFO-3 or F8BT, no reaction happened. This fact led to the presence of a larger hole extraction barrier as evidenced by the observed S-shaped I-V characteristics.

An efficiency improvement was also achieved for a dual anode interfacial layer based on electrochemically deposited polyaniline (PANI), **8**, nanofilms covered with PEDOT:PSS [50]. The superior performance of the dual HTL was ascribed to the increased conductivity of the double interlayer caused by the interactions between the PANI nitrogen atoms and the sulfonic groups of PSS. This led to an additional doping of the PANI film and decreased the series resistance of the PANI/PEDOT:PSS interface. Another successful example of double interlayers (polymer:PEDOT:PSS)

employed *in-situ* polymerized triphenylamine-containing polyperfluorocyclobutane (TPA-PFCB), **9** [51]. The implementation of a layer of TPA-PFCB between PEDOT:PSS and the ITO electrode improved the electron blocking ability of the hole selective layer.

One more interesting approach to replace PEDOT:PSS, consists of the use of crosslinkable materials forming a robust film insoluble in common organic solvents. The *in-situ* thermal crosslinking of TPD-BVB, **10**, displayed comparable efficiencies to PEDOT:PSS in inverted solar cells but showed superior long-term stability [43]. A similar situation was observed for NOSbF₆-doped crosslinked BT-BTPA, **11**, and IDT-BTPA, **12** [52]. The implementation of a double HTL composed of a thin layer of doped IDT-BTPA on top of non-doped BT-BTPA increased the electron-blocking ability of the interlayer and also established a good ohmic contact.

Conjugated polyelectrolytes (CPE), **13**, have been mainly employed as ETLs in organic solar cells and scarce attention has been paid to their evaluation as HTMs. This has been mostly motivated by the decrease of the ITO work function due to interfacial dipole interactions or to the relatively low electrical conductivities of most CPEs. Nevertheless, a thin layer of CPE (8 nm) proved to be a useful HTL, with polymer solar cells reaching an 8% PCE [53]. These results rely on its relatively higher and homogeneous electrical conductivity and on its neutral pH value. Its general applicability was also assessed in small molecule-based OSCs.

4.2.2.2 Small Molecules

The use of π -conjugated systems, commonly known as small molecules only to make a difference to the larger polymer materials, represents an alternative approach that could have certain advantages in the topic of organic electronics. Perhaps the most important feature to be highlighted is the fact that small molecules are always unequivocally characterized. Since the purity of organic materials becomes a critical aspect when it comes to their participation in charge transport processes, small molecules can be perfectly purified by applying several techniques so that the molecular structure is perfectly elucidated, and therefore do not have the problem of polydispersity and chain defects intrinsic to polymer chemistry. Regarding the processing of small molecules, due to their smaller size, thin films can be prepared by thermal evaporation, which normally allows better control of the morphology. Nonetheless, solution processing is also applicable to this type of organic materials.

Establishing a connection with the above-discussed polymer materials, apart from the utility of small molecules as additives in polymer HTLs,

thin films of molecular materials have been combined with PEDOT:PSS to define dual hole transporting layers. This approach has been used by inserting a pentacene, **14**, film between the blended active layer and a PEDOT:PSS anode buffer layer (Figure 4.3) [54]. The optimization of the pentacene film thickness (4 nm) enhanced the electromagnetic field distribution, contributing to a better light absorption, which subsequently resulted in a higher J_{sc} and PCE. Similar results were obtained for a dual HTL PEDOT:PSS/tetracene, **15** [55]. The acene, with a wide optical gap, played the role of exciton blocking layer. Moreover, the presence of the tetracene layer increased the crystallinity and modified the morphology of the zinc phthalocyanine in the flat heterojunction active layer, allowing a more efficient light harvesting and producing a significant improvement in the short-circuit current, which led to a PCE = 5.8%.

Triazatruxene-based materials typically behave as good hole transporters. Accordingly, N,N',N'' -tribenzyltriazatruxene, **16**, has been successfully used, in combination with MoO_3 , to form a dual hole transporting layer in flat heterojunction small molecule solar cells [56]. The organic film greatly improved the optical and electric field distribution inside the solar cell. Also, its high-lying LUMO blocked electrons escaping from the active layer. A fast hole mobility and reduced charge recombination was measured for the devices incorporating the tribenzyltriazatruxene and contributed to the improvement of J_{sc} and FF. Triazatruxene, **17**, and its N,N',N'' -trimethyl derivative, **18**, also admit solution processing in methanol, facilitating the fabrication of inverted organic solar cells [57]. Their good energy level alignment and charge mobility led to a noticeable rise of J_{sc} by selectively extracting holes from the active layer.

Chemical doping was a useful strategy to improve the hole conductivity of another fused carbazole system such as 1,8-dioctylcarbazolo[4,3-*c*]carbazole, **19** [58]. Then, this material was used as HTL in the fabrication of small molecule flat heterojunction solar cells with conventional and inverted architecture. Enhanced functioning was obtained for conventional devices, due to a better energy level alignment along the multilayer stack and the consequent minimization of charge accumulation.

The charge transport ability of the HTLs depends much on the thin film morphology, which can subsequently be modified by post-processing annealing. In this regard, a series of 5,10-dihydroindeno[2,1-*a*]indenes, **20–22**, with different diarylamino substituents were evaluated as hole transporters, showing better performance after thermal annealing due to their increased crystallinity and decreased roughness and surface energy [59].

Similarly, titanylphthalocyanine (TiPc), **23**, used as HTL in inverted solar cells, can experience a transition between phase-I (H-aggregate) and phase-II (J-aggregate) by vapor annealing. This change in the morphology can condition the solar cell performance [60].

The electronic properties at the anode/HTL interface can be altered by the presence of interface dipoles. That is the case of a lithium phthalocyanine (LiPc), **24**, interfacial layer [61]. The direction of the dipole induced by this HTL caused the upshift of the vacuum energy level, favoring the alignment of energy levels not only at the ITO/LiPc interface but also at the LiPc/ZnPc (donor) interface. Curiously, this was not observed for other phthalocyanines with similar ionization potentials.

A strong surface dipole also formed at the ITO surface after a thermally induced chemical reaction with a thin layer (1–5 nm) of evaporated $C_{60}F_{36}$ [62]. Fluorine-carbon bonds broke at the fullerene and new fluorine-indium bonds formed on the ITO surface. The resulting surface dipole reduced the ITO work function and caused a better energy level alignment between the Fermi level of the ITO and the HOMO of the donor material in the active layer. Additionally, it was observed that the surface modification with annealed $C_{60}F_{36}$ improved the morphology of the chloroaluminum phthalocyanine in the active layer. These two factors led to an increase of all the solar cell parameters, giving better results than a control device fabricated with PEDOT:PSS as HTL.

Diketopyrrolopyrrole (DPP) with appended *p*-carboxyphenylthiophene groups, **25**, was processed from alcohol solution (methanol or ethanol) for the fabrication of inverted solar cells [63]. This material formed part of a dual HTL combined with MoO_3 . After annealing the DPP film deposited onto the active layer, the formation of an improved crystalline nanostructure was observed, enabling better adhesion of the MoO_3 layer. The strong dipole generated from the interaction between the carboxylic groups and the metal oxide enhanced charge transport at the interface, producing higher J_{sc} reaching efficiencies of 7.6%.

Tetrathiophene functionalized with end-capped *p*-methoxyphenyl or *p*-cyanophenyl groups and alkyl chains, **26–29**, improved the inverted solar cell performance when compared to Alq_3 as HTL [64]. Although it is not a common situation, the oligothiophene showed absorbance at long wavelengths which contributed to an improved light absorption and the subsequent enhancement of the short-circuit current. This was confirmed by analyzing the effect of the HTL thickness. Besides, the HOMO alignment with the active layer contributed to improve hole extraction.

4.2.2.3 *Metals*

A very thin layer of gold (0.5 nm average thickness) can tune the anode work function and contribute to a better energy level alignment at the electrode interface [65]. Such a thin layer does not interfere with the transmittance of the transparent anode, since only 15% coverage of the electrode surface with gold nanodots has proved to be enough to exceed the performance of devices prepared with a 50 nm layer of PEDOT:PSS.

4.2.2.4 *Metal Oxides*

Transition metal oxides, such as MoO_3 , V_2O_5 , WO_3 or NiO , possess high work functions, optical transparency in the entire visible region, good charge carrier mobilities and environmental stability, which make them excellent candidates to be used as hole-transporting and electron-blocking materials in optoelectronic devices [66]. Metal oxide thin films can be formed by many different physical methods, including either solution or thermal evaporation techniques [67, 68].

Molybdenum oxide has gained significant attention and has become one of the most popular transition metal oxides as a cost-effective alternative HTL in organic solar cells. The reported efficiencies are quite comparable or superior to those achieved with PEDOT:PSS [69–71].

Despite MoO_3 behaving as an excellent hole injection material, there are evidences of its *n*-type nature owing to the proximity of its Fermi energy level to the conduction band minimum [72]. Consequently, due to its deep valence band edge, holes are not transported to the electrode through that valence band but via the shallow defect states created in its band gap due to the presence of oxygen vacancies. These states act as *n*-type dopants and give rise to the Fermi-level pinning at the MoO_3 /active layer interface. The hole extraction can then be explained by the injection of electrons from the electrode through these gap states to the MoO_3 /active layer interface where they recombine with the holes present in the HOMO of the donor. A direct relationship was observed between the depth of the trap states and the device performance [73]. Shallow traps, which formed upon vacuum annealing of MoO_3 -based devices, led to an enhanced mobility, allowing a more efficient hole transport and, consequently, providing better operational device stability. In contrast, the presence of deeper trap states, which formed in those devices annealed under nitrogen, produced an energy barrier at the active layer/HTL interface. Therefore, the accumulated charges had a detrimental effect on the device efficiency and stability in comparison to the vacuum-annealed ones.

Another interesting feature of MoO_3 is that its work function value (~ 6.8 eV) is quite sensitive to the film processing technique and the environment to which the films are exposed [74]. This can modify the film stoichiometry and, consequently, affect the device functioning. Thus, the work function of thermally evaporated MoO_3 films was higher than that of the evaporated films exposed to ambient atmosphere or the sputtered ones, whether in Ar or Ar/O_2 . The work function reduction was attributed to the contamination with atmosphere exposure and to the different stoichiometric composition. Accordingly, the highest V_{oc} and J_{sc} values were measured for the devices fabricated with the unexposed evaporated films.

Alternatively, the work function of molybdenum oxide films can be decreased by controlling the amount of reduced states (oxygen vacancies) and the hydrogen content by formation of different hydrogenated Mo oxides [75, 76]. Increasing the percentage of reduced species as well as the hydrogenation degree resulted in an invariable reduced work function in comparison to the stoichiometric MoO_3 films. This work function tuning also promoted an improvement of the overall device performance.

The importance of the energy level alignment between the electrode, the interfacial layer and the active layer, with the aim of achieving efficient hole transport and electron blocking, was validated by the comparison of MoO_3 with other transition metal oxides, namely WO_3 , Cu_2O , and NiO [77].

One of the most useful aspects of these inorganic interlayers comes from their remarkable effect on the device long-term stability. Although the mechanisms underlying the degradation processes are still controversial, the influence of light, temperature, moisture and oxygen exposure in the device stability has been investigated [78–81]. In this regard, it has been observed that the V_{oc} is the most affected parameter. It is believed that its decrease with time is associated with the change of the HTL work function due to the previously mentioned oxygen vacancies and lower oxidation states in MoO_{3-x} .

Solution-processed MoO_3 films, namely from sol-gel or nanoparticles, exhibited similar properties to those layers created by vacuum sublimation, with comparable or even larger efficiencies and stabilities than PEDOT:PSS [82–85]. Many novel solution processing methods have been reported, including, for example, film preparation by polymer-assisted deposition [86], low temperature processing from aqueous solution [87, 88], MoO_3 nanoparticles on MoS_2 nanosheets [89], or methanol dispersed solutions [90].

The benefits of using MoO_3 interlayers can be strengthened by working in synergy with other materials. In this regard, the coevaporation of MoO_3

and Au produced a smoother surface which increased the shunt resistance, resulting in an improved FF value while still preserving an optimal HTL transparency [91]. Alternatively, the insertion of a thermally evaporated thin layer of MoO_3 between CuI and the active layer resulted in an improved hole extraction attributed to the formation of more gap states in the MoO_x layers due to the interaction between both inorganic components at the interface [92].

Among the transition metal oxides, nickel oxide is the only one classified as *p*-type semiconductor. This oxide also admits solution or vacuum processing to be deposited as anode interfacial layer [93–95]. However, the deposition method or the post-deposition treatment can affect the NiO work function. For instance, NiO grown by pulsed-laser deposition presents a high enough conduction band minimum (~ 1.8 eV) to effectively block electrons, and a work function (~ 5.3 eV) that suitably matches the HOMO energy levels of common donor materials employed in solar cells [96]. Differently, when solution-processed NiO films are treated with O_2 -plasma, its work function increases, providing an optimized selective contact with the donor component in the active layer [97]. Thin film deposition processes can also alter the oxygen content in the resulting NiO layer, modifying its optical and electrical properties. For example, during the magnetron sputtering of NiO, the film resistivity and transmittance decreased upon increasing the oxygen content in the sputtering gas [98]. This reduced resistivity gave rise to lower series resistance, resulting in a higher FF and PCE.

Regarding the post-deposition treatment, one of the limiting aspects of the solution processing methods is the high annealing temperature required for the formation of NiO films after its deposition. To address this limitation, alternatives, such as the synthesis of NiO nanocrystals, were developed. However, in this synthesis it is necessary to avoid the undesirable reduction of NiO to Ni. This was successfully achieved by decreasing the NiO reactivity, using lithium stearate ligands to protect the NiO surface [99]. The resulting pure colloidal NiO nanocrystals showed a fairly good long-term stability and, when tested as HTL, led to higher PCE than PEDOT:PSS (6.3% vs. 5.2%).

Similarly to the rest of transition metal oxides, V_2O_5 interfacial layers have rendered better devices than those based on PEDOT:PSS hole transporting layers in terms of solar cell parameters and stability. Sol-gel-processed V_2O_5 , without any post-processing treatment, formed amorphous and smooth thin layers with identical electronic structure to thermally evaporated films (WF = 5.6 eV) [100]. These layers displayed a remarkable stability, maintaining almost 80% of the original PCE even after being stored for 400 h in air.

When V_2O_5 was deposited by solution processing during the fabrication of inverted devices, some diffusion of the oxide precursor into the active layer caused a J_{sc} decrease [101]. Nevertheless, the p -doping of the donor material, induced by the precursor infiltration, produced higher FF which partially compensated the J_{sc} loss.

Alternatively, the use of blends of V_2O_5 and WO_3 as complementary materials in HTLs boosted the performance of those devices including just one component [102]. This improvement was mainly attributed to the reduction of the leakage current and better light absorption due to the scattering of reflected light into the active layer.

Interestingly, in a more practical approximation, hydrated vanadium oxide films with different thickness were also evaluated as HTL on flexible substrates during the roll-to-roll fabrication of large area modules. The photovoltaic devices worked properly when tested under indoor and outdoor conditions [103].

Tungsten oxide represents another useful high work function transition metal oxide to be integrated as HTL in organic solar cells. The WO_3 nanoparticles processed from alcohol dispersion formed very functional smooth thin layers after a soft post-deposition thermal treatment of just 80 °C that has been applied to the fabrication of devices with both conventional and inverted architectures [104, 105]. After optimizing the film thickness, solar cells prepared under these mild conditions displayed device characteristics quite similar to other WO_3 HTLs prepared under more harsh conditions, such as O_2 -plasma treatment, or higher annealing temperatures, as well as to the PEDOT:PSS.

Also, WO_3 films grown from solution at room temperature whose hydrolysis and condensation reactions were completed after its storage in air overnight, exhibited a fairly good stability under air and humidity exposure or light soaking in air [106]. Consequently, in contrast to the rapid degradation of the PEDOT:PSS-based devices, only a reduction of ~10% of the initial PCE value was observed after nearly 200 h.

Regarding the processing of GeO_2 thin films, it is highly desirable to overcome the limitations of their high melting and boiling temperatures that make their thermal evaporation under vacuum a complicated process. Accordingly, solution processing approaches have been explored. The deposition from aqueous solution yielded pure GeO_2 films where no other germanium suboxides were detected [107]. Curiously, upon increasing the solution concentration two opposite effects were observed: whereas J_{sc} increased, due to the enhanced optical field location within the active layer, PCE decreased, due to poor thin film morphology caused by its low solubility in water. Nevertheless, the overall efficiency and stability of devices prepared with GeO_2 were better than those fabricated with PEDOT:PSS.

4.2.2.5 *Metal Salts*

Copper(I) iodide (CuI) has been successfully employed as HTL in organic solar cells with conventional and inverted architecture [108]. A curious feature of this ionic HTL is the significant change detected in its work function and valence band edge depending on the thin film processing. Deeper energy levels were measured for samples prepared by vacuum sublimation. Conversely, solvent interactions have been argued as the effect behind the higher energies measured for solution-processed thin films. It is worth highlighting the negligible solar cell sensitivity to modifications in the CuI film thickness, post-processing annealing or solvent, which reinforces the robustness of the hole transporting material. Devices prepared with CuI HTL showed longer stability than those prepared with PEDOT:PSS. Moreover, CuI HTL induces changes in the morphology of the active layer when compared to PEDOT:PSS-based solar cells.

Copper thiocyanate (CuSCN) is a metal pseudohalide intrinsic hole transporting semiconductor with a large optical band gap and a deep valence band edge. Its full characterization as semiconductor for solution-processed thin films prepared at low temperatures, make it a very interesting option for application in optoelectronic devices [109, 110]. The integration of CuSCN as HTL in bulk heterojunction devices (PBDTTPD:[60]PCBM) offered significantly better results than PEDOT:PSS (PCE = 7.20% vs. 5.94%). It is worth mentioning that the superior V_{oc} was not sensitive to the environment in which thin film solution processing was carried out [111].

4.2.2.6 *Carbon Nanotubes*

The renowned charge transport properties of carbon nanotubes make them very suitable materials to be applied as HTL in organic photovoltaics. In this regard, a thin film of solution-processed single-walled carbon nanotubes has been evaluated in bulk heterojunction polymer solar cells. Although a careful optimization of the film thickness (12.2 nm) was necessary to guarantee ITO coverage, light transmittance and acceptable sheet resistance, the resulting device parameters yielded better efficiency than PEDOT:PSS [112].

4.2.2.7 *Graphene-Based Materials*

The ideal 2D structure of graphene with an extended surface of sp^2 -hybridized carbon atoms conferred on this material excellent properties, such as large specific surface area, high transparency, excellent charge transport properties, superior mechanical strength, and high thermal

conductivity, which make it suitable for application in organic electronics in general and consequently in organic photovoltaics too [113, 114]. The most popular graphene derivative, namely graphene oxide (GO), has also become a very attractive material in organic electronics. The oxidized version of graphene can present many different functional groups, such as carboxyl, carbonyl, hydroxyl and epoxide, which make it particularly interesting due to the possibility of participating in chemical reactions to modify the physical and chemical properties of the material. Nevertheless, the disruption of the carbonaceous sp^2 network seriously affects the conducting properties of graphene oxide. Thus, due to its high electrical resistance, when GO is used as interfacial layer in organic solar cells, the device efficiency shows an evident dependence on the GO layer thickness [115, 116]. For this reason, fabrication methods to control GO film thickness have been developed to ensure the full coverage of the electrode while preserving a high film transparency and good electric contact [117]. Nevertheless, this drawback can be minimized by reducing graphene oxide. With this reaction a high percentage of the π -conjugated surface typical of pristine graphene can be recovered, consequently improving the charge transport in reduced graphene oxide (rGO). Moreover, from the morphological point of view, it is worth highlighting that using *p*-toluenesulfonyl hydrazine as reducing agent, instead of the usual hydrazine, significantly improves the quality of the solution-processed thin films, resulting in better device characteristics [118]. Similarly, very good conductivity is achieved with graphene quantum dots (GQDs), which also leads to smooth and homogeneous film morphology [119]. The GQDs-based HTLs outperformed GO and rendered devices with comparable efficiencies to PEDOT:PSS. Regarding the influence of the HTL on the microstructure of the active layer, it has been reported that the use of GO as HTL in CuPc-based solar cells had a beneficial effect on the device performance due to the increase of the grain size and crystallinity of the donor films deposited on it [120].

As just mentioned, chemical reactions on the surface of graphene and graphene oxide can modify the resulting films both in terms of morphology and electronic properties [121–123]. This modulation of graphene-based thin films, especially when they are used as interfacial layers, can be exploited to modify the device operation. For instance, the neutralization of the peripheral carboxylic acid groups of graphene oxide (GO) with cesium carbonate reduced the work function of the resulting GO-Cs to the extent that it could be successfully used as a fully functional ETL in combination with GO as HTL in the same device [124]. Alternatively, the work function of a GO interfacial layer could be continuously shifted upon increasing the concentration of 2,3,4,5,6-pentafluorobenzylphosphonic

acid due to its chemisorption to the GO surface [125]. This energy level tuning decreased the injection barrier and increased the surface recombination velocity, contributing to the improvement of hole collection and V_{oc} . Silane-functionalized GO (sGO) exhibited a slightly higher work function than GO, which enhanced its hole extraction ability and increased the solar cell efficiency [126]. Better electron-blocking ability was also achieved by functionalizing reduced GO with sulfonic acid groups (Sr-GO) [127]. When evaluated as HTL in bulk heterojunction (BHJ) devices with ICBA as acceptor, the formation of a surface dipole in the HTL/BHJ induced by the interactions between the SO_3H groups and the acceptor material in the blended active layer, resulted in better solar cell performance than r-GO.

Other methods that have been commonly used to increase GO conductivity consist of mixing it with certain additives. In this regard, the combination of GO with a polyfluorene derivative presented good packing between both components governed by strong noncovalent interactions between them [128]. As a result, a more efficient hole selective interfacial layer was obtained, which offered comparable efficiencies to PEDOT:PSS. Additionally, the surface doping of the polymers in direct contact with GO is one of the explanations given for the improved electrical contact and enhanced functioning of the devices fabricated with this mixed HTL [129]. Thin layers of GO ($\sim 3\text{--}4$ nm) have also been doped with single-walled carbon nanotubes (SWCNT), showing a conductance in the same order of magnitude as PEDOT:PSS whose thickness is usually tens of nanometers [130]. These GO:SWCNTs work well as hole transporting layers and can act as interconnecting layers in tandem solar cells, providing a good physical separation of the subcells while maintaining an effective electric contact.

Graphene oxide nanoribbons (GONR) combine the semiconducting properties of nanoribbons and the solution processing ability of GO. The hybridization of GONR with multiwalled carbon nanotubes (MWCNT) provided a functional interlayer for OSCs with similar efficiencies to MoO_3 [131]. The GONR/MWCNT work function (4.9 eV) decreased after the deposition of a polyethylenimine (PEIE) layer (4.2 eV) which enabled its simultaneous application as both HTL and ETL in the same device. Improved performance and stability were obtained when implementing GONR/MWCNT as HTL and GONR/MWCNT/PEIE as ETL in comparison to solar cells using transition metal oxides as selective interlayers. Similarly, the combination of inkjet-printed graphene nanoribbons (GNR) and CNT as HTL led to a remarkable efficiency of 7.6%, higher than those devices using a single component only: GNR (5.9%), CNT (4.5%) or PEDOT:PSS (7.3%) [132]. Other derivatives, such as the water-soluble graphene quantum rings (GQR), were used as PEDOT:PSS dopant

in hybrid solar cells. This doped HTL provided a better contact with the electrode and higher conductivities which reduced the device resistance and leakage currents, enhancing the PCE from 5.1% to 7.4% with respect to undoped PEDOT:PSS [133]. It was demonstrated that additional doping of PEDOT:PSS:GO interlayer with Au nanoparticles provided an efficient strategy that further enhanced the device performances [134].

4.2.2.8 Self-Assembled Monolayers

Functionalization of the electrode surface by self-assembled monolayers (SAMs) chemically anchors the material to be used as HTL, leading to a higher degree of hybridization at the interface than in the case of adsorbed hole transporting layers. This modification of the interface can be useful to obtain robust substrates with well-tuned properties. The chemisorption of organic molecules on the substrate surface can alter the electronic structure, enabling a modulation of the electrode work function as well as the interfacial dipole. Moreover, surface energies can be adapted by rational design of the molecule to be assembled with the aim of improving the compatibility between materials in different adjacent layers and preventing dewetting issues.

In this regard, TPDSi₂, **30**, or PABTSi₂, **31**, can form self-assembled monolayers resulting from the reaction between the SiCl₃ end-groups and the OH groups on the ITO surface (Figure 4.3). Additionally, anchored TPDSi₂ or PABTSi₂ can crosslink, forming a robust network. When these SAM precursors and the conjugated polymer (TFB), **32**, are spin-coated together, the crosslinking induced by exposure to air and annealing creates an interpenetrated network where the polymer chains get trapped, forming a robust layer [135, 136]. The transparency, charge mobility and energy level alignment of that layer make it an excellent HTL. Moreover, HOMO energy can be tuned by the different structures of the SAM precursors based on either a biphenyl or a bithiophene spacer. Accordingly, solar cells with different donors, namely MDMO and P3HT, displayed the same efficiency as those devices prepared with PEDOT:PSS but without any of its drawbacks. The crosslinked TPDSi₂:TFB layer has also been used in combination with PEDOT:PSS [137].

Self-assembled poly-3-methylthiophene (P3MT), **33**, can be synthesized following the surface-initiated Kumada catalyst polycondensation [138]. The robust self-assembled P3MT layers can be electrochemically doped to increase the carrier concentration and enhance its ability to work as HTL. Although BHJ solar cells approached the performance obtained for a reference device fabricated with PEDOT:PSS (5% vs. 6%), a lower FF

was measured for the P3MT HTLs. Nevertheless, an interesting advantage of the ITO substrates functionalized with P3MT SAMs is that they can be reused. A simple redoping process allows the use of recycled substrates that lead to devices with almost the same efficiency as the original substrates. A similar approach has been applied to a surface-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization of vinylcarbazol [139]. The poly(*N*-vinylcarbazole) (PVK), **34**, chains formed a brush-like surface. Moreover, these PVK chains can electrochemically crosslink to extend the conjugation of the anchored polymer layer. The use of this surface-grafted PVK as HTL in P3HT:PCBM solar cells, rendered better results than PEDOT:PSS.

Interface engineering induced by self-assembled monolayers was carried out with a series of *N*-(3-trichlorosilylpropyl)-*N,N*-diphenylamino derivatives, **35–39**, bearing a different number of fluorine atoms at the benzene rings [140]. Following this approach, a variation in the electron density is introduced using the fluoro substituents, while maintaining a similar molecular size. After a comprehensive characterization of SAMs on Si/SiO₂ and ITO surfaces, photovoltaic devices based on two different polymer bulk heterojunctions, namely P3HT/PC₇₁BM and PTB7/PC₇₁BM, were fabricated and characterized. It was observed that several solar cells with densely packed SAM-modified substrates performed better than solar cells prepared on bare ITO, confirming the benefit of self-assembled HTLs due to the selectivity in hole collection. Interestingly, a correlation was observed between the charge transfer rate at the SAM-modified substrate and the characteristic parameters of the solar cell, excepting FF. The monolayer linked through a propyl chain and having four fluorine atoms on the head group, **37**, led to results comparable to the traditional PEDOT:PSS layer in terms of V_{oc} , and J_{sc} . However, a noticeably lower fill factor affected the device efficiency.

As a continuation of this work, the packing density of the SAMs was optimized to improve the HTL operation. Since the surface coverage is conditioned by the steric hindrance of the head group anchored to the substrate, combining molecules with identical head groups but different chain lengths can improve the SAM packing density, defining a “super-saturated” surface [141]. Apart from the surface coverage, electronic properties of the substrate were influenced by the effective areal dipole. In agreement with these factors, a change was observed in the substrate work function that became essential to explain the solar cell functioning. Results very similar or even better than those obtained for PEDOT:PSS HTL have been achieved by the supersaturated heterogeneous SAM (PCE = 7.6%).

The use of SAM-based HTLs have also been reported for an ITO electrode covered by a thin film of gold (1 nm) and the subsequent self-assembly of 2-thenylmercaptan, **40** [142]. This simple strategy changed the ITO work function and improved both the V_{oc} and FF. Nevertheless, the gold film partially interfered in the sunlight absorption, causing a decrease in the short-circuit current. In any case, the efficiency of the solar cell was reported to be better than a model device prepared with PEDOT:PSS as HTL.

4.3 Hole Transporting Layers in Dye-Sensitized Solar Cells

Dye-sensitized solar cells, also known as photoelectrochemical solar cells, represent the breakthrough that proves the possibility of applying organic molecular materials to the fabrication of efficient photovoltaic devices. Their success resides in the ingenious combination of a mesoporous semiconducting electrode, an organic or organometallic dye for light harvesting and a redox system for the dye regeneration, coexisting in an extended surface.

The transparent electrode in dye-sensitized solar cells is commonly constituted by either ITO or fluorine-doped tin oxide (FTO). On the top of this electrode a layer of mesoporous semiconducting nanoparticles are sintered to achieve electronic conduction. In this case, TiO_2 is the material that has been more extensively used. The porous surface has to be completely coated by the thin film of the photoactive dye. Although an innumerable amount of sensitizers have been studied, those based on bis(isocyanato) bis(2,2'-bipyridyl)ruthenium(II) complexes traditionally exemplify the archetype in dye-sensitized solar cells. Following sunlight absorption, a fast photoinduced electron transfer takes place from the dye in its excited state into the conduction band of the oxide (Figure 4.4). This leaves the dye in its oxidized state, whose regeneration is accomplished by accepting an electron from a redox electrolyte. The most common redox system is I^-/I^{3-} , typically dissolved in an organic solvent. In turn, the redox couple is regenerated after the diffusion of I^{3-} to the surface of the back electrode, which is covered by a layer of a platinum catalyst to reduce it back to its I^- form and complete the charge transfer sequence that describes the functioning principles of dye-sensitized solar cells.

As expected, all the electron transfer processes require an intimate contact of the semiconducting oxide, the dye and the redox system, as well as an adequate correlation of the involved energy levels. The engineering of interfacial energetics and morphology becomes essential to avoid

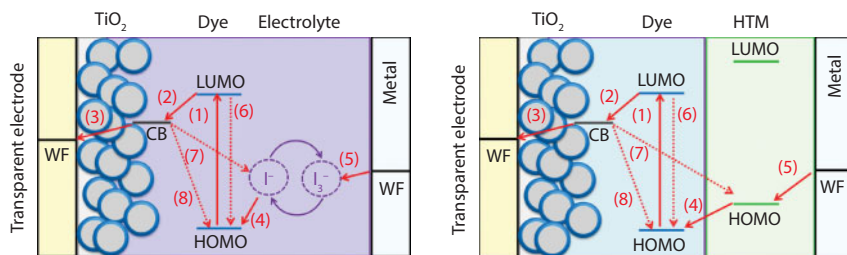


Figure 4.4 Schematic representation of the working principle in DSSCs (left) and ss-DSSCs (right). (1) Light absorption and dye excitation; (2) electron transfer from the LUMO of the dye into the conduction band of the mesoporous oxide; (3) electron transfer from the oxide into the transparent electrode; (4) electron transfer from the electrolyte or the HOMO of the HTM into the HOMO of the oxidized dye; (5) electron transfer from the back electrode into the redox electrolyte or the HOMO of the HTM. Possible relaxation processes: (6) dye relaxation prior to electron transfer; (7) electron transfer from the mesoporous oxide conduction band into the redox electrolyte or the HOMO of the HTM and (8) electron transfer from the mesoporous oxide into the oxidized dye.

secondary charge transfer processes, which would interfere with the optimum performance of the device. Among the common undesirable mechanisms it is worth mentioning: i) the relaxation of the excited state prior to the photoinduced electron transfer; ii) the back electron transfer from the semiconducting oxide to the oxidized dye; iii) the electron transfer from the mesoporous oxide or the transparent electrode to the oxidized species of the redox system.

A vast diversity of materials have been explored as an alternative to the above-mentioned typical components in the different constituting parts of a dye-sensitized solar cell. In any event, focusing our attention on the role of hole transporting materials, these materials represent an optional approach to the redox electrolyte [143]. This part of a DSSC has been one of the most investigated aspects, due to its critical influence in the charge transport process and its effect on the open-circuit voltage of the solar cell. It is important to note that the theoretical maximum of V_{oc} in dye-sensitized solar cells is determined by the Fermi level of the semiconducting oxide and the redox energy level of the electrolyte.

In spite of the remarkable efficiencies achieved in dye-sensitized solar cells with solution-based electrolytes, the volatility of the solvent or the possibility of electrolyte leakages becomes an issue for the device durability. Much effort has been put into looking for different strategies to find a solution to this problem, including the search for an optimum encapsulation system or the use of nonvolatile phases. The latter option includes the

utilization of gel and polymer electrolytes or ionic liquid electrolytes. All these approaches have the serious drawback of decreasing the efficiency of the solar cell when compared to the electrolytes in solution. One of the explanations that has been given for this result points toward the reduced ion mobility within highly viscous media. Nevertheless, a deeper understanding is still required for some elementary interface processes which the redox system intervenes in.

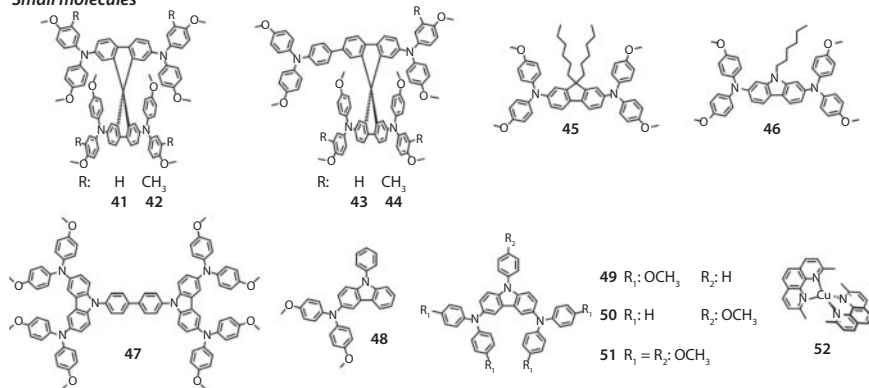
Another option to replace the liquid electrolyte in DSSCs consists of the use of hole transporting materials that can assist in the regeneration of the oxidized dye. This strategy originates in the so-called denomination of solid-state dye-sensitized solar cells (ss-DSSCs). In a different manner from the liquid electrolytes where charge transport is accomplished by ion diffusion, the hole transporting materials operate by charge carrier hopping. Unfortunately, the efficiencies reported for devices including hole transporters are lower than those achieved with the usual liquid electrolytes. As could be inferred from the contents discussed in previous sections of this chapter, energy level alignment and close contact between the mesoporous oxide, the dye and the hole transporting material become crucial to complete the charge transfer cycle. Accordingly, pore filling of dye-coated mesoporous TiO_2 with hole transporting materials becomes essential in solid-state dye-sensitized solar cells in order to achieve an efficient charge transfer for the dye regeneration. Otherwise, charge carriers can be lost through recombination processes, consequently affecting the V_{oc} and J_{sc} values. Besides, the HTL must have a HOMO energy higher than the dye to favor the dye regeneration and hole migration to the metal electrode. It is also important that hole transporting materials are transparent to the sun radiation so as not to interfere with the light absorption. Another valuable feature of HTLs in dye-sensitized solar cells is their charge carrier mobility, since it should be balanced with the charge transport in the semiconducting oxide to avoid charge accumulation within the device. A simple classification of the hole transporting materials used in dye-sensitized solar cells makes a difference between molecular materials and polymers (Figure 4.5).

4.3.1 Overview of Materials Used as Hole Transporting Layers

4.3.1.1 *Small Molecules*

The promising efficiencies achieved in solid-state dye-sensitized solar cells using spiro-MeOTAD, **41**, as hole transporting material, have made this molecule into a reference material. Nevertheless, its complicated synthesis is argued to increase the cost of device fabrication. Besides, its very

Small molecules



Polymers

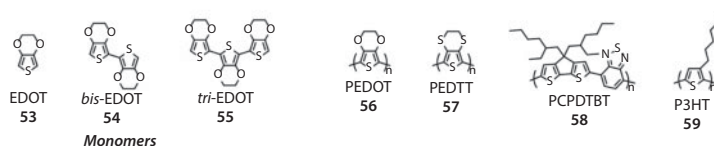


Figure 4.5 Chemical structures of small molecules and polymers used as hole transporting materials in dye-sensitized solar cells.

low hole mobility implies that spiro-MeOTAD has to be chemically doped. Typically, chemical dopants are species which promote the oxidation of the semiconducting HTL. As a result, more holes are produced, charge carrier density increases and the conductivity improves. Regarding spiro-MeOTAD doping, lithium bis(trifluoromethanesulfonyl)amide (LiTFSI), **92**, has been the most widely used dopant. Nevertheless, LiTFSI does not work directly as an oxidant species but instead favors the oxidation of spiro-MeOTAD by oxygen upon either light or thermal activation [144, 145]. Thus, it is necessary for the solar cell to be exposed to oxygen, at least in an initial stage, to trigger the spiro-MeOTAD doping. This methodology makes quite difficult to control the doping ratio since it will depend on the oxygen that has entered into the system during solar cell exposure. Additionally, *tert*-butylpyridine (*t*-BuPy), **93** [146], is another additive which is routinely incorporated into the hole transporting layer mixture to attenuate charge recombination. Finally, in those cases where an optimum efficiency is sought-after, a cobalt(III) complex, **94–96**, is also added to that mixture [147]. For these reasons, it would be advisable to find an alternative HTL that could mitigate any drawbacks, but maintain or improve the reported efficiencies.

In any case, the good results obtained with spiro-MeOTAD have also motivated interest in searching for the properties behind such a remarkable

performance [148]. In this regard, the effect of HTL morphology on solar cell stability has been studied for spiro-MeOTAD and three structurally related compounds, **42**–**44**, with methyl and phenyl groups attached to modify the crystallinity of the HTL [149]. A compromise must be reached between the crystalline and amorphous phases in the HTL. A completely amorphous layer will have a detrimental effect on the charge transport. On the other hand, a highly crystalline material inside the TiO_2 pores can affect the contact between the light absorber and the electrode. Accordingly, molecules **43** and **44**, which are amorphous, initially showed a worse solar cell operation. Nevertheless, thermal treatment of the solar cells (60 °C for 1000 h) affected the evolution of efficiency with time and revealed that DSSC fabricated with **43** and **44** degraded slower than those with spiro-MeOTAD. The latter displayed a dramatic decrease in the efficiency due to a thermally induced crystallization. In any event, the methylated **42**, which initially performed as well as plain spiro-MeOTAD (PCE = 4.8%) maintained the stability in the solar cell functioning even after long-term thermal treatment.

Carbazole-based materials represent an interesting alternative to spiro-MeOTAD as HTLs in solid-state DSSC and perovskite solar cells. The rich chemistry of the carbazole unit allows the modulation of its optoelectronic properties. Moreover, carbazole-based materials possess recognized charge transport ability. Bearing in mind that one of the strategies applied to improve the pore filling in ss-DSSCs consists of increasing the solubility of HTLs with the aim of using thicker DSSC to increase light absorption, alkylated fluorene and carbazole derivatives, **45** and **46**, have been used as HTLs and have been compared to spiro-MeOTAD [150]. Similar electronic structure and charge transport ability were confirmed for all three materials which should not limit the charge transfer processes within the device. However, whereas thin DSSC (2 μm thick) showed comparable results for all the tested materials, thicker devices (6 μm) evidenced a noticeable drop in the spiro-MeOTAD performance. Conversely, the more soluble carbazole derivative **46** maintained J_{sc} , V_{oc} , FF and PCE.

Likewise, two derivatives based on carbazole itself, **51**, and 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP), **47**, have been functionalized with the di(4-methoxyphenyl)amino groups typical of spiro-MeOTAD for comparison with this material [151]. Optical and electrochemical characterization showed similar features for all these materials. Nevertheless, the carbazole-based HTLs showed lower reorganization energy and higher hole mobility. As a result, DSSC prepared with the optimum LiTFSI dopant concentration offered better performance in the case of the CBP-based HTL (PCE = 6%), **47**, compared to spiro-MeOTAD (PCE = 5.5%). The latter HTLs

were also used in perovskite solar cells with comparable results, proving the potential of the CBP-based HTL.

Very similar carbazole derivatives have been studied to evaluate the effect of the number of aryl substituents attached to carbazole as well as the presence of methoxy groups on those aryl substituents, **48–51** [152, 153]. Better results were obtained for carbazole, **49**, with di(4-methoxyphenyl)amino groups on positions 3 and 6 and a phenyl ring on position 9. Despite the similar HOMO energies between the carbazole-based HTLs and spiro-MeOTAD the latter gave better V_{oc} due to a slower charge recombination. Nonetheless, the higher hole mobility measured for the trisubstituted carbazole led to an increased J_{sc} . It is worth mentioning that the effect of the HTL concentration as well as the processing conditions were also considered important factors to achieve a good filling of porous TiO_2 .

A structurally different alternative, such as bis(2,9-dimethyl-1,10-phenanthroline)-copper(I/II) complex **52**, has been used both as electrolyte and HTL in solid-state DSSC. Its combination with the usual additives (LiTFSI and *t*-BuPy) worked better than spiro-MeOTAD (8.2% vs. 5.6%) [154]. Good recovery of the oxidized dye by the Cu(I/II)(dmp)_2 , **52**, used as redox mediator was proved by photoinduced absorption spectroscopy. Moreover, photovoltage and current transient measurements revealed a fast charge transport and long electron lifetime in the solid-state DSSC with Cu(dmp)_2 HTL.

4.3.1.2 Polymers

Due to the large size of polymer chains, one of the main issues that has been spotted for these materials to affect the efficiency of solid-state DSSCs is the pore filling. Since a close contact between the different components in the solar cell is required to accomplish an ideal charge transfer process, the solution processing methodology commonly followed to directly apply the polymer materials, does not always permit a good infiltration into the mesoporous oxide. Accordingly, a frequent strategy consists of the deposition of the corresponding monomer precursors followed by *in-situ* polymerization inside the pores.

In this regard, poly(3,4-ethylenedioxythiophene) (PEDOT), **56**, is synthesized by photoelectrochemical polymerization of several pre-infiltrated monomers both in organic and aqueous media [155]. Since the reaction is initiated by the photogenerated holes in the HOMO of the dye sensitizer, this plays an essential role in the polymerization process and in the resulting polymer physicochemical properties. Besides, the dye also conditions the photoelectron recombination at the $\text{TiO}_2/\text{dye}/\text{HTM}$ interface and the

HTL infiltration depth. Accordingly, systematic studies carried out with different dyes proved their critical effect on the efficiency of solar cells processed under similar conditions [156, 157].

The choice of the monomers for the polymerization of PEDOT, mainly EDOT, **53**, *bis*-EDOT, **54**, or *tri*-EDOT, **55**, also determines the properties of the synthesized polymer inside the TiO_2 layer. It is important to use monomers having an oxidation potential lower than that of the dye to avoid its oxidative degradation. The monomer oxidation potential decreases as the number of EDOT units increases [158].

Thermal polymerization of EDOT has also been successfully applied to the synthesis of PEDOT HTLs [159]. The significance of the monomer structure was evidenced by the replacement of oxygen atoms in EDOT. When sulphur atoms were used instead, the resulting poly(3,4-ethylene-dithiathiophene), **57**, led to lower PCE mainly due to its lower electron conductivity causing higher interfacial resistance.

Other polymers traditionally used as donors in organic solar cells have also been incorporated as HTM in DSSCs. In agreement with this, PCPDTBT, **58**, was used in Sb_2Se_3 -sensitized devices, requiring optimized annealing conditions [160]. Blending PCPDTBT with PCBM improved the device performance. In the case of P3HT-based hole transporting layers, **59**, since the polymer molecular weight can influence the infiltration into the TiO_2 pores, it was observed that a non-uniform filtration of the polymer with higher molecular weight led to faster charge recombination rates and the subsequent V_{oc} decrease [161].

4.4 Hole Transporting Layers in Perovskite Solar Cells

Perovskite solar cells represent a very promising evolution of dye-sensitized solar cells since considerably high efficiencies have been recently achieved in a short time frame. The novelty of these devices is based on the use of organometal trihalide as light absorbers with the general formula AMX_3 , where A generally represents methylammonium, CH_3NH_3^+ , or formamindinium, $\text{HC}(\text{NH}_2)_2^+$, M corresponds to the metal cation (Pb^{2+} or Sn^{2+}) and X is the halide (Cl^- , Br^- or I^-). Different combinations of these components as well as hybrid perovskite structures containing different metal ratios or halide ratios have permitted the fine tuning of structural and electronic properties of these materials.

In general, perovskite solar cells have the same architecture as DSSCs, i.e., they are constituted by a transparent electrode covered by a layer of

TiO₂, which is in turn coated by the perovskite dye, and the structure is completed by a hole transporting material and the corresponding metal back electrode. In any event, it is worth highlighting some details that introduce certain differences with respect to the dye-sensitized solar cells. Although the typical layer formed by mesoporous TiO₂ nanoparticles has been extensively used in perovskite solar cells, it also admits the utilization of planar structures. This architecture involves the replacement of the mesoporous TiO₂ and its high-temperature sintering by an electron transporting layer, which can be deposited using standard methods. This planar structure also admits a conventional and inverted architecture.

Moreover, the use of hole transporting materials has been demonstrated to offer better efficiencies than liquid electrolyte in perovskite solar cells, affirming the significant progress towards the development of devices based on a solid-state design. Spiro-MeOTAD is by far the hole transporting material which has rendered the best results. However, as was previously mentioned for ss-DSSCs, the requirement of spiro-MeOTAD and its repercussions on the device fabrication cost makes the search for alternative HTLs very desirable. Additionally, of even more importance is that in perovskite solar cells the presence of hygroscopic dopants, such as LiTFSI, seriously affects the degradation of the photovoltaic device caused by atmospheric moisture. Thus, intensive research work has been done during the last few years exploring novel hole transporters that contribute to the promising development of perovskite solar cells. As expected, appropriate level alignment with the perovskite valence band (CH₃NH₃PbBr₃, -5.68 eV and CH₃NH₃PbI₃, -5.44 eV) and the metal electrode work function, good hole mobility, adequate interface morphology, close contact between the different materials and reduced charge recombination are mandatory properties for any hole transporting layer to be considered a useful alternative.

4.4.1 Overview of Materials Used as Hole Transporting Layers

4.4.1.1 *Small Molecules*

Despite the interest in finding materials that can replace spiro-MeOTAD, some aspects of this material are still worth being studied and subsequently used for any possible alternative hole transporting material (Figure 4.6). In this regard, the effect of the relative position of methoxy groups in spiro-MeOTAD has been analyzed [162]. The simple modifications of the *ortho*, **60**, *meta*, **61**, and *para*, **62**, position of the methoxy group affects the electronic structure and steric hindrance of the molecule. Accordingly, although the three isomers did not cause significant differences in the V_{oc}

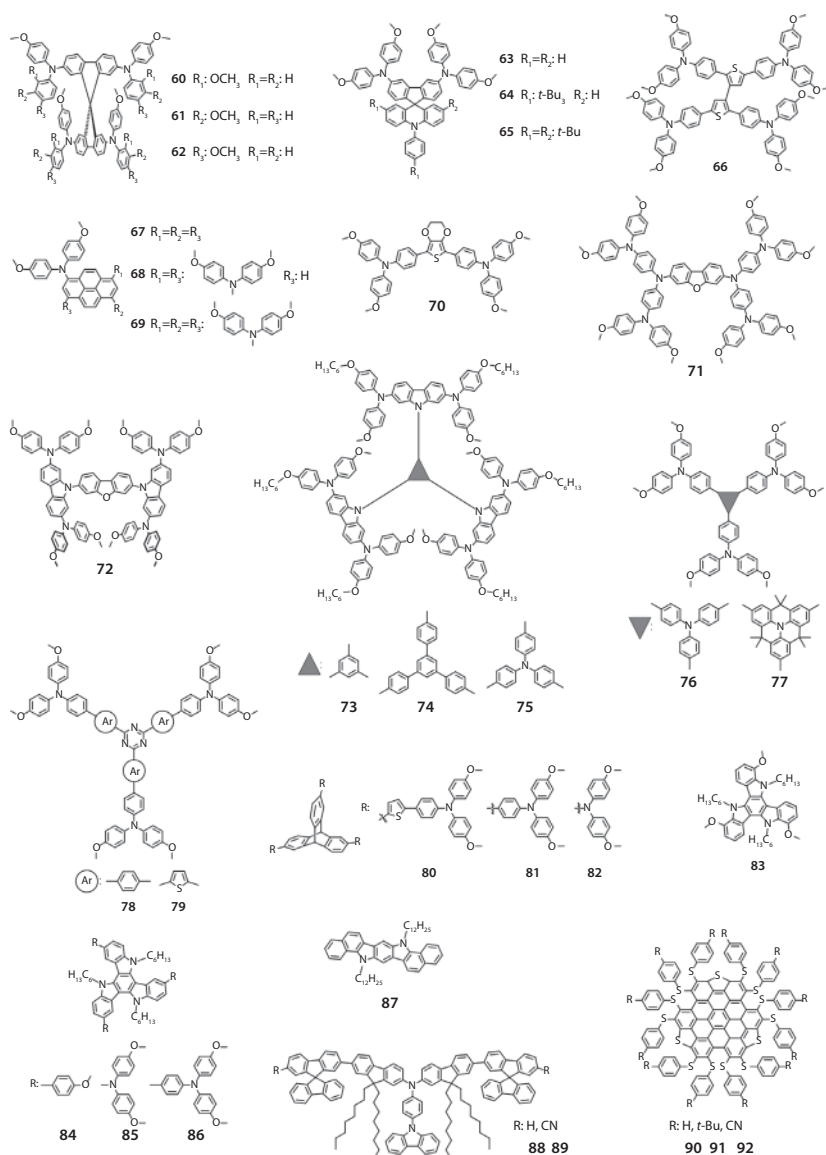


Figure 4.6 Chemical structures of small molecules used as hole transporting materials in perovskite solar cells.

and J_{sc} values of the solar cell, a remarkably enhanced FF was obtained for the devices fabricated with the *ortho*-substituted spiro-MeOTAD, **60**. In agreement with that result, this isomer displayed a lower series resistance, a higher shunt resistance and an efficiency of 16.7%.

Inspired by the spiro skeleton of spiro-MeOTAD, simplified spiro structures have been synthesized, **63–65** [163]. The HOMO energies and hole mobilities of these derivatives were similar to those of the spiro-MeOTAD model. Nevertheless, the novel structures might experience dissimilar packing in the solid state, influenced by the different bulky substituents attached. In turn, the different thin film morphology would also affect the coverage of the perovskite layer. When doping ratio was optimized, the spiro derivative, **64**, displayed good charge extraction from the perovskite absorber. Accordingly, higher J_{sc} and PCE were observed when compared to spiro-MeOTAD-based solar cells (16.6% vs. 14.3%)

Similarly, the twisted structure of spiro-MeOTAD was imitated by the cruciform conformation of a 3,3'-bithiophene core bearing four additional *N,N*-di(4-methoxyphenyl)aminophenyl substituents, **66** [164]. Due to the electronic structure of the hole transporter, a Co(III) complex, **97**, with a quite deep LUMO was required to dope the HTL [165]. This contributed to enhance J_{sc} and FF. Since the FF depends on the series and transport resistance as well as on charge recombination, these two aspects were analyzed. Whereas no significant differences were detected between the resistance of the new HTLs and spiro-MeOTAD, a remarkably reduced recombination kinetics was observed for the bithiophene-based HTL, presumably due to its torsional freedom allowing a better interaction with the perovskite, as well as extended delocalization of the radical cation by resonance.

The use of *N,N*-di(4-methoxyphenyl)amino groups or their extended triarylamine version based on *N,N*-di(4-methoxyphenyl)aminophenyl substituents, has become a recurring substructure used for the intuitive assay of several conjugated core systems with the aim of simplifying the synthesis of HTLs. This strategy was pioneered by the use of pyrene as a core building block, **67–69**. The attachment of one, three and four *N,N*-di(*p*-methoxyphenyl)amino groups modified the HOMO and LUMO energies of the HTM [166]. The comparison of tetrasubstituted pyrene derivative, **69**, and spiro-MeOTAD rendered very similar results. Nevertheless, the pyrene-based HTL exhibited a noticeably higher FF ascribed to its better hole transporting and electron blocking ability.

After optimizing the dopant ratio, a simple EDOT spacer connected to two di(*p*-methoxyphenyl)phenylamino units, **70**, displayed almost identical performance to spiro-MeOTAD (13.2% vs. 13.7%) [167]. It is worth highlighting that when the EDOT spacer was replaced by benzene or thiophene worse results were obtained.

Star-shaped hole transporting materials with C_2 symmetry, constituted by a benzofurane core and triphenylamine, **71**, or carbazole-based, **72**, dendritic structure have been compared [168]. The more flexible derivative with triphenylamine branches, **71**, reached almost identical values

to spiro-MeOTAD for all the characteristic parameters. Nevertheless, better stability was observed for the benzofurane-based HTLs after a 100 h test.

The dendritic structure of star-shaped molecules with C_3 symmetry has been successfully applied to the synthesis of HTLs which offered similar results to those obtained for spiro-MeOTAD. Core building blocks based on 1,3,5-trisubstituted benzene, **73–74** [169], triphenylamine, **75–76** [170], quinolino, **77** [171], 1,3,5-triazine, **78–79** [172], and tripticene, **80–82** [173], have been π -extended by attaching either *N,N*-di(4-methoxyphenyl) aminophenyl substituents or more rigid 2,7-disubstituted carbazoles. Solar cell efficiencies over 13% were reached for most of them after optimum doping with LiTFSI and *t*-BuPy. In general, these devices also presented better stability when compared to those fabricated with spiro-MeOTAD.

Indole-based systems with expanded conjugated surface, such as triazatruxene, also have a C_3 symmetry, **83–86** [174, 175]. Additionally, the conjugated system can be tuned by further extending their conjugated structure and by attaching methoxyphenyl substituents, **84–86**. The triazatruxene skeleton also admits the possibility of modulating the solubility by introducing *N*-hexyl chains. Besides, the optoelectronic properties of triazatruxene are appropriate to be integrated as HTL in perovskite solar cells. Although not all the derivatives responded to chemical doping, when the dopant ratio was optimized, triazatruxene, **84**, even outperformed spiro-MeOTAD (17.7% vs. 17.1%). The higher V_{oc} and FF were the parameters that decisively improved the solar cell efficiency, reaching a value of around 18%. Another related structure, such as π -extended indolocarbazole **87**, also surpassed the results obtained for a reference device prepared with spiro-MeOTAD [176]. The adequate electronic structure, good thin film morphology and high charge mobility contributed to improve FF. In this case no *N,N*-di(4-methoxyphenyl)aminophenyl groups were included in the structure of the HTM, showing that this kind of substituent might be an accessory.

Oligofluorene-based HTLs, **88–89**, have been employed in planar perovskite solar cells where the typical TiO_2 semiconducting layer covering the transparent electrode was replaced by another common electron transporting material such as ZnO. The devices prepared following a one-step procedure reached high efficiencies [177].

4.4.1.1.1 Additives for Hole Transporting Layers

As previously mentioned, the necessity of spiro-MeOTAD doping with LiTFSI, **93**, and *t*-BuPy, **94**, can become a problem for the optimization of the solar cell functioning. Apart from the sensitivity of the LiTFSI doping mechanism to the experimental conditions, depending on the

oxygen uptake upon air exposure, it has also been demonstrated that the hygroscopicity of that salt is one of the causes behind the solar cell degradation. For these reasons alternative additives have been explored to optimize the dopability of spiro-MeOTAD under more controlled conditions (Figure 4.7). Despite most of the research focusing on the reference spiro-MeOTAD, as long as the hole transporting material has an oxidation potential lower than the dopant, this difference will equally represent the driving force for the chemical doping to be effective. In other words, as long as the HOMO energy of the HTM is sufficiently higher than the LUMO of the dopant to promote an electron transfer process, the chemical doping will occur. Although several materials have been used as dopants for organic semiconductors [22], scarce solubility and low stability are common drawbacks of these species, which does not allow a straightforward application to the fabrication of solar cells. Therefore, the search for relatively stable dopants which could be adapted to a solution-processed methodology is a challenge.

In this regard, it was observed that the addition of small amounts (1 mol%) of Co(III) complex, **95**, to the usual HTL mixture (spiro-MeOTAD, LiTFSI and *t*-BuPy) considerably improved the conductivity, due to the direct oxidation of spiro-MeOTAD [147]. Interestingly, an increase of the PCE was observed after devices had been stored for a few days in the dark. It is also worth highlighting that the presence of Co(III) dopant contributed to maintain 80% of the photovoltaic efficiency after 40 days. An evolution of the Co(III) complexes has enabled a continuous improvement of ssDSSC and perovskite solar cells employing HTL chemical doping. In this regard, HTLs doped with complex **96** led to a significant increase in FF and J_{sc} [165]. However, an unexpected V_{oc} enhancement was

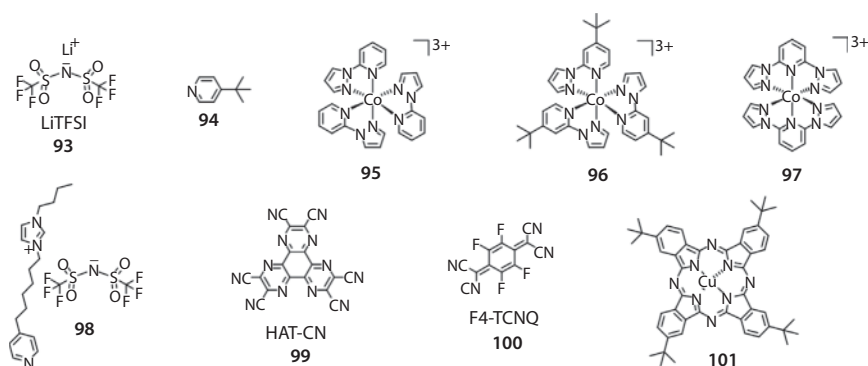


Figure 4.7 Chemical structures of additives or dopants for hole transporting layers in perovskite solar cells.

also observed. The origin of this V_{oc} raise is ascribed to a downshift in the spiro-MeOTAD Fermi level caused by an increase in the hole concentration resulting from doping. Consequently, the deeper Fermi level expands the energy difference with respect to the TiO_2 quasi-Fermi level and the corresponding V_{oc} increases. Moreover, dark current measurements revealed that HTL including complex **96** shows a better electron blocking ability. Similarly, very good results have also been obtained using AgTFSI (5.3 mol%) as *p*-dopant in the HTL mixture [178].

Regarding the control of the doping concentration, it has been shown that mixing spiro-MeOTAD with its own doubly oxidized species, spiro-MeOTAD²⁺(TFSI)₂, previously prepared by oxidation with AgTFSI, avoids the use of metal-based dopants and represents a valid strategy to remove hygroscopic components which severely affect the stability of the solar cell [179]. The combination of spiro-MeOTAD and spiro-MeOTAD²⁺(TFSI)₂ in the same layer results in a dismutation reaction to form the singly oxidized species spiro-MeOTAD⁺. The conductivity of spiro-MeOTAD with a 10 mol% concentration of spiro-MeOTAD²⁺(TFSI)₂ improved by four orders of magnitude. Curiously, although the fabricated solar cells were functional, they only reached their maximum efficiency after exposure to air. It is hypothesized that oxygen intervenes in surface passivation of the perovskite layer. This strategy has also been applied to simple carbazole-based HTLs [180]. Additionally, the attachment of aliphatic chains to the structure of the hole transporting material increases the hydrophobicity of the HTL and remarkably contributes to decrease the degradation caused by water.

The protonation of spiro-MeOTAD by protic ionic liquids such as HTFSI can also initiate the redox mechanism that results in spiro-MeOTAD doping [181]. Electron transfer from the neutral spiro-MeOTAD into its protonated counterpart, spiro-MeOTADH⁺ (10 mol%), produces the formation of the singly oxidized radical cation, spiro-MeOTAD⁺ and the radical of the protonated molecule spiro-MeOTADH. This radical could produce hydrogen gas with the concomitant formation of neutral spiro-MeOTAD which would reenter the cyclic reaction mechanism by accepting a proton. As previously mentioned for the metal-induced oxidations, the formation of the singly oxidized species, spiro-MeOTAD⁺, enhances the material conductivity. This acid-based doping strategy slightly improves the results obtained for the typical LiTFSI doping.

Mixing spiro-MeOTAD with dual functional ionic liquid, such as **98**, replaces the use of both LiTFSI and *t*-BuPy [182]. The imidazolium salt can work as a weak acid and promotes the protonation of spiro-MeOTAD that will get doped following the same mechanism described for HTFSI. Besides,

the role of *t*-BuPy can be played by the 4-alkylpyridine fragment present in the ionic liquid structure. Solar cell fabricated with the usual LiTFSI and *t*-BuPy additives and the new ionic liquid dopant showed very similar efficiencies, which confirm the adequacy of this dual functional strategy.

The use of strong electron acceptors, with a very low LUMO, as interfacial layers between the HTL and the metal electrode, operates in an analogous way as chemical doping [183]. Accordingly, a renowned hole transporting material, such as *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD), was deposited on a perovskite layer, followed by a very thin film (3 nm) of 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN), **99**, and finally the back electrode. Electron transfer can occur between the HOMO of the TPD (−5.3 eV) and the LUMO of HAT-CN (−5.70 eV), producing a charge transfer complex, which implies the formation of a dipole at the TPD/HAT-CN interface. As expected, the consequent increased concentration of charge carriers enhances charge transport. Besides, the interfacial dipole also contributes to electron blocking and better hole extraction. As a result, a decrease in charge carrier recombination and an increase in J_{sc} were observed. Regarding the metal electrode interface, the presence of strong electron acceptor species lowers the possible Schottky barrier, improving the contact by band bending. All these features led to a remarkable enhancement of the solar cell parameters with a special significance in the case of short-circuit current.

Copper phthalocyanine bearing peripheral *tert*-butyl groups (*t*-BuCuPc), **101**, have proved to be a useful additive for spiro-MeOTAD-based hole transporting layers [184]. The presence of *t*-BuCuPc in a 4.8 wt% concentration significantly increased shunt resistance, leading to higher FF, V_{oc} and PCE (18.5%). Additionally, the *t*-BuCuPc-doped spiro-MeOTAD showed a slower charge recombination. It is believed that the lower LUMO energy of *t*-BuCuPc when dispersed within the spiro-MeOTAD matrix enables the capture of the unwanted electrons present in spiro-MeOTAD, disrupting its percolation pathway. Conversely, the good HOMO energy match between the additive and the HTL matrix did not affect the hole transport.

Thiolated hexabenzocoronene electronic structure can be tuned by peripheral electron-releasing and electron-withdrawing groups, **90–92** [185]. This enables the modification of its HOMO energy when used as HTL. Surprisingly, despite the almost negligible hole mobility of the hexabenzocoronene-based material, the performance of perovskite solar cells was good. The use of thin films (60 nm) and the formation of Pb-S bonds at the perovskite/HTL interface might help the charge transfer processes. Nevertheless, doping with graphene nanosheets improved the conductivity

and consequently the solar cell efficiency (14%). Moreover, the highly hydrophobic nature of the HTL contributed to preserve the stability of nonencapsulated devices.

4.4.1.1.2 Dopant-Free Hole Transporting Layers

Although doped hole transporting layers have rendered very good results in the fabrication of perovskite solar cells, the use of dopants requires a precise optimization of the concentration ratio between the HTL matrix and the dopant species. Furthermore, depending on the stability of dopants this might become an issue concerning the solar cell degradation. It is also important to bear in mind that the more additives are incorporated into the fabrication of the solar cell, the more expensive the device will be. For all these reasons it would be very desirable to have hole transporting materials which can produce highly efficient solar cells without the necessity of adding any dopant (Figure 4.8).

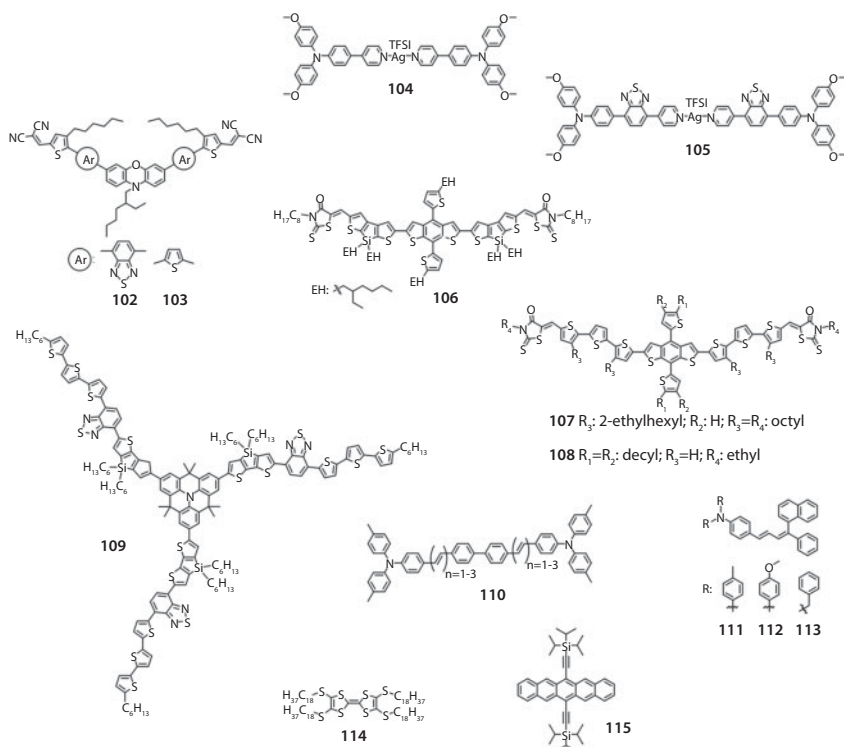


Figure 4.8 Chemical structures of dopant-free small molecules used as hole transporting materials in perovskite solar cells.

Recently, several organic materials based on a donor-acceptor (D-A) or acceptor-donor-acceptor (A-D-A) structure have demonstrated their ability to work as dopant-free HTLs in devices with high efficiency.

Phenoxazine core has been combined with benzothiadiazole-thiophene, **102**, or bithiophene, **103**, conjugated side structures end-capped by dicyanovinylene groups [186]. Their adequate HOMO energies and good hole mobilities improved the solar cell performances (PCE = 12.8%) when used as dopant-free HTLs.

Similarly, silver metal-organic complexes with conjugated ligands having a D-A structure, **104–105**, have shown good ability to work as HTLs [187]. When a benzothiadiazole spacer, **105**, was part of the HTL structure it contributed to lower the HOMO energy and to extend the π -conjugated surface. Accordingly, the right HOMO alignment resulted in a better V_{oc} and the expanded conjugation enabled a larger intermolecular overlap that improved the hole mobility.

Extended π -conjugated systems with A-D-A structure formed by dithienosilole-rhodanine external substructures and a benzo[1,2-*b*:4,5-*b'*]dithiophene (TBDT) core, **106**, have been studied as HTLs [188]. All the analyzed parameters (charge transport, charge extraction and charge recombination) confirmed the excellent behavior of this material as HTL, outperforming doped spiro-MeOTAD. This led to the highest PCE (16.2%) reported for a dopant-free HTL in perovskite solar cells. The main reasons behind that good functioning came from good interface energetics, also favored by the presence of a thin MoO_3 interlayer between the HTL and the silver electrode, and high charge mobility, which became especially important for an extended π -conjugated D-A system. The adequacy of this molecular design came from the previous good results reported for HTLs with the same TBDT core and rhodanine-end-capped terthiophene side structures, **107–108** [189, 190]. Moreover, several alkyl chains attached to the conjugated system significantly increased the hydrophobicity of the HTL, attenuating the degradation of the solar cell caused by moisture.

A star-shaped molecule with a sophisticated donor-acceptor structure, **109**, has also been synthesized and evaluated as HTL [191]. Interestingly, the absorption of this molecule in the visible range was argued to contribute to harvest the light transmitted by the perovskite. The SEM images showed that the star-shaped HTL uniformly covered the perovskite nanocrystals. The HOMO energy and hole mobility of the new HTL were appropriate for transferring electrons to the perovskite and transporting holes to the back electrode.

The combination of several donor and acceptor fragments within the same conjugated system is frequently associated with a complicated

synthetic route. Accordingly, any contribution coming from structurally simple molecules is always welcome. In this regard, two triarylamine units have been attached to a biphenyl by olefin spacers with different length, **110** [192]. Their HOMO energies and hole mobilities are similar to those of spiro-MeOTAD as well as the measured device efficiency (9.1% vs. 10.2%). It is worth highlighting that no significant degradation was observed after one week.

Structurally simple systems have also been synthesized by linking the naphthylphenylbutadiene unit to different tertiary phenylamine groups, **111–113** [193, 194]. The effect that the HTL thickness had on the solar cell functioning is noteworthy. Very thin HTLs prepared from diluted solutions were enough to get good pore filling and high solar cell efficiencies (PCE = 11.3–11.6%). Moreover, a daily measurement of the unsealed devices kept in the dark under ambient conditions displayed virtually no efficiency loss after one week.

Typical hole transporting materials, such as tetrathiafulvalene, **114**, bearing long alkyl chains at positions 2, 3, 6 and 7 have also been used as HTLs [195]. Curiously, the characteristic photovoltaic parameters were certainly comparable to those measured for devices fabricated with doped spiro-MeOTAD. Another renowned hole transporter, TIPS-pentacene, **115**, has been successfully used as dopant-free HTL [196]. The absorption of TIPS-pentacene in the visible range contributes to light harvesting, along with the perovskite, enhancing the photocurrent generation. Good V_{oc} is obtained due to the low-lying HOMO of TIPS-pentacene. Additionally, a large shunt resistance was observed which resulted in a lower leakage and reduced recombination. It is also worth mentioning that there is a negligible hysteresis in devices based on TIPS-pentacene HTL. Overall, this molecule worked noticeably better than doped spiro-MeOTAD (11.5% vs. 9.8%).

4.4.1.2 Polymers

The implementation of polymer HTLs has also been explored as an alternative to the prevalent spiro-MeOTAD in perovskite solar cells (Figure 4.9). Making the most of the vast diversity of polymers and copolymers traditionally employed as donor components in organic solar cells, some of them have been used as HTLs in perovskite solar cells with promising performances. In this regard, P3HT is considered one of the reference polymer HTLs. Since the energy level alignment between the HTL HOMO and the perovskite valence band ($\text{CH}_3\text{NH}_3\text{PbBr}_3$, -5.68 eV; $\text{CH}_3\text{NH}_3\text{PbI}_3$, -5.44 eV) becomes critical for the solar cell operation, the rational combination of

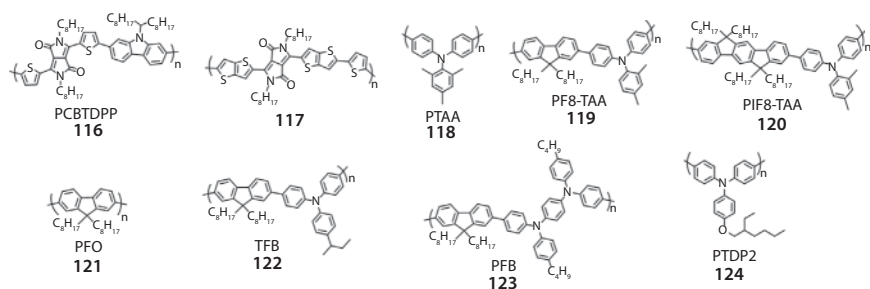


Figure 4.9 Chemical structures of polymers used as hole transporting materials in perovskite solar cells.

different electron-donating and/or electron-withdrawing fragments has been successfully applied to tune the electronic properties of various series of polymers. In this regard, diketopyrrolopyrrole (DPP)-based polymers, such as PCBTDP, **116**, have rendered perovskite solar cells with superior performance to P3HT [197]. The comparatively better results achieved with PCBTDP were ascribed to the weaker light-filtering effect, higher hole transport properties and lower charge recombination. Importantly, the stability studies revealed that the efficiency remained almost unchanged after a storage period of up to 900 h. Another DPP-polymer, **117**, was inserted as a thin film (~ 5 nm) between the perovskite and a MoO_3 layer, working as exciton blocker. The resulting device was again more efficient than the control solar cell fabricated with P3HT (10.8% vs. 6.62%) [198].

Moreover, the HOMO energy of the HTL also intervenes in the V_{oc} value, along with the energy of the TiO_2 conduction band. A comparative study was carried out by systematically modifying the HOMO energy in a series of structurally related triphenylamine copolymers combined with fluorene and indenofluorene moieties, namely PTAA, **118**, PF8-TAA, **119**, and PIF8-TAA, **120**. It was observed that deeper HOMO energies correlated with better V_{oc} . Furthermore, an impressive 16.2% efficiency was achieved for the PTAA HTL, which displayed better energy level alignment with the active layer [199]. A similar study was performed with polyfluorene derivatives PFO, **121**, TFB, **122**, and PFB, **123**, whose HOMO energies were modified by the presence of an increasing number of electron-rich triphenylamine moieties in the polymer backbone. The TFB showed a more suitable energy level correlation with the perovskite, which contributed to a more efficient charge extraction [200].

Even PEDOT:PSS has been used in perovskite solar cells. The PEDOT:PSS work function can be modulated by blending with PFI, **6** (Figure 4.3). The resulting PEDOT:PSS/PFI mixture presents a PFI-enriched surface that

matches the valence band of $\text{CH}_3\text{NH}_3\text{PbI}_3$, affording better device functioning than the neat PEDOT:PSS HTL [201]. Due to the good results reported for the pH-neutral conjugated polyelectrolyte CPE-K, **13**, in polymer solar cells, it was compared to PEDOT:PSS in inverted perovskite devices [202]. More uniform surface coverage was observed after the perovskite films were deposited on top of the CPE-K interfacial layer. Moreover, a superior hole transfer efficacy from the perovskite film to CPE-K was also evidenced by the faster photoluminescence decay times. The combination of these features resulted in the improved performance and better stability of CPE-K-based devices.

4.4.1.2.1 Doped Polymer HTLs

The previously mentioned benefits of molecular doping on the performance of HTLs have also been explored in polymer-based HTLs. Thus, the intuitive addition of LiTFSI to P3HT evidenced a remarkable conductivity enhancement, as well as HOMO energy decrease, rendering higher J_{sc} and better PCE than the pristine polymer [203]. The device efficiency was further improved when 2,6-di-*tert*-butylpyridine (di-*t*-BuPy) was combined with the lithium salt dopant due to an induced order in the P3HT side chains. A similar LiTFSI doping effect has been reported for PTAA, **118**, HTLs [204]. However, despite the efficiency improvement, the presence of Li^+ cations had a detrimental effect on the device stability. Polyaniline (PANI) interfacial layers have also improved their performance when doped with LiTFSI [205].

The renowned 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ), **100**, was also an effective *p*-dopant for PTAA HTLs in perovskite solar cells [206]. Upon optimization of the dopant concentration (1 wt%), insignificant changes were observed for J_{sc} and V_{oc} . Nevertheless, the reduced resistivity of the PTAA interfacial layer significantly increased the FF and consequently the PCE (17.5%).

Likewise, a series of poly(tetraphenylbenzidine) (PTDP)-based, **124**, HTLs were also doped with the tris(2-(1H-pyrazol-1-yl)pyridine) cobalt(III) complex [207]. As expected, the presence of the Co(III) complex in the polymer interlayer contributed to a significant improvement of the photovoltaic parameters. Moreover, the combination of LiTFSI and *t*-BuPy dopants with the Co(III) complex resulted in an even better device performance.

4.4.1.3 Metal Oxides

Transition metal oxide HTLs have also contributed to improve the performance and stability of perovskite solar cells. In this regard, the

implementation of a thin layer of MoO_3 between the anode and PEDOT:PSS in devices with inverted architecture considerably enhanced J_{sc} and FF [208]. This was attributed to improved charge collection efficiency and a decreased electron-hole recombination probability, resulting in an average PCE of 12.78%. Furthermore, the location of the oxide layer reduced the ITO roughness and protected the electrode from any possible etching caused by PEDOT:PSS, which resulted in only minor degradation after 10 days.

Different approaches have also been investigated regarding the applicability of NiO in perovskite solar cells. Good quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ films grown on top of NiO as HTL exhibited a high surface coverage [209]. The surface wettability and the work function of the NiO films deposited on ITO were modulated by UV-ozone treatment to provide a reduced charge transfer energy loss and improve the device operation. Alternatively, mesoscopic NiO nanocrystalline layers were combined with both solution-processed and low-temperature sputtered NiO_x thin films as hole selective contact [210, 211]. The mesoscopic layer acted as a mesoporous matrix, which avoided the presence of defects and improved the morphology of the light absorber. The efficiency of the solution-processed NiO_x was surpassed by the sputtered NiO after the optimization of the oxygen doping level and the mesoscopic NiO layer thickness. Additionally, Cu-doped NiO layers can further increase the device efficiency [212]. In this regard, Cu:NiO films prepared from low-temperature combustion process afforded HTLs whose optical and morphological properties were comparable to those of the films prepared by the sol-gel method. However, the combustion-derived Cu:NiO outperformed the sol-gel based HTL due to its superior electrical conductivity (PCE = 17.74%).

4.4.1.4 Metal Salts

The use of inorganic semiconductors as selective hole transporters has recently gained much attention due to their good conducting ability and the possibility of significantly reducing the cost of the optoelectronic device. In this regard, a thick layer of CuSCN (~600 nm) on top of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer contributed to an effective hole extraction and fast transport towards the electrode. The results were quite conditioned by the morphology of the subjacent perovskite. A two-step fabrication method aimed at obtaining thicker active layers minimized the possibility of having close contact between ITO and HTL [213]. The high sensitivity to the morphology of the perovskite layer in solar cells using CuSCN as hole transporting

layer has been further corroborated by the results coming from different fabrication methods [214] as well as post-processing annealing conditions [215]. Perovskite solar cells with inverted architecture have also been fabricated with CuSCN HTLs deposited either by conventional spin coating or electrodeposition. Subsequently, one or two-step methodologies have been used for the perovskite layer [216]. These methodologies have a critical effect on the roughness of the active layer which conditions the quality of the interfacial contacts and the device performance. The one-step method has resulted in the highest efficiency (16.6%) reported for perovskite solar cells with an inorganic HTL [217].

The incorporation of CuI in $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based cells provided encouraging results for its use as hole selective interlayer [218]. In contrast to spiro-MeOTAD, the high recombination in those devices containing CuI limited the V_{oc} values and restrained the achieved PCE. However, the better electrical conductivity of CuI, nearly two orders of magnitude higher than that of spiro-MeOTAD, resulted in a lower diode quality factor which accounted for the higher FF. Moreover, it was observed that the devices with CuI required storage for days to weeks to reach the maximum efficiency.

Magnetron sputtered CuAlO_2 inserted between the ITO electrode and PEDOT:PSS in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ -based cells significantly reduced the contact resistance due to its excellent conducting properties [219]. The conductivity and work function were dependent on the interlayer thickness. Thus, the optimal thickness which provided the best energy level matching between PEDOT:PSS and CuAlO_2 resulted in a PCE as high as 14.52%, in contrast to that obtained with only PEDOT:PSS (11.1%). Other inorganic materials such as kesterite $\text{Cu}_2\text{ZnSnS}_4$ provided comparable efficiencies to spiro-MeOTAD (PCE 12.75% vs. 13.23%) and lower device hysteresis [220]. Curiously, $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles induced a light absorption increase of the perovskite absorber, leading to superior J_{sc} values than those of spiro-MeOTAD. Since both HTLs provided the same V_{oc} , the device performance differences were related to the comparatively lower FF of the $\text{Cu}_2\text{ZnSnS}_4$ devices.

4.4.1.5 Carbon Nanotubes

Multiwalled carbon nanotubes (MWNTs) can enhance carrier concentration, charge mobility and electrical conductivity when added as dopant to a hole transporting layer [221]. However, their low work function can produce back electron transfer in the case of contact with the perovskite layer. Therefore, a hierarchical hole extraction layer formed by a film

of spiro-MeOTAD (containing LiTFSI and *t*-BuPy) deposited on the perovskite, followed by another layer of spiro-MeOTAD with a low content (0.5–1%) of MWNTs, led to an increase in the solar cell efficiency.

With the aim of avoiding carbon nanotube contacts at the perovskite surface, single-walled carbon nanotubes (SWNTs) can be wrapped by P3HT [222]. This composite can be directly deposited on the perovskite layer, enhancing the selective hole extraction without causing any electron recombination. Additionally, when pristine spiro-MeOTAD is deposited on the P3HT/SWNTs layer, it infiltrates the mesh-like structure and forms a stratified morphology. This benefits a sequential hole transfer from the active layer and significantly improves all the parameters of the solar cell (PCE = 15.4%). The same P3HT/SWNT composite has been combined with a thin insulating layer of either poly(methylmethacrylate) (PMMA) or polycarbonate which, when deposited between the HTL and the metal electrode, has rendered remarkable attenuation of the device degradation by thermal stress in ambient air and moisture [223].

4.4.1.6 Graphene-Based Materials

The properties of the perovskite absorbing layer can be modified by the presence of graphene-based materials. In this regard, $\text{CH}_3\text{NH}_3\text{PbI}_3$ films grown on reduced graphene oxide (rGO) exhibited better crystallinity with larger grain sizes, which lowered the number of grain boundaries [224]. Likewise, rGO showed high conductivity and good energy level alignment with the light-harvesting material. As a consequence, rGO-based devices outperformed those incorporating GO or PEDOT:PSS. When GO was deposited on top of the perovskite film, the reduction of the contact angle to zero considerably improved the contact between the perovskite and spiro-MeOTAD, enhancing the overall performance of the solar cell [225]. Graphene-based materials can reduce the adverse effects of the commonly used dopants on the device stability, especially Li-TFSI. The combination of rGO with pristine spiro-MeOTAD rendered devices with much higher efficiency than those fabricated with dopant-free spiro-MeOTAD [226]. The generation of additional hole extraction pathways through the observed protuberant rGO islands, which even contacted the electrode, contributed to a better hole transport in synergy with spiro-MeOTAD itself. More importantly, the use of rGO as the only additive in spiro-MeOTAD significantly improved the device stability in air, with only a 15% PCE degradation after 500 h, compared to doped spiro-MeOTAD with a 65% PCE reduction under the same conditions.

4.5 Concluding Remarks

The last years have witnessed the emergence and progress of organic and hybrid solar cells. These new types of photovoltaic devices are based on a multilayer architecture where an optimum combination of various materials with different properties is required to successfully complete the sequence of steps involved in the solar cell functioning, namely, charge carrier generation, transport and collection. This chapter has presented the essential roles that interfacial layers play in the improvement of the efficiency of this new generation of solar cells, focusing particularly on hole transporting layers. The conditions that control their mediation in the charge transport between the active layer and the electrodes, as well as their protective function for solar cell stability, have been discussed. A comprehensive review of the most recent advances in hole transporting materials has been made, including organic solar cells, dye-sensitized solar cells and perovskite solar cells. An extensive variety of materials having an organic and inorganic nature have shown that, despite the good results achieved in some cases, the “perfect” hole transporting layer does not seem to be available yet. Accordingly, the different research approaches based on polymers, small molecules, self-assembled monolayers, metal oxides, metal salts, carbon nanotubes and graphene-based materials, used either as single or combined components, pure or doped, have been summarized and organized to offer a good source of information, which is expected to be useful for future investigation of this interesting topic. Further development of hole transporting materials is still required, with the aim of achieving more efficient and stable solar cells that are suitable for industrial production in order to become a real alternative for solar energy utilization.

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Printable Solar Cells

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Abstract

Printable photovoltaic modules, along with other printed electronic devices, such as light-emitting diodes, thin film transistors, capacitors, coils, resistors, etc., are a low-cost alternative to the conventionally deposited devices. Due to its fabrication simplicity and the feasibility of using large-area flexible substrates, printable solar cell (PSC) is a prospective candidate in many application fields. Furthermore, light-absorbing layer of PSC is usually several orders of magnitude thinner than widely used conventional Si solar cells; thus production of PCS requires much less material, and in the case of printing deposition there is very little waste of material in comparison to other deposition methods. The possibility of using flexible large-scale substrates opens the door to multiple advanced application opportunities such as smart textiles, photovoltaic window shades, etc.

This chapter addresses a topic regarding key aspects of development, fabrication, and application with respect to PSC, mostly CIGS, perovskite and organic solar cells. First off, working principles, applicability of PSC, their merits and demerits, and future application possibilities are considered. Additionally, the chapter contains a description of a variety of different coating and printing technologies.

Keywords: Printable solar cells, thin film technology, printed electronics, printing, coating, CIGS, perovskite solar cells, organic electronics

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5.1 Introduction

Printable solar cells and, generally, printed electronics, offer cost-effective large-area deposition techniques for devices on a large variety of substrates regardless of their shape and thermal stability. Conductive or semiconducting electrically functional electronic or optical inks (organic, inorganic or hybrid) are deposited on the substrate, creating active or passive devices such as thin film transistors, capacitors, coils and resistors. Typically, materials for printable electronics are of organic origin (both polymers and small molecules), but not exclusively. Some new printable inorganic (silicon, silver, TiO_2 and many more) paste or hybrid materials (for instance, perovskite, nanocarbon, etc.) have also been developed.

Printed electronics offers a way of producing thin, lightweight, flexible and environmentally friendly products and also printable electrical components that can be integrated into conventional systems. Organic light-emitting diode (OLED) displays, smart clothing, solar cells, flexible displays, printed batteries, supercapacitors, memory or label-protection tags are just a few examples of the promising application of systems based on organic electronics. These new (usually organic-based) materials can be solubilized in a suitable organic solvent and therefore mass-volume production is achievable by proper printing techniques. This is a key factor for deployment of printed electronic devices in various applications since they can be extremely cost-effective compared to inorganic devices prepared by traditional techniques.

Printed electronics products are present on the market today. The current leader in the field of development and commercialization of printed electronics is a Norwegian company called Thin Film Electronics ASA. Memory labels, product protection and anti-theft tags that are all fully printed belong to their line of products. Konarka Technologies Inc. was a pioneer in the field of printed electronics, with a focus that was particularly aimed at production of fully printed solar cells, but this company has already ceased to exist.

There has been significant progress made in organic electronics entering the market in the last few years and it can be said with confidence that it is an ever-growing industry that has already started to generate significant profit. Sales of products that are fully based on organic electronics or that include printed components were 23–24 billion US\$ in 2014 and for the year 2024 are predicted to be over 70 billion US\$ (Smithers Pira 2013 and IDTechEx 2014).

5.2 Printable Solar Cells Working Principles

A *sine qua non* condition for printable solar cells is the possibility of wet processing, i.e., solution processing techniques. Considering application potential, today there are three types of solar cells which fulfill this requirement.

The first type is a copper indium gallium selenide solar cell (or CIGS photovoltaic cell) [1]. This type of solar cell is already in mass production, including solar panels where they are deposited onto flexible substrates; and along with cadmium telluride and amorphous silicon, CIGS is one of three mainstream thin-film PV technologies. However, the conventional manufacturing procedure is based on vacuum deposition of precursors, which negatively affects the final production cost. Moreover, up to now all the record efficiencies were recorded on glass substrates.

The second type is the perovskite solar cell [2], which has become a “superstar” in photovoltaic technology and has attracted the particular interest of research society due to its unique properties. As distinct from CIGS solar cells, record efficiencies of perovskite solar cells have been reached by solution processing. Layers of absorber, low-cost and high efficiencies make this type of photovoltaics one of the more commercially attractive technologies in the field. However, there are still some issues of toxicity [3] and stability [4] which need to be resolved.

Finally, the third type of solar cell is the bulk heterojunction organic photovoltaic (OPV) solar cell. The main advantages of the organic photovoltaics are a low production cost, flexibility, nontoxicity and color tunability. Nevertheless, among the three types of printable photovoltaics, organic solar cells possess the lowest power conversion (PCE) values, which stagnated at 11% [5, 6]. However, the nontoxicity and unbeatable low weight [7] of the organic photovoltaic cells still maintain their feasibility on the global market.

5.2.1 CIGS Solar Cells

A copper indium gallium selenide solar cell, or CIGS (see Figure 5.1) [8], is a thin-film photovoltaic cell, along with cadmium telluride (CdTe) and amorphous thin-film silicon (a-Si, TF-Si). Notably this is the only commercially available type of solar cell on the list. However, although it is predominantly manufactured by vacuum deposition it can also be successfully printed from precursors [9, 10]. It is one of the photovoltaic technologies with the most potential, which is assertively closing the efficiency gap

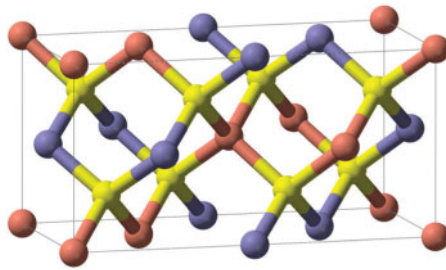


Figure 5.1 Chalcopyrite crystal structure of CIGS unit cell. Red = Cu, Yellow = Se, Blue = In/Ga.

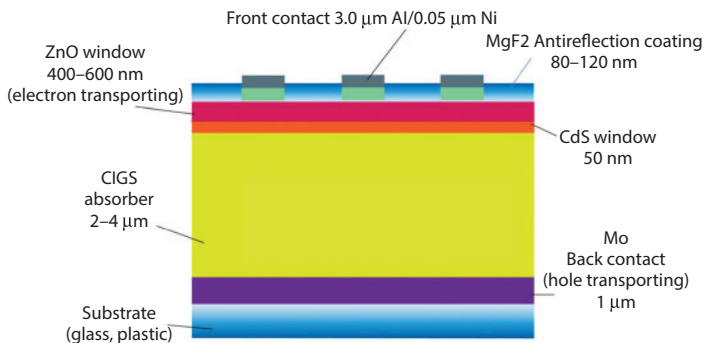


Figure 5.2 CIGS solar cell structure.

with silicon wafer cells [1]. A CIGS has broad spectra absorbing most of the sunlight [11] and very high extinction coefficient; thus, a much thinner film is required than that of other inorganic semiconductor materials. Record efficiencies reported by manufacturers are over 20% at glass substrates; at the same time, scientists from the Swiss Federal Laboratories for Materials Science and Technology have reported power conversion efficiency of 18.7% for flexible CIGS solar cells on plastics.

The main working principle of all solar cells (Figure 5.2) is based on the absorption of sunlight by photoactive semiconducting material (CIGS absorber). When photons are absorbed, electrons are excited from the ground-state molecular/atomic energy orbitals, creating electron-hole pairs or excitons. Excited electron can either dissipate the energy as heat and return to its initial orbital or travel through the cell until it reaches the electrode. Current flows through the material to reach the potential equilibrium and this electricity is captured. In the case of CIGS solar cells, the CdS/CIGS heterostructure is the key element in determining the electrical

and photoelectric characteristics of the device. In CIGS solar cells, the heterojunction is formed between the p-CIGS and n-CdS. The conductivity of CIGS is determined by a large density of the intrinsic defects, while the n-CdS is doped to a much larger extent by donors. This asymmetric doping causes the space charge region (SCR) to extend much further into the CIGS. As in CdTe solar cells, a thin layer of CdS serves as a “window” through which radiation penetrates into the absorber.

Like other above-mentioned thin-film technologies, these materials are thin enough to be flexible when deposited on plastic substrates. Flexible CIGS solar cells are already presented on the market; for example, the U.S. manufacturer SoloPower offers large-scale photovoltaic modules on plastic substrates. However, cadmium telluride and amorphous thin-film silicon are normally manufactured at high temperatures, while CIGS solar cells can be deposited at low temperatures (including printing). Even though for all types of thin-film solar cells the best performance normally comes from cells deposited on glass (>20% [1]), the advantages of low-temperature deposition of CIGS cells have erased much of this performance difference. Another advantage of using coating/printing techniques for CIGS solar cell manufacturing is that conventional vacuum procedures result in large wastage of the precursors, and as a result the supply of indium and gallium might become an issue. A recent publication by Lin *et al.* [9] reported on a low precursor wastage, cost-effective route for the fabrication of CIGS solar cells using an inkjet printing technique. Efficiencies exceeding 11% for inkjet-printed solar cells were achieved, which is a significant step towards the manufacturing of printed CIGS photovoltaics on the industrial scale. The development of CIGS cells is continuing, as they can be a good alternative to conventional silicon solar cells in terms of efficiencies, while at the same time maintaining all the advantages of thin-film technologies such as low cost and flexibility [1].

5.2.2 Perovskite Solar Cells

Recently, lead halide perovskite solar cells have attracted particular interest in research society due to several advantages they have over the traditionally used Si solar cells. One of the main advantages is the simplicity of perovskite photovoltaics processing. As distinct from silicon cells, perovskite solar cells do not require expensive, multistep processes at high temperatures and other expensive facilities. At the same time, hybrid organic-inorganic halide perovskite solar cells can be fabricated by solution process technology, including ink printing in a standard laboratory environment [12]. Moreover, detailed balance analysis [13] shows that the

efficiency limit of perovskite solar cells is about 31%, which approaches the Shockley-Queisser limit (33%). The above-mentioned properties of perovskite photovoltaics make them a commercially attractive option due to the demand for sustainable energy.

The extremely rapid increase of power conversion efficiencies from under 4% in 2010 to a record efficiency exceeding 22% in 2016, immediately made perovskite solar cells one of the most debated photovoltaic technologies in the short history of light harvesting. Similarly to the other technologies discussed in this chapter, lead halide perovskite active layer can be very thin—just a few hundred nanometers—for effective light absorption. Moreover, regarding the electronic structure, lead halide perovskite material is itself very versatile (see Figure 5.3). By playing with halide and organic precursors its band gap can be tuned from 2.52 eV for MAPbCl₃ to 1.5 eV for FAPbI₃ [14–16]; and partial substitution of lead with tin narrows the band gap to even lower values, down to 1.17 eV [15].

There is still an issue of the toxicity of lead-containing perovskite active layers, even though lead is widely used in car batteries; in this regard, this technology cannot be called “green.” Nevertheless, one of the interesting “environmentally responsible” approaches was reported in the *Energy & Environmental Science* journal [17], where old car batteries were used to manufacture lead halide solar cells. However, toxic lead can be substituted by tin [18, 19] or strontium [20]. Nevertheless, efficiencies of such cells lag behind lead-based perovskite absorbers. Out of all the possibilities, the best results were shown using methylammonium and formamidinium lead trihalides and their mixtures. Such lead halide perovskite solar cells have been created using a variety of solvent techniques and vapor deposition techniques, both of which have the potential to be scaled up with relative feasibility [21, 22].

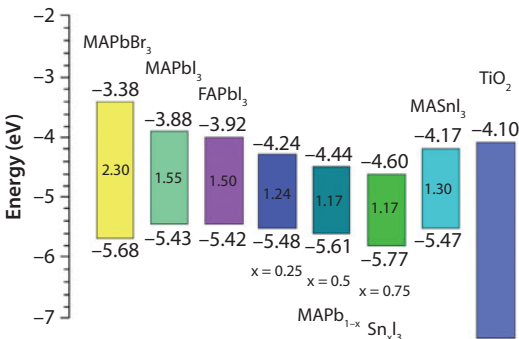


Figure 5.3 Band gap tuning of halide perovskite materials [15].

Another promising application of the perovskite solar cells is manufacturing of hybrid silicon-perovskite or CIGS-perovskite solar panels by depositing perovskites on top of conventional Si or CIGS solar cells (Figure 5.4). Wider in comparison with silicon, the band gap of perovskite will result in a broader absorption spectrum. Theoretically, this can be applied using existing Si solar panels and it may actually boost the silicon solar cell industry. Efficiency could exceed 30%, with the theoretical limit being around 44%. The improved performance would come from harnessing more solar energy. Perovskites have tunable band gap, which is, however, wider than that of silicon; thus the higher energy light would be absorbed by the perovskite top layer; at the same time, lower energy sunlight which passes through the perovskite would be absorbed by the Si layer. For example, Noel *et al.* [23] reported four terminal configuration tandem solar cells (two sub-cells are electrically isolated) based on microcrystalline-silicon-perovskite and CIGS-perovskite tandems. The authors reported a significant incremental increase of the efficiencies from 11% to 17% for mc-Si; for CIGS-based tandem power conversion efficiencies increased from 17% to 18.6%.

Several techniques [12, 24, 25] were reported regarding the wet-processed printing and coating manufacturing of perovskite solar cells, including screen and inkjet printing. The simplest way of precursor deposition is the so-called one-step solution-processing method, where a lead

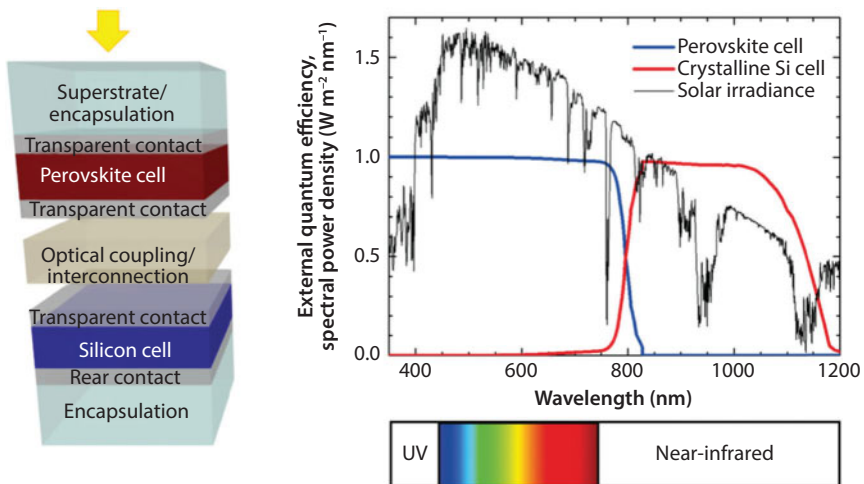


Figure 5.4 Tandem Si/perovskite solar cell structure (left) and absorption spectrum (right).

halide and an organic substituent are deposited from one solution onto a substrate. Subsequent or simultaneous annealing results in dense layers of well-crystallized perovskite material, due to the strong ionic interactions within the material (the organic component also contributes to a lower crystallization temperature). However, in most cases the layers contained cracks and pinholes and thus required the addition of other chemicals such as methylammonium chloride, as reported in ref. [12].

Several reports [26, 27] have shown that multistep procedures are more advantageous in comparison to simple one-step ones. Also, the vapor-assisted technique, where lead halide is annealed in the presence of methylammonium iodide vapor at a temperature of around 150 °C [28] showed its merits over solution processing, as it opens up possibilities to deposit multilayered solar cells over large areas [29]. Another technique using room-temperature solvent-solvent extraction produces high-quality crystalline films with precise control over thickness down to 20 nanometers across areas several centimeters square without generating pinholes [30]. In another solution-processing method, the mixture of lead iodide and methylammonium halide dissolved in DMF is preheated. Then the mixture is spin-coated on a substrate maintained at higher temperature. This method produces uniform films of up to 1 mm grain size [31]. Even though the above-mentioned techniques were applied using spin coating in a laboratory environment, the new findings assume that they can be successfully implemented using coating/printing technologies; thus these processes hold promise in terms of scalability.

5.2.3 Organic Solar Cells

An organic solar cell is a type of photovoltaic that uses semiconducting organic materials (polymer or small molecules) for light absorption and charge transport [32]. One of the most common organic photovoltaics is the polymer-fullerene, bulk-heterojunction solar cell. This type of solar cell is easy to process and potentially inexpensive; however, it still has some issues, such as limited efficiency [33–35] and long-term stability [36], compared to inorganic photovoltaic cells such as the commonly used Si, CdTe or GaAs solar cells. On the other hand, most of the materials used in organic solar cells are soluble and thus can be deposited by numerous printing and coating techniques. The optical absorption coefficient of organic molecules is high, thus a large amount of sunlight can be absorbed with a very thin layer, usually below a hundred nanometers. Therefore, they can be produced cost-effectively in large volumes on a great variety of substrates; organic photovoltaics can be deposited on textile [37]

and even on paper [38]. Also, the installation of flexible organic solar cells is extremely fast and facile, as was shown in Solar Park [39]. Moreover, organic solar cells show unbeatable weight-to-power ratio, which can be of utmost importance in such highly demanding fields such as aerospace engineering. One of the world leaders in research regarding the large-scale production of organic solar cells is Frederik C. Krebs from the Technical University of Denmark, who has published numerous papers regarding printing and coating techniques (e.g., see refs. [40–43]).

Another unique property of organic conjugated materials is their tunability by molecular engineering (e.g., changing the length and functional group of polymers). In this regard, altering functional groups of molecules can change the band gap, allowing for electronic and optical tunability. Consequently, tunable organic materials are advantageous not only in terms of their electrical properties but also in terms of their visual attractiveness, due to the fact that solar cells of any color can be made. For example, photovoltaic stained glass windows can be made of semitransparent organic solar cells of any visually pleasant colors, whereas inorganic or hybrid solar cells are mostly black, brown or grey.

Regarding the structure and fundamental operational principles, regular organic solar cells consist of a transparent anode created by one or two layers of organic semiconductor or their mixture and a metallic conductor such as aluminium cathode. Their function is based on photoelectric phenomena. To simplify things as much as possible, we can say that after absorption of light, charge carriers are generated. Charge carriers are transported to the electrodes and current is generated in the circuit. In the case of organic solar cells, the created particle is called an exciton [44], which is an electron-hole pair bonded together with the energy of approximately 0.4 eV. Excitons can dissociate within the electric field [45] of about 10^6 V cm^{-1} . The absorption of the light sometimes does not lead to charge carrier generation [46]. The exciton needs to be separated before the charge is transferred by the electrodes. The diffusion length of an exciton usually varies about 10 nm in the case of organic materials like polymers and pigments [47]. To ensure sufficient absorption of the light in the visible region, the active layer must be around 100 nm, which leads to a higher number of recombining excitons.

The very first solar cells were Schottky diodes consisting of the anode, one organic layer and the cathode. The devices were quite ineffective, as the photogeneration could only be realized within the small area or organic layer and metal electrode interface. More effective solar cells are based on photogeneration at the interface of two organic semiconductors, which is known as the heterojunction. Though in the case of bilayer, the

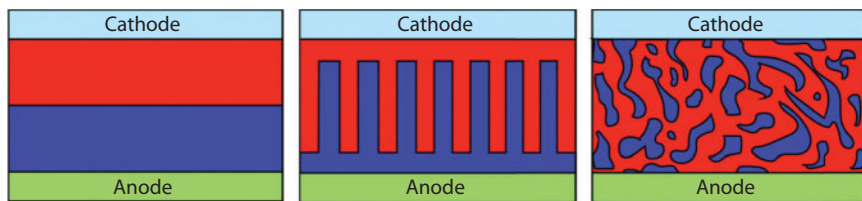


Figure 5.5 Types of organic solar cell junctions: planar junction (left), controlled heterojunction (center) and bulk heterojunction (right). Donor material and acceptor materials are depicted in blue and red colors respectively.

heterojunction is small and it is far from easy for charge carriers to reach it. That is why solar cells with bulk heterojunction are more suitable [48].

It has to be noted that there are a variety of junctions of organic solar cells (Figure 5.5). There are single layer, bilayer, discrete heterojunction, bulk heterojunction, graded heterojunction and continuous junction. However, we will dwell upon one type of junction, which is bulk heterojunction. This type of junction is predominantly processed by a solution procedure. Ease of processing and relatively high efficiencies [48] make this type of junction the most promising when mass production is considered.

5.2.4 Printable Charge-Carrier Selective Layers

All of the three main types of printable solar cells mentioned in this chapter require an effective charge carrier separation at the anode and cathode; thus, high electron/hole selectivity of both contacts is required. Contact selectivity staunchly depends on the band structure (or HOMO/LUMO levels for organic materials) of the interfacial materials, along with the high mobilities of one type of charge carrier and effective blocking of the other, i.e., unipolarity is required.

In most of the commonly used materials, charge carrier selective contacts are based on metal oxides, such as MoO_x , WO_3 , NiO_x , Al_2O_3 , etc., for hole injection/transport, and ZnO , TiO_2 , LiO , etc., for electron injection/transport. Usually deposition of these materials can be processed by vacuum evaporation (e.g., MoO_x , WO_3) or sol-gel method (e.g., ZnO , TiO_2), which are not suitable techniques if fully printable devices are considered. However, sol-gel is a solution-processable technique and mostly requires high-temperature post-deposition treatment (up to 300 °C and more), which on the one hand is not applicable for many flexible polymeric or textile substrates and on the other hand contradicts the idea of low processing temperatures of printable electronics. Nevertheless, there are

already commercially available metal oxide nanoparticle dispersion inks, which do not require high-temperature treatment.

Alternatively, one of the most promising candidates for a printable charge transport layer are carbon-based materials such as graphene [49], graphene oxide [50] or carbon nanotubes [51, 52] aqueous dispersions.

5.3 Solution-Based Deposition of Thin Film Layers

To give a broad-brush picture of coating and printing techniques for an industrial-scale production of printed solar cells, it can be noted that:

- Active material can be of organic (bulk-heterojunction OPV), inorganic (CIGS solar cells) or hybrid (perovskite solar cells) origin;
- Thin films can be produced by the deposition of an active material on a flexible (polymer foil, paper, textile, etc.) or non-flexible (e.g., glass) substrate;
- Deposition of an active material can be patterned (printing) continuous layer without a pattern (coating) by contact or contactless method.

There are a great variety of techniques that are suitable for preparation of thin films from a solution; however, several limitations reduce the usefulness of some of these techniques in practice. It is necessary to deeply consider which technique can be applied according to the desired outcome. First of all, many methods require large amounts of material and a lot of wastage is being produced. Secondly, for large-scale production it is of great importance to achieve good reproducibility, which is a challenging task. The third problem is that many of these techniques are suited only for small-scale laboratory applications but cannot be transferred to large-scale production. Spin coating can be named as a typical example of such a problem, where the most commonly used technique possesses good results on a laboratory scale but cannot be used in manufacturing as long as the maximum sample size is limited to only a few square centimeters. A lot of printing processes have been optimized for the preparation of large-volume devices and they will be briefly introduced in this chapter.

As previously mentioned, all wet processing thin film deposition methods can be basically divided into two categories: coating and printing processes. Coating can be described as a process of forming a film on a substrate without creating a complex pattern, whereas printing involves

the creation of a very well-defined film. It could be said that, considering *a priori* that the films are uniform, the thickness of a layer prepared by coating is the only parameter that is of concern [53]. Techniques can also be divided according to whether the substrate comes in direct contact with the deposition unit. In such cases we talk about contact methods, the other type is contactless methods.

5.3.1 Coating Techniques

As previously mentioned, coated films include no pattern in contrast to printed films. The thin film can be prepared by spraying, casting, smearing or painting over the surface. Techniques such as spin coating, doctor blade coating, spray coating, slot-die coating, curtain coating or knife-over-edge coating can be categorized as coating techniques [54].

5.3.1.1 Casting

Casting is definitely the simplest technique for preparation of layers. This procedure involves just a transport of ink on a substrate followed by drying of solvent. The only real advantage of this technique is that no special equipment is needed. It is possible to prepare films of good quality as well as thick films but the lack of control of film thickness, picture framing at the edges and sometimes even a precipitation of the ink during drying are significant drawbacks to the use of casting. Another problem could be control of the surface tension of the substrate and the fluid. The process of drying is inhomogeneous when the surface tension of the ink is dominant over the surface tension of a substrate.

5.3.1.2 Spin Coating

There can be no doubt that spin coating is practically the most widespread method for deposition of thin layers from the solution. It is used in microelectronics for application of polymeric photoresist on silicon wafers during preparation of transistors. It is also involved in some steps for manufacturing of CDs and DVDs. This technique has been the subject of many studies, for instance Norrman *et al.* [55]. The typical spin-coating operation involves placement of substrate on a vacuum pad and application of solution on top. The pad with the substrate rotates at a specified speed (up to several thousands of rotations per minute), which is the key parameter of this process. Fast evaporation of solvent and forming of layer occur, as can be seen in Figure 5.6. When the rotation is started the abundant material is ejected thanks to the high angular speed and only the preferable thin

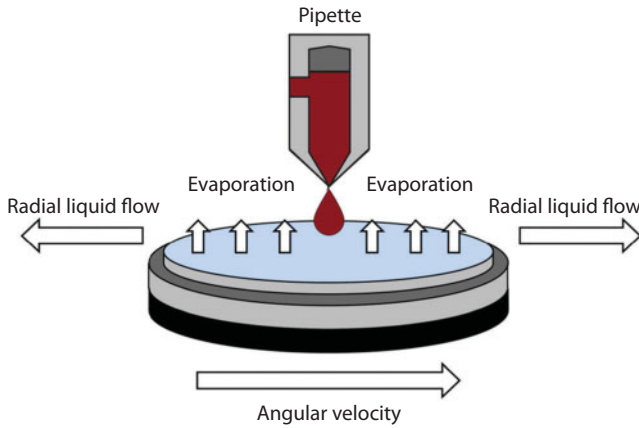


Figure 5.6 A typical spin-coating process.

film remains on the substrate. Resulting properties of the layers (thickness, homogeneity, topology, etc.) show excellent repeatability when using the same solvent and concentration of solid active material. It should be noted that it is not possible to achieve one specific value of thickness for the layer but instead a range of values can be obtained. Another disadvantage is that when deposition at an elevated temperature is needed, most of the commercially available spin coaters do not offer this option.

The thickness and morphology of the resulting layers strongly depend on rotational speed, viscoelastic properties of the ink, volatility, molecular weight and so on but are not very dependent on the amount of material deposited or the spinning time. The thickness of the layer can be roughly estimated from the empirical formula:

$$d = k_{spin} \cdot \omega^a \quad (5.1)$$

where ω is rotational speed ($\text{rev} \cdot \text{min}^{-1}$) and k_{spin} and a are empirical constants that take into account the physical properties of solvent, solute and substrate. Constant a typically attains the value around -0.5 . More detailed information can be seen in ref. [55]. It is also possible to start the rotation and apply the solution on the rotating substrate. This second approach is preferable when the solution is based on volatile solvent which would start to evaporate too quickly to form a homogenous layer. A relatively large area could be coated at once with very good homogeneity of the targeted layer (substrates up to 550 mm in diameter). However, the expression “relatively large” can be used only regarding laboratory-scale production.

Spin coating has found special application in the field of photovoltaics due to the fact that formation of thin film with relatively fixed thickness, morphology and topography of the surface can be easily reproduced. An excellent example of using spin coating in polymer solar cells is the preparation of P3HT-PCBM layer with 1,2-dichlorobenzene [56, 57]. Although lab-scale application of spin coating is extensive, it still remains to be seen whether the disadvantages of mass producing various products by this technique will be technically overcome in order for this technique to gain more popularity in the printed electronics industry.

5.3.1.3 Blade Coating

During blade coating, a sharp blade is placed in a defined position (10–500 nm) over the substrate to be coated and the coating solution is placed in front of the blade. The blade is then drawn with linear speed (usually several $\text{cm}\cdot\text{s}^{-1}$) across the substrate, forming the wet thin film layer of declared height. This process can be seen in Figure 5.7.

In theory the thickness of wet layer should be roughly half the distance between the substrate and the blade [54]. However, this parameter can vary significantly due to various physical phenomena such as the surface energy of the substrate, surface tension and viscosity of the solution. Forming of the meniscus between the blade and solution is another important criterion.

The thickness of a dry layer can be predicted by an empirical formula:

$$d = \frac{1}{2} \left(g \frac{c}{\rho} \right) \quad (5.2)$$

where g is the gap distance, c is the concentration of the solid material in solution (in $\text{g}\cdot\text{cm}^{-3}$) and ρ is the density of the solution (also in $\text{g}\cdot\text{cm}^{-3}$). All of the above could be a good reason for the greater popularity of spin-coating technique over blade coating.

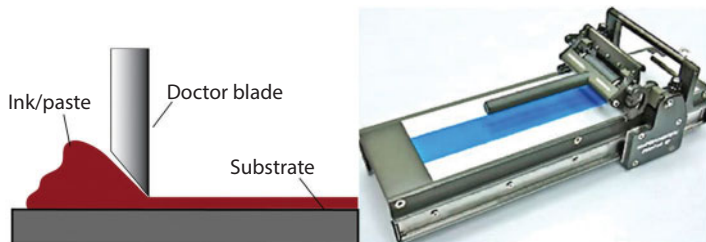


Figure 5.7 Illustration of the blade coating technique (left) and image of a blade coater (right) [58].

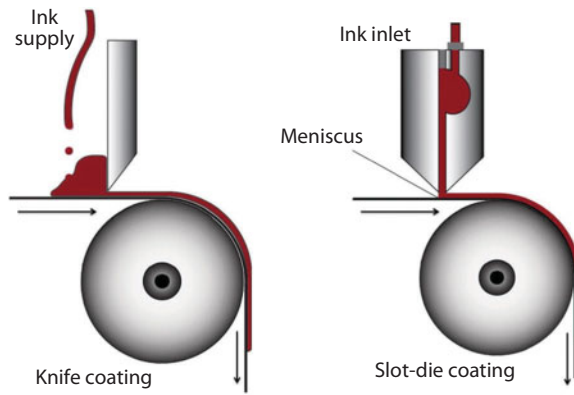


Figure 5.8 Basic principle of the rotary knife-over-edge and rotary slot-die coating methods [59].

It is usually stated that blade coating is a very parsimonious technique compared to the other coating techniques (such as spin coating), with almost no loss of the functional material. But a lot of material needs to be wasted when finding the optimal properties of the coated solution. Also, this method is not well suited for creation of prototypical devices. In the end, the amount of material that is wasted by this method can be easily compared to spin coating or the other methods.

The advantage of this process compared to spin coating is that it is possible to easily convert blade coating into roll-to-roll method where the flexible substrate is placed on a cylinder, as can be seen in Figure 5.8. In the last two decades, blade coating has experienced increasing interest for the fabrication of small-scale lab devices. One of the studies where blade coating was used as a deposition technique was the work conducted by Mens *et al.* Polymer solar cells based on a mixture of MDMOPPV and PC₆₀BM were manufactured and the crystallinity of the active material was determined by solid-state NMR. The crystallinity of layers deposited by this technique was higher compared to the spin-coated layers [60]. As of now, the use of roll-to-roll (R2R) printing is limited except for fully printed ZnO layer on the ITO [41].

5.3.1.4 Slot-Die Coating

Slot-die coating is a contactless high area deposition technique for preparation of thin layers with high uniformity. As it is a one-dimensional method, it is suitable for the manufacturing of multilayer polymer solar cells [41],

secondary batteries and electrodes for printed electronics [61]. This technique represents a unique combination of three key properties:

- **Premetered:** the coating thickness is predetermined by the feeding pump, coating speed and width of the mask and does not depend on any extra adjustments of the head.
- **Contact free:** the substrate is in contact only with the coating liquid which gives the advantage of avoiding scratches on the substrate.
- **Fully sealed:** the coating system is fully closed and solvents do not evaporate so that the concentration of ink is kept constant.

It is a quite simple technique where the ink is fed into the printing head with very well-defined shape. The real challenge is that the printing head is usually of very complicated design. It consists of an ink distribution chamber, feed slot and upstream and downstream lip, as shown in Figure 5.9. The internal mask (shim) is a critical part which is responsible for the resolution and the dimension of the slots. Both the shim and the whole printing head are made of stainless steel and the typical width of the printing mask ranges from 10–100 μm , while masks thinner than 20 μm are difficult to handle and the masks wider than 60 μm might require a more viscous ink for the correct deposition [61]. Theoretically, a very broad range of viscosities from less than 1 mPa·s up to several thousand Pa·s can be used, but when considering using the ink with relatively low viscosity (<20 mPa·s), the ideal width of the mask is roughly 25–50 μm . When using the low-viscosity ink a second supportive internal mask can be attached to help



Figure 5.9 Open slot-die head: (from left to right) ink distribution chamber, feed slot, lip and internal mask (shim).

prevent joining of the menisci of the two adjacent stripes. The R2R type of slot-die coating has been widely studied for high viscous inks at high speed deposition (>11 mm/min) [62].

The thickness of a wet film can be roughly estimated by the empirical formula:

$$d = \frac{f}{v_c \cdot w} \cdot \frac{c}{\rho} \quad (5.3)$$

where f is the flow rate (in $\text{cm}^3 \cdot \text{min}^{-1}$), v_c is the coating (or web speed) speed (in $\text{cm} \cdot \text{min}^{-1}$), w is the coating width (in cm), c is the concentration of the solids in the ink (in $\text{g} \cdot \text{cm}^{-3}$) and ρ is the density of the active dried material in the final film (in $\text{g} \cdot \text{cm}^{-3}$).

Interesting research was done by Krebs in 2009 [63] where a polymer solar cell based on the active material P3HT was prepared almost fully from the solution by slot-die coating. The bottom electrode based on nanoparticle silver was deposited on polyethyleneternaphthalate (PEN) substrate. An electron transporting layer of nanoparticle ZnO followed by an active layer of P3HT:PCBM and a hole transporting layer of PEDOT:PSS were all deposited by slot-die coating and only the top electrode was screen printed. No ITO layer was involved, which is a significant economic advantage, but the overall performance was a paltry 0.3%. All the layers were deposited in air and no vacuum was involved in the manufacturing process, which negatively affected the performance.

Similar research was conducted by Krebs [41] where ITO was introduced by screen printing and the other layers were either slot-die coated or deposited via knife-over-edge or screen printed. The top silver electrode was slot-die coated. The length of each individual stripe was 25 cm and the width was 0.9 cm. An active area for each individual stripe was 15 cm^2 . Performance was ten times higher compared to the fully screen-printed devices. The processing speed for all the layers was in the range of $40\text{--}50 \text{ m} \cdot \text{h}^{-1}$. Again, no vacuum steps were introduced.

Slot-die coating can also be used for production of polymer-based light-emitting diodes (OLEDs) [64] or more process-tolerant light-emitting cells (LEC) [65].

5.3.2 Printing Techniques

Printing techniques are typically contact methods (the one exception being digital inkjet printing) that allow a certain pattern to be deposited on the

substrate. Various printing techniques give a wide variety of achievable thickness and resolution of layers and speeds of deposition.

5.3.2.1 Screen Printing

Screen printing (Figure 5.10) is a two-dimensional (2D) technique, which means that complex well-defined patterns can be fully printed by this technique. The pattern is defined by open slots in an otherwise closed screen. The closed slots are usually filled with almost insoluble photo emulsion. The ink is deposited on top a screen and a so-called squeegee is drawn over the entire area of the screen. The ink is forced through the open image and deposited on a substrate. The mesh itself is placed in a snap-off distance above the substrate. The theory behind this subject has been described exhaustively (e.g., see ref. [66]).

A great advantage of screen printing is that it is fully roll-to-roll compatible, where the mesh is cylindrical and the squeegee is placed inside the rotating screen. The screen rotates with the same velocity as a substrate and a full print is conducted in each cycle by the stationary squeegee. It is possible to obtain much higher printing velocities with rotary screen printing (up to 180 m/min) than with flat-bed screen printing (0–35 m/min) [59].

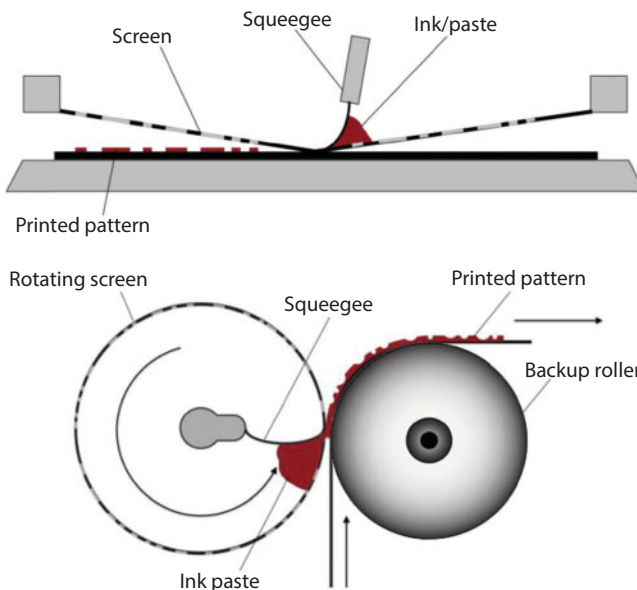


Figure 5.10 Schemes of flat-bed screen printing (top) and rotary screen printing (bottom) [59].

The logical disadvantages of this process are the high initial waste of material, since it requires a long time to adjust all the moving parts, and the high price of the rotary screens, hand in hand with the much reduced possibility of cleaning the screens. Basic schemes of both flat-bed and rotary screen printing can be seen in Figure 5.10.

It is difficult to consider screen printing as a deposition method for thin layers since the typical thickness of the layers ranges from less than 10 μm to more than 500 μm , which is partially given by the physical-chemical parameters of the inks. Typically inks with much higher viscosity than for the other methods are used (usually several tens or hundreds of Pa·s). Ink must be strongly viscous so that it does not pour through the open slots by itself. The resulting thickness of a dry layer depends on several factors such as the theoretical paste volume of the screen, V_{screen} , which is the volume between the threads of the screen and the thickness of emulsion, concentration of the solid in a ink, density and an empirical parameter called pickout ratio, k_p , which is dependent on factors like ink rheology, snap-off distance and snap-off angle, printing speed and squeegee force.

$$d = V_{\text{screen}} \cdot k_p \cdot \frac{c}{\rho} \quad (5.4)$$

where c is the concentration ($\text{g}\cdot\text{cm}^{-3}$), ρ is the density of material in the dry film (given in $\text{g}\cdot\text{cm}^{-3}$) and V_{screen} is the paste volume of the screen given in ($\text{cm}^3\cdot\text{m}^{-2}$).

Screen printing is currently used in the industry for printing conductors for flexible electronics and keypads. Only several cases of preparation of polymer solar cells have been reported; for example, in a study by Shaheen *et al.* [67] only the active layer (the blend of materials MDMO-PPV and PC_{60}BM) was deposited on a PEDOT:PSS by screen printing. The other layers were deposited by other techniques. The resulting power conversion efficiency (PCE) was 4.2%. There was another attempt by Aernouts *et al.* [68], where the active blend was MEH-PPV and PCBM, with the resulting PCE of 1.25% under standardized simulated solar illumination (AM 1.5 G; 100 mW/cm^2). A detailed investigation was done by Krebs *et al.* where blends of P3MHOCT/PCBM/ZnO were used as an active material [42]. Although the manufactured solar cells did not show good results, it was the first attempt to produce the whole device only by means of screen printing deposition method.

Very up-to-date research was done by Bondoni *et al.* [69], where terpeneol-based TiO_2 screen printing inks were thoroughly investigated as a very promising material for printing of a photoanode layer.

The very demanding requirements for the ink, such as low volatility and high viscosity, and the resulting thickness of the layer are somewhat limiting factors for use in the field of organic photovoltaics (OPVs). Polymer MEHPPV has suited these demands best up till now and it appears to be the top candidate from the polymer-based materials, as can be seen from this U.S. patent [70]. Commercially available PEDOT:PSS and silver inks exist and are usually used for preparation of various electrodes, conducting lines or semiconducting layers. As an example, rotary screen printing of PEDOT:PSS|ZnO electron transport layer is described in ref. [71]. A study was conducted on this topic to evaluate the influence of various silver paste solvents on the OPV characteristic.

Although correct formulation of the ink for screen printing is challenging at the moment, it is very likely that this deposition technique will gradually become more important in the field of organic PSC. Krebs *et al.* showed that real working devices can be processed at a very favorable price [42].

5.3.2.2 Gravure Printing

Gravure printing is a widely used high-volume printing method usually applied in the graphics industry [72, 73]. Using gravure printing, a high deposition speed of more than $15 \text{ m}\cdot\text{s}^{-1}$ can be achieved. In recent years, it has gained popularity in the field of printed electronics due to its potential for printing smooth layers with high resolution and the fact that a large variety of the materials could be deposited by gravure printing.

This technique is based on an ink transfer from the gravure cylinder to a substrate. A pattern is etched, mechanically or laser engraved on the gravure cylinder, which is immersed in an ink tank that is attached through a surface tension to the gravure cylinder and wiped by a doctor blade. Only the ink in engraved cells is then printed in a defined pattern on a substrate (Figure 5.11). The gravure cylinder itself is made of steel, while there is a thin copper plate that holds the predetermined pattern, and the upmost layer is made from chromium and works as a wear-resistant layer. A significant disadvantage of this method is the lack of possibility of changing a pattern. If a new pattern is to be introduced, the cylinder must be reshaped or a new cylinder must be purchased.

Gravure printing is easily adjustable for R2R since the substrate can be placed on an impression cylinder under some tension and through a series of winding and unwinding cylinders is still in contact with the gravure cylinder. Usually PEN (poly(ethylene 2,6-naphthalate) or PET (polyethylene terephthalate) are used as a substrate.

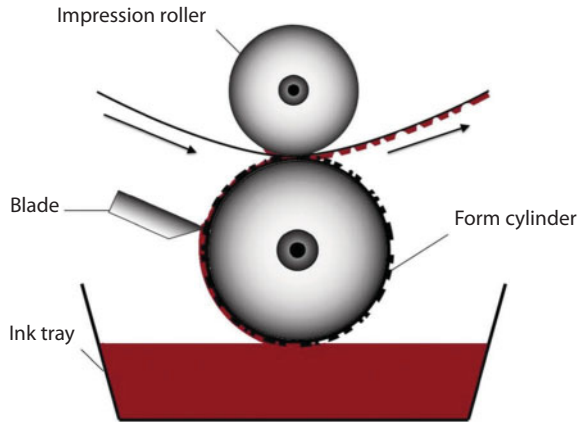


Figure 5.11 Basic principle of the rotogravure printing technique.

Thanks to the ability to print lines with resolution under 30 μm and the variability of materials that can be used, gravure printing is optimal for printing thin layer transistors (TFT) or functional traces for organic electronics. Interesting work was done with the material pBTTT, which was used for gravure printing of organic thin film transistor (oTFT), and silver source/drain (S/D) contacts were inkjet-printed. The thickness of the dry thin layer of pBTTT printed by gravure was 50 nm [74]. The privately owned company Thin Film Electronics ASA (TFE) is using rotogravure or flat-bed gravure in several applications. Development of fully printed oTFTs was done exclusively by this technique and Ag electrodes for commercially manufactured memory tags were also rotogravure-printed.

Thanks to its ability to print very thin (on the scale of ten nanometers) and homogenous layers, gravure printing has been used to prepare OPVs and OLEDs (organic-light emitting diodes) with similar structures. The typical active materials that have been most investigated are usually PEDOT:PSS and a mixture of P3HT:PCBM. One investigation involved the solvent composition and morphology wetting behavior of inks, among other things. Small modules with an area total of 15.45 cm^2 on PET substrate with indium tin oxide layer (ITO) were printed on a R2R compatible gravure printer. The efficiency of these modules was 1.92% but metallic electrodes were cathode evaporated [75]. Another interesting work was exhibited by Kopola *et al.* where the P3HT:PCBM active layer and PEDOT:PSS hole injection layer were gravure-printed and an effect of various engraving and printing parameters, ink compositions and printability parameters were examined. The obtained PCE from this work, 2.81%, is the highest obtained for gravure-printed OSCs (organic solar cells) [76].

Although a lot of work has been done in the field of gravure printing, in relation to printed electronics this work is primarily limited to flat-bed gravure printing. An example of the industrial use of rotogravure can be found in the Norwegian company TFE, which is using a fully compatible R2R rotogravure unit in large-scale component manufacturing.

5.3.2.3 *Flexographic Printing*

Flexography is a widely used technique, especially for foil substrates in the printing industry. It is a very quick printing method with speeds exceeding hundreds of meters per minute. The basic principles of this method, which can be seen in Figure 5.12, are based on an ink transfer from a soft printing plate to a substrate which is located on an impression cylinder. The transfer is handled by the raised area of the cylinder in the shape of a pattern. It works exactly in an opposite way than gravure printing. Suitable material for the printing cylinder is a rubber or some photopolymer of various types and chemical behaviors. The ink is transferred to the printing cylinder via a ceramic anilox cylinder which holds small engraved cavities on its surface. A doctor blade is attached above the cylinder and removes the abundant ink.

Demands for an ink rheology are similar to gravure printing with viscosities up to a few hundred cPs. The other parameters that could be tuned in order to optimize this process are printing speed, ink surface tension, nip force (the force of impact between printing and impression cylinders) and anilox cell geometry.

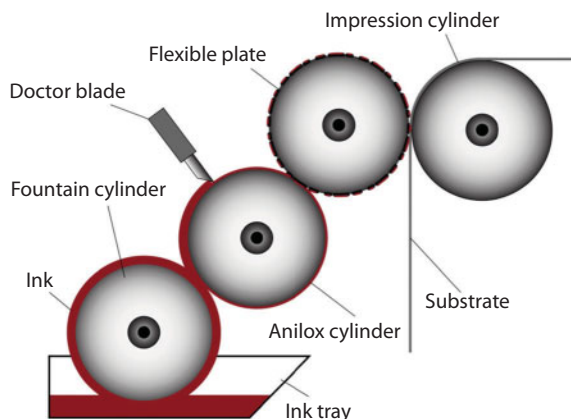


Figure 5.12 A simplified scheme of the flexographic printing process.

Flexography is not a broadly used technique in the field of OPVs and is mainly focused at the moment on printing layers of AgNP and PEDOT:PSS, both as electrodes. A paper-based OPV device has been prepared where transparent PEDOT:PSS acted as an anode layer on top of an active layer. This device exhibited a PCE of around 1.3% with an active surface of 9 mm² but the main application of flexographic printing for the area of OPVs is the deposition of silver-based inks for the grid of front electrode (sometimes referred to as flextrode). A variety of devices were prepared and examined, ranging from small lab-scale prototypes up to several-meters-long modules, based on flextrodes with either a honeycomb structure or one of slanted grid fingers [77]. It was shown that fabrication speeds exceeding 20 m·min⁻¹ are achievable.

Flexography can be used not only in the field of OPVs but also for printing electrodes, dielectric layers for OTFTs, paper-thin loudspeakers and various electroluminescent layers [78–80].

5.3.2.4 Inkjet Printing

Inkjet printing is a well-known technology used daily, and in the last 30 years it has found many interesting applications that go beyond the conventional printer [81]. This technique is based on the generation of a multitude of small droplets (typical volume is in the range of several picoliters) by a printing head. These droplets are then transferred in the form of a predetermined image on a substrate. A lot of interdisciplinary research had to be done in order to make this technique reliable. Good knowledge of fluid mechanics, electrostatics, optics, ink chemistry and many more fields needs to be exercised.

Inkjet printing can be divided into two distinct categories: continuous inkjet (CIJ) and drop-on-demand technique (DOD). Only DOD will be mentioned in this work since continuous inkjet does not meet the requirements for printable electronics. Among the biggest advantages of this method is that no hardware master is needed (compared to other techniques) since the image is in digital form and the resolution of targeted images can be achieved with little difficulty. Resolution ranges easily from 300–1200 dpi [54]. On the other hand, DOD inkjet suffers from several disadvantages as well. Printing speed is limited by the amount of nozzles and the biggest disadvantage is that the physical-chemical properties of the ink must be very carefully tuned so that fine droplets are created and form a sharp pattern on the substrate. Properties of inks suitable for application in the field of printed electronics cannot be tuned indefinitely.

The majority of modern DOD printing heads use piezoelectrically actuated transducers that eject droplets on demand when external voltage is applied to them. This voltage waveform induces a pressure pulse that is propagated through the ink in a chamber just behind the printing nozzles. Once the pressure pulse exceeds the threshold at the nozzle the droplet is ejected through a nozzle. The ink itself is contained within the chamber through surface tension and static pressure that further help to stabilize the meniscus at the nozzle. A simplified process can be seen in Figure 5.13.

Thickness of a dry inkjet-printed layer is given by the number of droplets deposited per area, volume of droplets and the concentration of solid in an ink:

$$d = N_D \cdot V_D \cdot \frac{c}{\rho} \quad (5.5)$$

where N_D is the number of droplets deposited per area in cm^{-2} , c is the concentration ($\text{g}\cdot\text{cm}^{-3}$), ρ is the density of material in the dry film ($\text{g}\cdot\text{cm}^{-3}$) and V_D is the volume of droplets in cm^3 .

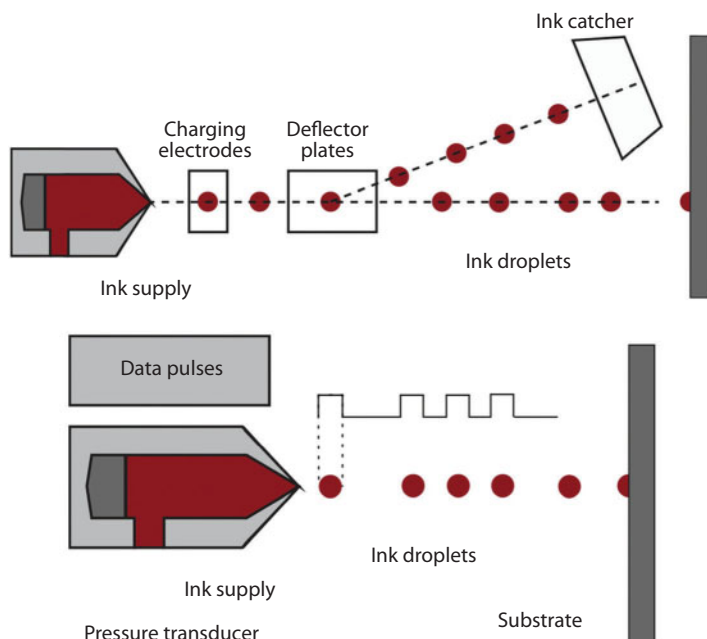


Figure 5.13 Difference between continuous inkjet (top) and DOD (bottom) [40].

The cooperation between the physical-chemical properties, such as viscosity of ink (dynamic viscosity in the range of approximately 4–30 cP), surface energy of the substrate, and surface tension of the ink, for forming droplet or stream of droplets (typically $> 35 \text{ mN}\cdot\text{m}^{-1}$), suitable mixture of solvents (sometimes 5–8 different, sometimes very volatile, solvents) and printing parameters, such as the drop distance, printing head, and printing velocity, requires a lot of adjustment in order to meet satisfying resolution, pattern definition and homogeneity [81, 82]. Because of these limitations it is currently hard to determine if this technique will find any suitable application in the field of printed polymer solar cells [54].

As mentioned earlier, when the voltage waveform is applied a droplet is shot from the nozzle with relatively high initial velocity. At this moment the droplet is still connected with the ink in the nozzle by a stretching ligament. At some point the ligament is broken and a surface tension of the liquid forces a droplet to take a spherical shape. If the ligament is long enough it can even form satellite droplets that negatively affect the resolution of layer.

Both the viscosity and the surface tension are dominant forces that control behavior of droplets and streams of an ink. It is useful to describe the behavior of forming droplets and films by dimensionless numbers. The Reynolds number, Re , describes the ratio between inertial and viscous forces in a fluid:

$$Re = D \cdot v \cdot \frac{\rho}{\eta} \quad (5.6)$$

where D is a characteristic length (jet length of droplet diameter), v is velocity, ρ is density and η is dynamic viscosity.

Another dimensionless number that takes into account the kinetic energy and surface energy is the Weber number, We :

$$We = D \cdot v^2 \cdot \frac{\rho}{\sigma} \quad (5.7)$$

where σ is surface tension.

An important number is the so-called Ohnesorge number, Oh , which describes the relative importance of viscous and surface forces:

$$Oh = \frac{We^{0.5}}{Re} \quad (5.8)$$

Interesting research was conducted by Martin *et al.* [81] where a window of printing conditions was determined for continuous inkjet and DOD in respect to the values of dimensionless criteria, which can be seen in Figure 5.14; and by Jang *et al.* where the interval of values of Z-number (inverse of Oh) was found out for the inkjet printing. This interval seems to be $4 \leq Z \leq 14$ [83].

It can be said that in recent years there has been increasing interest in using inkjet for the fabrication of OPVs on a lab scale. Both the active layers and PEDOT:PSS were printed in the form of homogenous layers and the material AgNP was printed in the form of grid as a current collecting unit. The reported inkjet printed cells with the highest PCE have achieved 3.7% so far with the active layer of PFDTBTP:PCBM [84]. In this study a lot of different mixtures of solvents were used (such as anisole/tetraline, p-xylene/tetraline, etc.) but the best results were obtained with a mixture of chloro/trichlorobenzene. Otherwise a lot of work has been done with the standard polymer P3HT. An interesting discovery was made on the use of additives which influence the morphology and optoelectronic properties of the active layer. The best result was achieved with 1,8 octanedithiol, which led to an efficiency of 3.71% [85]. It was also noted that additives have a strong influence on the overall performance of the solar cell. Surface morphology and printability of PEDOT:PSS in normal-structured OSCs could be enhanced by addition of glycerol or ethylene glycol butyl ether (EGBE). The addition of these substances resulted in PCE of about 3.16% [86].

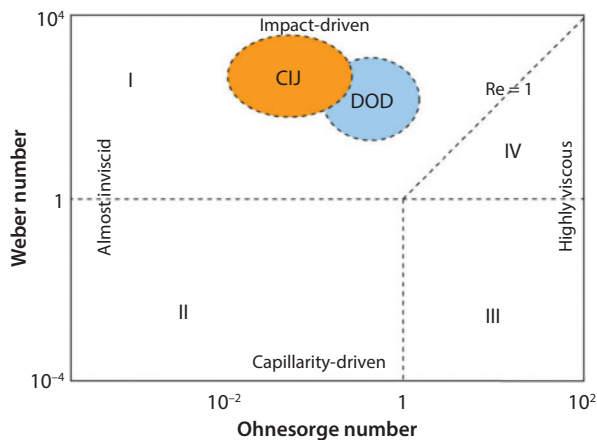


Figure 5.14 Schematic diagram showing four regimes of behavior of liquid drop based on the values of We and Oh [83].

Even though inkjet printing has seen its rise in the field of OPVs, there has been virtually no report on up-scaling this technique for high-volume application at the moment.

5.4 Characterization Techniques

5.4.1 Characterization of Thin Layers

In general, a layer is an object whose one dimension (thickness) is significantly smaller than the other two dimensions. When the thickness is small enough the material will start to exhibit the so-called quantum dimension phenomena which are unparalleled to the bulk objects. The two surfaces of a thin layer are so close to each other that the basic physical properties of these layers will show different behavior than expected. This can be said about the mechanical, thermic, optical and magnetic properties, just to a name few.

We typically talk about thin layers when the thickness of a material film ranges from 0.1 nm, which are monoatomic layers up to approximately 1 μ m. From this point of view the films prepared by a screen printing method might be problematic because they are usually thicker than several microns. But in this chapter these films will still be considered as thin films. In the 20th century thin film coatings experienced a tremendous rise and helped develop some modern day areas of technology and science. Multilayer metal and insulating films in microelectronics, semiconducting films in optoelectronics and stacks of dielectric films for optical coating, ceramic layers and many others can be taken as a short list of examples.

With respect to such a broad use of thin films and their significant contributions, techniques have been developed to classify them. All the parameters of thin films can be divided into three areas which affect the overall traits of films [87]:

1. Film thickness;
2. Film and surface morphology and structure;
3. Film and surface composition.

There are various methods that can provide us with information about the surface topography. Atomic force microscopy (AFM), which is a special type of scanning probe microscopy (SPM), is a commonly used technique similar to mechanical profilometry. A charged cantilever moves across the surface of a sample and interacts with the surface of the sample.

A displacement of cantilever is caused by this interaction, thereby causing a displacement of the laser beam on the photodiode. Profile topography can be obtained from the displacement of the laser beam.

Another important method is scanning electron microscopy (SEM), which is a type of electron microscopy where a sample is scanned by a focused electron beam. These electrons interact with atoms from the surface of the sample and secondary electrons are emitted. These electrons carry information about the sample.

Both of these methods have their advantages and disadvantages. Whereas AFM provides a 3D profile, the SEM provides only 2D images. There is no need to specially treat samples for AFM but for SEM a very expensive vacuum system must be applied. Higher resolution can be obtained by AFM but SEM gives significantly quicker, nearly real-time measurements.

5.4.2 Electrical Characterization of Solar Cells

In this part of the chapter we present a simple model for the characterization of solar cell efficiencies. Generally, the electrical characterization of photovoltaic cells is a complex problem, which includes the use of many various methods to gain deeper insight into the processes which can affect the efficiency and stability of the devices. Here, only the basics of electrical characterization are presented.

In the simplest approximation, photovoltaic cells can be modeled as a current source in parallel with a photodiode. Under dark conditions, where no photocurrent is generated, the solar cell indeed behaves like a diode. With light illumination, photocurrent is generated by the solar cell, as illustrated in Figure 5.15.

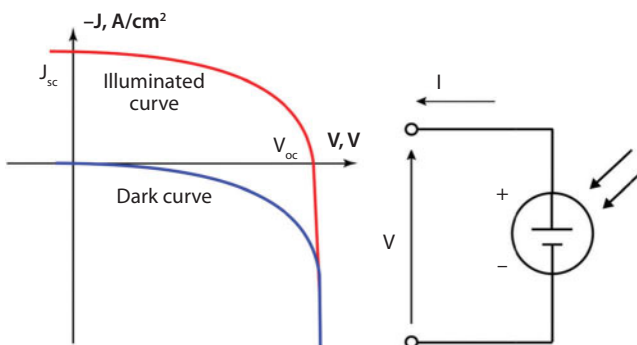


Figure 5.15 J - V curve of a photovoltaic cell and equivalent electrical diagram.

In the case of an ideal cell, the total current I is equal to the current I_ℓ generated by the photoelectric effect of the solar cell minus the diode current I_D , as shown in Equation 5.9:

$$I = I_\ell - I_D = I_\ell - I_0 \left(e^{\frac{qV}{kT}} - 1 \right) \quad (5.9)$$

where I_0 is the saturation current of the diode, q is the elementary charge of the electron, k is the Boltzmann constant, T is the cell temperature, and V is the measured cell voltage. Expanding the equation gives the simplified circuit model and the following associated Equation 5.10, where n is the diode ideality factor (typically between 1 and 2), and R_s and R_{sh} represent the series and shunt resistances that are described below in this chapter. Simple equivalent 1 diode circuit is depicted in Figure 5.16.

$$I = I_\ell - I_0 \left(e^{\frac{q(V+I \cdot R_s)}{nkT}} - 1 \right) - \frac{V + I \cdot R}{R_{sh}} \quad (5.10)$$

The J - V curve of a solar cell under light illumination is shown in Figure 5.15 and, it should be noted, that many performance parameters for the cell can be determined from this data.

As an example, a short-circuit current (I_{sc}) or more often short-circuit current density (J_{sc}), is an important parameter, which can be easily extracted from the I - V or J - V curve under illumination. The short-circuit current density J_{sc} corresponds to the short-circuit condition when the impedance is low and is calculated when the voltage equals 0, or simply intercrossing of the J - V curve with an axis of the ordinates, when $V = 0$. Another important parameter is an open-circuit voltage (V_{oc}), which occurs when there is no current passing through the cell.

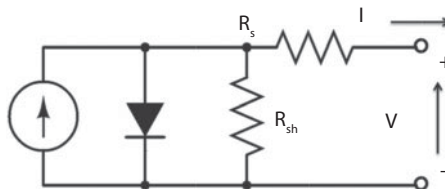


Figure 5.16 Simplified 1 diode equivalent circuit model for a photovoltaic cell.

The power produced by the cell can be easily calculated along the I - V sweep by the equation $P=I \cdot V$. At the I_{sc} and V_{oc} points, the power will be zero and the maximum value for power will occur between the two (Figure 5.17). The voltage and current at this maximum power point are denoted as V_{MP} and I_{MP} respectively.

The next parameter is the fill factor (FF), which is, in fact, essentially a measure of the quality of the solar cell. It is calculated by comparing the maximum power to the theoretical power (P_T) that would be output at both the open-circuit voltage and short-circuit current together. The FF can also be interpreted graphically as the ratio of the rectangular areas depicted in Figure 5.18, and can be calculated according to Equation 5.11.

$$FF = \frac{P_{MAX}}{P_T} = \frac{I_{MP} \cdot V_{MP}}{I_{sc} \cdot V_{oc}} \quad (5.11)$$

Finally, we have all the parameters to calculate the efficiency of the solar cell, which is the ratio of the electrical power output, P_{out} , compared to the solar power input, P_{in} , into the solar cell. Thus, efficiency can be calculated according to Equation 5.12:

$$\eta = \frac{P_{out}}{P_{in}} \Rightarrow \eta_{MAX} = \frac{P_{MAX}}{P_{in}} \quad (5.12)$$

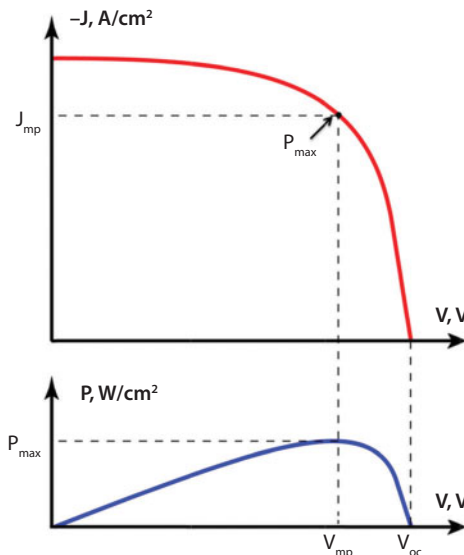


Figure 5.17 Maximum power for a J - V curve.

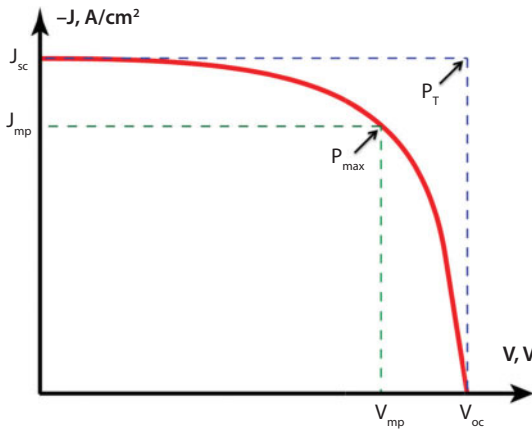


Figure 5.18 Getting the fill factor from the J - V curve.

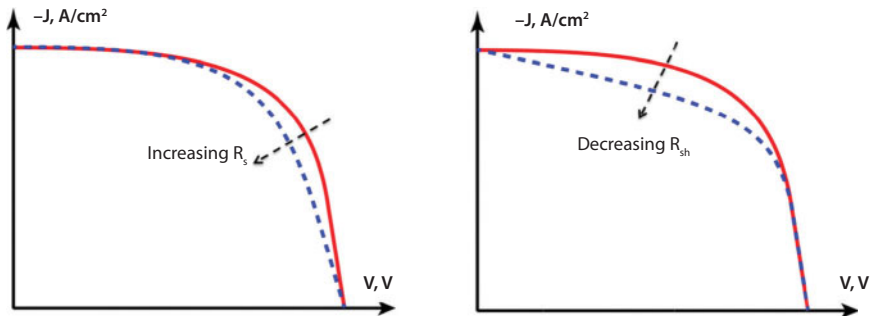


Figure 5.19 Effect of diverging R_s and R_{sh} .

where P_{in} is taken as the product of the irradiance of light, measured in W/m^2 or in suns ($1000 W/m^2$), with the surface area of the solar cell (m^2).

Other parameters which should be mentioned are a parallel shunt (R_{sh}) and series (R_s) resistances (Figure 5.19). During operation, the efficiency of solar cells is reduced by the dissipation of power across internal resistances. For an ideal cell, R_{sh} would be infinite and would not provide an alternate path for current to flow, while R_s is desired to be zero, resulting in no voltage drop before the load.

Usually series resistance corresponds to contact resistance and shunt resistance is a result of the non-ideality of bulk or interfacial parameters in the solar cells. Decreasing R_{sh} and increasing R_s will decrease the fill factor (FF) and P_{MAX} , as shown in Figure 5.19.

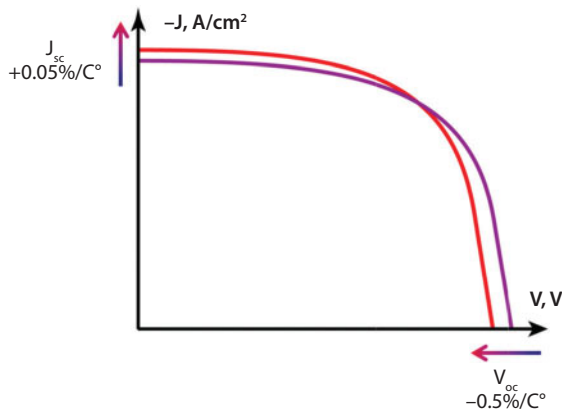


Figure 5.20 Temperature effect on the J - V curve.

The series and shunt resistances, R_s and R_{sh} , can be approximated from the slopes of the J - V curve at V_{oc} and J_{sc} , respectively.

During the characterization of solar cells, such an important parameter as temperature has to be taken into consideration. Figure 5.20 depicts the effect of temperature on a J - V curve. When a solar cell is exposed to higher temperatures, J_{sc} increases slightly, while V_{oc} decreases more significantly. Most of the modern software packages (e.g., Tracer 2) consider this parameter.

5.5 Conclusion

In conclusion, a future application of printed solar cells and overall printed electronics can be summarized. A roadmap in Figure 5.21 has been brought together by the experts from the Organic and Printed Electronics Association (OE-A), which is a group of more than 215 members from 31 countries from Europe, Asia, Australia and North America. The OE-A consists of material/equipment suppliers, research institutes and universities, producers and developers and end-users. The OE-A is assigned to the German Engineering Federation (VDMA), which is one of the key industry associations in Europe. The whole field of printed electronics has been divided by the experts of the OE-A into five subcategories such as OLED lightning, organic photovoltaics, flexible displays, electronic components and integrated smart systems. The up-to-date state is described for all the

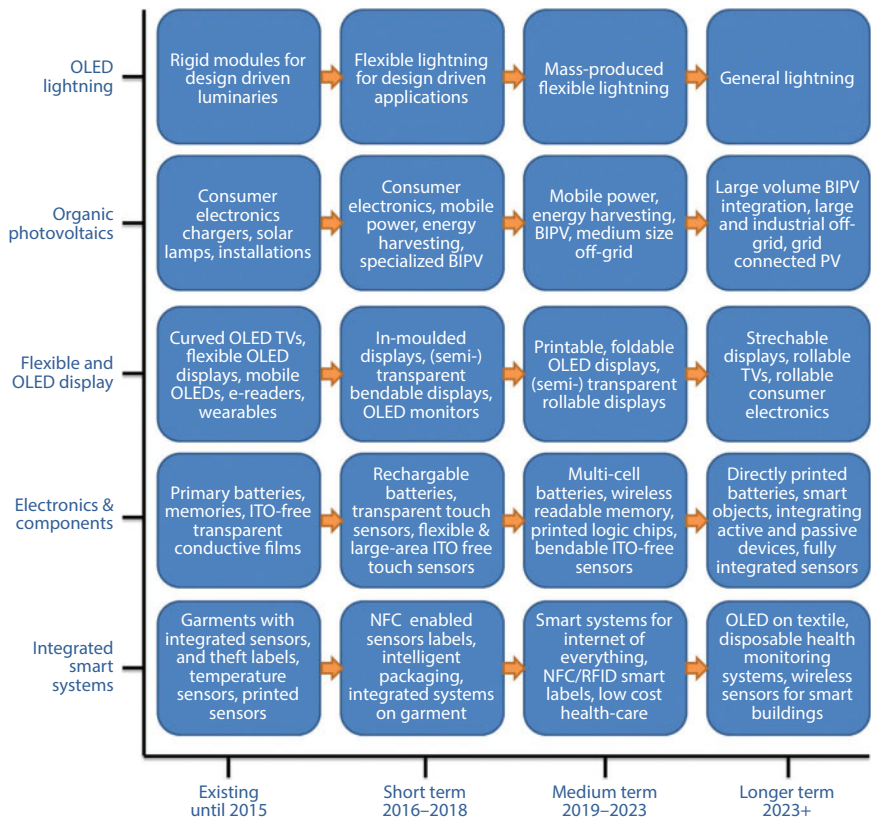


Figure 5.21 The Printed Electronics Association application roadmap, with the forecast for market entry.

categories and visions for further short-term and long-term (2023+) development are introduced together with a list of key technology parameters and so-called red brick walls for each of the five subcategories. These red brick problems represent technological problems and difficulties that need to be overcome in order to incorporate organic electronic devices into everyday life. Some of these problems might be:

- Performance and mobility of free charge carriers;
- Electrical barrier properties;
- Environmental stability;
- Flexibility of plastic substrate (improvement of a bending radius).

For instance, in the field of electronic components memory tags for brand protection are currently being developed and introduced and in the long-term fully printed batteries and other either active or passive components will be standardized. In the long term, the field of organic photovoltaics counts on standard solar cells having an efficiency of around 12–15%, and these cells will be fully building-integrated.

It is clear that printing and coating techniques are an excellent means for the mass-volume and high-speed production of various devices based on this new approach to electronics and therefore some of the potentially promising techniques that are currently being deployed in the field of printed electronics will be discussed in the following chapters.

It is notable that the preparation of fully printed electronic devices is extremely demanding and the results so far are not very convincing. Slot-die coating is well suited for applications where no pattern is needed but homogeneity and well-defined layer thickness is demanded, like in various planarization layers or blocking layers for charge carriers in OPVs.

Screen printing is a technique that gives well-defined pattern on one hand but puts severe demands on the physical-chemical properties of the ink on the other hand. This method finds application for deposition of electrodes for devices not based on ITO. Deposition of an active layer of MDMO-PPV:PCBM by screen printing with interesting PCE has been published. Since this technique can be modified for R2R printing it might be promising for mass-printing of active layers for OSC. Screen printing has also found application in the field of printed biosensors; an electrode grid with semiconducting PEDOT:PSS can be well printed using this technique.

Gravure printing and flexographic printing are in general similar methods and could be used for similar applications. Gravure printing is the most suitable technique in cases where the thickness of layers is of special concern and needs to be less than 100 nm. Together with flexography, this technique finds application for development of printed OTFTs; also, a good result in the field of organic solar cells was achieved by printing of an active layer of P3HT:PCBM.

Inkjet printing is the most versatile method since it needs only a digital master for printing. So far inkjet printing has been mainly used in the field of photovoltaics. At the moment the best results in OPVs were obtained with the inkjet printing technique but this does not necessarily mean that it is the best-suited technique. Inkjet printing is not R2R compatible and therefore it goes against the idea of mass-volume, high-speed manufacture of devices.

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Part II

ORGANIC MATERIALS AND PROCESS TECHNOLOGIES FOR PRINTABLE SOLAR CELLS

Spray-Coated Organic Solar Cells

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Abstract

Presented in this chapter is an overview of spray-coated organic solar cells. In the first section, a short introduction to the spray-coating method is given. Then there is a discussion of the available materials that can be coordinated with spray coating. Finally, the chapter ends with a presentation on the potential of spray coating in other organic electronics.

Keywords: Spray coating, organic solar cell, airbrush spray deposition, ultrasonic spray deposition, electrospray deposition, thermal annealing, solvent treatment

6.1 Introduction

Organic solar cells (OSCs) have been widely accepted as one of the highly potential candidates to solve the global energy crisis in an environmentally friendly and sustainable way [1]. Compared with conventional silicon solar cells, OSCs show several natural born advantages, including low cost of materials, high-throughput roll-to-roll production, mechanical flexibility and light weight [2–5]. However, although the power conversion efficiency (PCE) of OSCs has already been attributed to be over 11% for single junction devices by the constitution of novel low-band-gap material synthesis, it still does not fulfill pragmatic expectations [1, 6]. The shortage of reliable approaches which can satisfy both high efficiency devices

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and large-scale fabrication is a major limitation. The attention of scientists has been focused on the industrial high-throughput process rather than general method of spin coating and high vacuum thermal evaporation on the lab scale [7]. To realize large-scale coverage, various deposition techniques have been demonstrated in OSCs to be compatible with roll-to-roll (R2R) processing such as inkjet printing, screen printing, or doctor blading [1, 6, 7]. However, these techniques are suffering from stagnation due to the expensive equipment and strict requirements of materials. Hence, finding a well-established technique to match the state-of-the-art approach for high-efficiency OSC fabrication is a priority. As a result, spray coating, a well-established technique in graphic arts, industrial coatings and painting, has regained lots of attention recently.

6.2 Introduction of Spray-Coating Method

6.2.1 History of Spray Coating

Spray coating is a coating technique defined by how it works. A dynamic collection of drops dispersed in a gas is called spray. The process of forming a spray is known as atomization. The main uses of spray include distributing material over a cross section and generating liquid surface area. Although spray coating has been widely used for painting in commercial production, which is one of the cheapest solution processes, its application on OSC has been underexploited till very recently. In 2002, Fujita *et al.* proposed a novel method called “evaporative spray deposition from ultradilute solution” to prepare organic thin films [8]. After that, several groups realized high-efficiency OSCs by following this method. The PCE increased from 0.65% in 2002 to 7.6% in 2015 on polymer solar cell [8, 9], and to 13.6% on perovskite solar cell [3]. Although compared to the record efficient OSC based on spin coating, the PCE of spray-coated OSC is still a few percentages lower, it is still superior than all other R2R (roll-to-roll) matched techniques [10]. In the last decade there have been several equipment inventions according to the working dynamic of spray coating, which will be described in detail in the following sections.

6.2.2 Spray-Coating Equipment

6.2.2.1 Airbrush Spray Deposition

The first airbrush spray deposition (ASD) equipment was dependent on the definition, which was patented in 1876 by Francis Edgar Stanley [11].

Stanley and his twin brother later formed the Stanley Dry Plate Company where they invented a process for continuously coating photographic plates. No artistic images that used this “paint distributor/atomizer” exist or are as yet known. It took four years of further development before a working prototype was developed by Liberty Walkup, who re-patented the work under the name of “air-brush” [12]. His wife would later go on to be the founder of the Illinois Art School where airbrushing was taught to students from all over the world. The first certain “atomizing” type of airbrush was invented by Charles Burdick in 1893 and presented by Thayer & Chandler art materials company at the World Columbian Exposition in Chicago [13]. Burdick founded the Fountain Brush Company in the U.S. and launched the first series of airbrushes onto the market, which were essentially the same as a modern airbrush.

Figure 6.1 depicts the modern airbrush equipment, which can combine gas and solution together to spray out in the form of aerosol. Through the precise control of spray-coating parameters, including spray rate, gas pressure, and the amount of solution, we can optimize the film morphology by modifying the quality of atomized droplet, viscosity of solution and impact pressure of droplet hitting the substrate. An airbrush has the lowest cost compared with its counterparts in the spray-coating family, and also benefits from its convenient use by only pressing and twisting the trigger, flexible manual option during spray processing, and no limitations on the position and shape of objects. These advantages make the airbrush the most widely acceptable equipment by researchers. However, unstable fluent attributed to the nozzle being stuck by a large aggregation of materials in it, difficulty of optimizing the film quality due to the manual option on the control of spray parameter, and dirt inside the mixing room ascribed

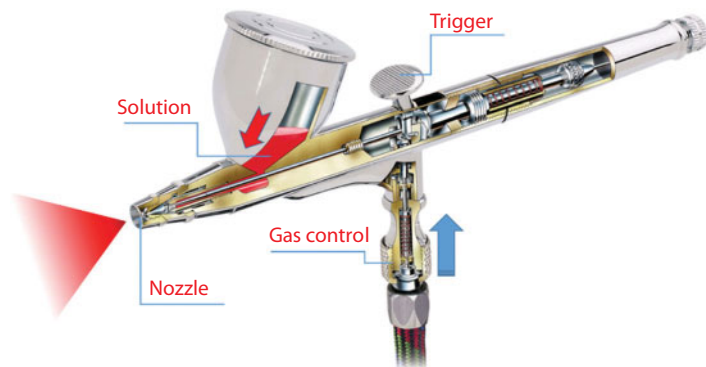


Figure 6.1 Illumination of the architecture of modern airbrush equipment.

to the protection design, all lead to the poor repeatability of OSC based on airbrush spray coating technique. The skills of a well-trained operator are urgently required in the application of airbrush spray coating at all times.

Generally, the ASD applied in the fabrication of OSC should use nitrogen (N_2) gas. Organic materials will degrade when exposed to the ambient air that contains water and oxygen. In this case, the solution should be atomized and broken into small droplets driven by N_2 , which follows the Bernoulli equation [14]:

$$P_0 + \rho gh + 0.5\rho v^2 = C \quad (6.1)$$

where C is the constant, P_0 is the environmental pressure, and ρgh is the pressure generated by gravity. These two terms are known as static pressure. $0.5\rho v^2$ is the dynamic pressure associated with fluid flow velocity. Bernoulli pressure tends to flow outward to break up droplets; meanwhile, the surface tension (ST) of the solution tends to keep the shape of droplets. In the initial stage of droplets being broken up, large droplets are broken into smaller size ones with decreased surface tension. The droplets will remain in the equilibrium state only when the Bernoulli pressure is equal to its surface tension.

The fluid mechanics can be described by Equation 6.2 [15]:

$$W = \frac{4\sigma}{d_0} \quad (6.2)$$

where σ is the ST of liquid, d_0 is the diameter of spherical droplets, and W is the Weber number. For hydrophilic organic solution, when $8 < W < 10.7$, the shape of droplets changes but does not break up; when $10.7 < W < 14$, breaking up of droplets will occur; when $W > 14$, droplets completely break up into smaller drops. With the increase of W , the diameter of droplets becomes smaller. Equation 6.3 is used to describe the diameter after atomization at the condition of $W > 14$ based on the aforementioned established mass transfer models.

$$d_0 \leq 14 \frac{\sigma}{\rho v^2} \quad (6.3)$$

We can find that with a large ST and small dynamic pressure, the large diameter d_0 is obtainable. The droplet diameter will change linearly due to the metastable shape and speed of droplets in the practical process of flying.

The other critical information in the spray-coating process is the impact of droplet on the substrate. For the purpose of spray coating a homogeneous film surface, we need to be very careful when dealing with the manual option. The impact value depends on the droplet size and the velocity of droplet, which can be determined from the flow rate of the solution and the gas pressure. The theoretical total impact (I) is shown in Equation 6.4 [16]:

$$I \propto Q \times \sqrt{P} \quad (6.4)$$

where I is the theoretic total impact, Q is the spray rate of solution, and P is the pressure of N_2 gas. A large droplet size and high velocity of the droplet yield higher impact values. The flow rate of the solution is the dominant factor in determining the droplet size.

After spray droplets impact the substrate, kinetic energy spreads the droplets and the liquid film accumulating on the outline of droplets, which follows Young's equation:

$$\cos \theta_C = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma} \quad (6.5)$$

where θ_C is the contact angle which strongly depends on the surface tension σ ; and σ_{SV} and σ_{SL} are the surface tension in solid-vapor phase and solid-liquid phase, respectively.

This aspect is critical in spray coating since a high surface tension liquid tends to create a spherical cap shape rather than forming a thin wet layer [17]. Also, the "coffee ring" effect will happen when high deposition rates are used [18]. Since large amounts of liquid require a longer evaporation time, the fluxes that create the coffee ring along the contact line are active for a longer time and bring larger amounts of solute to the contact line [18]. If we want to obtain homogeneous film, more treatments should be under consideration during or after ASD processing.

6.2.2.2 Ultrasonic Spray Deposition

Ultrasonic spray deposition (USD) is similar to airbrush deposition in its work mechanism. The only difference exists in how to disperse liquid into fine aerosol. In USD, an ultrasonic nozzle is used, which could use high frequency sound waves produced by piezoelectric transducers acting upon the nozzle tip that will create capillary waves in a liquid film (Figure 6.2). Once the amplitude of the capillary waves reaches a critical height (due to the power level supplied by the generator), they become too high to support themselves and tiny droplets fall off the tip of each wave, resulting in atomization [19].

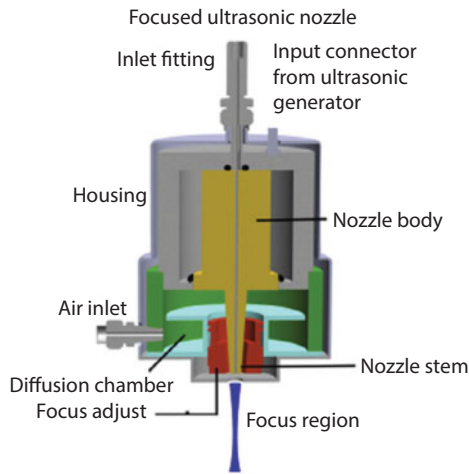


Figure 6.2 Generic description of the atomization process involved in ultrasonic nozzle systems; AccuMist™ ultrasonic nozzle with focused beam. (Reprinted with permission from Sono-Tek Corp. [22]; Copyright © 2014 Elsevier)

The phenomenon referred to as ultrasonic atomization has its roots in the acoustical physics of the late 19th century [20]. In 1962, Peskin and Raco proved a correlation between the atomized droplet size relative to Rayleigh's liquid wavelength [19]. In 1975, ultrasonic nozzles were first brought to market commercially by H. L. Berger. The first application of this ultrasonic nozzle was in home heating oil burners, in an attempt to create a more efficient burner and conserve fuel during the 1970s [21].

Subsequent uses of the technology include coating blood collection tubes, spraying flux onto printed circuit boards, coating implantable drug-eluting stents and balloon/catheters, coatings applied during float glass manufacturing, anti-microbial coatings on food, precision semiconductor coatings and alternative energy coatings for solar cell and fuel cell manufacturing [22, 23].

Attributed to the ultrasonic treatment on the liquid before spraying, the droplets size can be very small, which is comparable or even smaller than inkjet drops [24]. The only parameter that should be taken into consideration is the ultrasonic frequency. However, unfortunately, the frequency of an ultrasonic nozzle cannot be changed. For the different width requirement of pattern, you should carefully choose the nozzle accordingly.

6.2.2.3 *Electrospray Deposition*

High voltage is applied for dispersion in electrospray deposition (ESD) rather than mixed with gas as in airbrush spray coating (Figure 6.3). Ideally

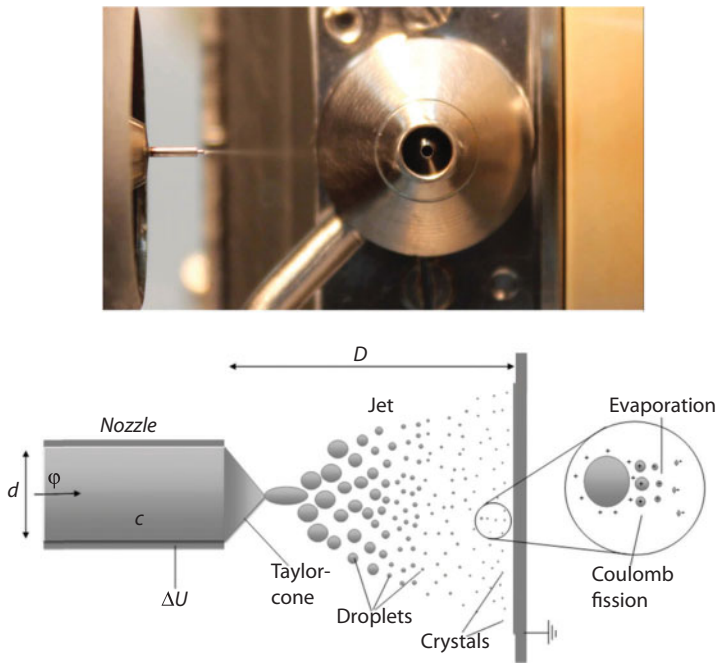


Figure 6.3 Process scheme of electrospray crystallization. Varied operation conditions: nozzle diameter (d), flow rate (f), concentration (c), potential difference (ΔU), and working distance (D). Solvent evaporation, Coulomb fission, and crystallization occur during the process. (Reprinted from [34]; Copyright © 2011 Wiley)

the liquid reaching the emitter tip forms a Taylor cone, which emits a liquid jet through its apex. Varicose waves on the surface of the jet lead to the formation of small and highly charged liquid droplets, which are radially dispersed due to Coulomb repulsion.

In the late 16th century, William Gilbert and Edward Wright described the behavior of magnetic and electrostatic phenomena, which is that a drop of water will deform into a cone in the presence of a charged piece of amber [25]. This effect is clearly related to electrosprays, even though Gilbert did not record any observation related to liquid dispersion under the effect of the electric field. In 1750, the French physicist Jean-Antoine Nollet noted that water flowing from a vessel would aerosolize if the vessel was electrified and placed near electrical ground. He also noted that similarly “a person, electrified by connection to a high-voltage generator, would not bleed normally if he were to cut himself; blood would spray from the wound” [26]. In 1882, Lord Rayleigh theoretically estimated the maximum amount of charge a liquid droplet could carry, which is known as

the “Rayleigh limit” [27]. This prediction that a droplet reaching this limit would throw out fine jets of liquid was confirmed experimentally more than 100 years later [28].

In 1914, John Zeleny published work on the behavior of fluid droplets at the end of glass capillaries, which presents experimental evidence for several electrospray operating regimes (dripping, burst, pulsating, and cone-jet) [29]. Fifty years later, Geoffrey Ingram Taylor produced the theoretical underpinning of electrospraying [30]. Taylor modeled the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone. He further worked to develop the “leaky dielectric model” for conducting fluids [31].

Figure 6.3 shows the scheme of the electrospray crystallization process and the investigated process parameters. There are several key parameters that can determine the final film morphology such as bias voltage, flow rate, syringe needle diameter, and the distance between the tip and substrate. The most critical one is bias voltage. The equation of the relationship between the applied voltage and the charged droplet size could be described as follows [32]:

$$r_j = \left(\frac{9\varepsilon\gamma}{2\pi^2} \right)^{1/3} \left(\frac{F}{I} \right)^{2/3} \quad (6.6)$$

From Equation 6.6, we can see that the increased current (I) will result in smaller size of droplet (r_j). As the voltage increases, the total amount of charge in the spray is also enlarged. When the droplets have high positive charge, the deposition of droplets would form more porous structure due to high repulsive force with a large spray angle [33].

The above three techniques stand for the major spray coating methods which are widely applied in the fabrication of OSC, no matter whether at lab scale or industrial scale. There is still some advanced spray-coating equipment to be created these days. However, due to the limited space herein we cannot introduce all of them.

6.2.3 Spray-Coating Treatment

Homogenous film is vital to OSC performance. In terms of organic materials, traditional spin-coating technique always results in a very smooth film with root mean square (RMS) roughness lower than 5 nm. However, the working mechanism of the spray-coating process is fundamentally different from that of the spin-coating method in regard to film formation. Also,

the OSCs fabrication via the spray process requires extensive know-how and comparatively high effort compared to the current state of the art [16]. Large distances between peak and valley of more than 20 nm are common in spray-coated film due to the stubborn coffee ring effect. Although there has yet to be a conclusion about the result of the coffee ring effect on OSC performance, it is obvious that too much peak and valleys existent in the film surface will lead to poor performance of OSC by introducing current leaking and high resistance. Under this circumstance, post treatments, such as thermal annealing and solvent annealing, are applied in the spray-coating process to overcome these issues.

6.2.3.1 Thermal Annealing

The self-assembly process of materials can obtain an optimized structure from wet phase to solid type, which is a benefit to the OSC performance. However, this stage takes a long period of time (above half an hour) due to the high boiling point of the solvent used, such as chlorobenzene (CB) or dichlorobenzene (DCB). Thermal annealing will significantly accelerate this stage by evaporating the residual solvent in a short amount of time (5–10 min). The aggregation of components in the bulk heterojunction (BHJ) active layer could form phase separation between donor and acceptor. Optimized phase separation offers a pathway for electron or holes to travel to correlated electrode, resulting in improved short-current density (J_{sc}) and fill factor (FF). Thermal annealing has been widely used in the fabrication of OSC for decades, especially in polymer solar cells. However, traditional thermal annealing requires samples to be put on a hot plate at high temperature inside the nitrogen box, leading to high fabrication cost. In 2013, our group introduced a novel process called *in-situ* annealing in the ASD [35]. *In-situ* annealing offers a similar polymer organization effect to traditional thermal annealing, which is lower temperature and less time-consuming (Table 6.1). A PCE of 2.9% is obtained in poly-3(hexylthiophene) (P3HT): [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM)-based OSC. Afterwards, we further extended *in-situ* annealing on the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole transport layer (HTL). The *in-situ* annealed OSC exhibits a 25.5% and 47.7% enhancement in FF and PCE, respectively, as well as about a two-fold improvement in the device lifetime [36]. Moreover, *in-situ* annealing is also applied to fabricate the nanoscale conductive patterns based on silver nanoparticle inks (Figure 6.4) [37]. A spray-coated silver electrode is realized by this *in-situ* annealing treatment, which gets rid of the need for an expensive vacuum evaporation system.

Table 6.1 Processing time of *in-situ* annealing and post-annealing treatment at one fabrication cycle [35].

Experimental steps	Post-annealing (sec)	<i>In-situ</i> annealing (sec)
Spray coating PSCs	120	120
Open nitrogen box	71	0
Transport cells to the hot plate	25	0
Annealing	300	0
Transport cells out of N ₂ glove box	30	0
Transport cells to OLED-V	45	45
Total time	591	165

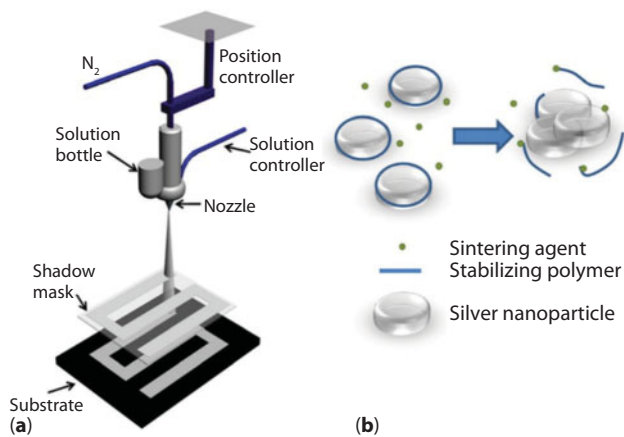


Figure 6.4 (a) Schematic diagram of the spray-coating apparatus; (b) Illustration of the sintering process of silver nanoparticle inks. (Reprinted from [37]; Copyright © 2014 Springer)

6.2.3.2 Solvent Treatments

In general, the quality of film fabricated through spin coating is largely dependent on the properties of the solution. Because of the different working mechanisms between spray and spin coating, the quality of spray-coated film is mainly related to the spray parameters, which have been described above. However, the solution properties are still indispensable to obtain the homogeneous film. There are a lot of works on the investigation of treatments in spray-coating solution. The most widely accepted one is the solvent treatment, especially the mix-solvent treatment.

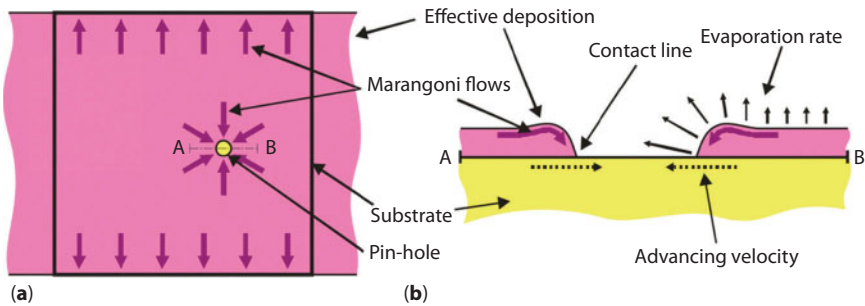


Figure 6.5 Schematic of the evolution of the liquid layer during the drying process: (a) top view of the liquid coverage of the substrate and its surroundings, together with the involved Marangoni flows; (b) Cross-section A-B: the enhanced evaporation rate at the contact line of the liquid layer with the substrate creates Marangoni flows from the bulk of the two-solvent system, establishing an advancing velocity for the contact line, which is able to recover unwetted areas. (Reprinted from [10]; Copyright © 2011 Wiley)

Figure 6.5 shows a schematic of the evolution of the liquid layer during the drying process. As we mentioned before, a large surface tension and contact angle usually lead to a poor wettability of the solution on the substrate, causing the film to undergo dewetting as it dries [38]. Various strategies can be used to reduce the surface tension of high surface tension liquids. One involves adding a surfactant to the liquid. A drawback of this method is that often the surfactant remains in the solid film and may negatively impact the electrical behavior of the solid film. Another strategy is to mix a secondary solvent with a lower surface tension than that of the primary one, which are called mix-solvent treatments here [10].

The secondary solution should be both miscible with primary solvent and compatible with the solute. With a higher vapor pressure (or lower boiling point) of secondary solvent, the film will dry faster. In this case, the coffee-ring effect is able to be eliminated. In addition, the mix-solvent system produces favorable spreading capabilities due to the Marangoni velocity [39]:

$$v_c^2(x) = \frac{1}{2\eta(x)} \frac{d\sigma}{dx} x(1-x)(-A_l\alpha_l + A_h\alpha_h) \quad (6.7)$$

where η is the viscosity of the film, σ the surface tension, x the volume fraction of the low surface tension solvents, A_l and A_h the evaporation velocity, α_l and α_h the activity coefficient of the low and high surface tension solvent, respectively. The introduction of secondary solvent not only reduces the contact angle of the mixture, but also enhances the spreading

of the deposited liquid into areas of the substrate not directly covered by the spray. An additional benefit of the Marangoni effect is a smoothening of the film surface, detected by Kojima *et al.* in 1993 [40].

Here are some examples of mix-solvent system, which have been demonstrated in efficient OSCs. Due to their wide compatibility to organic materials, CB and DCB are the solvents most widely used in OSC. However, their high boiling point causes them to be difficult to evaporate, and also results in the transfer of spray-coated film from liquid to solid state taking a long time. Girotto *et al.* use DCB:mesitylene at 70:30 vol% as mix-solvent system for P3HT:PC₆₁BM-based OSC, and obtained over 70% FF [17]. Compared with that, a single solvent system can only result in about 55% FF. Wang *et al.* also tried the combination of DCB:CB, DCB:chloroform (CF) in P3HT:PC₆₁BM active layer, resulting in 1% PCE enhancement from 3% to 4.2% [38]. Mix-solvent system also contains multiple solvents of more than two. Girotto *et al.* found that a mix-solvent system with PEDOT:PSS:deionized water:isopropyl alcohol ratio of 18:9:73 vol% is more favorable to achieve a pinhole-free hole transport layer [17]. Moreover, our group demonstrated an efficient mix-solvent system in 2015. A variety of combinations among CB, DCB, o-Xylene (o-Xy), and CF were investigated. We achieved a 34% improvement in the PCE of thieno[3,4-b]thiophene/benzodithiophene (PTB7):[6,6]-phenyl C71-butyric acid methyl ester (PC₇₁BM)-based OSC [9].

6.3 Materials for Spray Coating

6.3.1 Organic Materials

Organic solar cells have been a hot topic of research for decades due to their potential use in large-area, mechanically flexible and solution processable low-cost manufacturing techniques [1, 41–43]. In its current stage, spin coating is the most widely used method to fabricate solution-processed thin film at the lab scale. Due to the convenient and repeatable manipulation of spin coating, even an inexperienced person could handle it well after only practicing several times [1]. However, in terms of functional materials, spin coating has several disadvantages which restrict its potential for industrial application. Firstly, the material for spin coating needs to be well dissolved in a specific solvent for homogenous film. If some aggregation exists in the solution, the final film will suffer from very rough surface. Secondly, spin coating has a strict limitation on the viscosity of the solution. Solution with high viscosity would result in the

discontinuous coverage of the film surface. Finally, and most importantly, the spin-coating technique wastes a lot of material. At the very beginning, high spin rate will spin off almost 90% of the solution, leaving 10% of the solution on the substrate to further form the target film. In this case, 90% of the solution is wasted and cannot be reused anymore. This is the main reason for the high experimental cost in the present stage, especially in highly concentrated solution.

Taking all of the above into consideration, spray coating shows its unique advantage. First of all, high production speed and compatibility with various substrates become possible since the sprayed droplets are transferred from the spray nozzle to the substrate without direct contact to the surface [44]. Also, various materials with low solubility in less toxic solvent can be applied due to the low concentration of sprayed solution [45]. Moreover, the spray process can pattern the coated film within a sub-millimeter scale by using shadow masks [37]. Almost all the solution-processed materials are available in spray coating, including polymers, small molecules, carbons, metal oxide, and perovskite [1, 10, 35–37, 43, 46]. In the following section we will present a brief history of the material used in spray coating.

The active layer material that is most widely used to test the quality of a spray-coating approach is P3HT:PC₆₁BM. Figure 6.6 shows an example of spray-coated OSC based on P3HT:PC₆₁BM system. In 2007, Vak *et al.* realized the first spray-coated bulk heterojunction solar cells based on P3HT:PC₆₁BM by conventional handheld airbrushes [44]. Although the spray deposited film shows a relatively rougher surface than the spin-coated ones, pinhole-free and constant thickness films could be obtained. An optimized OSC shows 2.83% of PCE and 52% of incident photon to current conversion efficiency even though the device is fabricated in air. A PCE of 2.8% was really high at that time compared with 3.5% of spin-coated OSC. Further optimization focused on the spray parameters. In 2009, Giroto *et al.* used a single-pass technique to fabricate devices and obtained a PCE of 2.8% [47]. Hoth *et al.* obtained a PCE of 3.1% by using mix-solvent system of ortho-dichlorobenzene (oDCB) and 1,3,5-trimethylbenzene (mesitylene). They found that the solvent properties, such as boiling point, vapor pressure, viscosity and surface tension, have a massive impact on the topography [48]. In 2010, Chen *et al.* used multi-source spray coating for the fabrication of P3HT:PC₆₁BM OSC with a PCE of 2.8% [4]. This approach preserves the integrity of the layer morphology while forming an interpenetrating donor/acceptor network to facilitate charge transport. This method also allows the direct stacking of multiple photo-active polymers with controllable absorption in a tandem structure even without an interconnecting junction layer [4]. An investigation by Yu *et al.*

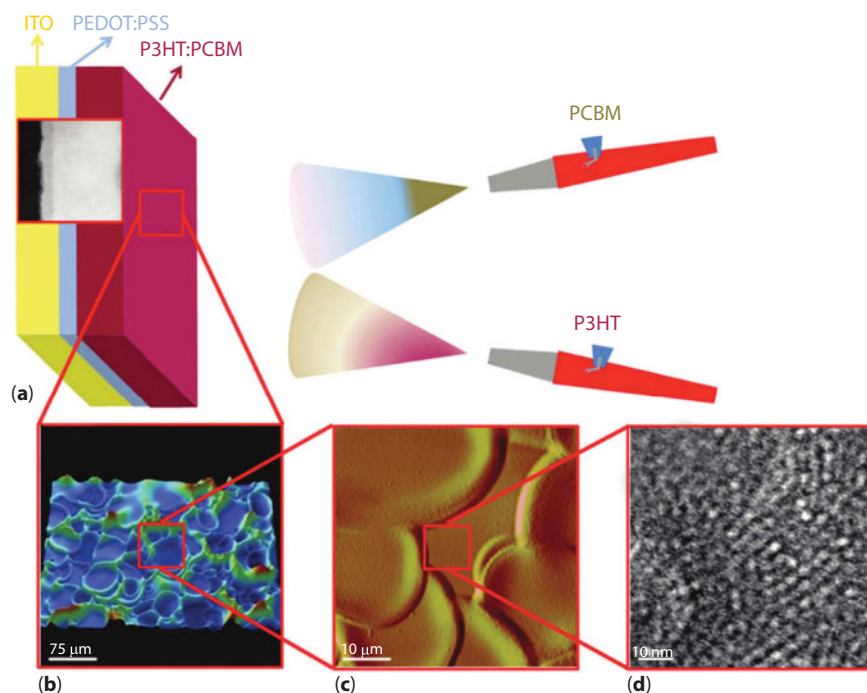


Figure 6.6 (a) Schematic of the alternating spray deposition apparatus. The device structure is shown with a TEM cross-sectional image, indicating the ITO/PEDOT:PSS/P3HT:PCBM layers starting from the left with well-defined interfaces. Zoom-in representative images taken from (b) optical profiler, (c) AFM, and (d) TEM of 150 °C annealed film from P3HT/PCBM alternating deposition. (Reprinted from [4]; Copyright © 2010 ACS)

detailed the effect of spray parameters on the film morphology. Through accurately controlling the droplet size, they obtained a PCE of 3.4% [16]. In 2011, Girotto *et al.* followed Hoth's work and further optimized the film by controlling the ratio in mix-solvent system [10]. They investigated the effects on uniformity of both fast drying and slow drying. A relatively high FF of 72% was obtained, which was the record FF of the P3HT:PC₆₁BM-based OSC at that time, including all methods. Finally, a PCE of 3.75% was achieved. This high PCE is hard to break in a short time, so many group are looking for other specific areas in the spray-coating technique.

Some people have found other alternative spray methods. In 2012, Ali *et al.* accomplished a solution-processed multilayer bulk heterojunction organic solar cell by electrospray deposition [49]. However, due to the unoptimized parameter, they could only attain a PCE of 2.17%. At the

same time, Kang *et al.* came up with a novel airbrush equipment which can be accurately controlled by computer [50]. They fabricated fully spray-coated devices by the use of zinc oxide (ZnO) electron transport layer (ETL) and PEDOT:PSS electrode. A PCE of 3.17% and 1.33% at a cell area of 0.36 cm² and 15.25 cm² were obtained, respectively. The other alternative method is post-treatment probes. In 2013, our group introduced *in-situ* annealing treatment to take the place of general high-temperature thermal annealing [35]. We found that the *in-situ* annealing treatment at low temperature not only corresponds to 12% enhancement of FF, but also results in a 13% increase of open-circuit voltage. More importantly, the post-annealing treatment takes 591 s at one fabrication cycle of the active layer, which is about 360% of that of the *in-situ* annealing process. By shortening the production time, more cells can be fabricated per unit of time, which means larger economic benefits for the practical application of PSC. In 2014, we applied *in-situ* annealing to fabricate PEDOT:PSS HTL, and further improved the PCE from 3.17% to 3.81% [36].

Recently, in order to achieve high PCE, other polymer systems have been employed despite P3HT. Although new polymers have been synthesized, spin coating seems to be the first choice to realize the demonstration of them for the process without any top skills. Only the widely used polymers have the chance to be coordinated with spray coating. In 2012, Saitoh *et al.* introduced spray coating in [N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT):PC₆₁BM system [51]. Although PCDTBT shows a relatively high PCE of 7.1% under spin coating, it seems to not work well under spray coating, which exhibits only 4% to 5% PCE [52–54]. Compared with PCDTBT, PTB7 is a better match with spray coating. In 2012, Kumar *et al.* demonstrated an OSC based on PTB7:PC₇₁BM active layer with PCE of 5.96% for the first time [55]. After that, the average PCE of spray-coated OSCs based on PTB7:PC₇₁BM was above 6% [9, 56]. By employing ternary solvent system, our group could accurately control the size of droplet and eliminate the coffee-ring effect, leading to a PCE of 7.62% [9]. In 2016, the highest PCE of 8.02% was obtained by Zhang *et al.* by using a novel polymer called poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl] (PBDTTT-EFF).

The device performance is largely based on what kind of active layer materials are used. By the exploration of novel materials, the performance of spray-coated OSC will gradually be enhanced.

6.3.2 Metal Oxide and Nanoparticles

Metal oxides have been widely applied in electronics for several decades and show some great advantages, like high transparency, when used as thin film, high electron transportation and tunable energy level. However, the general method used to deposit a thin film of metal oxide requires high annealing temperature and long annealing time, which is one of the reasons for the high costs in industrial fabrication. Therefore, scientists are looking forward to finding an alternative approach to realize gentle and environmentally friendly ways of fabricating metal oxide thin film. With the high potential of low temperature and fast deposition speed, spray coating is now applied as a general method to substitute lab-scale spin coating to build conductive thin film based on metal oxide and metal nanoparticles. In this section, we will list some brief examples of metal oxides and nanoparticles based on spray coating in recent years.

One of most popular metal oxides used in OSC, ZnO can be deposited by many methods. In 2012, Crossay *et al.* used ultrasonic spray pyrolysis deposited Al-doped ZnO (AZO) [57]. A resistivity of $3 \times 10^{-3} \Omega\text{cm}$, one of the lowest values reported in the literature for sprayed AZO, is obtained for a film thickness of 3 μm , maintaining a high optical transmittance of $> 74\%$. Kang *et al.* compared spin- and spray-coated ZnO by fabricating inverted structure OSCs [58]. The spray-coated ZnO layer shows a PCE of 3.17% under AM 1.5 simulated illumination and stability (480% of its original efficiency after 30 days), which is comparable to spin-coated ZnO. Geethu *et al.* found that by using spray coating, they could control the surface roughness of ZnO ETL, which can determine the final PCE of devices [59]. Another widely applied metal oxide is titanium dioxide (TiO_2). In 2012, La Notte *et al.* investigated the utilization of airbrushing in the fabrication of TiO_2 ETL in OSC [5]. They realized the low-temperature deposition of TiO_2 ($< 150^\circ\text{C}$) for the first time. In 2014, Sigdel *et al.* spray-coated ETL by mixing electrospun carbon nanofiber/ TiO_2 nanoparticle composite in dye-sensitized solar cells, resulting in a PCE of 7.22% [60]. In 2015, Kim *et al.* employed electrospray deposition to build mesoporous TiO_2 in perovskite solar cells, and obtained a PCE of 13.67% [33]. They further verified the possibility of large-area uniform TiO_2 film with a size of $10 \times 10 \text{ cm}^2$.

Different from metal oxide, it is hard to obtain a homogeneous film of nanoparticles through general spin coating. The nanoparticles are dispersed in the solvent. In this scenario, if the concentration is high enough to satisfy the requirement for solution viscosity of spin coating, the spin-coated film will suffer from large aggregation of nanoparticle. Such

aggregation not only leads to the high resistance of film surface but also plays a role as electron trap center. It is very difficult to control the quality of solution to obtain smooth film surface. However, this phenomenon does not seem to be a problem anymore when using spray coating, which could allow a very low concentration of solution to deposit homogeneous film (~ 1 mg/mL). Hence, many works based on metal nanoparticles and nanowires are able to be realized by spray coating. In 2012, Akter and Kim attained a spray-coated reversibly stretchable transparent conductive coating of silver nanowires with an average sheet resistance of ~ 35 Ω/sq [61]. In 2013, Choi *et al.* demonstrated a two-step spray-coating method for producing large-scale, smooth and flexible silver nanowire/PEDOT:PSS composite electrode, which also exhibited high transmittance of 84.3% and low sheet resistance of 10.76 Ω/sq (Figure 6.7) [62]. Krantz *et al.* also spray-coated silver nanowire as top electrode layer [63]. By getting rid of conventional vacuum deposition, the fabrication of OSCs will become accessible and cheap with low time cost. They demonstrated the possibility of spray-coated silver electrode by obtaining an OSC with a PCE of 2%. This result was also confirmed by Kang *et al.*, which showed an OSC with a PCE of 2.3% with spray-coated electrode [64]. In 2014, our group also realized an all-solution-processed OSC with spray-coated top electrode based on silver inks [37]. Recently, spray-coated silver electrodes with an average transmittance of 85% and 25 Ω/sq were continuously obtained, which have already been well matched with industrial fabrication requirements [65–68].

Besides pure metal nanowires, recently many groups have also been paying more attention to spray mix-metal nanoparticles. Dantelle *et al.* sprayed nanometer-sized YVO₄:Yb,Er particles to enhance the upconversion intensity [69]. Giusti *et al.* applied ZnO-SnO₂:F nanocomposite transparent electrode for energy application [70]. Kim *et al.* added Au nanoparticle into silver nanowire to clearly reduce the haze of the thin film of silver nanowire and get a 2% to 4% increase in total transmittance [71]. Kim *et al.* reported a novel tandem structure combining two different materials with complementary optical properties and microstructures, copper oxide (CuO) nanowires and cobalt oxide (Co₃O₄) nanoparticles, which can significantly enhance the light absorption of solar spectrum [72]. Zhu *et al.* spray-coated copper nanowire with PEDOT:PSS and reduced graphene oxide to reduce the surface roughness and improve the durability of the fabricated electrode [73]. Kwan *et al.* combined graphene oxide with silver nanowire to produce an ultra-stable transparent conducting electrode by keeping the gaseous environment oxygen free [74].

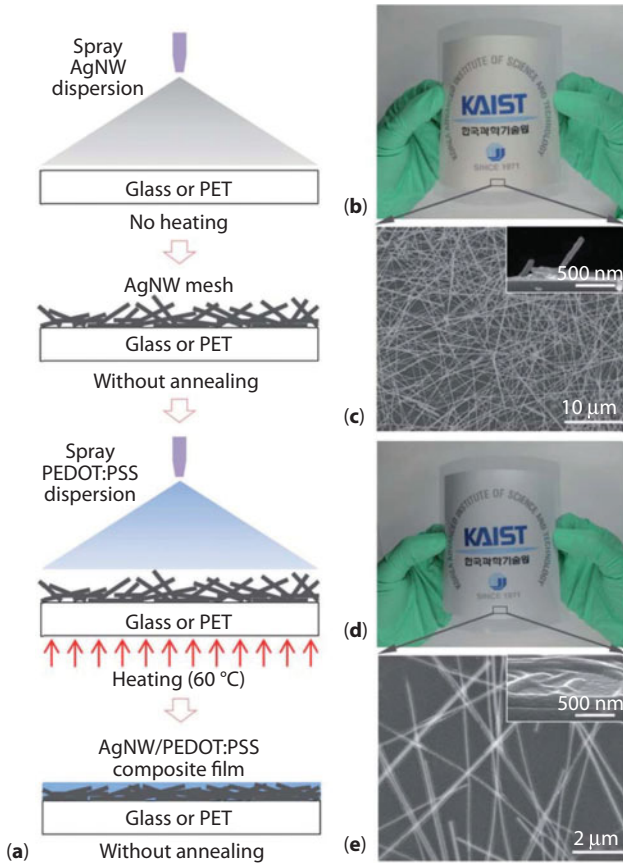


Figure 6.7 (a) Schematic diagram of the procedures for fabricating AgNW–PEDOT:PSS composite electrodes. (b) Photograph of the AgNW mesh deposited on a PET substrate (13×13 cm). (c) SEM image of the uniformly deposited AgNW mesh without a large difference in the density of nanowires. Inset shows the cross-section view of the AgNW mesh. (d) Photograph of the AgNW–PEDOT:PSS composite film deposited on a PET substrate. The mean transmittance was 81.7% (at 550 nm) and the sheet resistance was $11.3 \Omega \text{sq}^{-1}$. Their standard deviations were 2.84% and $1.85 \Omega \text{sq}^{-1}$, respectively. (e) SEM image of the AgNW mesh embedded in the PEDOT:PSS film. Connections between nanowires were maintained upon deposition of PEDOT:PSS. Inset shows the angled cross-section view of the composite film. (Reprinted from [62]; Copyright © 2012 Royal Society of Chemistry)

6.3.3 Perovskite

The rapid rise in efficiency of thin-film solar cells using organometal halide perovskite semiconductors has made this class of photovoltaic device a highly promising technology for solar energy conversion [75, 76]. Till now, the PCE of perovskite solar cell has already been above 20% [77].

However, such high efficiency is obtained in the small area devices based on lab-scale spin-coating method. There are two general methods for the formation of perovskite film, which are called one-step process and two-step process. The one-step spin-coating process with the mixed perovskite solution of methylammonium iodide (MAI) and lead iodide (PbI_2) gives poor film coverage due to the quick reaction between PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ [78]. Compared with that, in a two-step approach, MAI and PbI_2 are sequentially deposited in films and then thermally annealed to form methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), which is more easy to control and more repeatable. However, conventional spin coating would cause the non-full coverage of PbI_2 film, hard control of MAI and PbI_2 stoichiometric ratio, as well as the wastage of precursor. It is apparent that the path towards commercialization of solution-processed perovskite solar cells requires the development of fabrication protocols compatible with high-volume roll-to-roll or sheet-fed processing techniques [79]. Among the variety of large-scale solution approaches, spray coating shows ubiquitous advantages of depositing the film without wiping out the precursor film. Hence, spray coating has recently been applied in the fabrication of perovskite solar cells.

In 2014, Barrows *et al.* explored the use of ultrasonic spray coating as a deposition technique to create thin films of a perovskite precursor containing MAI and lead chloride under ambient conditions (Figure 6.8) [79]. They showed that spray coating could result in the same level of PCE as spin coating, over 11%. They suggested that by using some techniques, such as flash annealing or IR heating, the time-waste formation of perovskite film could be significantly shortened with low annealing temperature. In 2015, Boopathi combined spin and spray coating to deposit perovskite solar cell [80]. They spray-coated MAI droplet on the top of spin-coated PbI_2 film. A PCE of 11.66% was achieved for 100 nm of PbI_2 followed by 300 mL of MAI and annealing at 100 °C for 120 min. Complete diffusion of MAI into PbI_2 took place when a sufficient amount of MAI was provided, leading to highly crystalline and stoichiometric perovskite formation. Through controlling the substrate temperature, Ramesh *et al.* realized the full film coverage of MAI: PbI_2 droplet [80]. In 2016, a PCE of 14.3% was obtained by Shao *et al.* using a process that involves first the deposition of a low-crystallinity PbI_2 film and then subsequent spraying of MAI solution [81]. The PCE of spray-coated perovskite solar cell was further improved to 15.7% by Tait *et al.* through ultrasonic spray coating [3]. Concurrently pumped ultrasonic spray coating with differential rates enabled the rapid optimization of thickness, precursor ratios, and resulting pinhole-free layer crystallinity. The process is scalable and demonstrated 3.8 cm² aperture area modules with 11.7% measured PCE.

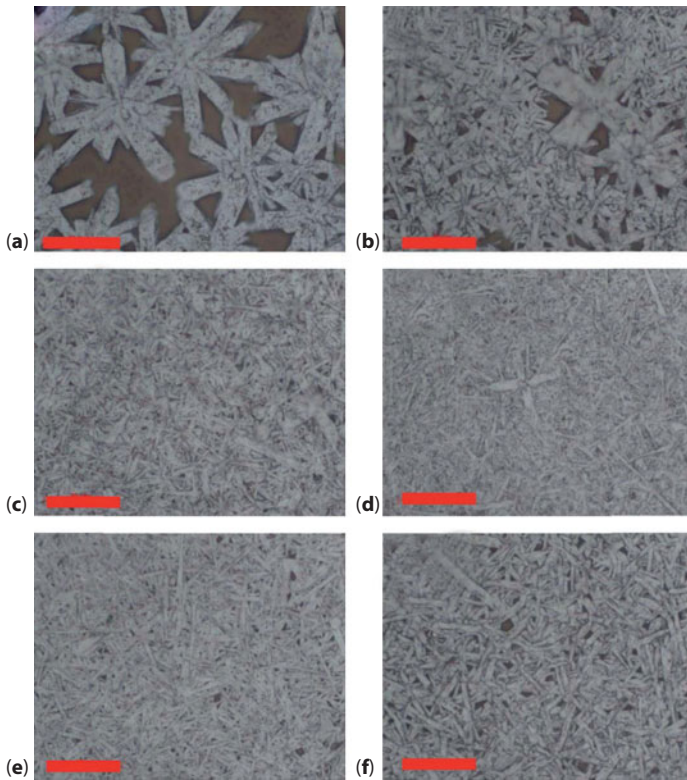


Figure 6.8 Optical microscopy images of spray-deposited thin films of methylammonium iodide and lead chloride on substrates held at a range of elevated temperatures: (a) 28 °C, (b) 38 °C, (c) 55 °C, (d) 75 °C, (e) 80 °C, (f) 87 °C. The scale bar in each image corresponds to 20 μ m. (Reprinted from [79]; Copyright © 2014 Royal Society of Chemistry)

For the consideration of toxicity of perovskite, till now, many groups are still focusing on the deposition of perovskite by easy to handle spin coating. However, the real effect of perovskite on the human body or environment is still under investigation. Therefore, it is still worth paying more attention to the spray-coating technique. In the long term, spray coating is one of the most available solution processes that matches the R2R approach in the industrial fabrication of solar cells.

6.4 Application of Spray Coating

In the above, we have collected the recent works pertaining to the application of spray coating on OSCs. However, due to its universality, spray

coating is suitable for almost every kind of electronic device which can be achieved by solution process.

In 2009, Southard *et al.* used airbrushed single-walled carbon nanotube (SWCNT) thin films with sheet resistivity $< 1 \text{ k}\Omega/\text{sq}$ and transparency $> 80\%$ as electrodes for pentacene and regioregular P3HT thin-film transistors (TFTs) [82]. They demonstrated that solution-processed electrodes can be patterned onto a flexible plastic substrate both directly (gate electrode with transparency $> 91\%$) and via transfer printing (source-drain electrode). In 2010, Chan *et al.* also fabricated organic thin-film transistor (OFET) by airbrushed P3HT [83]. They found that the transport-relevant molecular orientation at the organic-dielectric interface is similar for both spin- and spray-deposited P3HT. Not only are these values consistent with those reported before, but they may also explain why spin- and spray-deposited P3HT transistors perform comparably well. Since then, other OFETs based on spray-coated P3HT have also been verified by many groups [84, 85].

In 2013, our group spray-coated poly(methylmethacrylate) (PMMA) buffer layer between P3HT layer and gold electrodes in OFETs [86]. We characterized the morphology of spray-coated PMMA and found that the smooth and hydrophobic PMMA buffer layer primarily induced a better contact between organic layer and Au electrodes, resulting in a superior crystallization of P3HT layer. In 2014, we spray-coated OFETs in a top-contact structure by applying the biomaterial deoxyribonucleic acid (DNA) as a hole injection layer. Significant performance enhancement is obtained, which is attributed to the improved contact between Au electrodes and pentacene [37]. The dipole formation effect of the DNA hole injection layer can lead to an improved hole injection at the electrode/organic semiconductor interface. As DNA is a unique material which behaves in a particular way, lots of further research on the issue of charge injection improvement by DNA is still imperative. This study brings new insights into the utilization of biological materials in the field of organic electronics. In 2015, we further spray-coated water-soluble DNA on OFETs [87]. At that time, 5 times improvement on hole mobility was obtained. This work not only demonstrates the possibility of water-soluble DNA on the OFETs, but also provides new insights into the potential of biomaterials in electronics.

In addition to OFETs, other electronics based on spray-coated P3HT, carbon nanotube or metal nanowires have also been under investigation recently. Through spray-coated nickel and silver ink, foldable printed circuit boards on paper substrates were realized by Siegel *et al.* in 2010 [88]. Circuit boards printed on flexible paper- and fabric-based substrates offer new opportunities for inexpensive, disposable, configurable circuit boards

for portable applications where a circuit is required, but where the circuit may not be meant for continued use for months or years. In 2013, an organic photodetector (OPD) based on plastic optical fiber was realized by Binda *et al.* [89]. A fully sprayed OPD and ultra-thin OPD were then developed by Falco *et al.* and Liu *et al.* [90, 91]. In 2014, Gupta *et al.* developed a method of spray coating of crackle precursor for fabricating a crack template on flat and curved surfaces to obtain crack networks, which serve as sacrificial templates for depositing metal wire networks [92]. In 2016, a printed energy harvesting and storage circuit powered by ambient office lighting and its use to power a printed display was reported by Tuukkanen *et al.* [93].

6.5 Conclusions

In this chapter, we presented a brief introduction to spray coating technology, including its beginning, development and course of evolution. In addition, we included a detailed overview of recent investigations of spray coating in OSC and other electronics. As one of the most ubiquitous film formation techniques, spray coating with its unique advantages shows a high potential to be the major method applied in future industrial fabrication of electronics. To satisfy the different morphology requirements of thin film based on a variety of materials, adjusting the spray-coating parameters is a top priority. Hence, the spray-coating technique will evolve with the development of advanced materials, following the trends of the times and marching towards the future.

Acknowledgment

This research was funded by the Foundation of the National Natural Science Foundation of China (NSFC) (Grant No. 61675041) and the Foundation for Innovation Research Groups of the NSFC (Grant No. 61421002). This work was also sponsored by the Science and Technology Department of Sichuan Province via Grant No. 2016HH0027 and the China Scholarship Council (Grant No. 201506070069).

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Interface Engineering: A Key Aspect for the Potential Commercialization of Printable Organic Photovoltaic Cells

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Abstract

Power conversion efficiency (PCE) of polymer solar cells (PSCs) has overcome the milestone value of 10%, emphasizing their potential as next generation devices to replace silicon-based technologies as they can be fabricated through cost-effective printing techniques. Here, we demonstrate that interfacial interactions play a key role in improving two requirements for the commercialization of printable PSCs: increased device performances and decreased production cost.

Charge transport in conjugated polymers is related to their crystallinity and crystallite orientation. We demonstrated that crystallite orientation can be controlled by interactions between the active layer solution and the substrate. Combining the adequate crystallite orientation and device architecture, PSCs with high fill factors and PCEs can be fabricated with spin-coated active layer and evaporated metal electrodes. However, thermal evaporation generates large quantities of material and energetic wastes. With proper interface engineering, thermal deposition can be replaced with metal leaves lamination processes. Our systematic study based on metal leaves demonstrates that, by selecting the metal with the adequate adhesion to the underlying layer, high quality devices, with performances (PCE and stability) similar to their evaporated counterparts, can be fabricated. A PCE of 5.1% (record for laminated devices) was achieved with Au leaves.

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Nurdan Demirci Sankir and Mehmet Sankir (eds.) Printable Solar Cells, (235–262)

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Keywords: Organic solar cells, polymer solar cells, printed electronics, face-on crystallites, lamination, low-cost electronics

7.1 Introduction

Organic solar cells were first introduced in the 1980s after the breakthrough discovery from researchers at Kodak who fabricated the first devices with power conversion efficiencies (PCEs) of approximately 1% [1]. Since then, a large number of researchers have focused on developing this technology and PCEs of single cells now overcome the milestone value of 10% [2–5]. In fact, a major development was achieved with the introduction of conjugated polymers as they represent promising materials for low-cost fabrication not only of solar cells but also other electronic devices such as polymer light-emitting devices and organic thin-film transistors [6, 7]. One of the major advantages of conjugated polymer-based electronics is that the active layers can be deposited through solution processes. In fact, most of the research on polymer electronics focuses on the use of processes such as spin coating, dip coating, doctor blade, spray and/or printing. The first polymer solar cells (PSCs) were based on the bulk heterojunction active layer concept (BHJ-PSCs) in which a fullerene derivative is dispersed in a conjugated polymer matrix, resulting in a large amount of donor-acceptor interface and, consequently, a high quantity of generated charges [8, 9]. Since 2002, polyphenylene vinylene derivatives started gradually being replaced by poly(3-hexylthiophene) (P3HT) as electron-donating material and P3HT is still considered by many as the reference polymer for PSC fabrication [10]. Recently, copolymers synthesized using electron-donating and electron-accepting moieties have attracted a lot of attention as they result in the generation of polymers demonstrating high hole transport properties and absorption spectra spreading over a wide range of the visible spectrum [11, 12]. This new material development strategy led to a large number of reports demonstrating that PCEs over 7% can be achieved using specifically designed materials [13, 14]. However, these papers also clearly emphasize that particular attention should be given to the morphology of the active layer to achieve high device performances [13–15]. To control the morphology of the active layer, interface engineering at various levels needs to be taken into account.

In fact, PSCs have a rather complicated working principle in which the process of charge generation itself is controlled by the interface between donor and acceptor materials (Figure 7.1). Once light is absorbed by the donor or acceptor materials, the generated excitons need to diffuse to a

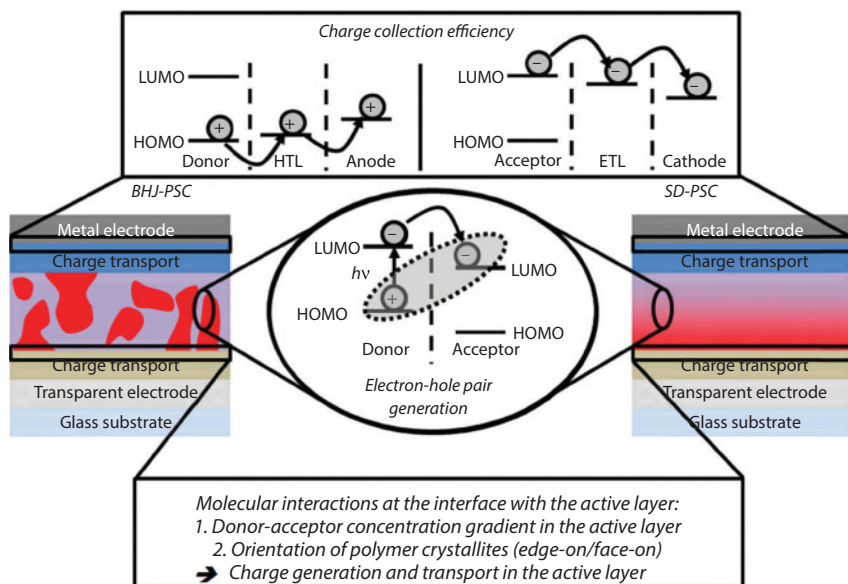


Figure 7.1 Schematic representation of the bulk-heterojunction (BHJ) and sequentially deposited (SD) active layer PSCs along with the interface-related mechanisms and effects in the device architectures.

donor-acceptor interface in order to undergo charge separation. The resulting charge-separated holes and electrons will then percolate to the anode and the cathode, respectively. In BHJ-PSC active layers, the donor and acceptor molecules phase separate and small donor-rich and acceptor-rich domains are formed. This strategy is beneficial to increase the interface between donor and acceptor domains but may also result in inefficient charge collection due to low percolation of the charges to the electrodes. Efficient charge transport can be obtained by inducing a vertical donor-acceptor concentration gradient in the PSC active layers where more electron donor material can be found close to the anode while a higher concentration of electron acceptor is in contact with the cathode. Vertical concentration gradients have the potential to reduce the series resistance (R_s) in the active layer as percolation is facilitated, but also to increase the shunt resistance (R_{sh}) which reflects the quantity of leak current in the devices [16]. Leak current is commonly associated with either donor or acceptor materials being in contact with the wrong electrode (e.g., high concentrations of electron donor at the interface with the cathode). To enhance charge selection at the electrode interface (reduce leak current), charge transport layers can be added between the active layers and the electrodes [16].

Over the past decade, various strategies to generate vertical concentration gradients in the active layers have been proposed. These include sequential deposition or transfer printing of donor-acceptor multilayer films with each layer containing a different donor-acceptor concentration [17, 18], the insertion of interfacial layers at the substrate/active layer interface [19], the addition of solvent additives to control the directional drying of the blends [20] or the formation of sequentially deposited diffusive bilayer PSCs (SD-PSCs) [21]. SD-PSCs are fabricated by first depositing a conjugated polymer layer (electron donor) followed by spin coating of a fullerene derivative (electron acceptor) from an orthogonal solvent. The solvent commonly used for SD-PSC fabrication is dichloromethane (DCM) as it swells the polymer network (without dissolving it), allowing for the fullerene derivative to gradually diffuse through the polymer layer. Depending on the fabrication conditions, this approach can readily generate vertical concentration gradients and donor- or acceptor-only buffer layers in PSC active layers. However, in SD-PSCs, donor and acceptor molecules cannot be intimately mixed, which may result in a lower amount of photogenerated excitons and charges.

Alternatively, the materials in contact with the active layer at its interface during either its deposition or post-deposition annealing can greatly influence the active layer morphology [22]. A self-assembled monolayer on the substrate which interacts with both donor and acceptor materials may generate a vertical distribution of the two materials within the active layer. In polymer field-effect transistors, modifying the functional groups present on the substrate surface has also proven to be an efficient strategy to induce the desired polymer crystallite orientation and obtain high field-effect mobilities [23]. In fact, in conjugated polymer thin films, two complementary charge transport mechanisms take place along the conjugated polymer backbone (intramolecular) and between neighboring polymer chains (intermolecular) [24]. In thin films of 50 nm or over, charge transport is governed by the intermolecular charge hopping along the π - π stacking direction of the crystalline parts of the polymer. Crystallite orientation, which can be controlled by the substrate/active layer interface, is therefore expected to play an essential role in the fabrication of PSCs with high charge collection efficiencies. In PSCs, which have a vertical device architecture, face-on crystallites should be beneficial as they enhance vertical charge transport while edge-on crystallites provide better charge transport properties in the lateral direction (Figure 7.2). Note that, considering the intrachain charge transport, edge-on crystallites may still provide a much more efficient hole transport compared to amorphous polymer phases.

The charge collection efficiency reflects the morphology of the active layer through the percolation paths for both positive and negative charges

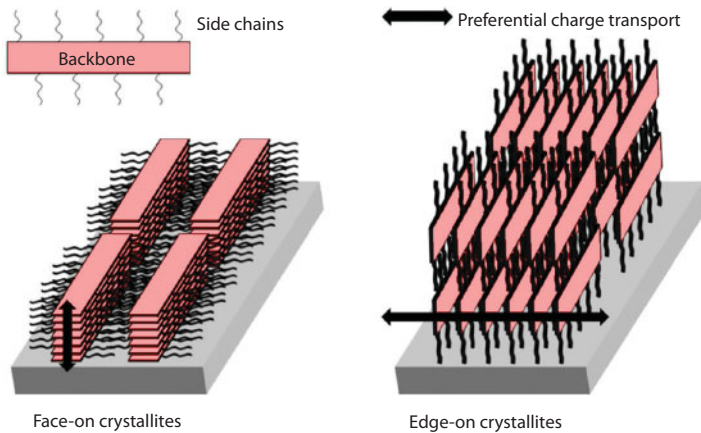


Figure 7.2 Schematic representation of face-on and edge-on crystallites and their preferential charge transport direction.

and the contact quality at the active layer/charge transport layer and charge transport layer/electrode interfaces. For instance, the quality of the interface between active layer and electrodes can largely contribute to reducing the R_s of the devices and, consequently, increase not only their fill factor (FF) but also their short-circuit current densities (J_{sc}). Furthermore, thermally evaporated metal electrodes may induce some degradation at the active layer/metal interface and alternative metal deposition solutions, such as lamination, have therefore been raising increasing interest in the organic electronics community [25, 26].

The possibilities to improve PSCs mentioned up to now have focused mainly on increasing their PCE. However, to be seriously considered as candidates for commercial applications, it is required that PSCs not only exhibit high PCEs but also high stability while maintaining a low production cost and ideally a high production output. Since 2004, reports on inverted device architectures using transparent cathodes and noble metals as the top anode have been steadily increasing [27–29]. In fact, in regular architectures, the use of calcium, aluminum (or other easily oxidizable metals) is at the origin of their low stabilities. Inverted architectures using top gold (Au) electrodes solve the stability issue and devices demonstrating stable performances around 3% have been previously reported [29]. However, using Au or silver (Ag) as the top electrode largely increases the production cost of PSCs, in particular, as the conventional method for metal electrode deposition (thermal evaporation) generates large amounts of waste material.

In this chapter, we present our recent results emphasizing the importance of interfaces not only to increase the PCE of PSCs but also to reduce

their cost of production through roll-to-roll compatible processes [30]. We will emphasize the effect of the different interfaces presented in Figure 7.1 through our studies on SD-PSCs and BHJ-PSCs. The results on P3HT:[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) SD-PSCs demonstrate that by controlling the donor-acceptor interface and active layer morphology, one can increase the J_{sc} and FF of the devices. For BHJ-PSCs, we used a naphthobisthiadiazole-based polymer (PNTz4T) in combination with [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) to demonstrate that the interactions at the active layer/substrate and active layer/air interfaces can strongly influence molecular orientation of the polymer as well as its crystallinity, which, in turn, leads to major increases in FF. Furthermore, in the PNTz4T:PC₇₁BM active layers, vertical crystallite orientation gradients are achieved which are more favorable for inverted PSC architectures. The resulting inverted devices exhibit enhanced charge collection efficiencies leading to PCEs over 10%. Finally, we demonstrate that the interface between the top metal electrode and the underlying layer (e.g., hole conducting layer in inverted device architectures) plays an essential role when it comes to decreasing the series resistance (R_s) of BHJ-PSCs. In fact, we compare devices fabricated with two processes, namely, the state-of-the-art thermal evaporation process, which generates large amounts of waste materials, and lamination of metal foils. Finding the adequate conditions for lamination to generate high quality interfaces allowed us to fabricate high efficiency (PCEs up to 5.1%) and stability devices for which the electrode deposition cost was reduced by a factor of approximately 200. Our studies therefore emphasize that to reach the challenging goal of PSC commercialization, particular attention should be given to the various interfaces present throughout the device architecture.

7.2 SD-PSCs Based on P3HT:PCBM Active Layers

7.2.1 Increase in Donor-Acceptor Interface through Nanostructuration of SD-PSCs

Although most of the research on PSCs has been focused on BHJ-PSCs, since 2009, the concept of SD-PSCs has developed as a potential alternative to BHJ active layers. This concept was first applied to P3HT:PCBM active layers, but has since then been expanded to higher performance polymers with PCEs reaching over 7% [31]. The polymer layer is typically deposited from conventional organic solvents, such as chlorobenzene (CB) or 1,2-dichlorobenzene (DCB), and, consequently, covered with the PCBM

layer from DCM. This fabrication method may induce a vertical donor-acceptor gradient which results in more efficient charge transport to the respective electrodes as compared to BHJ-PSCs. However, the interface between donor and acceptor is reduced, which can induce a decrease in the photogenerated charges and consequently, J_{sc} . For both non-diffusive bilayer and SD-PSCs, it is therefore essential to find methods to increase the amount of donor-acceptor interface in order to increase their J_{sc} . Nanostructuring of the P3HT layer, e.g., using porous alumina templates, has proved to be an efficient method to increase the J_{sc} of non-diffusive bilayer PSCs [32]. While the method presented by Hu *et al.* leads to the formation of interdigitated active layers in which both a large donor-acceptor interface and high charge transport properties should be generated, the PCE of the devices barely reached 0.01%. This may be due to the fact that the acceptor layer was deposited by evaporation of C60, which did not induce diffusion and molecular mixing of the donor and acceptor materials.

Recently, we introduced a method to fabricate nanostructured SD-PSCs by using phase separation between P3HT and polystyrene (PS) and selective removal of PS to generate nanoporous P3HT layers [33]. Figure 7.3 displays the morphological evolution of the nanostructured P3HT layer obtained by using a 25 PS wt%. By depositing PCBM from a DCM solution on the nanostructured P3HT layer, the nanopores are partially filled, resulting in a planarization of the P3HT:PCBM SD-PSC active layer. Using cyclohexanone, we then selectively dissolved PCBM to approximate the depth of diffusion of the acceptor molecules inside the P3HT network in both vertical and lateral directions. Through these AFM experiments, we were able to verify that PCBM does not diffuse until the bottom of the P3HT layer (a 15 nm buffer layer is left undissolved) and that PCBM diffuses inside the P3HT network in both vertical and lateral directions. Note that, after PS removal, nanostructured P3HT films are thinner than pure P3HT reference films and, therefore, have lower absorption intensities. Table 7.1 summarizes the evolution of J_{sc} and corrected J_{sc} (J_{sc} corrected by the absorption intensity of the P3HT layer) together with increasing pore dimensions.

The use of nanostructured P3HT for SD-PSCs fabrication also indirectly generated a strong vertical concentration gradient in the active layers, resulting in an approximately 30% increase in PCE for the nanostructured SD-PSCs compared to the flat interface reference devices. The PCE of nanostructured SD-PSCs prepared using 25 PS wt% exhibit average PCE values of 3.25%. These experiments clearly demonstrate that the performances of SD-PSCs are highly dependent on the quantity of donor-acceptor interface.

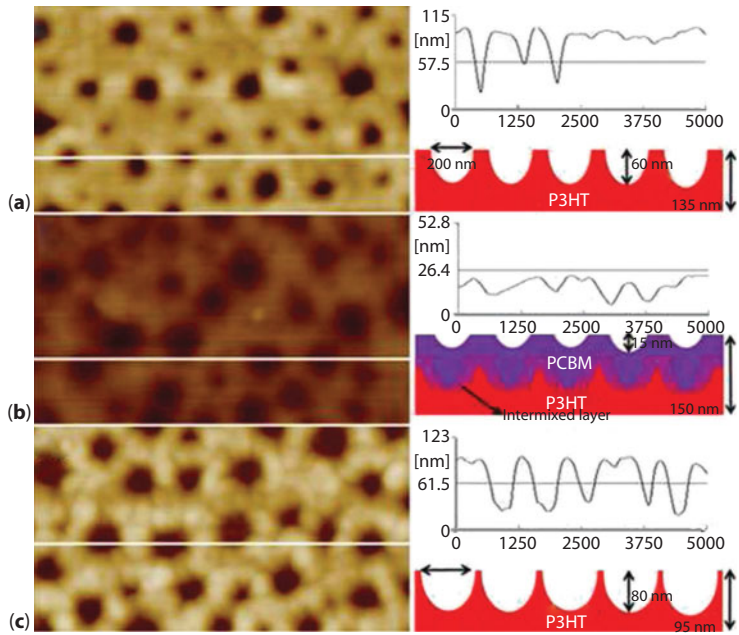


Figure 7.3 AFM micrographs, cross sections and schematic cross sections of nanostructured P3HT films (a) before and (b) after coating with PCBM from DCM, and (c) after removing PCBM molecules with cyclohexanone. (Reprinted with permission from [33]; Copyright © 2012 Royal Society of Chemistry)

Table 7.1 J_{sc} , optical and morphological properties of the nanostructured SD-PSCs. (Adapted with permission from [33]; Copyright © 2012 Royal Society of Chemistry)

PS (wt%)	J_{sc} (mA/cm ²)	Normalized absorption	Corrected J_{sc} (mA/cm ²)	Pore diameter (nm)	Pore depth (nm)
0	10.8	1	10.8	0	0
15	10.2	0.832	12.3	120	30
25	10.5	0.745	14.1	200	62
35	10.0	0.640	15.6	335	70

7.2.2 Generation of Vertical Concentration Gradient by Addition of Regiorandom P3HT in SD-PSCs

As mentioned previously, the hole conductive properties of p-type conjugated polymers are closely related to their crystallinity. Although regioregular P3HT (RR-P3HT) is highly crystalline, regiorandom P3HT

(RRa-P3HT) can be considered as a completely amorphous polymer material. When it comes to intimate mixing between P3HT and PCBM (network of small domains of a few nm), previous studies have reported that PCBM will generate smaller domains when associated with RRa-P3HT as compared to RR-P3HT [34]. Note that RR-P3HT and RRa-P3HT not only have different mixing properties with PCBM but also different absorption spectra, hole conductivities and highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) levels [35, 36]. The addition of RRa-P3HT to RR-P3HT in the first layer of SD-PSCs provides control over the quantity of PCBM which penetrates into the P3HT network [37]. However, as RRa-P3HT has a higher solubility in DCM and lower hole conducting properties as compared to RR-P3HT, the relative concentration of RRa-P3HT and RR-P3HT should be investigated to optimize active layer morphology and device performances. Through a systematic optical study, we observed the effect of gradually increasing the amount of RRa-P3HT (amorphous) to the crystalline RR-P3HT on the absorption spectra of the deposited films as well as their resistance to the PCBM layer deposited from DCM and their mixing properties with PCBM (Figure 7.4). Figure 7.4a clearly demonstrates that upon addition of RRa-P3HT, the overall absorption intensity as well as the relative absorption intensities around 560 and 610 nm, commonly ascribed to the strong inter-chain interactions, decrease. To estimate the amount of P3HT dissolved during the PCBM layer deposition process, we introduced A_i and A_f which correspond to the absorption ratio with respect to the pure RR-P3HT film and the decrease in P3HT absorption upon deposition of PCBM, respectively. Once the RRa-P3HT wt% (to the total amount of P3HT) exceeds 10 wt%, an abrupt decrease in absorption intensity of the P3HT film can

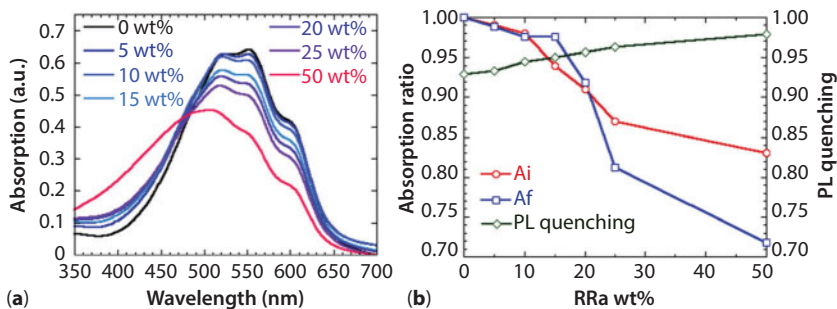


Figure 7.4 Evolution of (a) absorption and (b) absorption ratios and PL quenching of P3HT films with increasing RRa-P3HT wt%. (Reproduced with permission from [37]; Copyright © 2012 AIP Publishing LLC)

be observed. Furthermore, with RRa-P3HT wt% over 15 wt%, the P3HT film resistivity to PCBM deposition is strongly affected. By comparing the photoluminescence (PL) spectra of each film before and after PCBM deposition and normalizing with their absorptions, we were able to extrapolate the PL quenching ratio for each of the samples. PL quenching gradually increases with RRa-P3HT wt%, confirming that more intimate mixing can be obtained with larger amounts of amorphous P3HT. Note that all the samples were characterized after annealing at 140 °C for 10 min as this corresponds to the device fabrication conditions.

To further understand the effect of RRa-P3HT addition to the P3HT layer on the SD-PSC active layer morphology, we measured energy-dispersive X-ray spectroscopy elemental mapping (EDS) cross-section images of the devices finalized with 100 nm thick aluminum cathodes and annealed at 140 °C for 10 min. The annealing step may also induce diffusion of both P3HT and PCBM molecules, which usually results in the formation of larger aggregates [38]. The higher crystallinity of RR-P3HT therefore generates a higher degree of phase separation in the reference active layers which, after annealing, leads to the formation of a P3HT-rich layer close to the cathode and, consequently, a decrease in FF (high R_s as the P3HT-rich layer acts as electron-blocking layer). As emphasized in Figure 7.5, the formation of the P3HT-rich layer close to the aluminum

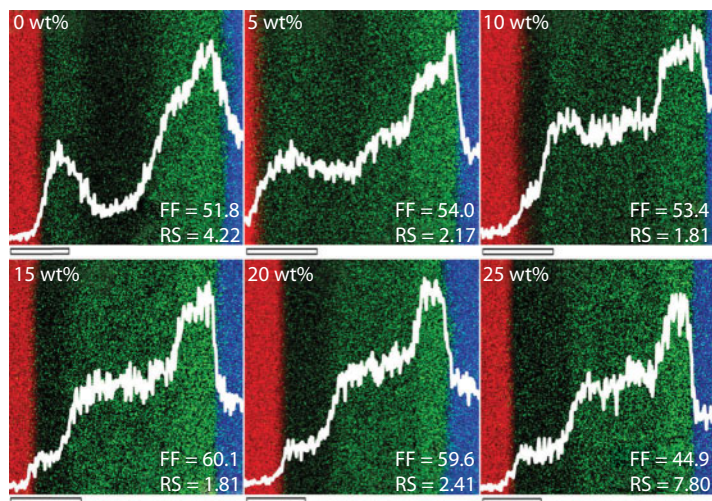
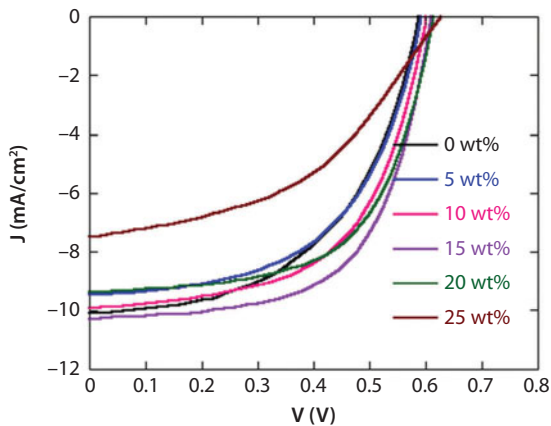


Figure 7.5 Evolution of the sulfur distribution (white lines), FF and R_s of active layers containing increasing RRa-P3HT wt%. The blue, green and red colors in the EDS images correspond to indium, sulfur and aluminum, respectively. The scale bar corresponds to 50 nm. (Reproduced with permission from [37]; Copyright © 2012 AIP Publishing LLC)

electrode gradually disappears upon addition of RRa-P3HT. This may be due to the more intimate mixing capacity of PCBM and RRa-P3HT with respect to RR-P3HT.

As the electron-blocking P3HT-rich layer gradually disappears, R_s decreases and FF up to 60% can be obtained for the devices prepared with 15 RRa-P3HT wt%. Note that these devices exhibit an almost ideal vertical concentration gradient with an intermixed layer displaying a vertical concentration gradient sandwiched between two buffer layers (P3HT- and PCBM-rich, respectively) of approximately 15 nm each [39].

In addition to a large FF increase, the intimate mixing between P3HT and PCBM, as well as the vertical concentration gradient, resulted in an enhancement of J_{sc} , in particular, when J_{sc} is corrected by the absorption of the film (Figure 7.6). In the J-V curves presented in Figure 7.6, the increase in PCE between the reference RR-P3HT device (3.09%) and the device containing 15 RRa-P3HT wt% (3.83%) can be clearly observed.



RRa-P3HT	J_{sc} (mA/cm ²)	Corrected J_{sc}	FF (%)	R_s (Ω/cm ²)
0 (wt. %)	10.05	10.05	51.8	4.22
5	9.49	9.70	54.0	2.17
10	9.93	10.37	57.0	1.87
15	10.34	11.26	60.1	1.81
20	9.40	11.26	59.6	2.41
25	7.45	10.55	44.9	7.80

Figure 7.6 J-V curves and photovoltaic characteristics of SD-PSCs prepared with increasing RRa-P3HT wt%. (Adapted with permission from [37]; Copyright © 2012 AIP Publishing LLC)

This study confirms that molecular interactions between donor and acceptors and the materials (donor or acceptor) at the interfaces with the electrodes play an essential role in improving the P3HT:PCBM SD-PSC performances. Note that higher device performances may be obtained if similar vertical concentration profiles can be obtained without introducing an amorphous material in the active layer. In fact, RRa-P3HT has lower charge transport properties compared to RR-P3HT, which is reflected in the high R_s obtained for the 25 RRa-P3HT wt% devices.

7.2.3 Generation of Vertical Concentration Gradient and Molecular Orientation by Rubbing P3HT in SD-PSCs

The introduction of the SD-PSCs concept was based on the fact that P3HT-rich and PCBM-rich layers at the bottom and top interfaces of regular device active layers can be readily generated through the sequential process. However, as demonstrated in Figure 7.5, a thin P3HT-rich layer is formed close to the cathode in pure RR-P3HT SD-bilayers. Increasing the resistance to PCBM penetration by adjusting the crystallinity of the polymer layer has been proven to generate extremely positive results and adequate donor-acceptor vertical concentration gradients [31]. Therefore, finding a process that not only increases the crystallinity of the polymer layer but also induces reorientation of the crystallites with more face-on crystallite concentration may be beneficial to increase PCE of SD-PSCs. Rubbing is a post-deposition process which has been used for many years in the liquid crystal display industry to orient polymer chains which are then used as substrate for consecutive layer orientation. In small molecules organic solar cells, it has also demonstrated its potential to orient electronically active layers and enhance their charge-transporting properties [40]. Moreover, Kajiya *et al.* demonstrated that rubbing P3HT films induces a large amount of face-on crystallite concentration and consequently, results in an enhancement of the vertical mobility in rubbed P3HT thin films [41]. Here, we applied rubbing with a nylon cloth to the P3HT layer prior to PCBM deposition during SD-PSCs fabrication process. We gradually increased the number of rubbing times and observed its effect on the active layer morphology (vertical concentration gradient and polymer crystallite orientation) as well as the device performances (Figure 7.7) [42].

Upon rubbing, the P3HT crystallinity increases, which controls the diffusion of PCBM molecules inside the P3HT network. Unlike the unrubbed active layers, with increasing rubbing times, a vertical concentration gradient is gradually generated within the active layers (Figure 7.7). As mentioned above, the generation of a vertical donor-acceptor concentration

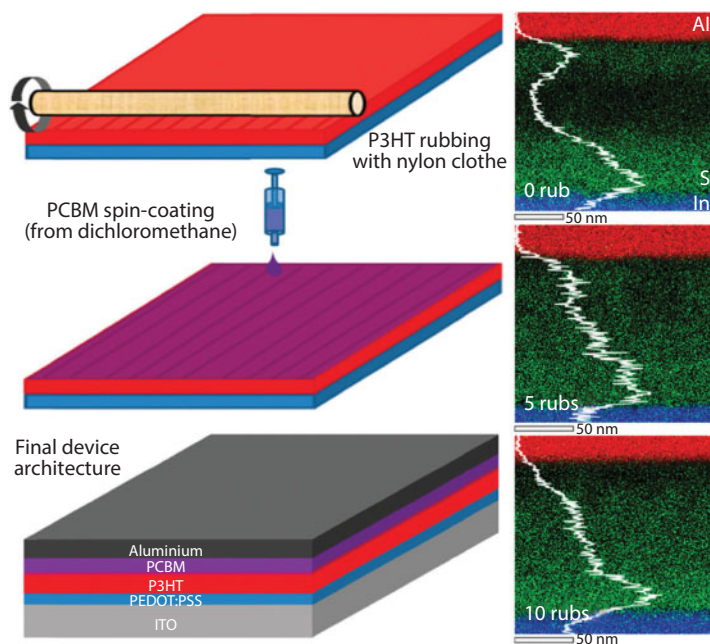


Figure 7.7 Schematic representation of the fabrication process of rubbed SD-PSCs and EDS profiles of unrubbed and rubbed devices. (Adapted with permission from [42]; Copyright © 2012 American Chemical Society)

gradient results in an enhancement of FF which, in the case of these SD-PSCs, increased from 52.6% (reference unrubbed devices) to 59.9% for 10 times rubbed P3HT layer devices.

The V_{oc} increase also suggests that rubbing induces a change in crystallite orientation as the energetic levels of P3HT edge-on and face-on crystallites may differ. We confirmed that rubbing of P3HT induces some reorientation of the polymer crystallites and generates more face-on crystallites by characterizing the samples using GI-XRD. Furthermore, in the incident 2D-XRD images, no crystallinity diffraction peaks from P3HT can be observed, confirming that the top part of the active layer is composed mainly of PCBM. Typical grazing and incidence 2D-XRD images for rubbed films are presented in Figure 7.8 along with the device performances. The highest average and maximum PCEs are obtained for 5 rubs and have a value of 3.81 and 3.99%, respectively. These PCEs are among the highest when it comes to P3HT:PCBM SD-PSCs and further emphasize how molecular orientation at the donor-acceptor interface can positively influence the performances of SD-PSCs.

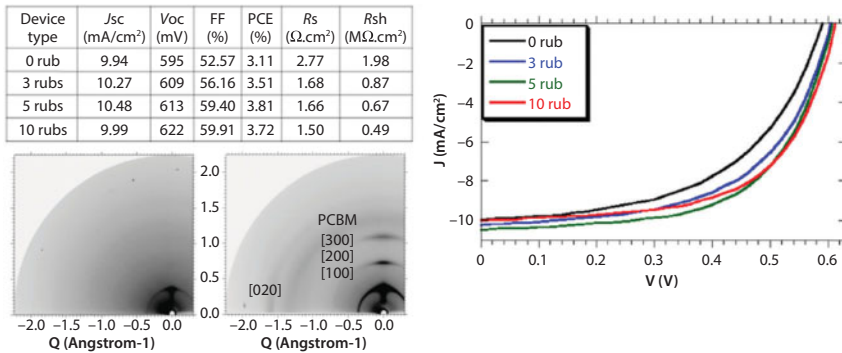


Figure 7.8 Average device performances, J-V curves and typical grazing (left) and incident (right) XRD of rubbed SD-PSCs. (Adapted with permission from [42]; Copyright © 2012 American Chemical Society)

7.3 High Performance BHJ-PSCs with Favorable Molecular Orientation Resulting from Active Layer/Substrate Interactions

Recent advances in polymer chemistry for optoelectronic applications have demonstrated the advantage of using donor-acceptor copolymers which can generate high performance PSCs as they display not only wide absorption spectra but also high charge transport properties. In particular, PNTz4T demonstrated very promising performances when associated with PCBM with PCE over 6% [12]. Here, we further studied active layers based on PNTz4T by associating it not only with PCBM (which contains a C60 fullerene) but also PC₇₁BM (which contains a C70 fullerene). The 250 nm-thick active layers were prepared under the same spin-coating conditions and the device architectures as well as the device performances are presented in Figure 7.9 [43].

Both the J-V curves and device characteristics demonstrate that PNTz4T:PC₇₁BM active layers result in higher performances compared to PNTz4T:PCBM ones. In particular, a higher J_{sc} can be observed in the case of PC₇₁BM. This can be easily explained by the fact that PC₇₁BM, which absorbs in the visible region of the spectrum, has a better spectral match with the sunlight emission spectrum. Additionally, an increase in FF can also be observed in PNTz4T:PC₇₁BM devices with values up to 66.8%. Figure 7.10 displays the 2D-XRD measurements on the two active layers in which differences in crystallinity (concentration of crystalline parts) and small variations in crystallite orientations can be observed. As demonstrated by Osaka *et al.*,

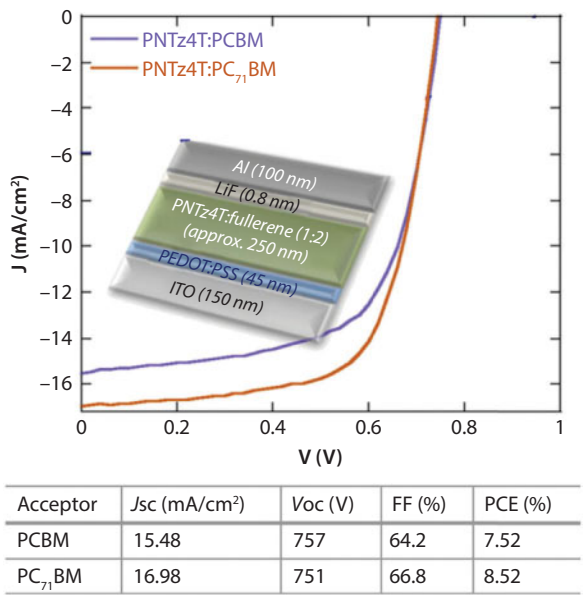


Figure 7.9 Comparative J-V curves and photovoltaic performances of PNTz4T associated with either PCBM or PC₇₁BM in regular BHJ-PSCs. (Adapted with permission from [43]; Copyright © 2015 Springer)

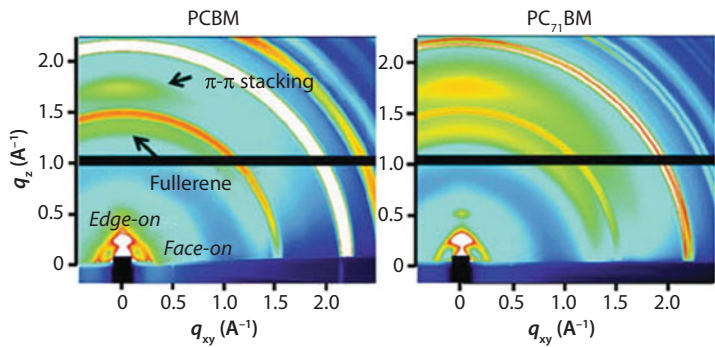


Figure 7.10 Comparative 2D-XRD of PNTz4T associated with either PCBM or PC₇₁BM in regular BHJ-PSCs. (Adapted with permission from [43]; Copyright © 2015 Springer)

the molecular orientation and crystallinity may be influenced by different molecular interactions between donor and acceptor molecules in the two active layers [12]. To avoid being misled by such variations related to different acceptor molecules, in the remaining part of this chapter, we will focus on the PNTz4T:PC₇₁BM combination when discussing PNTz4T-based BHJ-PSCs.

In conjugated polymer-based electronics, polymer crystallite orientation controls the hole-transporting properties and preferential hole transport directions. Previous reports suggest that conjugated polymer thin films deposited by spin coating have a tendency to generate a vertical distribution of crystallite orientation with more edge-on crystallites towards the bottom of the film and more face-on crystallites towards the interface with air, respectively [44]. However, as mentioned above, the surface properties of the substrate can also largely influence the polymer crystallite orientation. In fact, surface modification can directly influence the interactions between the polymer chains and the surface. The surface free energy of the substrate and, in particular, its compatibility with the solvent used for deposition, will therefore have major effects on the deposited film morphologies. Most BHJ-PSC active layers are deposited from either DCB or CB onto PEDOT:PSS (hole-transporting layer in regular device architectures) or ZnO (electron-transporting and work function modifying layer in inverted PSCs) layers. The surface free energies of PEDOT:PSS and ZnO are 73 and 40.5 mJ.m⁻², respectively [18]. Figure 7.11 displays the contact angles of DCB droplets (solvent used for PNTz4T:PC₇₁BM active layer deposition) as well as the results from two-dimensional GIWAXD analysis for PNTz4T:PC₇₁BM films deposited on PEDOT:PSS and ZnO substrates [2].

The difference in contact angles on the two surfaces (18.5 and 6.1° for PEDOT:PSS and ZnO, respectively) suggests that some variations in polymer crystallinity may be observed between the two samples. This is confirmed by the GIWAXD measurements in which the active layer deposited on ZnO clearly displays a larger face-on crystallite concentration as compared to the one deposited on PEDOT:PSS. To understand whether the face-on crystallites should be associated with the bulk properties of the thin films or with the polymer chains at the active layer/substrate interface, we gradually increased the active layer thicknesses and observed the influence of the thickness on their face-on to edge-on crystallite ratios. Upon increasing the active layer thickness from 50 nm up to 400 nm, a steady increase of face-on crystallite concentration can be observed. Both active layers deposited on PEDOT:PSS and on ZnO display a similar trend in face-on to edge-on ratios, suggesting that the active layer/air interface also plays a major role in the crystallite orientation. Taking into account previous studies involving thiophene-based polymers (such as P3HT), this strongly suggests that edge-on crystallites are mainly located close to the substrate/active layer interface while face-on crystallite-rich domains can be observed both in the bulk of the film and at the active layer/air interface (Figure 7.12) [2].

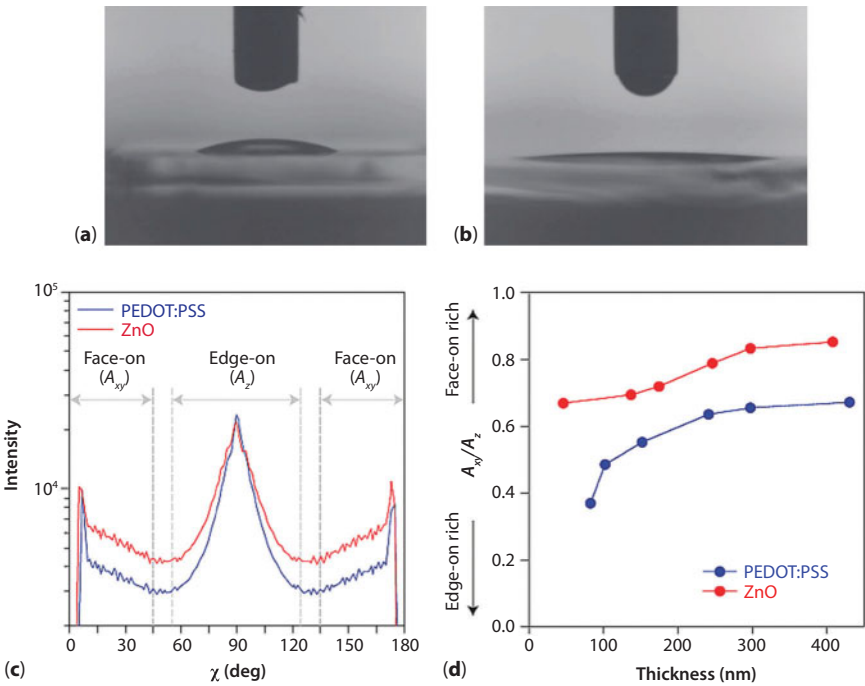


Figure 7.11 Contact angle measurements of DCB drops on (a) PEDOT:PSS and (b) ZnO surfaces. Comparative GIWAXD profiles (c) and thickness dependence of face-on to edge-on crystallite ratios (d) of active layers deposited on PEDOT:PSS or ZnO. (Adapted from reference [2]; Copyright © 2015 Nature Publishing Group)

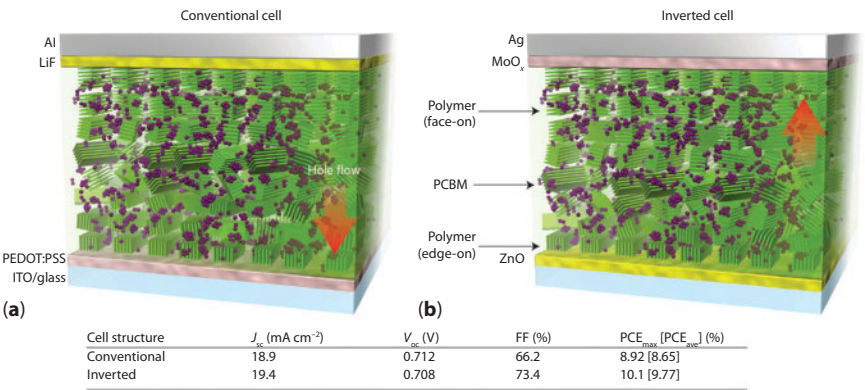


Figure 7.12 Schematic representation and device performances of regular and inverted PNTz4T:PC₇₁BM BHJ-PSCs. (Adapted from [2]; Copyright © 2015 Nature Publishing Group)

The generated crystallite orientation gradient in active layers deposited on both PEDOT:PSS and ZnO exhibits a edge-on-rich bottom layer which acts as “hole-blocking” layer. In fact, the vertical hole transport to the bottom electrode will be limited by the lateral hole transport properties of the bottom edge-on layer. On the other hand, the bulk and top face-on-rich layers favor the vertical movement of the holes towards the top of the active layers. This crystallite orientation gradient therefore favors inverted device architectures in which the holes need to move towards the interface with the top anode. The large increase in FF with values of 66.2 and 73.4%, respectively, for regular and inverted devices, further confirms our hypothesis that the vertical crystallite concentration gradient is favorable to inverted BHJ-PSCs. The best inverted PNTz4T:PC₇₁BM PSC reaches a PCE value of 10.1%, which is among the record PCEs for single junction BHJ-PSCs.

In addition to having longer lifetime due to the use of air-stable top electrode metals, inverted PSCs often exhibit higher performances as compared to their regular architecture equivalents. However, one of the main issues of inverted PSCs is that the metals that are used for top electrode deposition (commonly, Au or Ag) are more costly than those used in regular PSCs. In the following section, we will discuss a method to reduce the cost of top rare metals deposition by using a cost-effective lamination process.

7.4 Strongly Bond Metal Leaves as Laminated Top Electrodes for Low-Cost PSC Fabrication

Polymer solar cells are often referred to as low-cost alternatives to silicon-based technology. The active layer, which is solution processed and consists of thin films (small amount of active materials used), can indeed be considered as low cost. However, the top metal electrode, which is commonly deposited through vacuum evaporation, is one of the limiting factors to actually produce low-cost devices. In fact, to deposit the materials through vacuum evaporation, not only a large amount of energy is required (to produce high vacuum and heat the metals) but the process itself also generates a lot of material waste which remains on the evaporation chamber walls or on the mask used for electrode patterning. Previous studies have demonstrated that depositing the top metal electrodes through lamination can have a positive effect as the organic layer surface is not damaged during metal evaporation [45, 46]. One of the strategies to produce non-evaporate electrode deposition is to use high conductivity PEDOT:PSS as electrode,

which is deposited either by direct spin coating on the active layer or by transfer printing [17, 47]. However, to generate high conductivity PEDOT:PSS layers in a reproducible manner, particular attention should be given to the formulation (additives to generate the ideal PEDOT:PSS morphology and other additives to ensure that the PEDOT:PSS properly wets the surface of the active layer) and process conditions. Additionally, as a practical issue, even when used as electrode material, PEDOT:PSS cannot be contacted directly (to avoid damage) and therefore requires the deposition of metallic contacts.

Here, we propose 100 nm-thick metal leaves prepared by rolling and pounding as an alternative material to reduce the cost of metal deposition for inverted BHJ-PSCs by a factor of approximately 200 [48]. This factor was calculated taking into account the prices of pure metals used for evaporations (around 40 USD per gram for Au) compared with the cost of pounded metal foils (3 USD per sheet and 175 devices per sheet). The metals commonly used as anode in inverted BHJ-PSCs are Au and Ag. The devices are fabricated by depositing the P3HT:PCBM active layer on a titanium oxide (TiOx)-covered ITO substrate. A PEDOT:PSS hole conducting layer is then deposited on top of the active layer by adding a surfactant (Triton-X) to the PEDOT:PSS suspension to increase the wetting of the suspension on the active layer surface. The devices are then finalized by either Au or Ag evaporation (reference devices) or metal foil lamination and characterized without further encapsulation (Figure 7.13) [49].

Figure 7.13 and Table 7.2 summarizes the performances of the various devices after post-annealing (for evaporated devices) or lamination at

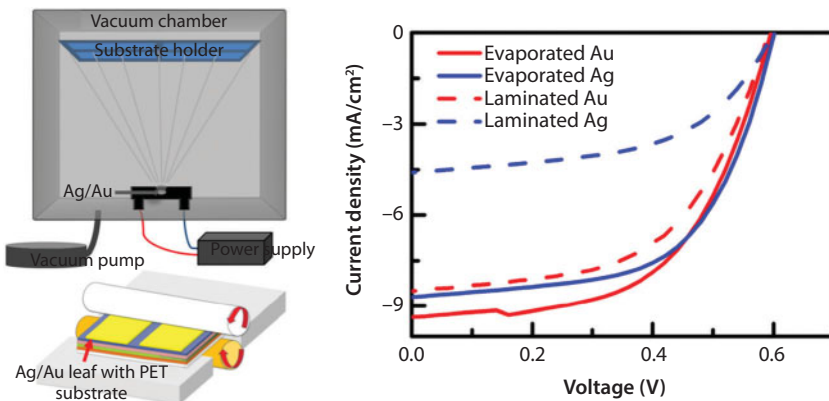


Figure 7.13 Schematic representations of the evaporation and lamination processes and comparative J-V curves of P3HT:PCBM BHJ-PSCs fabricated with the two metal deposition processes.

Table 7.2 Photovoltaic performances of laminated and evaporated top metal electrode P3HT:PCBM BHJ-PSCs.

Device	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_s (Ω .cm ²)
Evaporated Au	9.40	0.597	0.568	3.19	5.29
Laminated Au	8.28	0.593	0.572	2.80	5.33
Evaporated Ag	8.80	0.602	0.587	3.11	2.35
Laminated Ag	4.07	0.601	0.537	1.31	7.71

150 °C [49]. By comparing the J-V curves of evaporated Au and Ag devices, we can clearly observe that both devices result in very similar device performances (PCE of approximately 3.1%) with only a small variation in J_{sc} which is within experimental error. Au and Ag have work functions of 5.1 and 4.3 eV, respectively [50–53]. This suggests that a work function variation between these two values should not notably affect the device performances of the fabricated inverted BHJ-PSCs. Note that, for the metal foils, work functions of 4.9 and 5.0 eV were measured for Au and Ag, respectively. While the value for Au does not vary much between the evaporated and laminated thin films, Ag foils display a large increase in work function (approximately 0.7 eV) compared to evaporated Ag. This may be due to the fabrication (contamination) or storage (oxidation) conditions of the leaves. In fact, unlike the laminated Au devices which exhibit similar device performances to the evaporated devices, the laminated Ag devices display much lower photovoltaic properties. Taking into account the discussion above, we can eliminate the possibility that these lower performances are resulting from the change in work function. As a PEDOT:PSS layer (with a work function of approximately 5.2 eV) is deposited on the active layer prior to the metal electrode deposition, the variation in metal work functions may not play an essential role in these devices.

However, lower J_{sc} and FF can be observed for laminated devices compared to evaporated ones. Furthermore, laminated Ag devices display a higher R_s value compared to the other devices, which suggests that contact at the PEDOT:PSS/metal foil interface could be the issue. To fabricate high quality interfaces for efficient charge collection, a strong adhesion between the top metal layer and the PEDOT:PSS layer is necessary. Previous studies on metal lamination suggested that the addition of surfactants to the PEDOT:PSS layer enhanced the adhesion at the PEDOT:PSS/metal interface [46]. To understand whether the metal foils adhere to the PEDOT:PSS layer, we calculated the works of adhesion at the PEDOT:PSS/Au leaf ($W_{\text{PEDOT:PSS/Au}}$) and PEDOT:PSS/Ag leaf ($W_{\text{PEDOT:PSS/Ag}}$) interfaces and

verified whether they were higher than the works of adhesion at the metal leaves/poly(ethylene terephthalate) (PET) interfaces. PET is used as a substrate for metal foils handling prior to and during the lamination process to provide mechanical support for the thin and brittle metal foils. To laminate high quality electrodes, $W_{\text{PEDOT:PSS/metal}}$ should have a higher value compared to $W_{\text{metal/PET}}$.

To calculate W , we extrapolated the surface free energy for each of the solid (metal leaves, PEDOT:PSS and PET) surfaces (γ_s) through contact angle measurements with a selection of measuring liquids (CB, chloroform, DCM and benzaldehyde) using an optical tensiometer. Applying Owens and Wendt equation [54], we calculated the polar (γ_s^p) and dispersive (γ_s^d) components of γ_s for each surface. W at the interface between solid 1 (S1) and solid 2 (S2) can be calculated following Equation 7.1:

$$W_{S1/S2} = -2\sqrt{\left(\gamma_{S1}^d \gamma_{S2}^d\right)} - 2\sqrt{\left(\gamma_{S1}^p \gamma_{S2}^p\right)} \quad (7.1)$$

The preferential adhesion of metal leaves to either PET or PEDOT:PSS was estimated by subtracting the values of $W_{\text{PEDOT:PSS/metal}}$ by $W_{\text{metal/PET}}$. Here, we will refer to this value as lamination efficiency (L_{metal}), where a higher value of L corresponds to a stronger adhesion to PEDOT:PSS as compared to PET. The calculated values for L_{Au} and L_{Ag} are 0.23 and 0.21 mJ.m^{-2} , respectively. Note that the value obtained for Au foils is only slightly higher than that for Ag foils. However, $W_{\text{PEDOT:PSS/Au}}$ (66.2 mJ.m^{-2}) is relatively high compared to $W_{\text{PEDOT:PSS/Ag}}$ (62.5 mJ.m^{-2}). Together with the higher performances obtained for Au laminated devices, this confirms our suspicions that the lower PCE of Ag laminated devices may be related to a lower contact quality at the PEDOT:PSS/Ag foil interface. To verify this assumption, we performed optical microscope measurements of the metal foils transferred on the PEDOT:PSS surfaces and compared them with their evaporated equivalents (Figure 7.14). The results in Figure 7.14 clearly demonstrate that, unlike the smooth interfaces formed for evaporated metals, ripples are formed at the PEDOT:PSS/metal interface for laminated electrodes. In particular, the Ag metal foil surface exhibits a very large number of ripples which remarkably reduces the contact area of the electrode with PEDOT:PSS, which, in turn, reduces the J_{sc} and FF in the devices. While the surface of Au foils also displays some ripples, most of it still exhibits a smooth surface comparable with that of evaporated metals. The optical micrographs perfectly reflect the device performances and, in particular, the J_{sc} obtained for the various device types. Laminated Au devices display slightly lower performances compared to evaporate Au

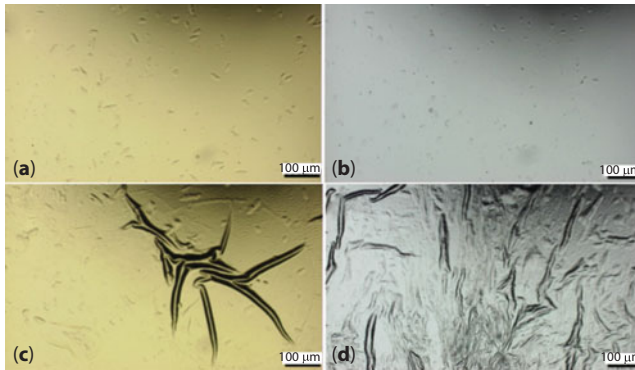


Figure 7.14 Surface optical micrographs of evaporated Au (a), Ag (b) and laminated (c) Au, (d) Ag deposited on PEDOT:PSS.

BHJ-PSCs (J_{sc} and PCE reduced by approximately 12% and similar FF for both devices).

On the other hand, comparing laminated and evaporated Ag devices, a 54% decrease in J_{sc} and 10% decrease in FF can be observed for laminated PSCs compared to the reference devices, resulting in a 60% drop of PCE. Note that the laminated Au devices exhibit similar PCEs compared with the evaporated reference devices but also demonstrate similarly stable performances under constant irradiation up to 15 hours (the experiment was stopped after 15 hours). This strongly suggests that no post-deposition Au delamination occurs in the case of Au laminated devices.

Additionally, this fabrication process, which considerably reduces the cost of production of inverted PSCs, can also be applied to higher performances conjugated polymer-based active layers such as PNTz4T:PC₇₁BM. In the case of PNTz4T:PC₇₁BM active layers Au laminated devices, we were able to obtain a J_{sc} , V_{oc} , FF and PCE of 15.1 mA.cm⁻², 726 mV, 46.1% and 5.1%, respectively. Note that the reference evaporated Au device has a PCE of 5.9%, which means that the drop in PCE by using Au lamination for PNTz4T:PC₇₁BM active layers is approximately 13% (similar value to that observed for P3HT:PCBM laminated Au devices). These results further emphasize the importance of interface quality and engineering to generate high performance devices. In fact, the laminated PNTz4T:PC₇₁BM inverted BHJ-PSCs exhibit record PCEs for laminated single-junction solar cell devices. Furthermore, our results suggest that, as long as a strong adhesion between the metal foils and the underlying layer can be obtained, this method has the potential to be applied not only to PSCs but virtually any electronic device requiring the use of thin metal electrodes. As the fabrication process was performed in atmospheric conditions through

a roll-to-roll compatible process, Au foil lamination opens a path to the fabrication of low-cost large-area photovoltaic devices which could revolutionize worldwide energetic requirements by providing PSCs affordable to anyone around the planet.

7.5 Conclusions

In summary, we have demonstrated that the requirements for commercialization of PSCs, namely, PCE, stability and low cost, can be achieved by engineering the various interfaces found in the devices.

Nanostructuration of the donor-acceptor interface in SD-PSCs results in a large increase in charge photogeneration efficiency. Furthermore, tuning the donor-acceptor vertical concentration gradient of SD-PSCs can be achieved by modifying the crystallinity of P3HT. Additionally, by using mechanical processes such as rubbing on the top surface (polymer/air interface) of P3HT films, one can induce face-on crystallite orientation favorable for vertical charge transport in P3HT:PCBM SD-PSCs, resulting in PCEs of approximately 4%.

In BHJ-PSCs prepared using PNTz4T:PC₇₁BM blends, crystallite orientation can be controlled by the interactions between the active layer and the substrate. More precisely, active layers deposited on ZnO display a higher face-on crystallite concentration with respect to those deposited on PEDOT:PSS. Moreover, a crystallite orientation gradient is generated along the vertical direction of the active layer with more edge-on and face-on crystallites, respectively, at the bottom and top of the thin films. The molecular orientation in PNTz4T:PC₇₁BM is therefore favorable for inverted devices which exhibit maximum FF and PCE values of 73.4 and 10.1%, respectively.

By developing a process based on the lamination of metal foils as top electrodes in inverted BHJ-PSCs, we were able to fabricate devices with similar (around 10% decrease in PCE) performances as their evaporated electrode equivalents. We verified that, to fabricate devices with high PCE and stability, particular attention should be given to the adhesion at the PEDOT:PSS/metal foil interface. In fact, with lamination of Au foils, which have a strong adhesion to the underlying PEDOT:PSS hole conducting layer, we were able to fabricate inverted BHJ-PSCs with PCE up to 5.1% while reducing the metal deposition cost by a factor of 200.

Our results not only emphasize the importance of interface engineering for PSCs fabrication but also open the path to commercialization of printed PSCs by providing innovative ideas to increase the device performances while maintaining a low fabrication cost.

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Structural, Optical, Electrical and Electronic Properties of PEDOT: PSS Thin Films and Their Application in Solar Cells

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Abstract

The structural, optical, electrical and electronic properties of poly(3,4-ethylene dioxithiophene):polystyrene sulfonate (PEDOT:PSS) thin films are investigated using transmittance spectrometry, atomic force microscopy, water droplet contact angle measurement, Raman scattering spectrometry, and photoelectron emission spectrometry. The fabrication parameters of the thin films were varied in order to determine which would improve the performance of the resultant PEDOT:PSS thin-film-based transparent conductive electrodes (TCEs) and hole-transporting materials (HTMs) in solar cells. For TCE applications, the experimental results lead to the conclusion that the necessary transparency and electrical conductivity of PEDOT:PSS (1:2.5 wt%) thin films can be simultaneously obtained by using a post-immersion treatment process which encourages the formation of connected conductive PEDOT channels and an increased carrier density in the PEDOT chains. On the other hand, the work function of the HTMs depends on the molecular structure of the PEDOT chains in the PEDOT:PSS thin films, which can be manipulated by varying the PEDOT/PSS ratio, spin rate, thermal annealing conditions and the viscosity of the PEDOT:PSS solutions. The work function

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of PEDOT:PSS thin films increases from 5.0 eV to 5.4 eV with an increase in the linearly oriented PEDOT chains, which results in an improvement in the open-circuit voltage of the solar cells.

Keywords: PEDOT:PSS thin films, molecular structure, free carriers, work function, viscosity

8.1 Introduction

Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) thin films were first used as the hole-injection contact in light-emitting diodes [1–4] and electrochemical devices [5–8] because PEDOT is a stable conductive polymer [9]. Owing to their high electrical conductivity [10–12] and large work function [13–15], the PEDOT:PSS thin films can be used as transparent conductive electrodes (TCEs) [16–18] or hole-transporting materials (HTMs) [19–21] in solar cells. PEDOT is a π -conjugated conductive polymer which is electrically attracted to an insulator-like PSS segment and therefore can be dissolved in aqueous solutions, which is beneficial in terms of the fabrication cost because PEDOT:PSS thin films can be easily obtained using solution processes. PEDOT:PSS (1:2.5 wt%) aqueous solutions are widely used as the starting material for the fabrication of transparent conductive electrodes (TCEs). The electrical conductivity is usually smaller than 1 S/cm when a PEDOT:PSS (1:2.5 wt%) thin film is deposited on top of a glass substrate using the spin-coating method due to the poor connection between the PEDOT chains in the PEDOT:PSS thin films. The electrical conductivity of PEDOT:PSS (1:2.5 wt%) thin films can be dramatically increased from ~ 1 S/cm to ~ 1000 S/cm using various treatment methods [10, 17, 18]. These modified highly conductive PEDOT:PSS (1:2.5 wt%) thin films can be used as stand-alone TCEs for ITO substitutes. Previous reports [22, 23] have explained the increased electrical conductivity in the modified PEDOT:PSS (1:2.5 wt%) thin films as being due to the partial removal of the insulator-like PSS segments and the formation of conductive PEDOT three-dimensional (3D) networks [24]. The starting material for the HTMs is a PEDOT:PSS (1:6 wt%) aqueous solution. The spin coating of a p-type PEDOT:PSS thin film on top of an n-type ITO/glass sample can lead to an improvement in the open-circuit voltage (V_{oc}) of the solar cells, and block the electron recombination from the conduction band in the active layer to the Fermi level in the ITO thin film.

The transparency, electrical conductivity and work function of PEDOT:PSS thin films is greatly dependent on their molecular structure which consists of amorphous PSS segments, PEDOT-PSS core-shell

clusters and linear PEDOT islands [24]. Under air-dried conditions, there is no clear segregation between the amorphous and crystalline phases, which indicates that the PEDOT chains are randomly distributed in the PEDOT:PSS thin films. After annealing in air at 120–160 °C for 10–20 min, uniformly distributed PEDOT-PSS core-shell clusters form with an average diameter of ~40 nm, which is close to the film thickness. The PEDOT-PSS core-shell clusters are separated by amorphous PSS polymers, which impede carrier transports in the transverse direction. The core-shell clusters are hole-transporting pathways, which means that the work function of the PEDOT:PSS thin films is dominated by the molecular structure in the PEDOT-PSS core-shell clusters. This PEDOT molecular structure can be manipulated by varying the PEDOT/PSS ratio [14, 25], spin rate [15, 26], thermal annealing conditions [26, 27] and viscosity of the PEDOT:PSS solutions [28].

This chapter will explore the correlation between the properties of the PEDOT:PSS thin films and the photovoltaic performance of the resultant solar cells. The molecular structure of the thin films is characterized by examining the Raman scattering spectra. The free carrier density of the PEDOT chains in the PEDOT:PSS thin films can be determined by fitting the transmittance spectrum with a transfer matrix method [29] and Drude model [30]. The work function of the PEDOT:PSS thin films is measured by a photoelectron emission spectrometer. The hydrophilicity and surface roughness of the PEDOT:PSS thin films are assessed using a homemade contact-angle imaging system and an atomic force microscope (AFM), respectively.

8.2 Chemical Structure of PEDOT:PSS

The chemical structure of PEDOT:PSS is depicted in Figure 8.1a. The positively charged PEDOT chains and negatively charged PSS chains are attracted through Coulomb interaction. The molecular structure of the PEDOT chains can be a benzoid form and or a quinoid form, as shown in Figure 8.1b. The benzoid form has a coil conformation, while the quinoid form has a linear or expanded-coil conformation. Both the benzoid form (coil conformation) and quinoid form (linear or expanded-coil conformation) can coexist in a PEDOT:PSS thin film. Theoretical studies reveal that the PEDOT chain is bent towards the PSS moiety and, thus, PEDOT:PSS is likely to form a partially coiled or helical structure [31]. Figure 8.1c presents the Raman fingerprints of a PEDOT:PSS thin film, which can be used to investigate the chemical structure of PEDOT:PSS thin films [32–34].

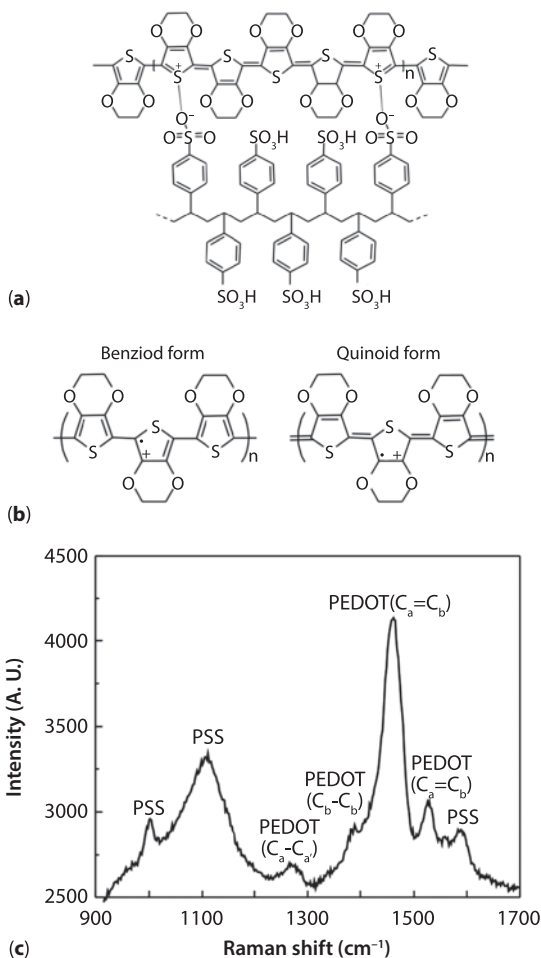


Figure 8.1 (a) Molecular structures of PEDOT and PSS polymers. (b) Benzoid and quinoid forms of PEDOT polymers. (c) Raman fingerprint of a PEDOT:PSS (1:6 wt%) thin film.

The vibrational modes of the PSS segments are located at 1110 cm^{-1} and 1000 cm^{-1} , while the vibrational modes of the PEDOT chains are located at 1524 cm^{-1} , 1452 cm^{-1} , 1383 cm^{-1} , and 1272 cm^{-1} , which have been assigned to the $\text{C}_a=\text{C}_b$ asymmetrical, $\text{C}_a=\text{C}_b$ symmetrical, C_b-C_b stretching, and C_a-C_a inter-ring stretching vibrations, respectively. The band between 1400 cm^{-1} and 1500 cm^{-1} , which corresponds to the $\text{C}_a=\text{C}_b$ symmetrical vibration on the five-member ring of PEDOT, can be used to distinguish the molecular structure of the PEDOT chains [11, 25, 33, 35, 36]. Conceptually, the benzoid form of PEDOT is a de-doping state while the quinoid form is a

doping state, which means that the carrier concentration in the PEDOT chains is proportional to the quinoid form/benzoid form ratio. In other words, the quinoid form of PEDOT (doping state) has a larger work function when compared with the benzoid form (de-doping state).

8.3 Optical and Electrical Characteristics of PEDOT:PSS

For a quinoid form of PEDOT chains in PEDOT:PSS thin films, the electrons are removed from the PEDOT chains due to the strong electron attraction of the sulfonate groups in the PSS segments, which results in the generation of free carriers with lattice distortions (positive polarons). The generation of polarons increases the electrical conductivity, optical transparency in the visible region and reflectance in the infrared region of p-doped PEDOT polymers [37, 38]. In p-doped PEDOT polymers, two polaron states (P1 and P2) are created in the midgap of the π - π^* transition. Figure 8.2a presents the electronic structure of a heavily p-doped PEDOT polymer. Figure 8.2b presents the transmittance spectrum of a PEDOT:PSS thin film (1:6 wt%) on glass substrate. The transmission drop in the violet region is due to the absorption of the glass substrate. The transmittance in the visible region (400 nm to 700 nm) is higher than 88%, which indicates that the exciton transition in the PEDOT chains is nearly completely suppressed due to the generation of polarons. The strong free carrier effect results in a reduced transmittance in the long wavelength region, which indicates that doping of the PEDOT polymer by PSS produces a heavily p-doped organic semiconductor. The resultant broad absorption

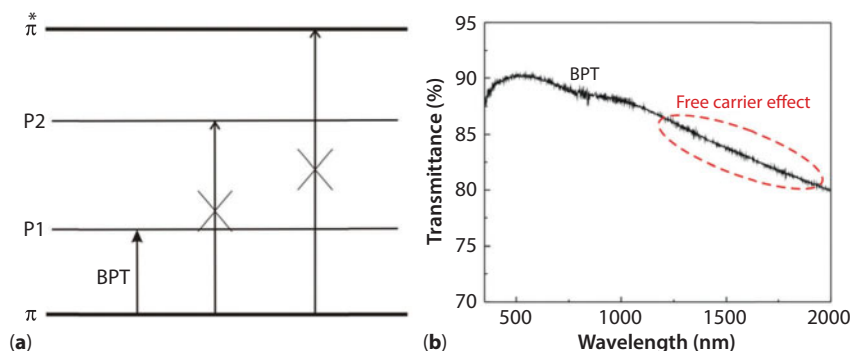


Figure 8.2 (a) Electronic structure of p-doped PEDOTs. (b) Transmittance spectrum of a PEDOT:PSS thin film deposited on glass substrate.

drop (570–1050 nm) can be assigned to the bipolarons transition (BPT) from π to P1. The absorption peak of the PSS polymers is located at ~ 260 nm [39] while the broad photoluminescence of the PSS polymers ranges from 413 nm (3.0 eV) to 1033 nm (1.2 eV) [38]. The PSS polymer is highly transparent in the near-infrared region, which indicates that the free carrier density of the PSS segments in the PEDOT:PSS thin film is quite low and suggests that they act as electrical insulators when compared to the PEDOT chains. This means that the PEDOT chains in PEDOT:PSS thin films are the hole transport pathways, which is confirmed by the conducting AFM images seen in refs. [40, 41].

The transmittance of the PEDOT:PSS thin film (1:6 wt%) decreases monotonically with the wavelength in the near-infrared region, which is similar to the transmittance spectra of conductive transparent oxide films (Al-doped ZnO, Ga-doped ZnO and ITO) [42–44]. This means that the free carrier density of the PEDOT chains in the PEDOT:PSS thin film is higher than $1 \times 10^{20}/\text{cm}^3$. However, the PEDOT chain connectivity dominates the electrical conductivity of the PEDOT:PSS thin films and impedes the determination of the carrier characteristics (carrier density and carrier mobility) of the PEDOT chains in the films when using Hall measurements. The PEDOT chain connectivity can be evaluated by examining various AFM images (phase, adhesion and current) [11, 41, 45]. Owing to the disconnected PEDOT chains, it is not easy to use electrical measurement methods to investigate the carrier characteristics of the PEDOT chains in PEDOT:PSS thin films. In our previous report [11], the carrier characteristics of the PEDOT chains can be obtained by fitting the near-infrared transmittance spectrum of the PEDOT:PSS thin film with the transfer matrix method and the Drude model. Figure 8.3 presents the transmittance spectra and fitting curves of the PEDOT:PSS thin films on glass substrate [25]. The PEDOT:PSS nanocomposite thin film can be viewed as an effective medium because the PEDOT chains are randomly distributed within the PSS host. In the near-infrared region, the dielectric constant of the PSS segments is assumed to be 2.56 while the dielectric constant of the PEDOT chains can be described by the free carrier model (Drude model) as follows:

$$\varepsilon_{\text{PEDOT}} = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + j\nu_c)}, \quad (8.1)$$

where ε_{∞} is assumed to be 2.56 [46]; ω_p is the plasma frequency of the free carriers; ω is the angular frequency of the incident lights; and ν_c is the collision frequency of the free carriers. The free carrier density, carrier

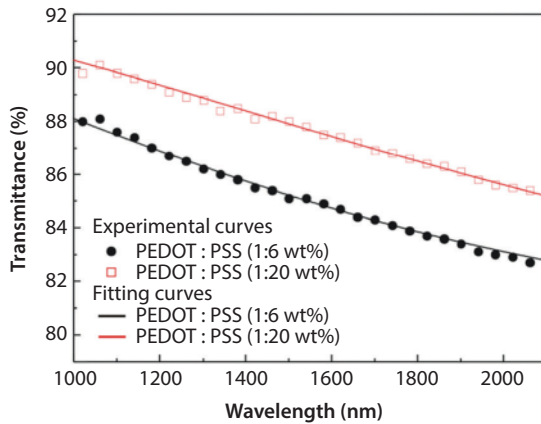


Figure 8.3 Transmittance spectra of the PEDOT:PSS thin films on glass substrate. (Reprinted with permission from [25])

Table 8.1 Free carrier density, carrier mobility and local conductivity of the PEDOT chains in the PEDOT:PSS thin films. (Adapted with permission from [25])

PEDOT/PSS ratio	N_{PEDOT} ($1/\text{cm}^3$)	μ_{PEDOT} (cm^2/Vs)	σ_{PEDOT} (S/cm)
1/6	1.191×10^{21}	5.32	1014
1/20	1.438×10^{21}	8.36	1923

mobility and local conductivity of the PEDOT chains can be calculated by $N_{PEDOT} = \varepsilon_0 m_h^* \omega_p^2 / e^2$, $\mu_{PEDOT} = e / m_h^* v_c$ and $\sigma_{PEDOT} = \varepsilon_0 \omega_p^2 / v_c$, respectively, where ε_0 is the absolute permittivity, the effective carrier mass, m_h^* , is assumed to be $0.3 m_e$ [47]; m_e is the electron mass; and e is the electric charge. The effective dielectric constant of a PEDOT:PSS thin film can be obtained using the Maxwell Garnett model [48]. During the curve fitting process, the dispersive dielectric constant of the glass substrate and the thickness of the PEDOT:PSS thin film have to be known and are fixed, while the plasma frequency and collision frequency are varied. The dielectric constant of the PEDOT chains is adjusted in order to fit the experimental data. After the curve fitting process, the free carrier density, carrier mobility and local conductivity of the PEDOT chains in the PEDOT:PSS thin film are obtained and are listed in Table 8.1. The experimental results show that the local conductivity of the PEDOT:PSS (1:20 wt%) thin film is larger than that of the PEDOT:PSS (1:6 wt%) thin film because of the

larger free carrier density and the higher carrier mobility in the PEDOT chains. This result implies the conformation of the PEDOT changes from a benzioid-like form (coil conformation, de-doping state) to a quinoid-like form (linear conformation, doping state) with a decrease of the PEDOT/PSS ratio, which is also confirmed by the Raman fingerprints of the PEDOT:PSS thin films at the $C_a = C_b$ stretching mode ($\sim 1450\text{ cm}^{-1}$) in the five-member ring of PEDOT chains.

8.4 Electronic Characteristics of PEDOT:PSS

PEDOT is a conjugated thiophene-derivative polymer, which can be doped to achieve high electrical conductivity. Thiophene-derivatives fall into the class of nondegenerate ground-state polymers [49–51], which results in polaron or bipolaron states for charged defect in the polymer. A polaron is a radical-ion coupled with a local geometry relaxation, which has electron spin resonance characteristics. At higher doping concentrations, the paired polarons form a doubly charged spinless bipolaron which has a strongly localized lattice relaxation. Figure 8.4 presents the electronic structures of the neutral PEDOT, lightly p-doped PEDOT and heavily p-doped PEDOT. The energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PEDOT polymers can be increased from 1.6 eV [52] to 2.6 eV [37] by doping with PSS polymers, which is the signature of heavily p-doped conducting polymers [37]. The band gap widening effect of the PEDOT polymers is due to the fact that bipolaron states entering into the gap are taken from the HOMO and LUMO edges. In heavily p-doped PEDOT polymers, the conduction mechanism is highly unexpected in the sense that all bands are either completely filled or vacant and that mobile spinless bipolarons, not electrons, transport the current. The Fermi level of the PEDOT:PSS thin films can be

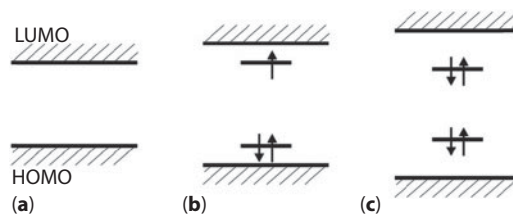


Figure 8.4 Energy level scheme of the self-localized states in PEDOT polymers. (a) Band edge of a neutral PEDOT polymer; (b) polaron state formed upon the addition of an extra electron; (c) spinless bipolaron state formed upon the addition of a second electron.

manipulated to increase from -5.20 eV to -5.44 eV by increasing the PSS/PEDOT ratio from 10 to 46 [40]. For a heavily p-doped PEDOT:PSS thin film, the Fermi level (E_F) is close to the HOMO energy level (E_{HOMO}) [53]. Therefore, the LUMO energy level (E_{LUMO}) of a PEDOT:PSS thin film can be determined by the relation: $E_{LUMO} = E_F + E_G$ when the optical band gap, E_G , is known.

8.5 Highly Conductive PEDOT:PSS Thin Films

These heavily PSS polymer doped p-type PEDOT polymers can be expected to serve as high-performance TCEs in organic optoelectronic devices due to their high transparency in visible region (400–700 nm) and the high carrier density ($\sim 10^{21}/\text{cm}^3$) of the PEDOT polymers. However, the electrical conductivity of PEDOT:PSS (1:2.5 wt%) thin films is lower than 1 S/cm which is far smaller than that of ITO thin films (~ 7000 S/cm). The main reason for this is the poor connection between the PEDOT chains in the PEDOT:PSS thin films, as shown in Figure 8.5d, which impedes electrical conductivity. However, the electrical conductivity of the thin films can be increased from 0.84 S/cm to 1210 S/cm using a post-immersion treatment process [11]. There is a gradual increase in the PEDOT chain connectivity with an increase in the immersion time of the PEDOT:PSS thin film in an ethylene glycol/hexafluoro-isopropyl alcohol solvent mixture, as shown in Figure 8.5d–f. The increase in the PEDOT chain connectivity is widely explained as being due to the partial removal of PSS polymers [22], which results in a lot of holes, as shown in Figure 8.5a–c. After the post-treatment process, the free carrier density of the PEDOT polymers increases from $5.0 \times 10^{20}/\text{cm}^3$ to $8.2 \times 10^{20}/\text{cm}^3$, which results in an improvement in the local conductivity of the PEDOT polymers from 944 S/cm to 1284 S/cm. This result is due to the conformational change of the PEDOT chains from a benzoid-like form to a quinoid-like form, as confirmed by the Raman fingerprints of the PEDOT:PSS thin films [11, 25, 33, 35, 36].

In previous studies [16–18], it was found that PEDOT:PSS thin-film-based TCEs could be fabricated on top of glass (plastic) substrates using various pretreatment and post-treatment methods. The addition of alcohols to the PEDOT:PSS (1:2.5 wt%) aqueous solutions during pretreatment can increase the electrical conductivity of the PEDOT:PSS (1:2.5 wt%) thin films from 0.2 S/cm^{-1} to 103 S/cm^{-1} due to the preferential solvation with cosolvents [54]. When an ethanol-water pretreated PEDOT:PSS thin film is used as the anode electrode, a moderate power conversion efficiency (PCE) of 2.87% can be achieved in P3HT:PCBM-based solar cells. The

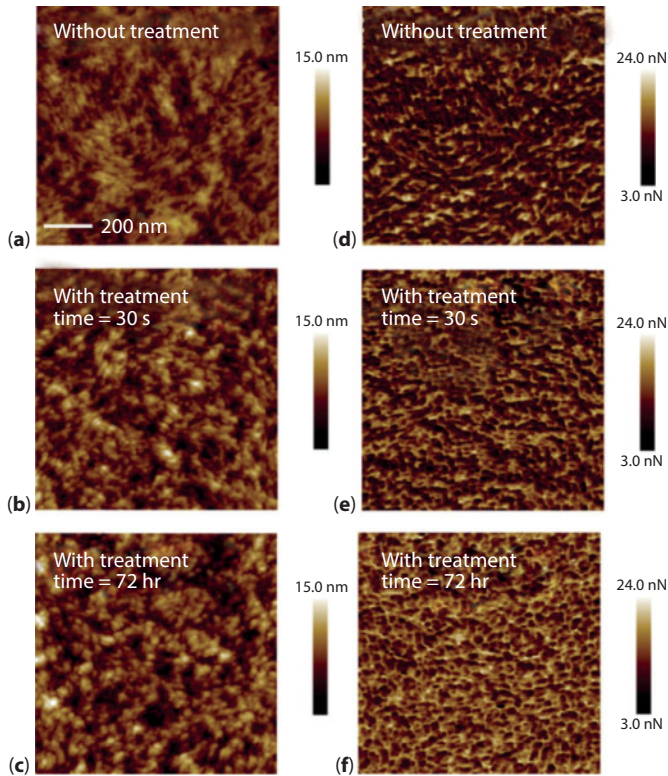


Figure 8.5 Atomic force microscopic images of PEDOT:PSS thin films: (a–c) images of the topography; (d–f) adhesion images. (Reprinted with permission from [11])

electrical conductivity of the PEDOT:PSS (1:2.5 wt%) thin films can be increased from 0.3 S/cm to 1050 S/cm (1100 S/cm) by using a dipping (dropping) method with methanol solvents as part of the post-treatment process [22]. The electrical conductivity of PEDOT:PSS (1:2.5 wt%) thin films can be further improved to 1336 S/cm when a co-treatment (dip and drop) method is used during the post-treatment process [22]. When the methanol post-treated PEDOT:PSS thin film is used as the anode electrode, a high PCE (3.71%) in P3HT:PCBM-based solar cells can be realized. The use of formic acid [12] and H_2SO_4 [55] in the post-treatment process can improve the electrical conductivity of the PEDOT:PSS thin films from 0.3 S/cm to 1900 S/cm and 3065 S/cm, respectively.

The open-circuit voltage (V_{oc}) (0.58 V) in glass/PEDOT:PSS (1:2.5 wt%)/P3HT:PCBM/Ca/Al solar cells is lower than the V_{oc} (0.61 V) in glass/ITO/PEDOT:PSS (1:6 wt%)/P3HT:PCBM/Ca/Al solar cells [11] because the work function of the PEDOT:PSS (1:2.5 wt%) thin films is smaller than

that of the PEDOT:PSS (1:6 wt%) thin films. However, the work function of modified PEDOT:PSS (1:2.5 wt%) thin films is expected to increase because of increasing the free carrier density of the PEDOT chains.

8.6 Hole-Transporting Materials: PEDOT:PSS Thin Films

The role of the HTM in solar cells is to extract positive carriers (holes) and to block negative carriers (electrons) from the light-absorbing material. Therefore, the HOMO energy level (LUMO energy level) of the HTM needs to be higher than that of the light-absorbing material (active layer), as shown in Figure 8.6. In an ideal solar cell, the V_{oc} can be defined as the energy difference between the LUMO of the electron acceptors and the HOMO of the HTMs. Therefore, the highest theoretical V_{oc} is the optical band gap of active layers when the LUMO (HOMO) of the electron acceptors (HTMs) is equal to the LUMO (HOMO) of the active layers. However, the exciton dissociation and carrier extraction efficiencies at the active layer/HTM (active layer/electron acceptor) interface, which influence the short-circuit current density (J_{sc}), is proportional to the driving electric force which is created due to the energy difference between the HOMO (LUMO) of the active layer and the HOMO (LUMO) of the HTM (electron acceptor). It is clear that there is a trade-off between the V_{oc} and J_{sc} [56], which reduces the maximum efficiency of Shockley-Queisser limit in p-n junction solar cells.

Under a suitable thermal annealing process, the HOMO and LUMO energy levels of the PEDOT:PSS (1:6 wt%) thin films are -5.2 eV and -2.6 eV, respectively, which is an appropriate HTM for solar cells. In

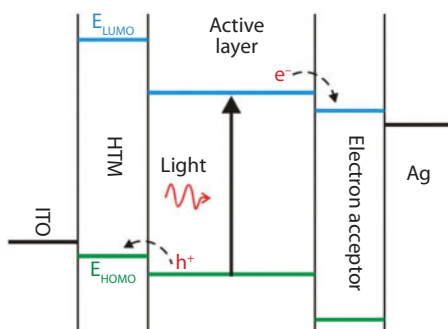


Figure 8.6 Electronic structure of planar solar cells.

addition, the diameter of PEDOT-PSS core-shell clusters are close to the thickness of the PEDOT:PSS thin films, while the PEDOT-PSS core-shell cluster is a PEDOT-rich nanoparticle. This means that the extracted holes can propagate to the anode electrode through the PEDOT-rich nanoparticles. In a previous report [25], we showed the local conductivity of the PEDOT chains in the PEDOT:PSS (1:6 wt%) to be higher than 1000 S/cm, which results in an excellent exciton dissociation (carrier extraction) at the interface between the PEDOT:PSS and the active layer [21]. Therefore, it is possible to increase the V_{oc} without reducing the J_{sc} by lowering (increasing) the LUMO energy level (work function) of PEDOT:PSS thin films. In previous reports [14, 15, 25–28], it was discovered that the work function of the PEDOT:PSS thin films could be increased by varying the PEDOT/PSS ratio, spin rate, thermal annealing condition and viscosity of PEDOT:PSS solutions.

8.6.1 Effect of PEDOT/PSS Ratio

The work function of the PEDOT:PSS thin films can be increased by decreasing the PEDOT/PSS ratio, as shown in Figure 8.7a, which is determined using a photoelectron emission spectrometer. When the PEDOT/PSS ratio decreases from 0.4 to 0.05, the work function (V_{oc}) of the PEDOT:PSS thin films ($CH_3NH_3PbI_3$ -based solar cells) increases from 5.02 eV (0.77 V) to 5.23 eV (0.90 V). The increase in the work function (0.21 eV) of the HTM is nearly contributed to the improvement in the V_{oc} (0.23 eV) of the solar cell. Figure 8.7b presents the current density-voltage (J-V) curves of the $CH_3NH_3PbI_3$ -based solar cells fabricated using the different PEDOT:PSS

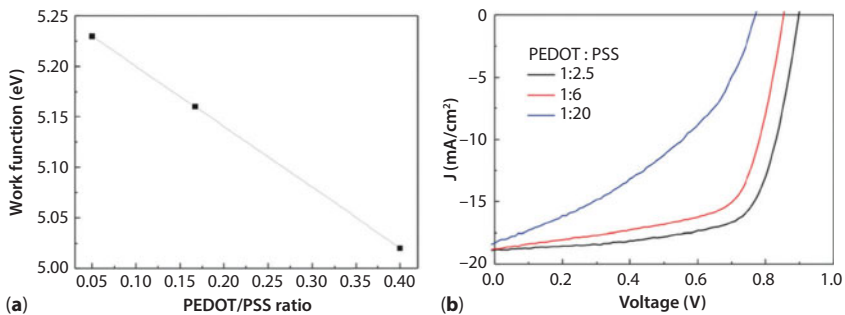


Figure 8.7 (a) Work functions of the PEDOT:PSS thin films. (b) Current density-voltage (J-V) curves of the $CH_3NH_3PbI_3$ -based solar cells fabricated with the different PEDOT:PSS thin films under one-sun illumination (AM 1.5G, 100mW/cm²). (Reprinted with permission from [25])

thin films [25]. The work function of the PEDOT:PSS thin films increases with a decrease in the PEDOT/PSS ratio due to the conformational change of the PEDOT chains from a benzoid-like form to a quinoid-like form. The possible reason for this is that the PEDOT aggregation (benzoid-like form) is suppressed due to the excess PSS polymers and thereby forming linear PEDOT chains (quinoid-like form) doped by PSS segments. However, the excess PSS polymers would degrade the performance of optoelectronic devices due to the low stability of PSS polymers in high-moisture environments [57]. In addition, the value of J_{sc} is not reduced (see Figure 8.7b) when the PEDOT/PSS ratio decreases from 1/6 to 1/20, which originates from the increased local conductivity of the PEDOT polymers (see Table 8.1).

8.6.2 Effect of Spin Rate

The spin rate influences the thickness of the PEDOT:PSS thin films and the evaporation speed of the PEDOT:PSS aqueous solutions during the spin-coating process. Usually, the PEDOT:PSS thin films are deposited on top of ITO electrode as the HTM in solar cells. In order to avoid the electron injection from the active layer to the ITO electrode, the ITO surface has to be completely covered by the PEDOT:PSS thin film which is an electron-blocking layer (EBL). In references [15, 58–60], it can be found that the optimal thickness of PEDOT:PSS (1:6 wt%) thin films is about 40 nm for ITO-based organic (perovskite) solar cells.

The work function of the PEDOT:PSS (1:6 wt%) thin films can be increased from 5.15 eV to 5.39 eV by increasing the spin rate from 3000 rpm to 6000 rpm, which results in a (an) decrease (increase) in the thickness (surface roughness) of the PEDOT:PSS thin films from 55 nm (1.43 nm) to 25 nm (2.19 nm) [15]. Therefore, it is predicted that the V_{oc} of the solar cells can be improved by increasing the spin rate of the PEDOT:PSS aqueous solutions. The photovoltaic performance of the mixed-organic-cation (MOC) perovskite-based solar cells is listed in Table 8.2. The experimental results show that the V_{oc} of the solar cells increases from 0.932 V to 0.979 V with an increase in the spin rate for the fabrication of the PEDOT:PSS thin films, which originates from the increased work function of the PEDOT:PSS thin films from 5.15 eV to 5.20 eV. In addition, the J_{sc} of the MOC perovskite-based solar cells can also be increased from 19.45 mA/cm² to 20.96 mA/cm² due to the better exciton dissociation efficiency, which is confirmed by a photoluminescence (PL) quenching experiment, as shown in Figure 8.8. In order to avoid the strong light absorption of the PCBM thin films in the violet region, the samples are

Table 8.2 Photovoltaic performance of the mixed-organic-cation perovskite-based solar cells under 1 sun illumination (AM 1.5G, 100mW/cm²). (Adapted with permission from [15])

Spin rate (rpm) ^a / TK(nm) ^b /Rq(nm) ^c	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
3000/55/1.43	0.932 ± 0.025	19.45 ± 0.12	67.4 ± 0.5	12.21 ± 0.15
4000/46/1.66	0.940 ± 0.093	20.09 ± 0.17	65.9 ± 0.6	12.45 ± 0.22
5000/37/1.84	0.979 ± 0.016	20.96 ± 0.14	64.7 ± 1.2	13.28 ± 0.37
6000/25/2.19	0.953 ± 0.010	20.66 ± 0.39	56.3 ± 4.9	11.08 ± 0.83

^aSpin Rate: spin rate of PEDOT:PSS thin film.

^bTK: thickness of PEDOT:PSS thin film.

^cRq: surface roughness of PEDOT:PS thin film.

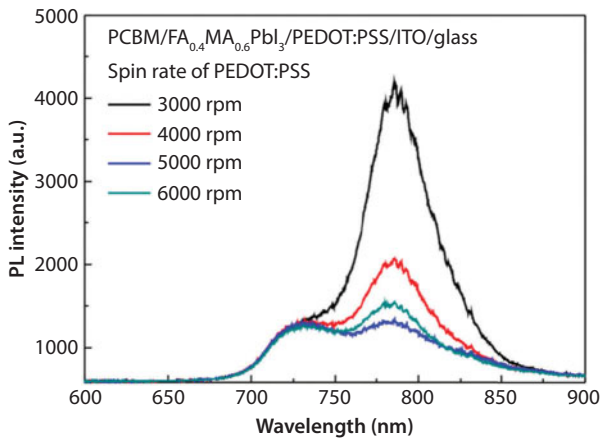


Figure 8.8 Photoluminescence spectra of PCBM/FA_{0.4}MA_{0.6}PbI₃/PEDOT:PSS/ITO/glass samples. (Reprinted with permission from [15])

illuminated from the glass side by a 405-nm laser source. The prominent PL peaks at the wavelengths of 720 nm and 770 nm are emitted from the PCBM thin films and the MOC perovskite (FA_{0.4}MA_{0.6}PbI₃) thin films, where FA and MA are formamidinium (HC(NH₂)₂) and methylammonium (CH₃NH₃), respectively. Half of the photo-generated excitons in perovskite thin films can self-dissociate due to the small exciton binding energy (2 meV ~ 70 meV) [61–66]. The residual excitons must diffuse to the interfaces for the generation of photocurrents. Therefore, better

exciton dissociation results in a lower PL intensity which corresponds to the higher J_{sc} .

The V_{oc} and J_{sc} (see Table 8.2) are simultaneously enhanced by increasing the spin rate of the PEDOT:PSS thin films from 3000 rpm to 5000 rpm. However, the fill factor (FF) of the MOC perovskite-based solar cells decreases from 67.4% to 56.3% with an increase in the spin rate of the PEDOT:PSS thin films from 3000 rpm to 6000 rpm. The trend of the FF of the solar cells is proportional to the trend of the thickness of the PEDOT:PSS thin films, which reflects the fact that the surface of the ITO thin films is not completely covered by the thin PEDOT:PSS layers and the contact between the perovskite and the ITO decreases the FF due to the carrier recombination at the perovskite/ITO interface. When the spin rate increases from 5000 rpm to 6000 rpm, the carrier recombination at the perovskite/ITO interface results in the simultaneous reductions in the V_{oc} and J_{sc} , leading to an optimal average PCE of 13.28% for the inverted MOC perovskite-based solar cells.

8.6.3 Effect of Thermal Annealing Temperature

For air-dried PEDOT:PSS thin films [24], the PEDOT chains are randomly distributed in the PEDOT:PSS thin films, which means that there is no clear phase separation between amorphous and crystalline phases. Therefore, the extremely low electrical conductivity in air-dried PEDOT:PSS thin films originates from the homogeneous distribution of insulating PSS polymers which impedes the formation of conductive PEDOT channels. The thermal annealing treatment is an important process used to form the conductive PEDOT-PSS core-shell clusters (PEDOT-rich nanoparticles) embedded in the insulating PSS polymers and serving as the carrier extraction pathways in the HTM of solar cells. The electrical conductivity and work function of PEDOT:PSS thin films can be manipulated by altering the annealing temperature after the spin-coating process [26, 27].

PEDOT:PSS thin films can be fabricated on top of various hydrophilic substrates using solution processes such as spin-coating, spray-coating, and roll-to-roll processed methods. The residual solvent (water) can be removed by thermal drying [67], vacuum drying [47] and microwave-assisted drying methods [68], which strongly influences the optical and electrical properties of the resultant PEDOT:PSS thin films. During the evaporation process of the residual solvent, the PSS segments can be aggregated to form the PSS clusters which results in the separation between the PSS segments and the PEDOT chains. Then, the PSS segments and PEDOT

chains are rearranged to form the conductive PEDOT-PSS core-shell clusters which dominate the electrical and electronic properties of PEDOT:PSS thin films.

In a PEDOT:PSS aqueous solution, the PEDOT chains are attracted to the PSS segments, which are dissolved in an aqueous solution. When the water molecules evaporates from the PEDOT:PSS aqueous solution by heating the substrate, the aggregations of PSS segments and PEDOT chains weaken the electrical attraction between the negative PSS segments and the positive PEDOT chains. Therefore, the evaporation rate of water molecules strongly influences the aggregation degrees of PSS segments and PEDOT chains, which determines the electrical and electronic properties of the resultant PEDOT:PSS thin films. Conceptually, the fast evaporation rate of water molecules restrains the aggregations of PSS segments and PEDOT chains, which maintains the quinoid-like form of PEDOT chains doped by PSS segments. This means that the faster evaporation rate of water molecules results in the higher free carrier density of PEDOT chains in p-type PEDOT:PSS thin films. Therefore, it can be predicted that the work function of PEDOT:PSS thin films is proportional to the thermal annealing temperature. However, the PSS degrades via ruptures in the sulfonate group from styrene when the annealing temperature is larger than 260 °C, which results in a significant reduction in the V_{OC} of P3HT-based solar cells due to the reduced work function of the p-type PEDOT:PSS thin films. When the thermal annealing temperature is higher than 260 °C, the reduced work function of p-type PEDOT:PSS thin films originates from the reduction of PSS content in PEDOT:PSS thin films, which decreases the p-type doping concentration in PEDOT chains.

8.6.4 Effects of Viscosity of PEDOT:PSS Solutions

In the previous subsections (8.6.1–8.6.3), the effects of the PEDOT/PSS ratio, spin rate and thermal annealing on the properties of PEDOT:PSS thin films and the corresponding photovoltaic performance of the resultant solar cells were discussed. The main conclusion is that the molecular structure of the PEDOT chains in the PEDOT:PSS thin films can be manipulated by varying the PEDOT/PSS ratio, spin rate and thermal annealing temperature. To explore the dynamics of the formation of PEDOT:PSS thin films, the viscosity of the PEDOT:PSS aqueous solution is varied by adding a series of alcohols (methanol, ethanol and isopropyl alcohol) which have different boiling points and viscosities (see Table 8.3).

It is well known that the synthesis of conductive PEDOT:PSS polymers involves the polymerization of EDOT in an aqueous solution containing

Table 8.3 Properties of the solvent additives and the modified PEDOT:PSS thin films (Adapted with permission from [28]).

Solvent additive	Boiling point (°C)	Viscosity (cp)	Surface roughness (nm)	Contact angle (°)	Work function (eV)
Methanol	64.7	0.545	1.53	42	5.06
Ethanol	78.4	1.074	1.47	58	5.10
IPA	82.6	1.960	1.76	49	5.12

long PSS segments, with sodium perfluorates as the oxidizing agent. It is indicated that the conductive PEDOT:PSS polymers in the aqueous solution have a linear molecular form. The fabrication process of modified PEDOT:PSS thin films is described below. Methanol, ethanol and isopropyl alcohol (IPA) are individually added to a PEDOT:PSS (1:6 wt%) aqueous solution, and the volume ratio of water to alcohol is 1:2. The modified PEDOT:PSS aqueous solutions are spin-coated onto the top of the ultraviolet-ozone treated glass substrates, then subjected to thermal annealing at 150 °C for 20 min. After that, the modified PEDOT:PSS/glass samples are cooled on a steel plate at room temperature.

The surface roughness of the PEDOT:PSS thin films is measured using a contact-mode atomic-force microscope. The water droplet contact angle of the PEDOT:PSS thin films is determined by a homemade optical microscope imaging system. The surface morphology and water droplet contact angle of the modified PEDOT:PSS thin films are shown in Figure 8.9. The use of high viscosity (boiling point) solvents for thin-film deposition by a spin-coating method results in a large (small) surface roughness [69]. This means that the surface roughness of the modified PEDOT:PSS thin films is related to the viscosity and boiling point of the solvent additives. The surface roughness and water droplet contact angle of the modified PEDOT:PSS thin films are listed in Table 8.3. The trend of the water droplet contact angle on the surface of the modified PEDOT:PSS thin films is inversely proportional to the trend of the surface roughness of the modified PEDOT:PSS thin films, which implies that a flat PEDOT:PSS thin film has a low surface free energy. The change in the surface free energy of the modified PEDOT:PSS thin films indicates that the arrangement of the structure of the PEDOT chains and PSS segments has changed, which implies that the electronic properties of the PEDOT:PSS thin films can be manipulated by the addition of solvents. To investigate the electronic properties of the modified PEDOT:PSS thin films, a photoelectron emission spectrometer is used to measure the work function (see Table 8.3). The work function of the

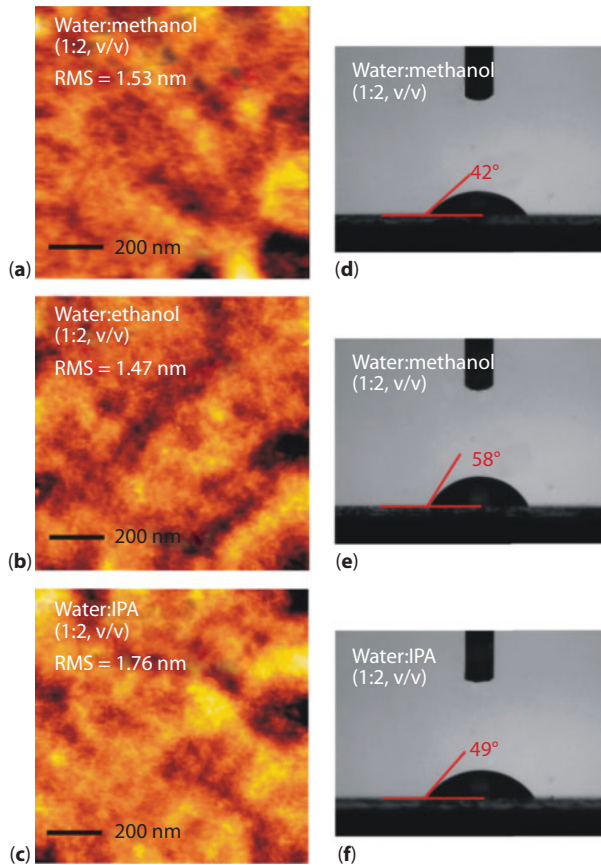


Figure 8.9 Atomic-force microscopic images (a,b,c) and water droplet contact angle images (d,e,f) of the modified PEDOT:PSS thin films (Reprinted with permission from [28]).

modified films is proportional to the viscosity of the solvent additives. The increase in the work function is due to the conformational change of the PEDOT chains from a benzoid-like form to a quinoid-like form, which can be confirmed using the Raman scattering spectra [11, 25, 33, 35, 36].

The experimental results show that the modification of PEDOT:PSS thin film leads to a larger work function and high local conductivity, which is predicted to be advantageous to the V_{OC} and J_{SC} of the resultant solar cells. The higher work function and high local conductivity are produced through the addition of an IPA solvent which increases the viscosity of the PEDOT:PSS solutions and thereby suppresses the aggregation of PSS segments and PEDOT chains during the thin-film deposition process to maintain the linearity of the PEDOT chains.

8.7 Directions for Future Development

The PEDOT:PSS thin films can be used as the TCE or HTM in solar cells due to their high transparency in the visible region, high electrical conductivity and large work function. The transmittance of the PEDOT:PSS thin films can be larger than 90% in the visible region due to the formation of bipolarons, which effectively suppresses the π - π^* transition of the PEDOT polymers. The electrical conductivity can be close to the local conductivity due to the formation of conductive PEDOT channels in the PEDOT:PSS thin film. The work function of the p-doped PEDOT polymers can be adjusted by tuning the molecular structure of the PEDOT chains in the thin films. As a consequence, it is clear that the structural, optical, electrical and electronic properties of the PEDOT:PSS thin films can be arbitrarily manipulated by tailing the molecular structures of PEDOT:PSS nanocomplexes.

The conductivity ($\sigma = eN\mu$) of materials is proportional to the carrier concentration (N) and carrier mobility (μ) in materials, where e is the electric charge. To optimize the intrinsic (local) conductivity of the PEDOT chains in PEDOT:PSS thin films, the carrier concentration and carrier mobility must be simultaneously increased. One of the ways to do this is to change the molecular structure of the PEDOT chains from a benzoid form (de-doping state) to a quinoid form (doping state) by decreasing the PEDOT/PSS ratio (see Table 8.2). The theoretical carrier concentration in heavily p-doped PEDOT chains can be calculated as follows:

$$N_{PEDOT} = \frac{1}{V_{PEDOT}}, \quad (8.2)$$

where V_{PEDOT} ($= a \times b \times c = 0.78 \text{ nm} \times 1.18 \text{ nm} \times 0.69 \text{ nm}$) [70] is the volume of a EDOT unit in the PEDOT chain. Therefore, the theoretical carrier concentration in a p-doped PEDOT chain (quinoid form) can be estimated to be $1.575 \times 10^{21}/\text{cm}^3$. The theoretical carrier concentration in the PEDOT chain is slightly larger than the experimental value (see Table 8.2), which implies that each EDOT unit in the PEDOT:PSS (1:20 wt%) thin film is almost doped by the PSS polymer. So far, the highest electrical conductivity of the modified PEDOT:PSS (1:2.5 wt%) thin film has been 3300 S/cm [71], which was measured by the van der Pauw four-point probe technique. However, the carrier concentration and carrier mobility of the modified PEDOT:PSS (1:2.5 wt%) thin film are not provided in ref. [71]. To the best of our knowledge, the highest reported carrier mobility in PEDOT:PSS thin films is 53.8 cm^2/Vs [72]. Therefore, the optimal

electrical conductivity of a PEDOT:PSS thin film is predicted to be larger than 13557 S/cm ($= 1.6 \times 10^{-19} \text{C} \times 1.575 \times 10^{21} \text{cm}^3 \times 53.8 \text{ cm}^2/\text{Vs}$), to be used as a standalone electrode.

However, it is known that PEDOT:PSS thin films are unstable under humid environments [73] or high temperature treatments [9, 73]. To improve the stability, a sulfonated poly(imide) (SPI) polymer can be substituted for the PSS polymer. However, the doping concentration of a PEDOT:SPI thin film is lower than that of the PEDOT:PSS thin films due to fewer doping sites. The carrier concentration in the PEDOT chains can be increased to $10^{23}/\text{cm}^3$ so that when the conductive PEDOT-based polymer is synthesized using iron trifluoromethanesulfonate as the oxidant it exhibits metallic behaviors [74]. The results show that the structure, optical, electrical and electronic properties of stable conductive PEDOT-based polymers can be adjusted to obtain the desired characteristics by using different chemical dopants.

8.8 Conclusion

A comprehensive study has been carried out to explore the structural, optical, electrical and electronic properties of PEDOT:PSS thin-film-based conductive transparent electrodes and hole-transporting materials under various fabrication conditions. The formation of bipolarons in the heavily p-doped PEDOT polymers, which dominates the optical, electrical and electronic properties of the PEDOT:PSS thin films, results in high transparency in the visible region (suppressed exciton transition), a transmission drop centered at the wavelength of 810 nm (π to P1 transition), and a reduction in the transmittance in the long wavelength region (free carrier effect).

For the PEDOT:PSS (1:2.5 wt%) thin-film-based conductive transparent electrode, the removal of the excess PSS polymers greatly increases the electrical conductivity from ~ 1 S/cm to ~ 1000 S/cm due to the formation of a 3D PEDOT network and an increase in the local conductivity in the PEDOT chains. Moreover, the highest electrical conductivity of PEDOT:PSS thin films is predicted to be larger than 13557 S/cm, which is higher than the highest reported experimental value (3300 S/cm). Therefore, there is still room for improvement of the electrical conductivity of PEDOT:PSS thin films.

For the PEDOT:PSS thin-film-based HTMs, the work function, which is related to the molecular structure of the PEDOT chains, can be manipulated by varying the PEDOT/PSS ratio, spin rate, thermal annealing

temperature and viscosity of PEDOT:PSS solutions. The work function of the linear PEDOT chains (quinoid form, doping state) is larger than that of the coiled PEDOT chains (benzoid form, de-doping state). Owing to the high exciton dissociation (carrier extraction) at the PEDOT/light-absorbing material interface, the open-circuit voltage of solar cells can be increased without reducing the short-circuit current density of solar cells when increasing the work function of the PEDOT:PSS thin film.

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Part III

PEROVSKITES AND PROCESS TECHNOLOGIES FOR PRINTABLE SOLAR CELLS

Organometal Trihalide Perovskite Absorbers: Optoelectronic Properties and Applications for Solar Cells

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Abstract

Solution-processed organohalide perovskites are recognized as the most promising photoactive material for the next generation solar cell fabrication. In recent years, the power conversion efficiency of organohalide perovskite-based solar cells has surpassed 20%, which highlights their excellent potential for solar cell applications. This chapter discusses the optoelectronic properties of organohalide perovskite absorbers. In addition, some points related to the process of perovskite-based solar cell fabrication are also discussed. Finally, the importance of further research in the area of organohalide perovskites is outlined, especially that which is connected to their stability and commercialization.

Keywords: Organohalide perovskite, optoelectronic properties, perovskite-based solar cells, solar energy conversion

9.1 Introduction

Efficient solar energy conversion to electricity becomes absolutely essential for future energy generation due to the rapid depletion of fossil fuels. Currently, photovoltaic (PV) solar cells and photothermoelectric generators

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are used widely to convert sunlight photons into electrical energy [1]. Recently, a new class of thin film photovoltaics called perovskite-based solar cells (PSCs) have emerged as the third-generation solar cells [2]. The efficiency of these PSCs has increased drastically from 3.8% to more than 20.1% in only a few years of research [3, 4]. The simple fabrication process, low cost, and high efficiency of PSCs makes them a good alternative to traditional silicon, thin films, quantum dots, and dye-sensitized solar cells [5]. In a typical PSC, a thin layer of perovskite absorber is located between the electron (ETM) and hole (HTM) transport materials (Figure 9.1). Carriers are produced in the perovskite absorber upon the absorption of solar photons and their separation occurs through the ETM and HTM layers.

Perovskite absorbers used for PSC fabrication can generally be described by the formula ABX_3 (where A is usually organic methylammonium CH_3NH_3 cation, B = Pb or Sn cations, and X = Cl, Br, or I anions). Figure 9.2 shows the typical basic crystal structure of ABX_3 perovskite material. This structure consists of corner-sharing X anion octahedra, B cations located at their centers and the A cations between them [6]. In the case of organic-inorganic hybrid perovskite absorbers, the choices of A and B cations are limited by the stability of the resulting structure. On the other hand, organic-inorganic $CH_3NH_3BX_3$ (B = Pb or Sn, X = Cl, Br, I) hybrid perovskites have been utilized successfully for PSC fabrication [7–10]. Boriello *et al.* theoretically showed that the electronic properties of organic-inorganic $CH_3NH_3BX_3$ perovskite materials strongly depend on the structure of the inorganic network [6].

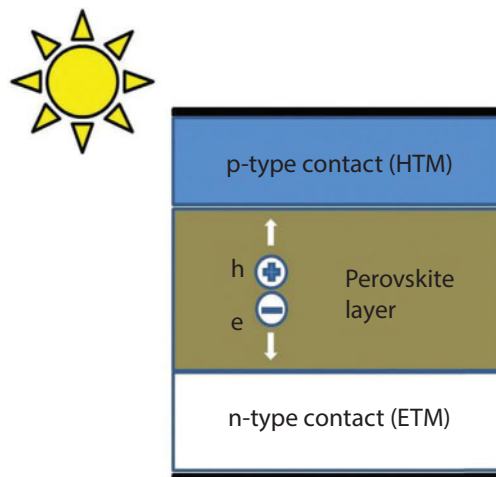


Figure 9.1 Schematic representation of a typical PSC structure.

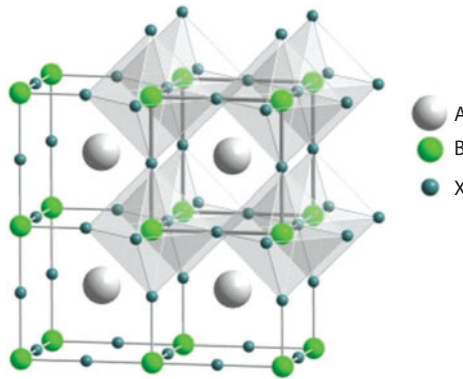


Figure 9.2 Basic crystal structure of ABX_3 perovskite material. (Reprinted with permission from [6])

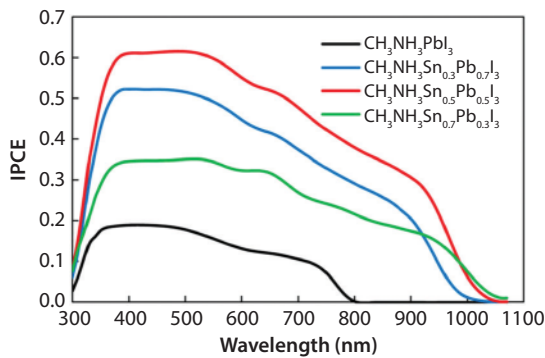


Figure 9.3 IPCE curves for $CH_3NH_3Sn_xPb_{(1-x)}I_3$ /P3HT solar cells. (Reprinted with permission from [14])

9.2 Optical Properties of Organic-Inorganic Perovskite Materials

The linear optical absorption coefficient of a commonly used $CH_3NH_3PbI_3$ is approximately equal to $5.7 \times 10^4 \text{ cm}^{-1}$ at 600 nm [11]. The calculations have suggested that this value is higher than those of conventionally used CdTe, CuInSe₂, and Cu₂ZnSnSe₄ thin-film-based solar cells [12]. On the other hand, $CH_3NH_3PbI_3$ absorbs incident photons up to 800 nm [13]. Several strategies were developed to extend the absorption limit of $CH_3NH_3PbI_3$. For example, Ogomi *et al.* showed that partial replacement of the Pb cation with a Sn cation leads to band gap narrowing [14]. Figure 9.3

shows that the incident photon-to-current efficiency (IPCE) threshold of their devices reached up to 1060 nm. However, one should consider the problems related to the poor Sn^{2+} stability during the PSC fabrication.

The variation of halide ions in the final perovskite composition is another way to extend the absorption limit of $\text{CH}_3\text{NH}_3\text{PbI}_3$. For example, I ions can be partially or fully replaced with Br and/or Cl ions, which causes band gap narrowing due to different covalent bonding with a metal cation [15–17]. As a result, the absorption spectrum of a mixed perovskite structure can be tuned within the entire visible spectrum [18].

In addition, the optical properties of the perovskite can be influenced by the A cation in the ABX_3 structure. A smaller or larger A cation can cause the lattice distortion in the perovskite structure. This lattice distortion leads to changes in the B-X bond length, which helps determine the band gap of the system [17]. For example, the effective ionic radius of formamidinium is larger than the methylammonium [19]. Therefore, lattice expansion is expected, which leads to a red-shift in the absorption spectra of the formamidinium-based perovskite absorber [20, 21].

9.3 Charge Transport Properties

In addition to the excellent light-harvesting properties, organic-inorganic ABX_3 perovskites also show efficient electron and hole transport properties. Photoexcitation of the perovskite absorber leads to the generation of electron-hole pairs, which can exist as free carriers or excitons [22]. The electron and hole diffusion lengths were estimated to be around 130 and 100 nm, respectively, for samples prepared from a $\text{CH}_3\text{NH}_3\text{I}+\text{PbI}_2$ mixture [11]. Another study [23] suggested that the electron-hole diffusion lengths can exceed 1 μm (roughly 1069 for electrons and 1213 for holes) in a $3\text{CH}_3\text{NH}_3\text{I}+\text{PbCl}_2$ mixture. Therefore, the electron-hole diffusion lengths can be controlled by mixture engineering. Owing to the long electron-hole diffusion lengths, more electrons and holes can reach the PSC photoelectrodes to produce an external electrical current.

On the other hand, several groups reported the possibility of ultra-long diffusion lengths (more than a hundred micrometers) in single-crystal-based PSCs [24, 25]. Therefore, single-crystal perovskite can also work efficiently without a mesoporous scaffold layer due to the long carrier lifetime and long electron-hole diffusion lengths. For example, the efficiency of a simple planar heterojunction-structured PSC based on a single-crystal perovskite absorber was reported to be 19.3% [26].

9.4 Electron Transporting Materials (ETM)

The performance of PSCs can be strongly affected by the design of the ETM layer. First, a thin compact blocking layer (BL) with no pores and defects is required for most PSCs. This BL can be fabricated by a range of methods, such as solution-based methods, ALD, PLD, sputtering, etc. In the next step, a mesoporous layer with different nanostructures can be deposited on the surface of the BL. This mesoporous layer provides a large contact area (better charge collection) between the ETM and perovskite absorber. Inorganic thin films are frequently used to form an ETM layer. Among them, inorganic TiO_2 is widely used because of its excellent electronic properties, low cost, chemical stability, and availability. The conduction band minimum of TiO_2 is equal to 4.1 eV [27], which is lower than that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (this guarantees direct electron injection from the perovskite absorber to the TiO_2). TiO_2 can also be used as an efficient hole-blocking layer due to the very low position of the valence band maximum [28]. Furthermore, the compact layer of a TiO_2 film has a very high electron diffusion length, which is over 1 μm [29]. Owing to well-established protocols, the TiO_2 layer can be engineered precisely with the desired morphology and dimensions to achieve the best PSC efficiency.

Other inorganic semiconductors, such as ZnO , SrTiO_3 , SnO_2 , and WO_3 , are also used as the ETM layer in PSCs. All these oxides have a much higher reported electron mobility than TiO_2 [28]. In addition, these materials have unique properties that can be employed to construct the ETM. For example, the ferroelectrical properties of SrTiO_3 can help reduce charge recombination at the interface. On the other hand, large-sized SrTiO_3 particles strongly reduce the photocurrent, which can be resolved by further SrTiO_3 size optimization [30]. ZnO does not require a sintering process, which is very convenient for the mass production of flexible devices. On the other hand, ZnO suffers from photocorrosion, which makes the device unstable. WO_3 has a smaller band gap and can be fabricated relatively easily with a range of morphologies. A recent study suggested that charge recombination can be suppressed at the WO_3 /perovskite interface, which resulted in a much higher PCE [31]. SnO_2 has better electronic and optical properties, and can be a promising material to replace TiO_2 in the future [32, 33].

9.5 Hole-Transporting Materials (HTM)

Several aspects should be considered seriously during the selection of an appropriate HTM for PSCs: a) excellent hole mobility, b) low cost,

c) good film-forming properties, and d) suitable energy level. Small molecules and conducting polymers were employed widely at the early stages of PSC research. Spiro-OMeTAD is one of the most well-known polymers employed as the HTM layer. For example, Eperon *et al.* reported efficiencies above 10% in fully thin-film solution-processed PSCs using a spiro-OMeTAD as the HTM layer [10]. In the following year, Yang *et al.* demonstrated stable 15% efficiency for large-area PSCs using spiro-OMeTAD in PSCs [34]. Poly(triaryl amine), or PTAA, is another high-mobility polymer that demonstrated 12% efficiency in the first tests with a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite absorber [35]. On the other hand, the efficiency of PSCs with PTAA as the HTM layer was improved up to 16.2% [9]. The use of organic HTMs simplifies the process of PSC fabrication. At the same time, most organic HTMs require some additives to enhance their electronic properties [36]. In addition, organic HTMs can be degraded easily under UV light exposure.

To date, many researchers have actively explored inorganic p-type semiconductors to replace organic HTMs in PSCs. For example, Zhu *et al.* used well-known p-type NiO nanocrystals as the HTM in inverted planar PSCs [37]. They reported an optimized efficiency of 9.11% with a 30–40 nm NiO film thickness. According to their results, thicker NiO films resulted in a high series resistance. CuO , Cu_2O , and CuO_x , and other well-known p-type materials, were also recently employed to construct the HTM layer [38–40]. The efficiency of copper oxide-based PSCs varied in the range of 8.23–17.1% (depending on the material type and cell preparation method). In addition, copper oxide-based PSCs exhibited superior performance in the stability tests when compared to polymer-based PSCs. Copper iodide CuI also provided better J_{sc} stability and higher FF when compared to organic spiro-OMeTAD [41]. However, V_{oc} is limited due to the high recombination rate in the CuI layer. In another study, researchers reported an average 15.6% efficiency for inverted planar PSCs with a copper thiocyanate CuSCN p-type material [42]. Therefore, adopting the proper inorganic HTM could be a solution for achieving better stability and device performance.

9.6 Perovskite Solar Cells Architectures

Figure 9.4 shows the possible architectures used for the construction of PSCs. Similar to the DSSCs' structure, n-type metal oxide nanoparticles (NPs) were used to fabricate mesoporous thin films. In the early stage of research, there were no techniques for high-quality perovskite films;

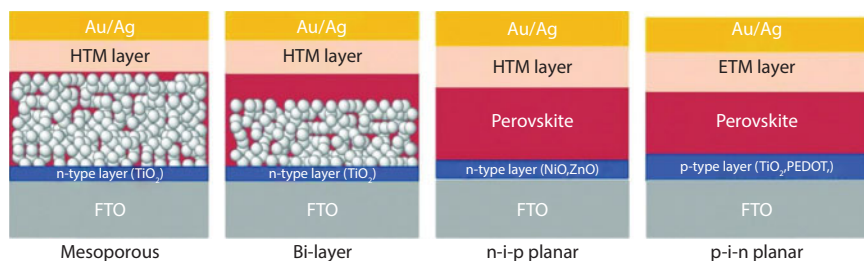


Figure 9.4 Schematic representation of the mesoporous, bi-layer, n-i-p and p-i-n architectures in PSCs. (Reprinted with permission from [43])

thus, the mesoporous configuration helped achieve high-efficiency PSCs [43–45]. The main disadvantages of the mesoporous configuration are deposition process and high-temperature annealing process. Therefore, it is difficult to realize a uniform, crack-free mesoporous film for large-scaled devices. In addition, mesoporous devices generally have weak light absorbance at wavelengths ≥ 700 nm and a relatively low V_{oc} . On the other hand, with the rapid development of various PSC fabrication techniques, the formation of a mesoporous structure has become less important.

The bi-layered structure has an additional perovskite capping layer on the top of a mesoporous perovskite-sensitized scaffold [46]. In such a configuration, the mesoporous layer in the bi-layered structure is usually thinner compared to a regular mesoporous PSC. The deposition of a high-quality perovskite capping layer was shown to be a very critical parameter to achieve high device efficiency [46]. Bi-layered PSCs have demonstrated higher cell efficiency, up to 15% [47], and negligible hysteresis. On the other hand, the deposition of an additional high-quality perovskite capping layer makes the entire fabrication process more complex.

The concept of simplified planar n-i-p and p-i-n originated recently with the extensive analysis of perovskite properties. As already discussed, perovskite materials have good ambipolar charge transporting properties. A study of Al_2O_3 -based PSCs showed that the mesoporous TiO_2 -based film is not necessary for efficient device construction [48]. Snaith *et al.* constructed a planar mesoporous layer-free PSC with 15% efficiency using a vapor-phase deposition method [49]. Another study used a room-temperature solution method to fabricate a device with 15.7% efficiency [50]. Therefore, simplified planar devices can also demonstrate high efficiency compared to complex nanostructured PSCs. On the other hand, the J-V hysteresis of planar devices is inferior to that of nanostructured PSCs.

9.7 Perovskite Deposition Methods

The quality of a perovskite film is one of the most important factors that determine the efficiency of PSCs. Therefore, major research efforts have been focused on the deposition of high-quality perovskite thin films. To date, several methods have been reported: a) dual-source vapor deposition, b) vapor-assisted solution deposition, c) one-step solution deposition, and d) two-step solution deposition.

In the dual-source vapor deposition method, perovskite films were formed through simultaneous evaporation from two separate sources under high vacuum conditions (Figure 9.5). As a result, semitransparent large-scaled high-quality perovskite thin films can be obtained easily on the substrate [49]. The same method was later used to fabricate an inverted PSC [51]. A thin perovskite film was sandwiched between the two photoelectrodes coated with organic molecules. This configuration showed a remarkably high efficiency of 12%, which highlights the possibility of flexible organic module designs. On the other hand, this deposition method has many disadvantages. For example, one should control the precursor ratio, which is a critical point for perovskite structure formation, adjust the evaporation temperature, and maintain a high vacuum in the chamber.

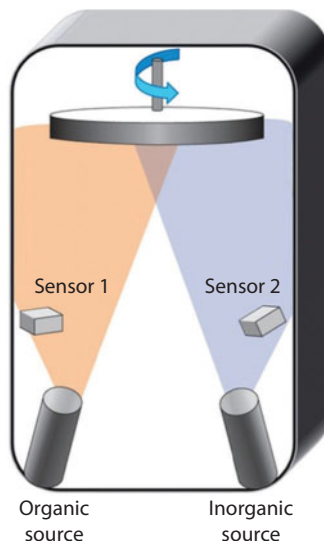


Figure 9.5 Schematic representation of the dual-source vapor deposition method. (Reprinted with permission from [49])

To overcome the difficulty in controlling the ratio of precursors, vapor-assisted solution deposition was introduced to prepare the planar PSCs [52]. In this method, PbI_2 films were deposited on the surface of fluorine-doped tin oxide (FTO) glass coated with TiO_2 BL. These films were then annealed in $\text{CH}_3\text{NH}_3\text{I}$ vapor at 150°C for 2 h (in N_2 atmosphere) to form a perovskite layer. The resulting perovskite film showed excellent surface coverage and a uniform grain structure. The high efficiency of the prepared device (12.1%) highlights the versatility of this approach.

Simplicity, rapid processing and low cost makes the solution-based preparation of perovskite films quite popular among researchers. Various solution-based deposition techniques can be grouped into two main strategies: one-step and two-step deposition. Figure 9.6 shows the differences between these processes. In the one-step deposition process, the precursor solution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is generally prepared by mixing the PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ powders at a 1:1 mole ratio in high boiling point polar solvents [54]. This precursor is further used for coating process. The annealing process was applied as the next step to form the final perovskite structure. The quality of the final perovskite structure is determined by film shrinkage during the annealing process, which is due to solvent removal.

In a typical two-step procedure, the PbI_2 was first deposited on the surface of BL. Subsequently, the $\text{CH}_3\text{NH}_3\text{I}$ layer was deposited on top of the PbI_2 film. The as-deposited PbI_2 layer can also be dipped into a solution of $\text{CH}_3\text{NH}_3\text{I}$. Finally, the sample was annealed to obtain a perovskite film. The main problem of the two-step procedure is volume expansion, which

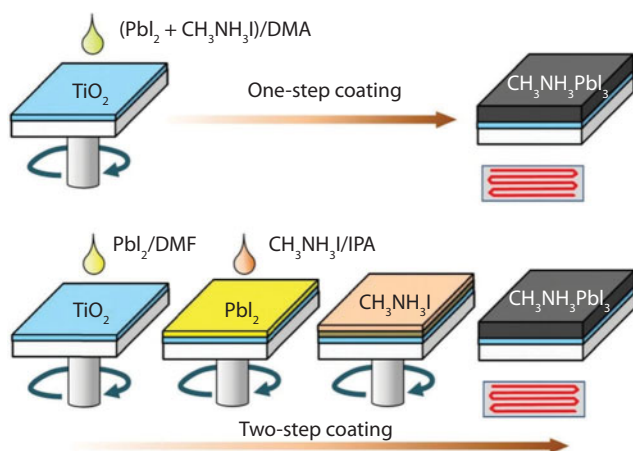


Figure 9.6 One-step and two-step solution deposition methods. (Reprinted with permission from [53])

occurs in PbI_2 films due to organic molecule intercalation. On the other hand, the two-step coating process resulted in better photovoltaic performance compared to the one-step coating [53]. The morphology, precursor concentration, and annealing temperatures [8, 54, 55] of the perovskite films can strongly influence the photovoltaic properties of PSCs. Therefore, these parameters can be due to the simplicity of the solution-based deposition methods.

9.8 Photoexcited States

Photoexcited states of organometal halide perovskites have been studied extensively for more than two decades. In 1994, Hirasawa *et al.* reported that the photoexcited states in $\text{CH}_3\text{NH}_3\text{PbI}_3$ are Wannier-type excitons [56]. Several studies suggested that these Wannier-type excitons have very low binding energies, in the range of 20–98 meV [56–58]. Owing to the low binding energies, a large amount of free charge carriers can be generated. Recent studies have shown that the carrier/exciton ratio can be controlled by the excitation wavelength and light intensity. For example, D’Innocenzo *et al.* showed that a large number of excitons can be formed with increasing the photoexcitation density [59]. On the other hand, Sheng *et al.* could control the carrier/exciton ratio via the excitation wavelength [60]. Thus, controlling the carrier/exciton ratio can be one of the key factors for improving the photovoltaic properties of the PSCs.

9.9 Hysteresis

The hysteresis in PSCs is a mismatch in the J-V curves scanned in the forward (short-circuit $\rightarrow$ open-circuit) and reverse (open-circuit $\rightarrow$ short-circuit) directions [22]. Snaith *et al.* reported the first hysteresis in planar PSC [61]. The inability to measure the real power output of PSCs has recently made hysteresis a very hot topic [43]. For example, hysteresis was also observed in other PV devices such as DSSCs, CdTe, and amorphous silicon-based solar cells. Several origins of the hysteresis in PSCs have been proposed:

- a. Photo-induced ion migration. This mechanism was well explained by the time-dependent drift of ions under an applied electric field, as shown in Figure 9.7 [62]. In this case, the hysteresis induced by ion drift in the perovskite layer can be suppressed effectively by lowering the scan rate

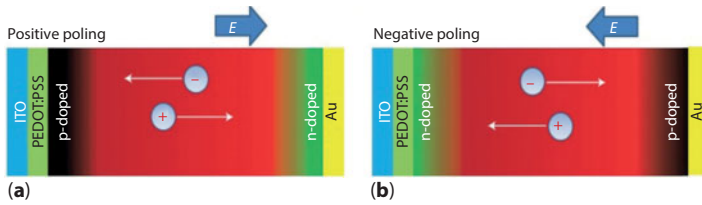


Figure 9.7 Ion migration mechanism in perovskite during (a) positive and (b) negative poling. (Reprinted with permission from [62])

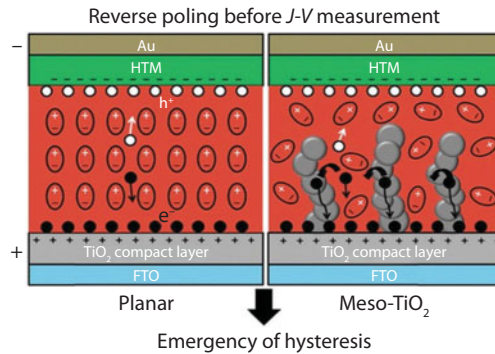


Figure 9.8 Ferroelectric polarization mechanism in PSCs. (Reprinted with permission from [65])

[22]. Theoretical calculations also confirmed the existence of photo-induced ion migration in PSCs [63].

- b. Ferroelectric polarization. A simulation study performed by Frost *et al.* [64] suggested that hysteresis occurs due to the internal electrical field associated with microscopic polarization domains inside the perovskite materials. In this case, the domains could align themselves with the external electric field (Figure 9.8). The counter ferroelectric polarization field reduces the charge separation, which can also be a reason for the observed hysteresis in PSCs [65, 66].

Note that mesoporous TiO_2 -based PSCs exhibit less hysteresis compared to planar PSCs. One possible reason could be the direct electron injection into the TiO_2 scaffold, which reduces the polarization effects in perovskite [22]. Furthermore, the polarization properties of perovskite are strongly influenced by the preparation conditions, type of organic cation, and halide ions, etc. [67]. Therefore, the fabrication conditions and measurement details should be controlled carefully to eliminate the hysteresis in PSCs.

9.10 Stability in Humid Environment

The presence of moisture leads to degradation of organometal trihalide perovskites [68]. Therefore, PSCs are usually fabricated under inert or dry vacuum atmospheres with minimal H_2O . In addition, several other methods have been proposed to reduce the contact of perovskite absorber with air moisture. A water-resistive coating or encapsulation can be used as an inexpensive and quick solution. For example, water-repellent PSCs with polydimethylsiloxane (PDMS) films showed excellent hydrophobicity [69]. On the other hand, bond strengthening between the organic cations and metal halide can improve the resistance of perovskites to moisture [70]. Physical separation of perovskite films has also been investigated. Niu *et al.* introduced Al_2O_3 as a post-modification material to reduce the degradation of perovskite [71]. Control and Al_2O_3 -modified PSCs were exposed to sunlight for 18 h ($t = 35^\circ\text{C}$ and humidity of 60%). They found that Al_2O_3 -modified PSCs showed much better stability to humidity than the control devices. In another report, the researchers used a ZnO layer in inverted p-i-n devices to prevent the degradation of perovskite material [72]. They reported that the PSCs retained approximately 90% of their original efficiency after 60 days storage in ambient environment. At the same time, the control samples with organic molecules were degraded completely within 5 days of storage. A recent study, however, suggested that the crystallinity of perovskite films could be improved by annealing under mild moisture conditions (approximately 30% of humidity) [73]. Accordingly, PSCs with better performance can be obtained. In addition, stable PSCs were recently prepared under ambient conditions with a very high humidity of 70% [74]. Therefore, the perovskite properties should be investigated further under different atmosphere conditions.

9.11 Stability Under UV Light Exposure

In most cases, TiO_2 is used widely in PSCs to form a planar or mesoporous ETM layer. On the other hand, TiO_2 is also known as an efficient photocatalyst for oxidizing organic molecules under UV light [75]. According to a recent study [76], the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was transformed to PbI_2 after 12 h of light exposure. This UV degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ can be explained by taking the surface chemistry of TiO_2 into account. Figure 9.9 shows the possible degradation mechanism, which can be divided into several steps:

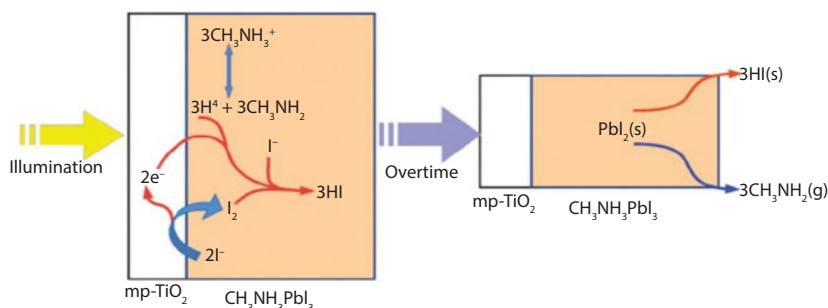


Figure 9.9 Degradation mechanism of $\text{CH}_3\text{NH}_3\text{PbI}_3$ under light exposure. (Reprinted with permission from [68])

- $2\text{I}^- \leftrightarrow \text{I}_2 + 2\text{e}^-$ (TiO_2 extract the electrons from iodide anions at the interface between TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$)
- $3\text{CH}_3\text{NH}_3^+ \leftrightarrow 3\text{CH}_3\text{NH}_2 \uparrow + 3\text{H}^+$
- $\text{I}^- + \text{I}_2 + 3\text{H}^+ + 2\text{e}^- \leftrightarrow 3\text{HI} \uparrow$

Therefore, a simplified reaction that occurs during the long light exposure can be rewritten as:



This type of degradation can be reduced by introducing an additional passivation layer at the interface between $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$. The same authors [76] reported that devices with an additional passivating Sb_2S_3 layer retained approximately 65% of their initial efficiency, while the devices without a Sb_2S_3 layer decreased to almost 0%. The other possible way to prevent the UV light degradation of PSCs is to place a UV filter or spectral converters in front of the TiO_2 . The spectral converters can simultaneously absorb UV photons and emit visible light photons. The generated visible light photons can be then reabsorbed by the perovskite layer, which results in enhanced light harvesting by PSCs. Recently, Chander *et al.* fabricated PSCs with a nanolayer of $\text{YVO}_4:\text{Eu}^{3+}$ spectral converters [77]. This kind of structure can mitigate the UV light induced degradation in PSCs.

9.12 Stability at High Temperatures

Generally, thermal annealing is an essential step to form high quality perovskite films. On the other hand, exposure to high temperatures can

also cause the degradation of perovskite films [78]. Therefore, understanding the stability of perovskite films at high temperatures is very important, because solar modules will be exposed to direct sunlight illumination. Philippe *et al.* examined the influence of different annealing temperatures on the stability of perovskite [79]. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films were placed in a high vacuum chamber to suppress the moisture-induced degradation. Heating even at 100 °C for 20 min led to degradation of the perovskite film. In another report, good quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were formed when annealed under vacuum conditions at 100 °C for 30 min [80]. On the other hand, annealing of the same $\text{CH}_3\text{NH}_3\text{PbI}_3$ film at 140 °C and 160 °C caused the formation of PbI_2 as evidenced by XRD. Many studies confirmed that the perovskites can be decomposed at temperatures higher than 140 °C [81, 82]. The origin of perovskite film degradation can be the temperature-induced flow of the component materials due to thermal evaporation, phase segregation and separation. The decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ may lead to the formation of PbI_2 , CH_3NH_2 , and HI as the final products, which is similar to the light-induced degradation process. Furthermore, high temperatures can cause device architecture degradation, interlayer diffusion, contact degradation, etc. Thus, the mechanisms of PSCs degradation at high temperatures should be reported carefully.

9.13 Additives

Several studies suggested that the organometal trihalide perovskites are quite sensitive to some impurities. In particular, small amounts of chemical additives in the perovskite precursors can enhance the crystallinity, surface coverage, device performance, etc. For example, better surface coverage, crystallinity, and device performance was observed when the NH_4Cl additive was added to perovskite precursor [83]. Methylammonium chloride MACl was also added as an additive to the precursor solution of PbI_2 and methylammonium iodide MAI [84]. The authors could enhance the photovoltaic performance of PSCs by adjusting the initial ratio of MAI, MACl, and PbI_2 in the precursor solution. In another report, a so-called DIO (1,8-diiodooctane) additive was added to the initial precursor solution [85]. The DIO-modified perovskite films showed better surface coverage and crystallinity than those prepared without additives. The mechanisms for the additive-related improvements in PSCs are still unclear. On the other hand, the results suggested that additives can also play an important role in future PSCs design.

9.14 Conclusions and Outlook

This chapter discussed briefly the importance of organometal trihalide perovskites for future optoelectronic applications. The results showed that organometal trihalide perovskites combine three important tasks required for solar cell operation: a) excellent light absorption, b) carrier generation, and c) ambipolar transporting. The optoelectronic properties of perovskites can be tuned easily by several controllable parameters, such as composition, annealing temperature and time, environment conditions, and additives. The simple processing technology makes the PSCs more reliable over existing solar technologies. For example, organometal trihalide perovskites are suitable for cheap roll-to-roll processing, while their efficiencies are much higher than those of polymer solar cells [4]. This simplified roll-to-roll configuration guarantee lower cost processing and simplicity in design.

The rapid development of organometal trihalide perovskite-based solar cells is encouraging but many issues need be resolved. Figure 9.10 shows that the efficiencies of PSCs have improved quickly within the last several years. This improvement was faster than for any other thin film-based photovoltaic device. On the other hand, the operational stability of PSCs also should be taken into account for real solar light harvesting applications. To date, the operational stability of PSCs under different conditions was not properly investigated. As discussed earlier, organometal trihalide perovskites are vulnerable to moisture, temperature, UV-light exposure,

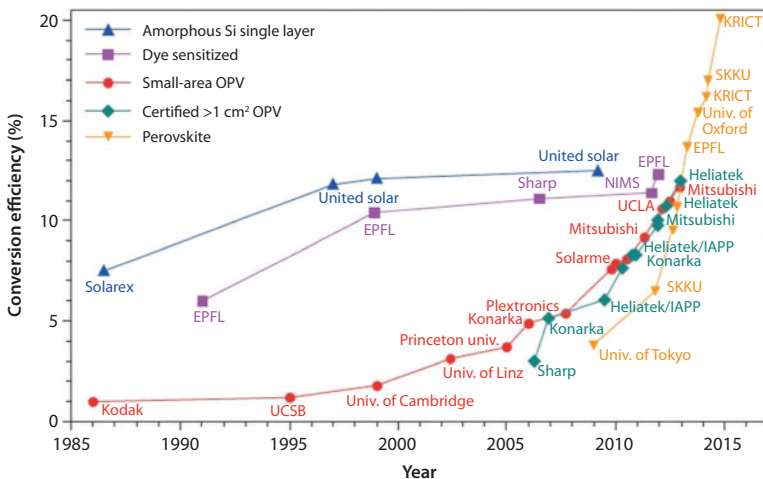


Figure 9.10 Reported efficiencies for some thin films based photovoltaic devices. (Reprinted with permission from [86])

etc. Therefore, the degradation mechanisms should be studied to predict the behavior of perovskites under different conditions. Note that the development of a stable device can take many years of research. PSCs should demonstrate 10% efficiency loss after 1000 h of operation to pass the standard International Electrotechnical Commission damp heat test (85 °C, 85% relative humidity) [86]. Obviously, the present stability results are very far from practical applications. In this regard, encapsulation may resolve the moisture-induced degradation mechanism. UV-light can be blocked or transformed to visible light using spectral convertors. Thermal-induced degradation mechanism should be investigated in detail to determine the optimal perovskite growth conditions [87]. In addition, the acceptability of lead Pb in so-called “green technology” is still a hot topic. However, a recent study suggested that even in the case of catastrophic module failure, Pb contamination of the environment is not so critical [88]. To eliminate the potential toxicity, one can replace Pb with Sn in perovskite. On the other hand, chemical instability of Sn and low efficiency of Sn-based PSCs also limits their usage.

Obviously, excellent optical and electronic properties of perovskites in combination with low cost processing makes them a potential candidate for future optoelectronic devices. Therefore, making these PSCs stable over long periods of time will be a promising research focus that will allow the utilization of PSCs for outdoor sunlight harvesting.

Acknowledgment

This work was financially supported by BK21 PLUS program at the Department of Physics and Astronomy, Seoul National University.

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Organic-Inorganic Hybrid Perovskite Solar Cells with Scalable and Roll-to-Roll Compatible Printing/Coating Processes

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Abstract

Organic-inorganic hybrid perovskite solar cells (PeSCs) are on the brink of causing a seismic breakthrough in solar cell technology. Unlike other solar cell technologies, PeSCs combine high efficiency with solution-based processing, which is not possible in other solar cell technologies thus far. Solution-processing enable dramatic cost reduction in production as high throughput vacuum-free manufacturing becomes possible. The record efficiency of PeSCs with solution-processed absorber layer has rapidly climbed from 3.8% in 2009 to above 22% in 2016. The challenge remains to demonstrate scalable production method that embodies the unique merits of PeSCs to enable dramatic improvement in power-to-cost ratio. The combination of a roll-to-roll (R2R) manufacturing line, all-solution based printing and coating methods, and low embedded energy in the processing steps represents high throughput and low-cost production scheme. Today, research in PeSCs is geared towards issues of production and scalability. This chapter provides an overview of various printing and coating methods that are suitable for low-cost solution-based R2R production of PeSCs. Additionally, an overview on PeSC technology is given and the state-of-the-art materials and methods are discussed with respect to their scalability.

Keywords: Organic-inorganic hybrid perovskites, solar cells, roll-to-roll, printing and coating, flexible

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10.1 Introduction

Solar cells are a clean and abundant energy resource. Current solar cell technologies have the technical capacity to meet the total annual world energy demand. Solar cells with a power conversion efficiency of 12% installed on only 2% of the land area on earth can power more than four times the current total world energy consumption [1]. Many solar cells currently on the market operate at even higher efficiency levels. Silicon solar cells, which hold 90% of the solar cell market, deliver 15–17% efficiency. In recent years, the uptake of solar cells has rapidly expanded, with a 20–30% year-on-year growth rate. This is attributed to a confluence of factors, including the improvement in the technology and manufacturing alongside the increasing cost of conventional energy. Current solar cell installations supply 242 GWp of the electricity in the world, which is 10 times higher than a decade ago [2, 3]. However, the massive potential, the prevailing technical capability, and the rapid growth trends seen in recent years have failed to make a significant impact in the world energy scenario. Only 1.1% of net world electricity is currently met by solar cells [1, 2]. The impact of solar cells has long been hindered by the lack of cost competitiveness. Thus, a disruptive technology is needed to deliver a dramatic improvement in the power-to-cost ratio and to rise above the benchmark that silicon solar cells have set in terms of efficiency, stability, and cost.

Organic-inorganic hybrid perovskite-based solar cells (PeSCs) may just be the much needed breakthrough in the field of solar cells. Its solution-processability offers the possibility for fast production via industrial roll-to-roll (R2R) manufacturing while delivering high efficiency. PeSCs achieved a record efficiency of 22% in the year 2016 with less than 10 years of development while silicon solar cells took more than 80 years to reach a record efficiency of 25% [4, 5]. The rapid increase in record efficiency of PeSCs in such a short period with the possibility of further improvement has piqued the interest of many different scientific fields. This is evident in the skyrocketing number of scientific publications from 1 in the year 2009 to nearing a thousand in the year 2016 [6] (Figure 10.1a). In addition to high efficiency, low-cost production is of utmost importance to achieve cost competitiveness against conventional energy resources. This requires replicating efficiency reported in the laboratory while scaling-up with the use of low-cost materials and a production method that enables high throughput production with low embedded energy in the processing steps.

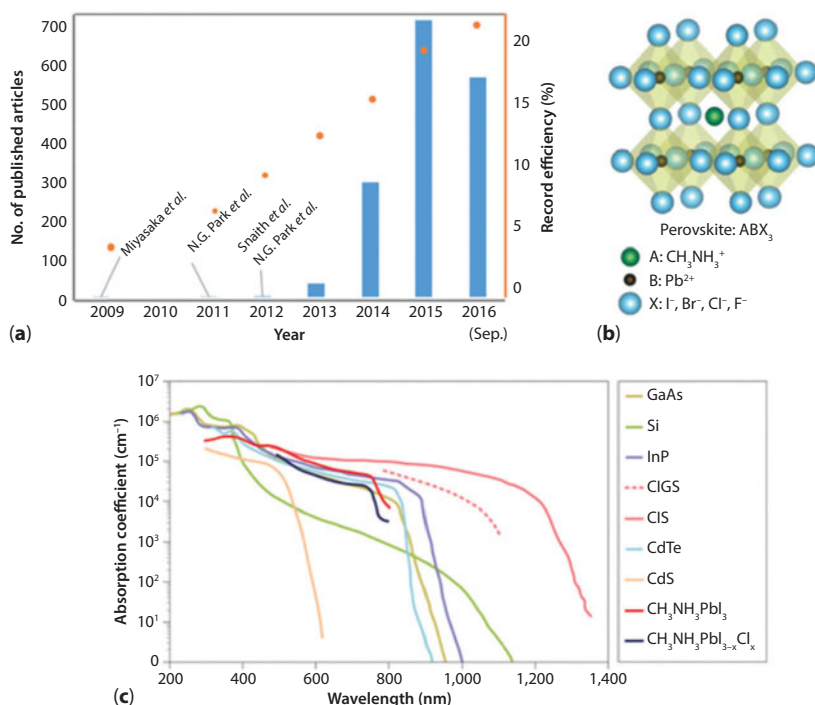


Figure 10.1 (a) Number of publications of PeSCs (bar graph) and record efficiency since 2009. Data on publications collected from Web of Science and on efficiency from NREL and various literature sources (see ref. [6–8]). (b) Crystal structure of cubic metal halide perovskites with the generic chemical formula ABX_3 . Absorption coefficients as a function of wavelength of various solar cell technologies. (Figure 10.1b reprinted with permission from [9]; Copyright © 2015 Material Research Society. Figure 10.1c adapted with permission from [10]; Copyright © 2014 Macmillan Publishers Ltd)

Research focus is now geared towards investigation of scalable production methods as efficiencies above 15% are routinely reported for laboratory cells. This chapter aims to provide readers with an encompassing overview of the technology and R2R printing and coating processes for cost-effective industrial production of PeSCs. The state-of-the-art cell performance and the materials and processing methods employed in the fabrication of laboratory cells are presented. Their relevance to and compatibility with low-cost R2R processing are also discussed. Current developments in printed and coated PeSCs are also presented. Finally, the chapter concludes with a future outlook.

10.2 Optoelectronic Properties

Today, a record efficiency of 22% is reported for PeSCs [7, 8]. The achievement of such a high efficiency is made possible through an understanding of the inherent optoelectronic properties of the organic-inorganic hybrid perovskite materials, hereafter referred to as perovskites. The perovskite crystal structure belong to the cubic lattice system and are described by the general formula ABX_3 (Figure 10.1b). The type 'A' atoms are occupied by an organic mono-cation (e.g., $CH_3NH_3^+$) and are placed at simple cubic position at the cube corners (0,0,0), type 'B' are divalent metal cation (Pb_2^+ or Sn_2^+) which occupy the body-center position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the type 'X' are halide mono-anions (I^- , Cl^- , Br^-) which occupy the face-center positions ($\frac{1}{2}, \frac{1}{2}, 0$).

Many of the key characteristics of perovskites surpass those of the preceding technologies, including dye-sensitized solar cells (DSSCs), organic solar cells, and in some cases, even silicon solar cells. Their low band gap (up to 1.5 eV) covers a large portion of the solar spectrum similar to CdS and GaAs (Figure 10.1). Unlike silicon solar cells, PeSCs have a direct band gap which leads to negligible non-radiative recombination. The absorption coefficient of perovskites ($1.5\text{--}0.5 \times 10^4 \text{ cm}^{-1}$ at 550–700 nm) is higher than silicon ($6.39\text{--}1.39 \times 10^3 \text{ cm}^{-1}$) at 300 K, thus allowing the fabrication of thin film in PeSCs with typical thickness ranging between 200–500 μm whereas silicon solar cells typically employ 200–500 μm thick films [11]. Single-crystal perovskites show charge carrier diffusion lengths of 10 μm and very low trap-state densities on the order of 10^9 to 10^{10} per cubic centimeter, which is comparable to the best crystal quality used in silicon solar cells [12]. Similar to silicon solar cells, the exciton binding energy in perovskites is only a few microelectron-volts. Thus, excitons dissociate spontaneously, leading to the generation of free charge carriers at room temperature [13, 14]. This is in sharp contrast with organic solar cells where exciton binding energy in conjugated polymers can be up to 0.5 eV. Organic solar cells therefore require more complex structures in order to induce exciton dissociation. In particular, acceptor materials (such as C_{60} and its adducts) of distinct energy offsets are used in intimate mixtures [15]. Additionally, electron and hole diffusion lengths in solution-processed triiodide perovskites ($CH_3NH_3PbI_3$) are 110 and 130 nm, respectively, while they are an order of magnitude higher in mixed halide variants ($CH_3NH_3PbI_{3-x}Cl_x$) [16, 17]. Such diffusion lengths in solution-processed perovskites are significantly higher than in solution-processed organic conjugated polymers (~ 10 nm) and thermally deposited organic molecules (10–50 nm), and comparable to GaAs [16, 17]. Perovskites also

have significantly higher carrier mobilities. The reported values of carrier mobility vary significantly which can be attributed to a range of empirical factors including large differences in the morphologies of the perovskite films; nonetheless electron mobility μ_e up to $66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been experimentally obtained, while theoretical predications suggest ~ 100 to greater than $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are possible depending on defect density [18, 19]. Regardless, the reported charge mobilities are significantly higher than organic solar cells where low mobilities ($\mu_h \sim 10^{-4}$ – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$) limit carrier lifetime and impede in charge transport [18–20]. The combination of these properties makes PeSCs a promising photovoltaic technology.

10.3 History

The term perovskite refers to the cubic crystal structure of calcium titanate (CaTiO_3). It was discovered by the German mineralogist Gustav Rose in 1839 and named in honor of the Russian mineralogist Lev Perovski. In optoelectronics, the first inorganic perovskite semiconductor, cesium lead halide (CsPbX_3 , $\text{X} = \text{Cl}, \text{Br}, \text{or I}$), was reported by Danish scientist Moeller in 1958 [21]. Subsequently, cesium was replaced with methyl ammonium cation (CH_3NH_3^+) by German scientist Weber in 1978, thus reporting the first organic-inorganic hybrid perovskite [21, 22].

Thirty years later, perovskites were reported in the development of DSSCs by Miyasaka and coworkers in 2009. DSSCs were suffering from poor efficiency attributed to the low absorption coefficient and narrow absorption band of the dyes in addition to the complex charge generation mechanism. The leakage of liquid electrolyte was also a major issue limiting stability and commercialization of DSSCs. As an alternative to the then existing dyes, Miyasaka and coworkers demonstrated perovskites as visible light sensitizers decorating the mesoporous TiO_2 surface and reported an efficiency of 3.81% and 3.13% with methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) and methylamine lead tribromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$ or MAPbBr_3), respectively [23]. The efficiencies of these cells were improved to above 6% in a following study by N. G. Park and coworkers [24]. However, the liquid redox electrolyte caused fast dissolution of the perovskite sensitizers, thus rapidly deteriorating efficiency by 80% in a matter of 10 minutes. Two subsequent independent studies, both of which were almost simultaneously published in 2012, sought solutions to the poor stability of the perovskites in liquid electrolyte. Instead of the liquid electrolyte, a solid hole-transport material, 2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) was used to make solid-state DSSC (ssDSSC). A hero cell

efficiency of 9.7% was reported which was a breakthrough in ssDSSCs [25]. Simultaneously, a collaborative study between Snaith and Miyasaka *et al.* used perovskites in ssDSSCs and reported an efficiency of 9.2% [26]. In addition, this study made a significant observation—the replacement of mesoporous TiO_2 by mesoscopic Al_2O_3 dielectric scaffold led to higher efficiency (10.2%). This was attributed to Perovskites' n-type semiconductor properties with significantly higher conductivity of the perovskite than TiO_2 . The absence of mesoporous TiO_2 meant that charge generation did not depend on a sensitization process. Hence these cells no longer belonged to the DSSC group. Snaith termed the device “meso-superstructured solar cells.” In a following study, Snaith and coworkers further observed that nanostructuring was not even necessary and that a planar configuration in fact led to a high efficiency of 15.4% with evaporation and 8% with solution-process [27]. This marked the separation of PeSCs from DSSCs. The finding here highlighted high-temperature processes unnecessary and opened up the possibility of R2R production of PeSCs.

10.4 Device Configurations

A typical DSSC structure is shown in Figure 10.2. It consists of dye molecules adsorbed onto nanocrystalline TiO_2 film which is sandwiched between a transparent conductive electrode (TCE) and a counter electrode (EL). An electrolyte containing a redox couple is infiltrated between the electrodes. Additionally, the TCE is covered with a compact TiO_2 film which forms the electron selective layer (ESL). The dye molecules adsorbed onto the TiO_2 surface absorb solar light which then injects electrons into the conduction band of the TiO_2 . The dyes which are oxidized upon losing electrons are regenerated to neutral state by accepting electrons from the electrolyte. The electrolyte in turn is replenished by the charge injecting electrode. In order to increase the active contact surface between the dye and TiO_2 , several micron thick mesoporous film of TiO_2 is employed.

The earliest cell configuration in PeSCs was the mesoporous structure which was directly adapted from DSSCs. In mesoporous PeSCs, the dyes and the liquid electrolyte are simply replaced by perovskite and a solid hole-selective layer (HSL), respectively, as shown in Figure 10.2. Shortly after the initial trials of perovskites as dye replacements in DSSCs, the differences in charge generation mechanisms between DSSCs and PeSCs were understood. Unlike in dyes, the exciton binding energy in perovskites was very small leading to spontaneous dissociation of exciton upon photon absorption by the perovskites. Further insights into the working principle and photophysics of PeSCs can be found in various other sources [43–45]. Thus, TiO_2 did

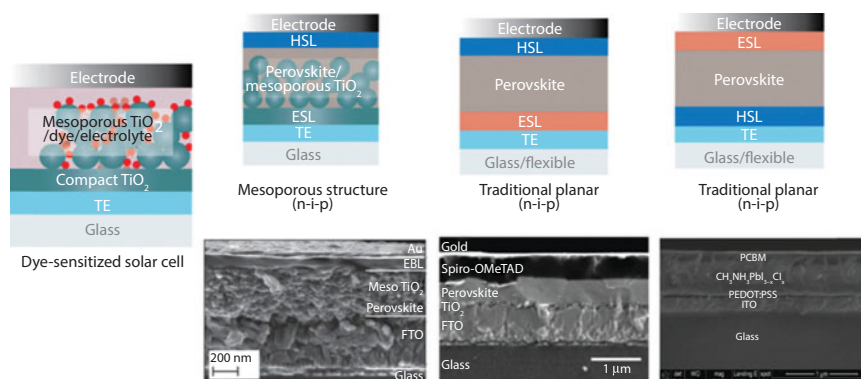


Figure 10.2 Schematic illustration of cross section of a dye-sensitized solar cell and the three most common configurations of PeSCs. SEM images correspond to the configurations shown directly above them. (SEM images: Mesoporous structure from ref. [28]; Copyright © 2013 Macmillan Publishers Ltd. Traditional planar structure from ref. [29]; Copyright © 2016 John Wiley & Sons. Inverted planar structure from ref. [30]; Copyright © 2014 American Chemical Society. Reprinted with permission)

not contribute to charge generation mechanism and therefore the meso-structuring of TiO_2 was no longer necessary in PeSCs. Thus, planar structures in PeSCs was explored and have today evolved into two distinct classes: the traditional planar and the inverted planar structures (Figure 10.2).

The traditional planar structure is composed of Substrate|TCE|ESL|Perovskite|HSL|EL wherein electrons are collected at the TCE side and the holes at the back electrode. In the inverted structure, the direction of charge collection is reversed which is achieved by reversing the ESL and HSL layer. Thus, the inverted structure is composed of Substrate|TCE|HSL|Perovskite|ESL|Electrode. In these triple-junction structures, the perovskite forms the intrinsic semiconductor and ESL and HSL work as n-type and p-type charge extraction layers, respectively. Thus, the traditional and inverted structures are often referred to as “n-i-p” or “p-i-n” structure, which reflects the sequence of junctions with respect to the substrate.

In the early stages of development, solution-processed organic halide precursors led to higher efficiency in the mesoporous configurations than in the planar configuration. This was attributed to the shorter path of charge carriers in the mesoporous configuration. As TiO_2 infiltrates into the thickness of the perovskite layer in mesoporous structure, the diffusion of charges are over 10–20 nm which is significantly lower than the maximum charge diffusion lengths in solution-processed perovskites (>100 nm) [16]. However, the mesoporous structure is complex and requires multi-step high temperature (>500 °C) sintering processes for the TiO_2 compact layer and for the mesoporous TiO_2 layers. The replacement of the thick

mesoporous TiO_2 layer with a thinner dielectric scaffold requiring lower processing temperature was successfully demonstrated [31]. Yet, the compact ~ 100 nm thick TiO_2 ESL layer in these cells still required a processing temperature of around 500°C for 30 minutes or longer.

Over time, the planar structures have also improved to reach high efficiencies. The first planar structure composed of Glass|FTO| TiO_2 |absorber|spiro-OMeTAD|Ag was briefly reported to illustrate the semiconducting nature of the organic lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and an efficiency of 1% was reported [26, 27]. Soon thereafter, this planar structure was fabricated employing co-evaporation and solution-processing, which led to hero-cell efficiencies of 15.4% and 8.4%, respectively [27]. However, these structures still employed a TiO_2 compact layer which required prolonged sintering at high temperature. The next significant study demonstrated that TiO_2 could be replaced by ZnO which requires no annealing steps at all and reported efficiencies of 15.7% and 8% on glass and flexible substrate respectively—the efficiency on glass substrate was similar to the efficiency of control devices fabricated by co-evaporation employing TiO_2 [32]. These results highlighted the great potential of planar structure PeSCs for high throughput R2R manufacturing via all-solution processes.

The traditional planar configuration was initially the most cost-efficient structure since it is compatible with flexible substrate and high sintering temperatures are not needed. However, cells of this configuration showed large photocurrent density-voltage hysteresis with respect to forward and reverse scan direction. The origin of hysteresis is still under debate and a number of factors have been reported for explaining the dynamic hysteresis behavior which include unbalanced photoexcited electrons and holes at the interfaces due to inefficient extraction of photoexcited carriers, dynamic trapping and detrapping processes at interfaces, and band bending due to ion migrations and/or ferroelectric polarization [33–35]. This has led to the adoption of inverted planar configuration, which combines the developments of various materials from the field of organic solar cells. The inverted structures show negligible hysteresis [36] and use low energy steps in the processing, which makes them compatible with flexible substrates, and are reportedly air-stable due to the hydrophobicity of [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM)—the most commonly employed ESL in inverted structures. High efficiency exceeding 18% is reported for cells with inverted planar structure [33, 36].

Other less explored device configurations includes p-n structures in the planar configuration. In this structure, the perovskites act as p-type

semiconductor forming a double junction with an n-type metal oxide layer. It is the most simple and parsimonious structure as it eliminates the HSL and thus saves material and processing cost. However, so far an efficiency of only 6% is reported for p-n planar junction whereas above 18% is reported for the triple junctional planar structures [33, 37]. Additionally, mesoporous structures with inverted p-i-n configuration have also been reported in recent years. The p-i-n structure employs a p-type metal oxide, such as NiO_x , in combination with dielectric mesoporous scaffold of Al_2O_3 . The Al_2O_3 can be processed at lower temperature than required for TiO_2 which generally forms the mesoporous scaffold in mesoporous structure [38–40]. A hero efficiency of 9% has been reported [38–40].

Regardless of the similarities and differences in charge generation mechanism of the different device configurations, the question remains on how these structures can be scaled-up via low-cost processes while maintaining efficiency. Ultimately, the structures that deliver the lowest cost of electricity, whether achieved with high efficiency or by lowering the cost of materials and processing, or a combination of both, will be the most competitive. With respect to efficiency, mesoporous structures have achieved an efficiency of 20% while planar structures employing TiO_2 have achieved an efficiency above 19% [41, 42]. This suggests that mesoporous structure may be a futile pursuit beyond theoretical studies. In contrast, an efficiency of above 18% has been achieved with planar structure that avoids TiO_2 and is compatible with low-cost polymer flexible substrates for fast manufacturing [33]. Thus, the planar configurations appear more lucrative. The mesoporous structure can be favorable if significantly higher efficiency and stability can be achieved with this structure upon scaling-up in comparison to the planar structures. The technology at the current stage is too nascent to give clear evidence on performance versus cost of any of the structures. Further development in the near future will elucidate which configurations have the highest potential at maximizing performance-to-cost ratio.

10.5 Functional Materials

As described above, PeSCs typically consist of a number of critical layers including the electrodes, ESL, HSL and the Perovskite absorber itself. Each of these need to be carefully selected based on their energy levels to ensure efficient current extraction and high open circuit voltage. In Figure 10.3,

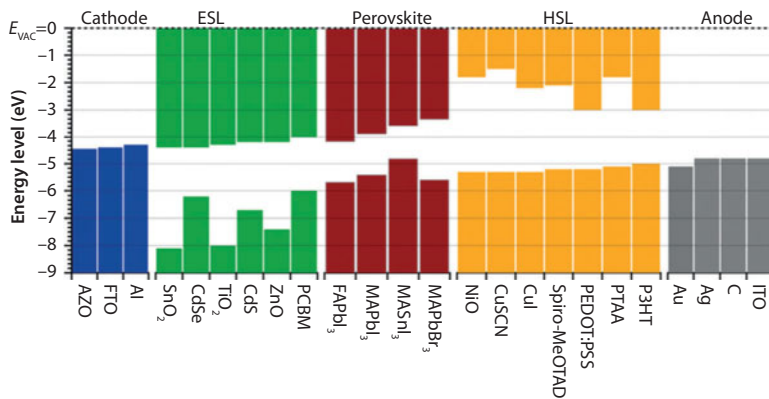


Figure 10.3 Collection of materials employed in various functional layers in the PeSCs with their respective energy level. (Reprinted with permission from [40]; Copyright © 2016 Society of Photo Optical Instrumentation Engineers)

the energy levels of materials employed in various functional layers of PeSCs are shown [40]. Here, the alignment of energy level between the different functional layers can be distinguished. This list is not exhaustive but represents the most common ones. The following sections give further details on materials and processing of each of these device components.

10.5.1 The Organic-Inorganic Halide Perovskites

A plethora of perovskite variants have been investigated and many of them lead to high efficiency. The earliest perovskites were based on methylammonium lead trihalides, specifically $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr₃) [23]. Since then, various material strategies have been explored to replace and/or supplement one or more elements in these trihalide perovskites for improved device efficiency and stability. Mixed halide formulations, such as $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ or $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{Cl}_x$, have significantly improved optoelectronic properties compared to the trihalide formulations [23, 26]. The organic cation methylammonium was replaced with a related compound of ethylammonium ($\text{CH}_3\text{CH}_2\text{NH}_3^+$) and formamidinium ($\text{NH}_2\text{CHNH}_2^+$) which also showed good photovoltaic performance [46–49]. Formamidinium lead triiodide (FAPbI₃)-based PeSCs have achieved 20% efficiency with solvent engineering to enable uniform film growth [41]. Most recently, complex compositions composed of mixed organic cation and halides, such as $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$, have shown state-of-the-art performance with efficiency reaching 20% [50].

On the other hand, lead-free perovskites are of interest due to the toxicity concern associated with Pb. Environmentally friendly elements such as Tin (Sn^{2+}) [51, 52], germanium(II) (Ge^{2+}) [53], antimony(III) (Sb^{3+}) [54], and bismuth(III) (Bi^{3+}) [55] have been explored [56, 57]. However, the photovoltaic performance of lead-free PeSCs still tags far behind Pb-based ones. Sn seems to show most promise. Sn is theoretically more ideal as Sn-based perovskites lead to lower band-gap than lead-based perovskites. An efficiency of 6% was reported in two independent studies [51, 52]. Despite numerous follow-up reports [58–63], no further improvement in efficiency has taken place. There are several challenges associated with the use of Sn. Sn is more susceptible to oxidation and cells reportedly degrade rapidly in air [58]. Secondly, the fabrication of uniform film with Sn-based perovskites is more challenging due to the rapid crystallization at room temperature [64]. Recently, the use of additives in formamidinium tin iodide ($\text{NH}_2\text{CHNH}_2\text{SnI}_2$) have enabled higher efficiency with improved layer uniformity and improved stability [65]. However, the efficiency of lead-free PeSCs is still around 6%. Most recently, complex composition containing both Pb and Sn with mixed cations comprising $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ have enabled 15% efficiency with no hysteresis following a two-step deposition process. Additionally, this composition has lower band gap (1.2 eV) than trihalides (1.5 eV), which has resulted in a short-circuit current of 27 mA/cm^2 , albeit with lower V_{oc} than trihalide perovskites (~ 1 V).

The perovskites can be deposited via vapor deposition or solution deposition method, however, the latter is more relevant for low-cost manufacturing. Solution-deposition of perovskite can be achieved through a one-step deposition route or a sequential process involving two deposition steps. In the one-step process, a solution is prepared by mixing the inorganic halide compound with the organic halide. In the simplest form, a precursor solution is prepared by blending lead halide with organic iodide which forms a perovskite layer upon film deposition. For example, PbI_2 is blended with MAI to form a perovskite film of MAPbI_3 . Mixed halides can be used to create mixed halide perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ [23, 26]. In the two-step sequential deposition process, separate solutions of the lead halide and the organic halide are prepared separately and deposited sequentially. For example, the PbI_2 solution is deposited first forming a PbI_2 film. In the second step, the MAI solution is deposited on top of the PbI_2 film, which converts it into perovskite [28].

The one-step process is a simpler low-cost approach for industrial production as it involves only one processing step, however the formation

of uniform defect-free films is difficult due to the uncontrolled precipitation or rapid crystallization of perovskites. Therefore, reproducibility remains a major challenge with one-step devices [29, 66–68]. Recent advances to address this challenge include either (i) retarding crystallization by controlling solvent composition and additives or (ii) inducing rapid nucleation by quenching strategies (solvent and/or vapor) such that crystallization is uniform throughout the deposited film [42, 45, 69]. In contrast, in the two-step process, the PbI_2 precursor solution transforms to uniform and compact film upon deposition in the two-step process more easily. The challenge here is to achieve complete conversion of the dense PbI_2 film into perovskite upon subsequent deposition of the organic halide. Furthermore, the conversion process requires volume expansion, which can induce pin-holes and film inhomogeneity in the perovskite films. Many processing strategies are reported to avoid this challenge, as reviewed in detail elsewhere [45]. Briefly, the main strategies involve reducing the crystallinity of the PbI_2 film and controlling the volume expansion. The former approach, for example, involves the creation of an amorphous PbI_2 film. Dimethyl sulfoxide solvent is reported to form complexes with PbI_2 , forming an amorphous film which leads to homogenous conversion of PbI_2 , in turn improving efficiency and reproducibility of the cells [69]. Similarly, adding a non-stoichiometry amount of MAI into the PbI_2 solution is reported to significantly reduce crystallinity and enable rapid and uniform conversion to perovskite upon deposition of the subsequent MAI [70]. There are numerous reports on solutions to tackling the challenges associated with both the one-step and the two-step processes. Most of the reported devices have an area less than 0.1 mm^2 . Hence, the main challenge will be scaling this up and achieving high reproducibility and maintaining high efficiency.

10.5.2 Electron-Selective Layer

The most commonly used ESL in all device configurations is TiO_2 . In the mesoporous structure, it forms both the compact layer and the mesoporous template. Other metal oxides have also been investigated in mesoporous structure. ZnO [71] has been used as both the compact layer and the mesoporous scaffold. While SiO_2 , Al_2O_3 [26, 31], SrTiO_3 [72], and ZrO_2 [73] have been used in forming the mesoporous scaffold on top of a TiO_2 compact layer. In the traditional planar n-i-p structure, TiO_2 , ZnO [32, 74, 75], graphene/ TiO_2 composite [76], SnO_2 [77, 78], CdSe [79], and CdS [80] have been employed. SnO_2 -based devices are particularly

promising achieving an 18% efficiency with vacuum deposition [77] and 17% with solution processing [78]. In the inverted p-i-n structures, PCBM, PCBM/ZnO and PCBM/TiO₂, are most commonly employed [36]. Most ESL materials can be solution-processed, however different sintering conditions may be required depending on the precursor formulations [81].

10.5.3 Hole-Selective Layer

Early reports of PeSCs employed spiro-OMeTAD as the HSL, the standard HSL material for ssDSSCs. However, it is an expensive material which has encouraged the investigation of various HSLs from other fields such as organic solar cells. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), NiO_x, MoO₃, VO_x and a variety of conjugated polymers, including poly(3-hexylthiophene-2,5-diyl) (P3HT), the most common absorber material from the field of organic solar cells, have been successfully employed as the HSL in PeSCs [36, 82–85]. To date, PEDOT:PSS is the most common HSL in the p-i-n structure. Recently, highly doped Li⁺-doped Ni_xMg_{1-x}O was reported with a high efficiency up to 20% [86]. However, the processing requires high-temperature spray pyrolysis which is similar to TiO₂ fabrication. Alternatively, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) is reported to be a better HSL than PEDOT:PSS because of its higher conductivity and appropriate energy levels for high open-circuit voltage. An efficiency of 19% with an open-circuit voltage of 1.1 V and short-circuit current density of 22 mA/cm² was achieved in a p-i-n planar structure with no hysteresis in the J-V curve [87, 88].

10.5.4 Transparent Electrode

Indium-tin-oxide or ITO (In₂O₃:Sn) is the most used transparent electrode. It has high optical transparency and low sheet resistance. However, Indium is a scarce element, its supply is geographically confined, and it is in very high demand as it is a universal transparent electrode used in the optoelectronic industry. In addition, ITO is processed with vacuum methods and its patterning incurs large material wastage. Thus, ITO is an expensive material which is subject to large cost fluctuations, and is laden with future supply concerns. Finally, ITO is a highly brittle material which can be a drawback for handling of flexible PeSCs and its integration in various flexible applications [89, 90].

ITO-free transparent electrodes are needed for ensuring no supply constraints in the future of PeSCs as well as for reducing the materials and

processing cost. The market for ITO-free alternatives is rapidly expanding and numerous alternatives are available, many of which can meet the processing objectives of PeSCs. Metals grids, nanowires, conducting polymers, inorganic oxides, carbon nanotubes and graphene have been investigated in organic solar cells ITO [89, 90]. Nanowires and a composite electrode made of metal grids and PEDOT:PSS can deliver significantly higher transparency and conductivity than ITO [89, 90]. Furthermore, some ITO-free transparent electrodes have high transparency and low sheet resistance ($<1 \Omega/\square$) which has enabled scaling up to large area modules without loss of efficiency [91] and in further scaling up of *in-situ* interconnected modules during R2R processing [92]. Additionally, these ITO-free alternatives, which are also R2R printed on flexible substrates under ambient conditions, have led to significant reduction in cost and environmental footprint of organic solar cells [89, 92]. Similar strategies for PeSCs can be envisioned as processing challenges are gradually overcome. Recent reports have successfully employed ITO-free electrodes in PeSCs based on PEDOT:PSS and metal grid/PEDOT:PSS to realize extremely flexible and lightweight PeSCs with efficiency of 12% and 14% respectively [93, 94].

10.5.5 Counter Electrode

In traditional planar structures, Ag or Au is employed while Al is mostly used in inverted planar configuration. Al is a low work function metal which is highly susceptible to oxidation. The use of Al can be circumvented by using a bilayer of ZnO|Ag on top of the ESL layer (such as PCBM). Most PeSCs reported employ an evaporated counter electrode, however printing of the counter electrode is possible. Screen-printed Ag or carbon [75] and blade-coated carbon [95] have been used to produce vacuum-free perovskites. The efficiencies of cells with printed electrode however are much lower than with evaporated ones. This can be attributed to the use of Ag and carbon printable ink formulations which are developed for other “inert” applications. In PeSCs, the solvents in these inks tend to diffuse into the cells, which damages the underneath layers [75]. Such challenges are similar to those encountered in organic solar cells and likely to be overcome as materials are adapted specifically for PeSCs [96]. There are several strategies which can alleviate and even eliminate this challenge. It has been shown that ink-jet printing of certain silver formulation on PEDOT:PSS can avoid the solvent penetration and enable photovoltaic performance similar to cells with evaporated electrodes [97, 98]. It is likely that as research focus shifts from perovskite absorber, such strategies will be explored and will pave the way for vacuum-free PeSCs.

10.6 Spin Coating

Most materials involved in PeSCs are suited to be processed with solution-based methods. In fact, most materials employed in PeSCs except the absorber layer have already been processed in large-scale production of organic solar cells using solution-based printing and coating methods [92, 99]. Numerous benchtop machines with scalable printing and coating methods exist, yet most research laboratories rely on spin coating. The technique is borrowed from the electronics industry where it is traditionally used to coat thin films of photoresist on CDs, displays, integrated circuits, etc., which are generally on discrete small area substrates. Now it has become a preferred method for thin film formation in the research phase of new solar cell technologies, particularly organic solar cells [100] and most recently, PeSCs.

In spin coating, a solution is applied to the slowly rotating substrate which is then accelerated to a high speed, typically 1000 rpm and above. The solution undergoes a radial flow under centrifugal forces and most of it is swept off the substrate. Concurrently, evaporation takes place which ultimately dries the film leaving behind a thin film (Figure 10.4) [101]. Film thickness and uniformity is controlled empirically by optimizing the solution composition (solution concentration, solvent, additives, etc.) and

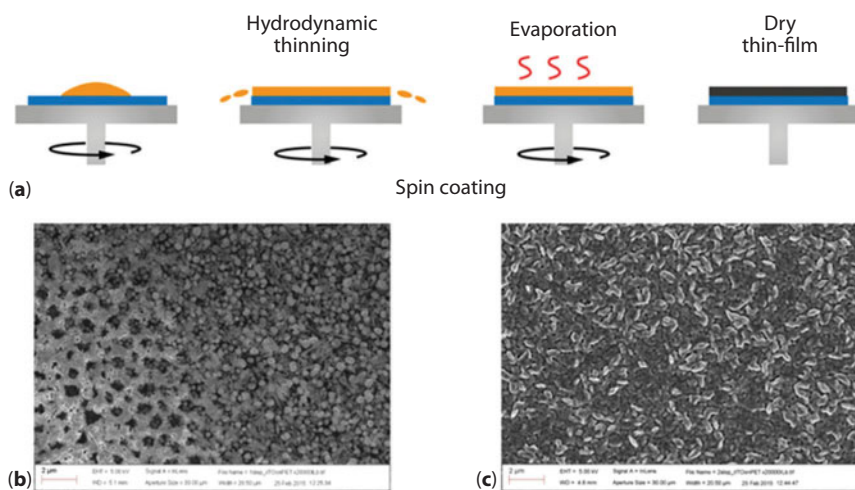


Figure 10.4 (a) Process of film formation in spin coating. (b) Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ film morphology with spin coating on flexible PET substrate via: (a) spin-coating 1-step method and (b) 2-step method. (Figure 10.1a adapted with permission from [101]; Copyright © 2013 The Royal Chemistry Society)

coating conditions (spin speed, acceleration, number of steps, etc.). Once the film is formed, additional drying/annealing steps can be carried out. In PeSCs where device performance is highly dependent on the perovskite film quality, spin coating may offer an advantage. To a degree, the dynamics of the spin-coating process enable simultaneous “quenching” of the film while ink spreading and evaporation are taking place. Hence, film uniformity is largely determined by the spin-coating process and before any subsequent additional annealing steps. In other film formation techniques, ink spreading and drying are more discrete processes and film formation is at a much slower rate than that of spin coating.

The dynamics of film formation in spin coating have been studied for many different materials [101, 102]. The spin-coating process is known to cause phase separation in organic solar cells where donor and acceptor molecules are intermixed in one solution [103]. We have also found that the morphology varied dramatically across a large-area substrate of a spin-coated perovskite film using the one-step method (Figure 10.4) while uniform films were obtained via the two-step process. Recent development in controlling film formation including the use of additives and different solvents among other strategies may alleviate the problem with one-step process [41, 45].

Spin coating is a facile laboratory technique, however, it has some severe limitations. Patterning is not possible and material wastage is high. Most importantly, it is not a scalable method and not suitable for large-area high throughput production. Thus, the findings of many studies, especially those directly relating to film characteristics, will be inconsequential in knowledge transfer to large-scale industrial processing where alternate scalable printing and coating methods will be employed. The high efficiencies touted in the literature are based on spin coating and meticulously controlled strategies for very small areas which can grossly misrepresent what could be feasible upon scaling-up production on an industrial scale. Thus far, spin-coated PeSCs in planar structures have resulted in above 20% efficiency on glass [36] and 15.6% on flexible PET substrate [104]. These efficiencies remain to be achieved with scalable processing methods. Current reports employing one or more scalable processing steps on flexible substrate have only achieved cell efficiency in the 10–12% range (Table 10.1). It is yet to be seen whether efficiencies achieved with spin coating can be attained with low-cost R2R compatible printing and coating methods. Perhaps the main reason why spin coating continues to be an unquestioned technique is because of the availability of existing infrastructure and the lack of knowledge on scalable printing and coating methods that are likely to share a future with the industrialization of PeSCs. To this

Table 10.1 Overview of scalable printing and coating methods employed in PeSC research as of Sep 15, 2016. All cells were characterized under 100 mW cm⁻² at AM 1.5G. Abbreviations and chemical formulas are expanded in the footnote.*

Device structure	Perovskite deposition method	Perovskite layer thickness [nm]	Scalable printing and coating method employed	Functional Layer processed with scalable printing and coating method	Ambient or N ₂ for processing of Perovskite layer	Active area of the cell [cm ²]	Power conversion efficiency of champion cell [%]	Ref.
Glass/ITO/ZnO/CH ₃ NH ₃ PbI ₃ /doped P3HT/Ag	2-step	300–500	Slot-die	PbI ₂ layer only	Ambient	0.10	11.6	[121]
Glass/ITO/ZnO/CH ₃ NH ₃ PbI ₃ /doped P3HT/Ag	2-step	500	Slot-die	All layers except ITO and Ag	Ambient	0.10	11.96	[74]
PET/ZnO/CH ₃ NH ₃ PbI ₃ /P3HT/Ag	2-step	NA	Slot-die/Screen	All layers except ITO	Ambient	0.2–0.5	2.60	[75]
PET/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /Cl ₂ /PCBM/ZnO/Ag	1-step	NA	Slot-die/Screen	All layers except ITO	Ambient	0.2–0.5	4.90	[75]
Glass/ITO/TiO ₂ /CH ₃ NH ₃ PbI ₃ /spiro-OMeTAD/Au	1-step	400	Spray	Concurrent spray of perovskite forming solutions and spectator ions	N ₂	0.13	13.7	[135]
Glass/ITO/TiO ₂ /CH ₃ NH ₃ (1 Br _{1-x} I _x)/spiro-OMeTAD/Au	1-step	400	Spray	Concurrent spray of PbCl ₂ /MAI and PbBr ₂ /MABr	N ₂	0.13	6.8	[135]
Glass/ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	1-step	220	Spray	Perovskite layer only	N ₂	0.10	9.7	[133]
Glass/ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /PCBM/Ca/Al	1-step	330	Spray	Perovskite layer only	Ambient	0.025	11.1	[134]
Glass/ITO/ZnO/CH ₃ NH ₃ PbI ₃ /P3HT/Ag	2-step	500	Spray	PbI ₂ via slot-die and MAI via spray	N ₂	0.10	7.48	[68]
Glass/ITO/TiO ₂ /CH ₃ NH ₃ PbI ₃ /spiro-OMeTAD/Ag	1-step	250	Spray	Brush and spray of perovskite layer	Ambient	0.20	3.52	[137]
Glass/ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /Cl ₂ /PCBM/LiF/Al	1-step	390	Spray	Spray-coating of all except the electrodes	Ambient	0.04	9.9	[136]
Glass/FTO/TiO ₂ /CH ₃ NH ₃ PbI ₃ /Au	1-step	3400	Spray	Spray coating of TiO ₂ and Perovskite via single step	Ambient + Annealed in N ₂	0.04	6.9	[37]
Glass or PET/ITO/TO ₂ /CH ₃ NH ₃ PbI _{3-x} Cl _x /Spiro-OMeTAD/Ag	1-step	295	Spray	Spray coating of the perovskite layer	Ambient	0.065	11.2 (glass) 8.1 (PET)	[128]

(Continued)

Table 10.1 Cont.

Device structure	Perovskite deposition method	Perovskite layer thickness [nm]	Scalable printing and coating method employed	Functional Layer processed with scalable printing and coating method	Ambient or N ₂ for processing of Perovskite layer	Active area of the cell [cm ²]	Power conversion efficiency of champion cell [%]	Ref.
Glass/FTO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ Cl/PCBM/Al	2-step	460	Spray	Spray coating of the perovskite and PCBM layer	Ambient + annealed in N ₂	0.3	5.08	[138]
Glass/PEDOT:PSS or c-OTPD+TPACA/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	1-step	3.1	Doctor Blade	Doctor blade of only perovskite precursor	N ₂	0.0725	12.80	[143]
Glass/ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ Cl/PCBM/Al	1-step	350-400	Doctor Blade	Doctor blade of only perovskite precursor	N ₂	0.0314	9.52	[142]
Glass/ITO/PCBM/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ Cl/PCBM/bis-C60/Ag	1-step	350	Doctor Blade	Doctor blade of all layers except ITO and Ag	ambient	0.10	10.71	[145]
PET/ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ Cl/PCBM/bis-C60/Ag	1-step	350	Doctor Blade	Doctor blade of all layers except ITO and Ag	ambient	0.10	7.52	[145]
Glass/ITO/Modified PEDOT:PSS/CH ₃ NH ₃ PbI ₃ Cl/PCBM/bis-C60/Ag	2-step	NA	Doctor Blade	Doctor blade of perovskite layer only. Uniform large area was shown.	Ambient+N ₂	>0.10	10.15	[140]
Glass/ITO/PTAA/CH ₃ NH ₃ PbI ₃ Cl/PCBM/C60/BCP/Al	1-step	NA	Doctor Blade	Doctor blade of only perovskite layer	N ₂	NA	12.1	[144]
Glass/ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ Cl/PCG60BM/Ag	1-step	150-200	Doctor Blade + Spray	Doctor blade of PEDOT:PSS and spray coating of Ag nanowire	Ambient + N ₂	0.104	8.5	[141]
Glass/FTO/TiO ₂ /meso-TiO ₂ /CH ₃ NH ₃ PbI ₃ Cl/Spiro-MeOTAD/Au	1-step	200	Ink-jet	Ink-jet printing of perovskite layer only	Ambient + N ₂	0.04	12.3	[171]
Glass/FTO/TiO ₂ /CH ₃ NH ₃ PbI ₃ +C	2-step	>500 nm (interpenetrating with carbon)	Ink-jet	Ink-jet printing of mixed solution of CH ₃ NH ₃ I+C	Ambient + N ₂	0.15	11.6	[172]
Glass/ITO/PEDOT/PbI ₃ :NH ₃ CHNH ₃ PbI ₃ :CH ₃ NH ₃ PbI ₃ /PCBM/Ca/Al	2-step	NA	Ink-jet	Combinatorial Ink-jet printing of two organic cation sources: CH ₃ NH ₃ I and NH ₃ CHNH ₃ PbI ₃	Ambient + N ₂	NA	11.1	[173]

*NA: not available; PEDOT:PSS:poly(3,4-ethylenedioxy-thiophene);poly(4-styrenesulfonate). PCBM: [6,6]-phenyl-C 61 -butyric acid methyl ester. PTAA: poly [bis(4-phenyl)](2,4,6-trimethylphenyl)amine; P3HT: Poly(3-hexylthiophene-2,5-diyl). TPACA: (2)-2-cyano-3-(4-(diphenylamino)phenyl)acrylic acid. c-OTPD: Cross-linked N4,N40 -bis(4-(6-(3-ethyloctan-3-yl)methoxy)hexyl)phenyl)-N4,N40 -diphenylbiphenyl-4,40 -diamine. BCP:2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

end, the following sections will elucidate the considerations for scaling up on the R2R manufacturing line and also discuss various printing and coating methods. Many of these methods are down-scalable and in fact exist in benchtop variants.

10.7 Roll-to-Roll Processing

Roll-to-roll (R2R) implies a continuous manufacturing process that involves the use of a flexible substrate (web) moving between two rolls—an unwinder roll feeding the flexible substrate mounted on a roll and a rewinder roll collecting the flexible substrate on another roll. Between the unwinder and the rewinder rolls, one or more deposition (additive) and/or elimination (subtractive) fabrication technique can be mounted. Many treatment stations can also be included. For example, a printing station (additive), a convection oven (treatment) and a laser-structuring (subtractive) can form a simple R2R set-up. Multiple additive and subtractive units as well as treatment methods can be mounted on a single continuous R2R line capable of producing several layers in one R2R run. Alternatively, R2R processing can be broken down into discrete steps where one or a few layers are processed in one run and the roll is re-fed into the line to be further processed. Regardless of the set-up, R2R manufacturing is an efficient and cost-effective method allowing high throughput and low-cost production in comparison with batch processing. In general, R2R machines are more complicated and consist of an unwinding roll, a cleaning unit, web guide, corona unit, drying units, one or more printing and coating stations, tension-sensor rollers, traction roller, and several transfer rollers. An example of semi-industrial R2R equipment is shown in Figure 10.5.

10.8 Substrate Limitation

The fast R2R manufacturing requires the use of flexible substrates. In most cell configurations, the transparent electrode is directly processed on top of the substrate. Thus, the flexible substrate must be optically transparent to fully transmit incident light into the absorber layer. Additionally, the flexible substrate must be dimensionally stable in the temperature range required for the processing of all layers comprised in the solar cell. Otherwise, registration problems can arise that can hamper the patterning of successive layers and undermine technical yield. In large-scale production of large-area modules, one aim is to increase the geometric fill factor.

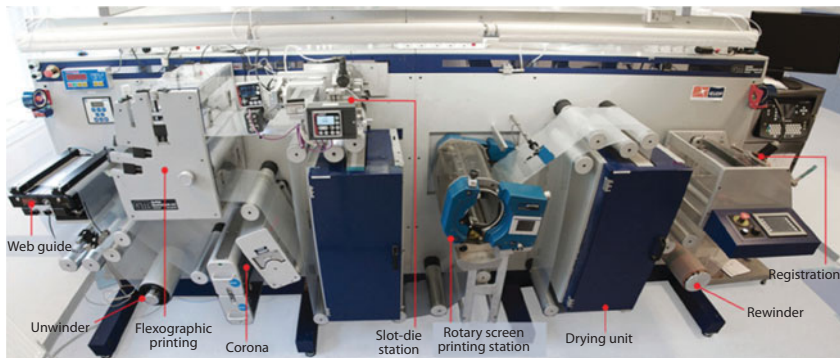


Figure 10.5 A semi-industrial R2R printing and coating machine. (Reprinted with permission from [105]; Copyright © 2012 Woodhead Publishing Ltd.)

This involves maximizing current generating area and minimizing non-active areas (such as area used for interconnections and contact) on the substrate. High geometric fill factor can be achieved with high resolution patterning which highly relies on registration in additive processes [106]. Flexible substrates with high dimensional stability are therefore needed.

Most flexible substrates are made of thermoplastic polymers. Polyethylene terephthalate (PET) is most commonly used as a substrate for flexible solar cells and offers dimensional stability up to 150 °C. Polyethylene naphthalate (PEN) is an alternate flexible thermoplastic substrate which can offer thermal resistance up to 200 °C [107]. The most thermally stable flexible substrates on the market are polyamide films. These films offer dimensional stability between 350–400 °C. However, they are typically colored and hence they are not ideal to be a substrate of PeSCs. This generally rules out R2R production of the mesoporous structures on plastic substrates because they need higher thermal processing. Unless the efficiency achieved with the mesoporous structures far outweighs material and processing complexity, this configuration will not be competitive in comparison to the planar configurations which are compatible with low-cost flexible polymer substrate. Alternatively, flexible metal foils can be used where high process temperatures are required. However, metal foils are opaque and require the development of transparent counter electrode. Metal foils and polyamide films are also expensive compared to low-cost PET and PEN substrates.

The earliest report on flexible PeSCs employed PET as a substrate in an inverted p-i-n planar structure with solution-processed TiO_x . Efficiencies around 6% were achieved on both glass and flexible substrates [108]. Thereafter, cells based on traditional planar n-i-p structure

were fabricated on PET substrate with the use of ZnO as ESL and an efficiency of 8% was achieved. Recently, the same n-i-p planar configuration has enabled a record efficiency of 15.6% [104]. The vast improvement in efficiency is achieved with the use of additives to control perovskite film morphology and by balancing conductivity between the ESL (ZnO) and the HSL (PTAA). The latter specifically also alleviates hysteresis in the J-V curve. Currently, cells employing metal substrates are reported with the state-of-art efficiency of 13%, however the cells are meticulously prepared circumventing various development challenges. Here, the titanium foil substrate is clipped together with PEN/ITO/PEDOT:PSS and perovskite precursor is subsequently infiltrated between the clipped electrodes [109]. Additionally, ITO-free electrodes in combination with PET substrate have enabled extremely lightweight and flexible PeSCs. A power-to-weight ratio of 23 W g^{-1} which surpasses any of the previous solar cell technologies could be realized with 12% efficient ITO-free flexible PeSCs. These cells have been employed in powering aviation models [93] (Figure 10.6). However, this state-of-the-art efficiency and exciting results on flexible substrates are achieved with spin coating. The results cannot be extrapolated for R2R compatible processing.

10.9 Printing and Coating Methods

Solution-based additive printing and coating methods as well as the use of highly flexible substrates allow high throughput R2R manufacturing. Vapor deposition techniques such as chemical vapor deposition (CVD), sputtering, and evaporation can also be mounted on a R2R set-up. However, vapor-based techniques are generally much slower and more costly compared to solution-based printing and coating methods. Printing speeds of 100–500 m/min can be easily achieved in an industrial-scale R2R set-up using a variety of different printing and coating techniques, although coating methods are generally slower than printing methods.

Printing and coating methods can be distinguished based on their ability to produce patterns. In printing, the motif patterned on a printing form is reproduced on a substrate by transferring ink from the motif to the substrate through physical contact (Figure 10.7). Inkjet printing is a newer printing technique where the printing form is digital and no physical contact is necessary. Printing methods are therefore two-dimensional and complex patterns can be easily achieved. In contrast, film formation with coating methods is achieved with or without physical contact by pouring, spraying, blading, smearing, and brush painting

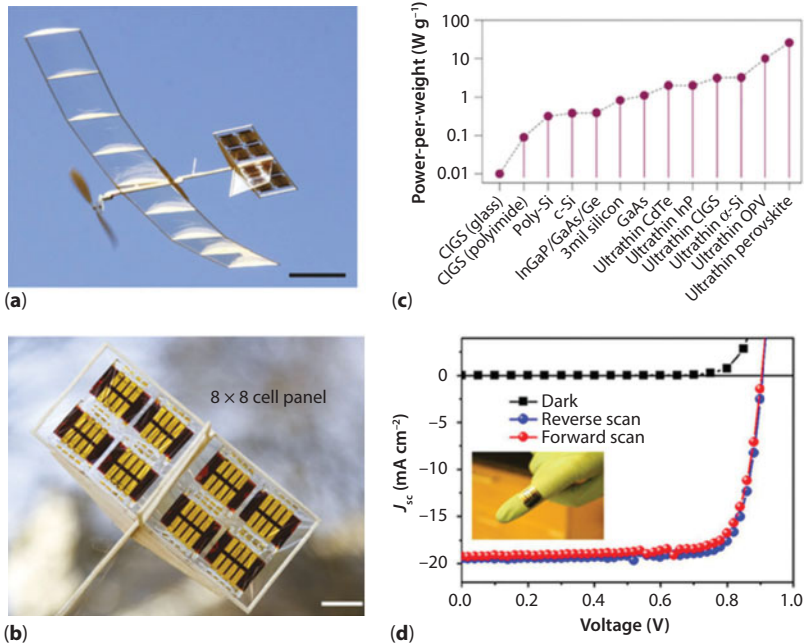


Figure 10.6 (a) Snapshot of a model plane powered by flexible and lightweight ITO-free PeSCs based on PEDOT:PSS as transparent conductor. (b) A close-up picture of the PeSCs integrated in the model plane. (c) Power-to-weight ratio of PeSCs in (a) and (b) is compared with other solar cell technologies (d). J-V curves in reverse and forward scan measured under 1000 cm⁻² AM 1.5 G in yet another ultra-thin perovskite solar cell with an Ag grid/PEDOT:PSS as TCE (inset shows a photograph of the solar cell wrapped around a finger). (Figure 10.6a–c reprinted with permission from [93] and Figure 10.6d reprinted with permission from [94]; Copyright © 2015 Macmillan Publishers Ltd.)

(Figure 10.8) [110]. Hence, coating methods offer no freedom of patterning in themselves. However, limited patterning can be extracted from some coating methods with the use of masks. For example, a flow mask is used in slot-die coating to enable coating of multiple stripes and a shadow mask is used in spray coating to reproduce patterns on the mask. However, only low resolution patterns can be achieved with coating methods by employing masks.

10.9.1 Coating Methods

10.9.1.1 Slot-Die Coating

Slot-die coating involves the controlled supply of ink to a moving web through a slot die head. The slot-die head in turn receives a regulated

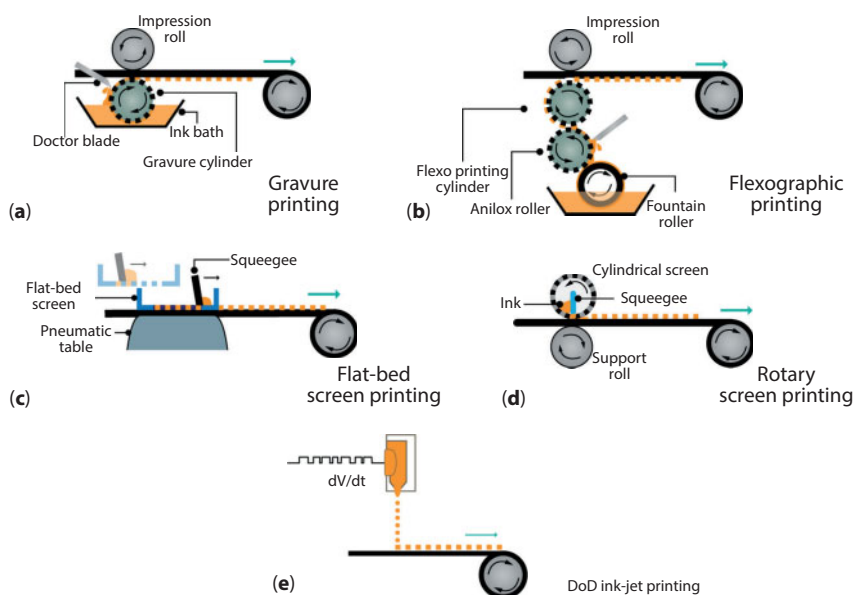


Figure 10.7 Schematic illustrations of selected printing methods.

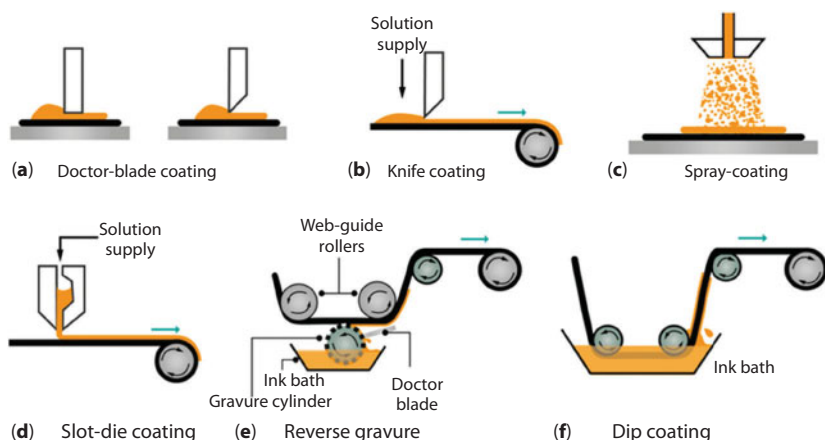


Figure 10.8 Schematic illustrations of selected coating methods.

supply of ink from an ink stock with the use of a pump. A stable meniscus is formed between the slot die head and the web, and a uniform wet film formed as the web moves (Figure 10.8). The slot die head is composed of two halves made from machined metal blocks, which contain a distribution chamber, feed slot, and an up and down stream lip. In between the

two halves sit a flow mask and meniscus guide, which are made from thin sheet metal. The design of the flow-mask and meniscus guide are customized to enable coating in the form of stripes. Thus, the width and number of stripes are predefined with the use of flow-mask and meniscus guide (Figure 10.9). Detailed information on slot-die coating technique can be found in various handbooks on coating [111, 112].

Slot-die coating is a pre-metered technique which means that printed wet-layer thickness is determined by a set of input parameters: flow rate, printed width, and web speed. Additionally, the ink and the surface properties determine maximum thickness achievable. In general, slot-die coating is used to coat inks with viscosity ranging from 1 m Pa·s to above a thousand Pa·s [118]. Low viscosity inks enable fast coating and fast drying. Most inks in PeSCs and organic solar cells have low viscosity. Thicker flow masks are typically

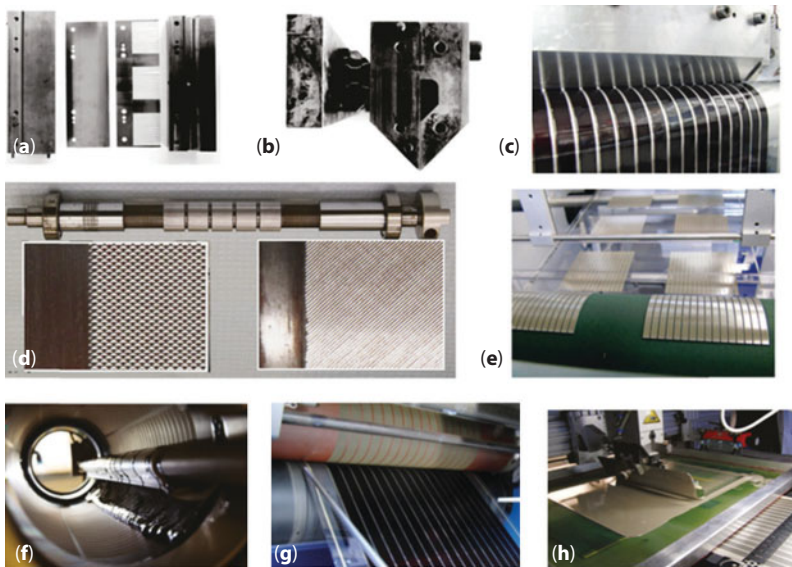


Figure 10.9 (a) A disassembled slot-die head showing meniscus guide (second from left) and flow mask for stripe coating (third from left). (b) Side view of an assembled slot-die head. (c) Slot-die coating of an ink in progress. (d) A gravure printing roll. Insets show the difference in engraving patterns on the printing roll in gravure printing (left) and in reverse gravure (right). (e) Flexographic printing in progress. Relief features on the flexographic printing cylinder can be seen. (f) The inside of rotary screen taken during printing of PEDOT:PSS. (g) Rotary screen printing of silver. View from outside the rotary screen roll. (h) Flat-bed screen printing of Ag in progress. (Copyrights: [a-b] from [113], Copyright © 2014 Technical University of Denmark; [c,g,h] from [114], Copyright © 2015 John Wiley and Sons Inc.; [d] from [115], Copyright © 2016 Elsevier; [e] from [116], Copyright © 2012 Elsevier; [f] from [117], Copyright © 2014 Technical University of Denmark. All figures reprinted with permission)

required for high viscosity inks to avoid clogging the slot. Typically, a 25–50 μm thick flow mask is employed for low viscous inks in organic solar cells, whereas a 100 μm thick mask was found essential to coat 200 mPa.S viscous PEDOT:PSS [118]. A wet layer thickness of 70 μm , which corresponded to a dry layer thickness of 20 μm of PEDOT:PSS, was successfully accomplished with slot-die coating [119]. In PeSCs, the theoretically optimum absorber layer thickness for maximum absorption is above a micron (2 μm for $\text{CH}_3\text{NH}_3\text{PbI}_3$). However, the optimum layer thickness for maximum efficiency is an optimization between maximizing absorption and minimizing recombination coupled with other practical matters. Recombination rates can be minimized when the layer thickness is below the charge carrier diffusion lengths which is ~ 100 nm for the triiodide and ~ 1 μm for mixed halide variants. Practically, however, layer thicknesses below 100 nm result in poorly functioning cells due to the challenges with pin-holes and layer inhomogeneity. As such, a layer thickness between 300–500 nm is pursued for MAPbI_3 and mixed halide perovskites [11, 120]. This thickness range could be easily achieved using slot-die coating by optimizing the solution composition and the slot-die coating parameters.

In contrast to spin-coating, slot-die coating incurs no loss of materials as all the ink/solution supplied to the head becomes part of the final film. Slot-die coating is, however, limited for patterning purposes. It is a one-dimensional method and patterning is only possible in the form of stripes, where the width and the number of stripes are determined by the design of the flow mask and of the meniscus guide (Figure 10.8). Slot-die coating is the most facile and scalable method. The only difference in going from laboratory to industrial production is the size of the slot-die head.

To date, slot-die coating has rarely been investigated in PeSCs [74, 75, 121]. A lab-scale low-cost 3D printer was transformed into a slot-die coater by Vak *et al.* and was investigated as a facile lab method to fabricate organic PeSCs [121]. Initially, only the PbI_2 layer was slot-die-coated while the remaining layers were fabricated by other methods: MAI was dip-coated, P3HT as HSL was spin-coated and electrode was evaporated. The resulting performance was above 11%. In a subsequent study by the same group, all layers except the electrodes were slot-die-coated. The coating conditions for PbI_2 were optimized to achieve optimal microstructure that could lead to complete permeation of the MAI into the PbI_2 film enabling complete conversion into perovskite. The best 12% efficiency was achieved by storing the PbI_2 film in an enclosed space and then using a N_2 quenching step immediately after coating of MAI on-to the PbI_2 layer [74]. These reports demonstrate the applicability of slot-die coating in printing of perovskite. However, glass was used as a substrate and as such the result does not set a benchmark for industrial feasibility.

The scalability of both the one-step and two-step was investigated in a subsequent study [75]. Additionally, the impact of spin coating versus slot-die coating and the impact of flexible PET substrate versus glass substrate were also highlighted. Cells via one-step and two-step process were fabricated using slot-die coating of all layers except the back electrode, which was screen printed. Both one-step and two-step processed cells on glass substrate using spin coating and with printed electrode resulted in similar efficiency (albeit significantly lower than evaporated electrodes), the efficiency dramatically decreased for both processes when slot-die coating and flexible substrate were employed. Post-analysis showed that flexible substrate and slot-die coating method led to dramatically different absorber morphologies, as evident in the AFM images (Figure 10.10) [75]. This study especially highlighted that spin coating is not a scalable technique for PeSCs and the results obtained with spin coating cannot be

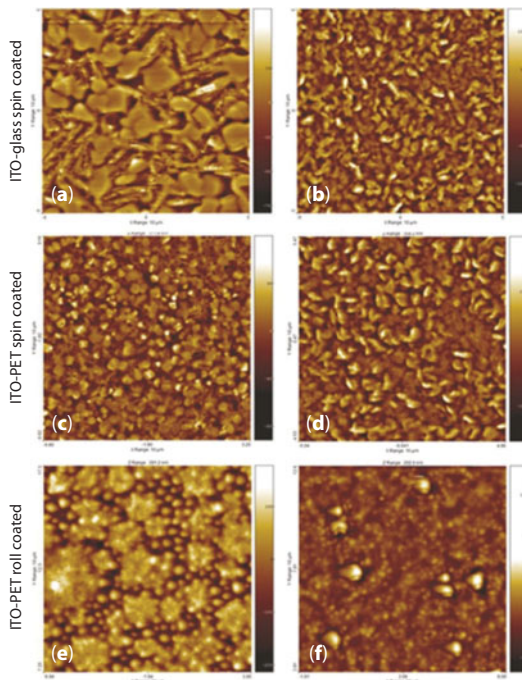


Figure 10.10 Influence of substrate and coating method on the perovskite absorber morphology processed from one-step and two-step methods. One-step process: (a) spin-coated on glass/ITO/PEDOT:PSS, (c) spin-coated on PET/ITO/PEDOT:PSS, (e) slot-die-coated on PET/ITO/PEDOT:PSS. Two-step process: (b) spin-coated on glass/ITO/ZnO, (d) spin-coated on PET/ITO/ZnO substrate, (f) slot-die-coated on PET/ITO/ZnO. (Reprinted with permission from [75]; Copyright © 2015 John Wiley and Sons Inc.)

reproduced with the industrially relevant methods because of the different dynamics dictating film formation. The cell efficiency in this study was lower compared to the ~12% in a corresponding two-step process previously reported [74]. This can be attributed to three main differences: the lack of accurate optimizing of PbI_2 film as N_2 quenching and enclosed storage was not carried out, the use of flexible substrate, and the use of screen-printed electrode in this study.

10.9.1.2 *Spray Coating*

Spray coating involves spray application of the aerosols to a substrate (Figure 10.8). The name is a misnomer as a continuous wet film coating is not generated upon coating. Film formation is a multistep process in spray coating which involves atomization of liquid solution or mixture, droplet flight and evaporation, droplet impact on the substrate, droplet spreading, receding, recoiling, drying, solute adhesion and bonding to itself and to the substrate [122]. Spray coating is differentiated by the method involved in the atomization for solution-based coating. There are numerous advanced spray-coating methods, including thermal spray, plasma jet, flame spray, arc discharge spray, flame, etc., but these methods are mostly used with solid materials. Some of these methods are also used in the deposition of other inorganic optoelectronic materials [123]. For PeSCs purposes, the preferred spray-coating method is one that is compatible with solution processing without the need for high temperature or low pressure to create atomization. Nozzle-based and ultrasonic nozzle-less solution spray coating are employed in the fabrication of PeSCs. Wet-layer thickness is determined by rate of ink feed (speed of spraying), opening of the nozzle in the case of nozzle-based spray coating or the area of piezoelectric head in the case of nozzle-less ultrasonic coating, consistency of the coating, and the percentage of volatile material in the solution [124].

Spray coating has been employed in both traditional planar structure and inverted planar structure. In traditional planar structure, spray pyrolysis is a common approach to deposit the compact TiO_2 film [28, 125–127]. In this method, spray coating of TiO_2 precursor is carried out in conjunction with a substrate maintained at high temperature. The temperature of the substrate, generally at 400–500 °C, is needed to ensure decomposition of organic compounds in the precursor solution into volatile gases. It is quite clear that such a deposition method is not suitable for low-cost scaling up of PeSCs and the advances made in ESL that require no annealing makes such an approach redundant in the future of PeSCs [81]. Recently, a compact

TiO_2 was used as ESL layer on flexible PET substrate. Instead of high-temperature sintering, which was incompatible with the flexible substrate, a photonic curing of the spin-coated TiO_2 was successfully carried out [128]. Photonic sintering is R2R compatible and has been previously used for printed Ag nanoparticle on flexible substrate as well as for thermocleavable absorber layer based on conjugated polymers that require high-temperature steps [129–132]. Thus, TiO_2 can be employed on flexible substrates if need be with the use of photonic sintering. This was employed in the fabrication of PeSCs with a spray-coated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ absorber layer on a flexible substrate via the one-step process. Devices with 6.5 mm^2 area gave 8.1% efficiency, but exhibited large hysteresis with the efficiency reduced to 6.9% in opposite IV scan direction. In contrast, corresponding spray-coated PeSCs on glass substrate in which TiO_2 was thermally annealed at 500°C showed above 11% efficiency in both scan directions with negligible hysteresis.

In a contrasting report, both one-step and two-step processes were investigated with the use of spray coating using a commercial airbrush. Instead of TiO_2 , this report employed ZnO. The film quality of perovskite layer was observed to be very poor in one-step method due to the fast kinetics of crystallization and the slow coalescing of spray-coated droplets which resulted in pin-holes. The sequential, 2 step process was also attempted but led to a defective, non-uniform PbI_2 film. To overcome this, slot-die coating was used to deposit the PbI_2 followed by spray coating of MAI. This formed a good quality 500 nm perovskite film, and a device efficiency of 7.5% on glass was achieved [68].

Other reports have employed spray coating in inverted planar structure. A simple spray-coating set-up consisting of an airbrush pen, an air compressor, and a hot plate was employed to deposit continuous perovskite films on spin-coated PEDOT:PSS HSL under a N_2 environment. A cell efficiency of 10.20% was achieved on a 10 mm^2 area. However, the efficiency was dramatically reduced to 6.88% and 4.66% on scaling-up the area to 60 mm^2 and 342 mm^2 , respectively, highlighting the challenges in film quality control using spray coating and with perovskite materials [133].

A major obstacle in achieving high-efficiency PeSCs via any technique is the processing under ambient conditions due to the rapid degradation of the perovskite film. In small laboratory devices using spray coating, this issue is circumvented by coating in a glove box. However, processing in a glovebox is not scalable nor economical. Therefore, efforts have been dedicated towards processing of PeSCs under ambient conditions. Nozzle-less ultrasonic spray coating has been used to generate uniform perovskite

films fabricated from one-step method. In this method, ultrafine aerosol is generated upon contact of the spray solution with an ultrasonic vibrating tip which is made of a piezoelectric element (Figure 10.11). Efficiency up to 13% has been reported using this method for deposition of perovskite while other layers are processed under a combination of ambient, glove-box, and vacuum conditions [37, 128, 133, 134]. Similarly, a combinatorial ultrasonic spray-coating method was employed in fabricating $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer from a combination of Pb-containing precursors (PbAc_2 , PbI_2 , and PbCl_2) with $\text{CH}_3\text{NH}_3\text{I}$ [135]. In this method, these precursor solutions from two different sources were pumped and mixed in the spray nozzle prior to aerosolization. Such a method proved to be a facile route for optimizing various parameters while enabling full surface coverage with negligible pinhole density, thus leading to an efficiency of 15.7% for small-scale devices and 11.7% for 3.8 cm^2 cells.

In most instances, spray coating has been used to deposit just one of the device layer (Table 10.1) [30, 137, 138]. A recent study reported the fabrication of inverted PeSCs where all but the electrodes were spray-coated using an ultrasonic spray coater. An average efficiency of 7.1% with a peak

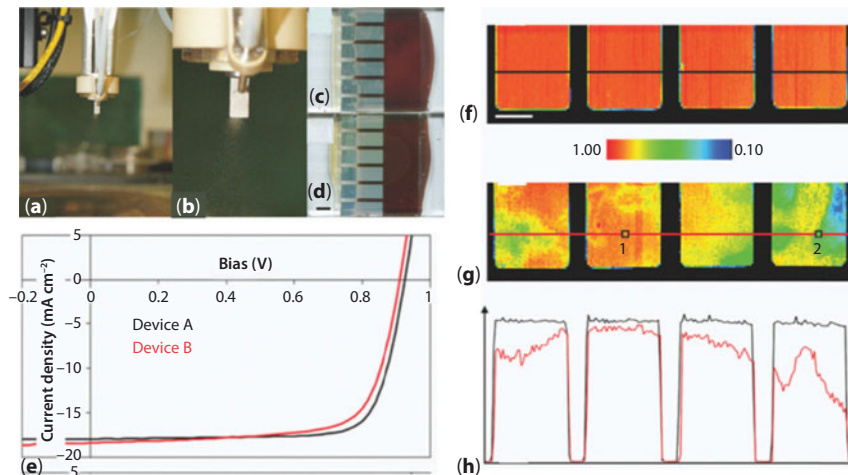


Figure 10.11 Nozzle-less ultrasonic spray coating is compared with spin coating. (a) Photographs of the spray-coating head under operation and (b) a close up, (c) spray-coated cell and (d) spin-coated cell (scale-bar inset is 2 mm), ϵ J-V curve of spin-coated (Device A) and all spray-coated cell (Device B). (f) Laser beam-induced current (LBIC) mapping of: (f) spin-coated cells and (g) of spray-coated cells. (h) The line profile of the current along the scan direction shown in Figure (f–g). (Reprinted with permission from [136]; Copyright © 2016 John Wiley & Sons)

efficiency of ~10% was achieved. In contrast, similar devices using spin coating led to a 12.1% average efficiency and 12.8% peak efficiency on a 4 mm² area. The lower efficiency for spray-cast cells in comparison to spin-coated cells was attributed to the reduced film uniformity and lower surface coverage of the perovskite film [136] (Figure 10.11). In comparison, similar cells with slot-die coating of all but the electrode layer under ambient conditions resulted in a maximum efficiency of 12% on a 10 mm² area, which appears to be the highest for any large-scale compatible processing technique [74].

The motivation for pursuing spray coating in PeSCs is to demonstrate scalable processing of PeSCs. While the intention is good, the method is misguided. Although spray-coating is a R2R compatible method, it is impractical for fabrication of multilayer structures in a continuous R2R processing for large-scale production of PeSC modules. Spray coating is a zero-dimensional technique and patterning is not possible. The use of masks may enable patterning, however, resolution will be extremely limited. It may provide useful in monolithic cells where the cell designs are not intricate. However, large-area PeSC modules are comprised of *in-situ* interconnected cells which in themselves are a multilayer structure. The cells which are in the shape of long stripes are generally separated by a distance of 1–2 mm before interconnection. Certain layers in the multilayer cell require narrow and precise offset with respect to the underlying layer. This requirement for fine patterning laterally as well as across the multilayers of each cell is a very challenging task with the use of spray coating, albeit not impossible [139]. However, it will be extremely throughput limiting and will most likely lead to poor technical yield. Additionally, masking would incur high material wastage. Alternatively, spray-coating may prove useful in subtractive R2R production where patterning is achieved through elimination by laser-structuring.

10.9.1.3 Doctor Blade Coating

Doctor blade coating is a spreading technique in which a suitable amount of ink is placed on a substrate. A blade is positioned over the substrate at a set gap width from the substrate. The height of the blade is adjustable so that the width of the gap is set to the desired film thickness. The blade is then moved past the standing ink leaving a sheared trail of a uniform film (Figure 10.8). The wet film is not necessarily the gap width between the substrate and the blade for low-viscosity solutions and may depend on many factors, including the ink properties, the coating conditions, as well as the shape of the blade. The film thickness approaches half of the gap

width for a rectangular blade whereas the film thickness approaches full gap width in bevelled blade (Figure 10.8) [124].

Doctor-blade is most suitable for coating over rigid substrates such as glass. In fact, it is the primary manufacturing method for ceramics for building materials. While potentially useful with flexible substrates when used in conjunction with a pneumatic table to position them, such a set-up could be throughput limiting.

Doctor blade coating has been used to deposit all the various, including photo active layer, ESL, HSL, and Ag electrodes, in organic solar cells [116]. In PeSCs, doctor blading has been used in combination with other deposition methods to achieve high efficiency cells. For example, PEDOT:PSS, TiO_2 and perovskite layers were fabricated by doctor blade coating while the other layers were spin-coated to achieve efficiency as high as $\sim 17\%$ [140–145]. In one instance, complete PeSCs, except for the Ag electrode, were fabricated with doctor blade under ambient conditions and an efficiency of 10.71% was achieved with good reproducibility on glass and 7.52% on flexible substrate [145]. This is in the same range as similar devices with mixed halide absorber layer fabricated under ambient conditions using spray coating. In another significant study, the surface coverage problem of the perovskite layer on the underlying PEDOT:PSS HSL was overcome by modifying the surface ion density of the HSL and inducing an electrostatic interaction between the perovskite absorber and the HSL. This was achieved by the addition of poly(4-styrenesulfonic acid) (PSSH) in the PEDOT:PSS HSL which induces an electrostatic interaction between the sulfonyl functional groups in PEDOT:PSS and perovskite precursor ions (Figure 10.12). All demonstrations of doctor blade coating thus far are based on the one-step process requiring prolonged annealing steps exceeding 1 hour, which are not ideal for low-cost, fast R2R processing.

The advantages of doctor blade coating include simplicity of the set-up, adaptability to various inks, and R2R compatibility. On the other hand, the disadvantages include lack of edge control and a lack of patterning as only one stripe, albeit of various widths depending on the width of the blade, can be coated at one time. This can be a serious bottleneck in its applicability to doctor blade in large-scale manufacturing as a commercial module is envisioned to comprise of a number of interconnected cells in the shape of stripes. Such a geometry is the most ideal geometry because it minimizes power losses due to high sheet resistance of the transparent electrode [139]. Nevertheless, doctor blade coating can be used for R2R coating ESL layer in the n-i-p structure such as ZnO and TiO_2 over the entire surface of the pre-patterned transparent electrode on a flexible substrate. These metal oxides have low conductivity and do not hamper electrical performance of the

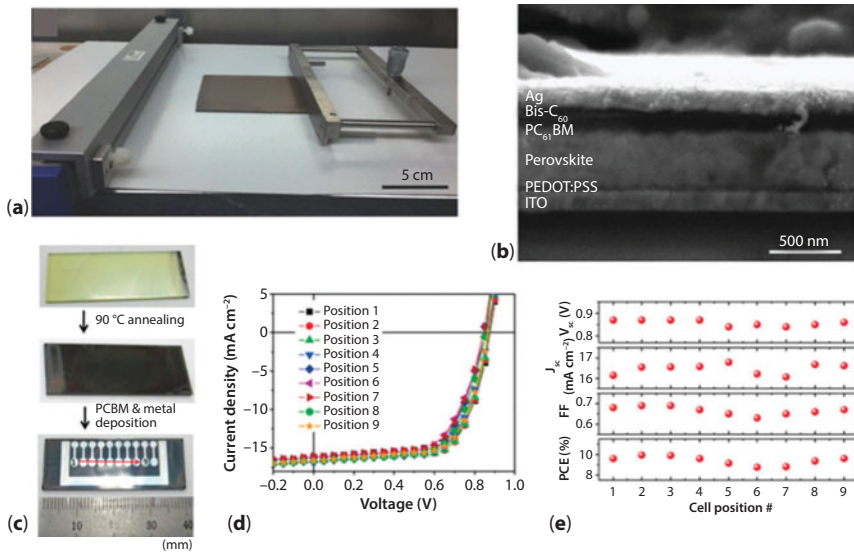


Figure 10.12 (a) Benchtop blade-coating equipment. A blade-coated perovskite film is shown. (b) SEM cross section of an all-doctor-blade-coated PeSC except for the electrodes. (c) Photographs of a blade-coated large-area (15 mm × 40 mm) perovskite film shown before and after thermal annealing process and the completed cells after electrode deposition. (d) J-V curves measured under AM 1.5 irradiation at 100 mW cm⁻² conditions. All the positions correspond to the cells position on a single substrate, as shown in (c). (e) Variation in the photovoltaic parameters as a function of cell position on the substrate which proves excellent film uniformity. These cells were made by modifying the surface ion density of the HSL PEDOT:PSS layer to retard perovskite crystallization. (Copyrights: [a,b] from [145], Copyright © 2015 John Wiley and Sons Inc.; [c-e] from [140], Copyright © 2015 Elsevier. All figures reprinted with permission)

striped cells upon interconnection to form modules. In contrast to doctor blade coating, however, slot-die coating can coat multiple stripes of varying widths with simple modification of the meniscus guide and the flow mask, which can be easily machined at low cost. In addition, slot-die coating has proven to be the most suitable and fastest technique for coating ZnO in organic solar cells with coating speed as high as 10 m/min in a semi-industrial R2R processing line [91, 106].

10.9.1.4 Knife Coating

The technique can be thought of as doctor blade coating made compatible for continuous coating (Figure 10.8). Unlike in doctor blade coating, the knife is stationary coating the web is moves. An ink reservoir supplies a constant supply of ink before the knife which spreads to a film as the web moves. Like doctor blade coating, knife coating cannot create patterns and

therefore is perhaps applicable only to coat metal oxide or other low conductive charge selective layers on top of the transparent conductor on substrate in striped modules. Knife coating of ZnO was used in organic solar cells [118] and resulted in film defects. These defects in the film were most likely caused due to the low viscosity of ZnO combined with its less than 50 nm thickness requirement—which is challenging with knife coating. In contrast, slot-die coating enables fast and facile solution deposition of low viscous ink and is particularly suited for thin film. We have coated 20 nm thin films with ZnO with no difficulties.

10.9.1.5 Reverse Gravure Coating

Reverse gravure coating, also known as micro-gravure coating or kiss coating depending on the roll system, consists of two key components in its simplest form: a reverse gravure cylinder and two web-guide rolls (Figure 10.8). The surface of the reverse gravure cylinder is engraved with micro helical recessed patterns characterized by line density, spiral rib angle and depth of the recesses (Figure 10.9). These patterns can be separated by dead regions to enable coating of multiple stripes at the same time. During coating, the gravure cylinder is partially immersed in an ink bath before coating and any excess ink is removed from the cylinder using a doctor blade immediately before the reverse gravure cylinder is brought in contact with the web. The coating is achieved by bringing the gravure cylinder in contact with the web which is held in uniform tension by two web-guide rolls. The direction of web movement is opposite to the rotational direction of the gravure cylinder, such that coating proceeds by ink pick out from the recesses and a shearing process induced by the movement of the web opposite to the rotational direction of the reverse gravure cylinder. Layer thickness is determined by the ratio of the web speed and the rotational speed of the gravure cylinder. Both parameters can be varied or only web speed can be varied while keeping the gravure speed constant. The characteristics of the engraved patterns on the coating cylinder, which includes line density, spiral angle, and depth of the cells, can be modified to further control film thickness and uniformity. Additionally, varying ink properties can offer an additional parameter for controlling film thickness. Technically, coating speed of several meters per minute is possible but requires fine tuning of the features of the gravure cylinder with respect to the ink to be deposited. Commonly encountered defects include ink splitting at the web separation from the contact roller which can be circumvented by reducing web speed. Additionally, the shearing principle of the method is not ideal for multilayer structure which leads to scratches. This problem has been solved by introducing a non-contact method where

a meniscus is generated between the web and the gravure cylinder. The meniscus is generated by briefly touching the gravure roll with the web and lift-off at the beginning of a coating run, whereafter coating proceeds by the opposite movement of the web and the gravure roll [115].

Recently, reverse gravure was studied in detail in the fabrication of organic solar cells. Three successive layers comprising ZnO|organic active layer|PEDOT:PSS were consecutively coated [146]. Line density on the reverse gravure cylinder was critical to achieve uniform films across the coated width. Once this parameter was optimized, film thickness along the coating direction was rather precisely (± 20 nm) controlled by simply varying the coating speed and web speed. The non-contact meniscus coating approach was adopted for the processing of multilayer in consecutive reverse gravure coating runs. The device performance was similar to another study where the same three layers were slot-die coated in a similar configuration [139]. In a separate study, the shearing nature of the gravure method was exploited to produce highly oriented large-area perovskite nanowire with lengths reaching 15 mm and applied in photodetectors [146].

10.9.2 Printing Methods

10.9.2.1 Gravure Printing

Gravure printing is a fast printing technique that relies on reproducing the image pattern defined on the gravure cylinder onto the web. This printing method is commonly used in high volume production of magazines and catalogues with speeds exceeding 15 m/s. The image pattern is composed of micro volumetric cells engraved on the gravure roll. These cells are uniformly filled with ink as the gravure cylinder is partially immersed in an ink bath, followed by removal of excess ink with the use of a doctor blade. Printing is achieved by bringing the web in contact with the gravure cylinder and the application of nip pressure by the impression roller, which results in ink pick-out (Figure 10.7). Surface tension of the ink is critical for successful ink transfer. Similar to reverse gravure printing, the thickness of the film depends on the characteristics of the engraved cells, the coating parameters, and the ink properties. The engraving parameters, such as cell density, depth, width, screen angle and stylus angle, can be adjusted in order to achieve optimal printing of the ink. Unlike in reverse gravure coating, the web movement is in the same direction of rotation of the gravure cylinder. Another distinction is in the features on the gravure cylinder. Whereas reverse gravure cylinder has a helical line pattern, gravure printing has engraved cells such that dot-by-dot ink transfer takes

place allowing high resolution two-dimensional printing. The differences in the cell pattern on gravure cylinders are shown in Figure 10.9. The third distinction is in the method of bringing the web in contact with the gravure cylinder. In reverse gravure, two web-guide rolls are used, each of which can control the web tension in the coating region, which is separate from the overall tension of the web maintained between the unwinder and rewinder rolls. In gravure coating, the web-guide rolls are absent and instead an impression roller is used. Ideally, gravure printing is suitable for low viscous inks at very high speeds. The print quality is highly dependent on the ink rheology, web speed, and the pressure of the impression cylinder. Printing speed of up to 900 m/min can be achieved but relies on careful optimization of parameters, particularly the surface tension of the ink.

So far, gravure printing has not been reported for PeSCs. However, valuable experiences and lessons can be gathered from the development in gravure printing of various functional layers in other electronic fields. PeSCs share several materials in common with several other fields and the lessons learned from these fields can spearhead the applicability of gravure printing in PeSCs. Gravure printing can print with high resolution, and as such it has been widely reported for printing the fine grid pattern of transistors and other functional materials for printed electronics, including organic light-emitting diode and organic solar cells [147–157]. Typical materials printed using gravure include Ag patterns, PEDOT:PSS and P3HT:PCBM, which have been studied in detail for printability via gravure [152–161]. Fine Ag grid pattern with a line width of 10–20 μm have been accomplished with gravure printing [152, 160].

10.9.2.2 *Flexographic Printing*

Roll-to-roll (R2R) flexographic printing is a fast printing method suited for high resolution two-dimensional printing with high throughput and low material wastage. Like gravure, flexographic printing enables high speed printing of up to 15 m/s (900 m/min) and a resolution down to 10 μm . It differs from gravure printing mainly in the fact that the transfer of the ink is performed by the relief/elevated features on the flexo printing cylinder as opposed to engraved cells in gravure printing (Figures 10.7 and 10.9). A printing plate made of an elastomeric or photopolymer carries the image motif as relief patterns on the surface and is mounted onto the printing cylinder. To achieve uniform layer of ink on the flexo printing roll, ink transfer is achieved from an anilox roller which is made of steel with a finely textured ceramic or chromium surface. The surface of the anilox roller is engraved with micro volumetric cells. A third roller, a fountain

roller, which is partially immersed in the ink bath, is placed in contact with the anilox roller to enable continuous transfer of ink to the anilox roller. Alternatively, the fountain roller can be eliminated and the anilox roller can be directly partially submerged in the ink bath. During printing, the cells in the anilox roller are evenly filled with ink via the chambered doctor blade or the fountain roller. Excess ink in the latter case is scraped off with the doctor blade. The ink from the anilox roller gets transferred to the image relief on the printing plate cylinder whereby only the relief gets inked while the recessed areas remain ink-free. Thus, the anilox roller appears to contain the negative pattern of the image motif on the printing cylinder. Finally, the ink from the printing cylinder is transferred to the web rolling over the impression roller with the use of nip pressure. With web movement in the same direction as the flexo printing cylinder, image from the flexo printing cylinder is continuously reproduced on the rolling web (Figure 10.7).

Like gravure, flexographic printing has been applied to printing narrow Ag grids with line widths below 100 μm to reinforce the conductivity of ITO on PET [162]. It was later adapted in organic solar cells where flexographic printing of conductive Ag grids directly on PET was carried out at a speed of 20 m/min. Higher speeds are possible with longer drying time. By overlying this Ag grid with a rotary screen-printed ZnO and slot-die coated with PEDOT:PSS, a conductive transparent electrode, as ITO replacement, was mass fabricated in a high speed R2R process [91, 106]. When Ag grid forms part of the transparent conductor, photocurrent loss occurs due to shading caused by the Ag grid. High resolution prints with uniform height are desirable for optoelectronic application in general and thin film organic-based solar cells in particular, in which multiple thin films are built upon the transparent conductor layer. To find a printing method to this end, flexographic printing, inkjet printing, and thermal imprinting were compared. Both inkjet and flexographic printing resulted in 100 μm wide Ag grid line whereas 16 μm wide Ag grids were achieved with thermal imprinting. Nonetheless, flexographic printed Ag were processed at 70 m/min whereas thermal imprinting required two process steps with the highest of the two steps enabling 6 m/min throughput [163]. Flexographic printing is also used to print high conductive PEDOT:PSS as the last layer on top of a gravure printed P3HT:PCBM in an organic cell under ambient conditions fabricated on a paper substrate [161]. Additionally, a modified flexographic printing method is employed as a facile lab-scale roll coating of Ag electrode using screen-printable formulations in organic solar cell [164]. Recently, flexographic printing has been explored for printing of multi-busbar contacts in silicon solar cells [165]. From these advances in various fields, it appears

that flexographic printing will prove to be a very useful technique in the printing of many components, including Ag grids as ITO replacement and/or PEDOT:PSS counter electrode, and it may prove equally suitable for high throughput printing of perovskite absorber layer as well.

10.9.2.3 Screen Printing

The screen printing process involves a screen made of a mesh of a woven material made of synthetic fiber or steel held in tension to a frame. The mesh is filled with an emulsion that is impervious to the coating solution (stencil). The image print is achieved on the screen by removing the stencil by a photochemical process using a shadow mask, thus leaving the image area open and permeable to ink. Printing is achieved by forcing the ink through the open areas in the screen by using a squeegee. In this manner, the pattern (print image) on the screen is reproduced onto the substrate. During printing, the screen is placed above the substrate at a certain “snap-off” distance of few millimeters. The diameter and the thread count of the mesh determine the amount of ink deposited on the substrate. Layer thickness is influenced by force of squeegee, screen parameters, the snap-off distance, the speed of squeegee, and rheology of the printing paste. Rotary screen printing can be in flat-bed as well as rotary format (Figure 10.7). The rotary screen printer is suitable for fast throughput large-scale production as the overhead cost is higher than flat-bed screens. Flat-bed screen printers, like doctor blading, require the use of a pneumatic table to position flexible substrate.

Unlike flexographic and gravure printing, screen printing is inherently suitable for printing very thick layers often above 500 nm to several hundred microns. This has been proven to be useful in printing contacts using screen printable formulations of Ag microparticles. The method is used in metallization of silicon solar cells as well as in the printing of front and back electrodes in organic solar cells [115, 139, 166, 167]. Some reports suggest that thin layers up to 40 nm can be achieved by using a steel mesh [167]. With rotary screen printing of Ag and PEDOT:PSS, an infinite number of modules can be interconnected *in situ* whilst processing. This method would prove extremely beneficial for perovskite solar cells if its efficiency can be maintained. This would mean that the installation bottleneck, as experienced in discrete module assemblies of silicon and other solar cells, will be overcome. Installation and balance of system cost (BOS) is a major deterrent to reducing the cost of power in photovoltaics. The BOS cost, including installation, can determine up to 80% of the cost of electricity [168].

10.9.2.4 Inkjet Printing

Inkjet printing is a two-dimensional technique that allows the formation of fine patterns of inks from suspensions or solutions with high resolution up to 1200 dpi and frequency of 100 kHz. It is a well-known printing method in the graphics, textile, and ceramic industries where under demanding conditions, web speed exceeding 10 m min^{-1} is used [169]. It is a non-contact printing method wherein printing is achieved by directing a steady jet of ink droplets to the substrate and the pattern is present in the form of a digital motif. There are three distinct classes of inkjet printing, namely continuous inkjet (CIJ), drop on demand (DOD), and field- or flow-induced tip streaming (FITS) [170]. The DOD inkjet printers are most advanced and are increasingly being applied in processing of functional films, including in solar cells. In DOD inkjet printers, the required amount of ink droplets are generated with the use of piezoelectric or thermal actuators that are located in the ink chambers. In piezoelectric-based systems, an electric signal controls the mechanical deformation of the piezo plate. Upon the application of voltage, the piezoelectric material deforms and sends a pressure pulse to the ink, forcing it out of the nozzles in the form of droplets (Figure 10.7). Each ink requires optimization of the waveform of the applied voltage to form stable droplets. The applied frequency determines the amount of drops released per second and therefore the printing speed.

The main advantage of the DOD system is that the patterns are digital motif patterns which can be altered in the software without incurring overhead cost (other than the designer/operator) whereas all other printing methods require the replacement of the printing form for each desired pattern which can be time-consuming and costly. The freedom of design and high resolution patterning is the main advantage of inkjet printing compared to all other printing methods. Additionally, there is no material wastage. The disadvantages include limited printing speed compared to gravure, flexographic, and rotary screen printing. Additionally, inkjet printing requires intensive ink development to generate stable droplets. Film formation is complex as droplets undergo spreading, receding, recoiling, drying, bonding, etc., which is different for different substrates and inks. Meticulous optimization of the ink properties is critical to achieve successful printing runs in an industrial setting. Nozzle clogging in industrial inkjet, which is comprised of above 500 nozzles, can be a technical nuisance.

Inkjet printing has been employed in deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber via both one-step and two-step processes in either planar or mesoporous structures. A precursor mixture of MAI and PbI_2 dissolved in γ -butyrolactone was inkjet-printed on mesoscopic TiO_2 and a device efficiency of 12.3% with an average value of 11.2% was achieved [171].

Similarly, MAI plus carbon ink mixture was inkjet-printed on as-deposited PbI_2 film to transform spin-coated PbI_2 film to $\text{CH}_3\text{NH}_3\text{PbI}_3$, which led to an interpenetrating seamless interface between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer and the carbon hole-extraction electrode. Cells with a markedly reduced charge recombination were achieved compared to those with the carbon ink alone, with device efficiency of 11% [172]. In another study, a desktop multi-channel inkjet printer was converted as a rapid screening tool for organic cations. By assigning an RGB code on the computer softwear, the compositional ratio of FAI and MAI was controlled *in situ* and deposited on spin-coated PbI_2 film. The precision and control of the method led to greater reproducibility [173].

Inkjet printing has been widely explored in organic solar cell for the printing of PEDOT:PSS [174], Ag grids as ITO replacement [129, 130, 174, 175], Ag back electrodes [97, 98], metal oxides, including ZnO [176], and conjugated polymer such as P3HT:PCBM [177]. In fact, all inkjet-printed devices were successfully shown in laboratory scale [177] and using industrial-scale printheads for large-area cells [169]. The advantage of inkjet printing is the freedom of design it offers compared to all other printing methods which require costly masters each time the pattern is changed. This has been illustrated in an all inkjet printed and functional organic solar cells in the shape of a Christmas tree (Figure 10.13).

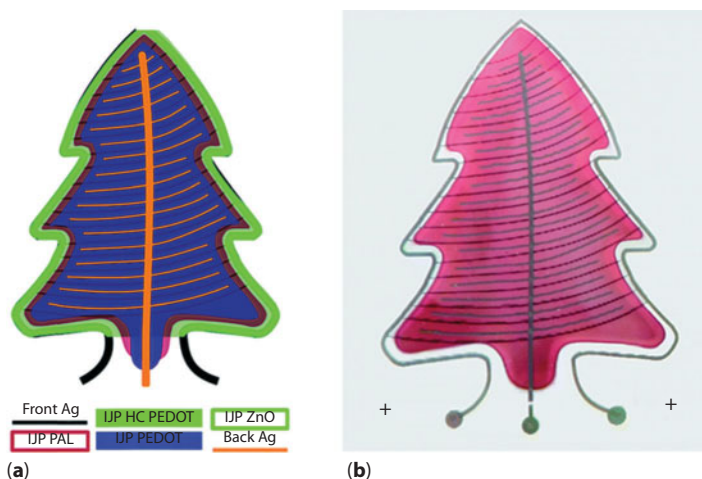


Figure 10.13 Freedom of design offered by inkjet printing and its applicability in printed solar cells. (a) Schematic representation of printed layers lay-out of organic solar cells in the shape of a Christmas tree, (b) a photograph of a fully inkjet printed ITO-free organic solar cell including the electrodes. (Reprinted with permission from [169]; Copyright © 2015 Royal Society of Chemistry)

10.10 Future Outlook

The technology of PeSCs could potentially be a game changer. The efficiencies of these solution-processed thin-film PeSCs are already nearing that of silicon solar cells. Initially, major challenges were faced in the areas of both defect-free film formation and stability. Research to date has thus primarily focused on increasing efficiency and achieving reproducibility. Numerous solutions to improving film quality and eliminating film defects have enabled better layer uniformity and increased reproducibility. However, the universal use of spin coating in research may limit the implication of these results in industrially relevant processing in the future factory of PeSCs.

The future factory of PeSCs will be a dramatic shift from the current factories of silicon or inorganic thin-film solar cells to a low-cost and extremely high throughput industrial process. R2R processing on flexible substrates and the deposition of all layers via ambient printing and coating methods will catapult PeSCs toward commercial feasibility. Materials and device configurations currently being developed on a laboratory scale, are geared toward such a production scheme and are delivering promising outcomes. However, the translation from research-scale to industrial-scale production is hampered by the use of spin coating as the primary laboratory film deposition method. The findings based on spin-coated films may not be applicable in an industrial setting as film formation dynamics in the R2R printing and coating methods are completely different from spin coating. This is evident in the large gap in record efficiency between spin-coated cells (above 20%) and those employing one or more scalable printing method (12–13%) (Table 10.1). Thus, spin coating should be replaced with scalable deposition methods, many of which are available in cost-effective and easy-to-operate benchtop variants, to bridge the divide between research and industry.

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Inkjet Printable Processes for Dye-Sensitized and Perovskite Solar Cells and Modules Based on Advanced Nanocomposite Materials

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Abstract

The application of new materials on conductive substrates and possible commercialization of new types of solar cells, such as dye-sensitized and perovskite solar cells, have created an urgent need for new methods of deposition with priorities in the uniformity of the films and cost-effectiveness. Inkjet printing is considered a low-cost technology which may reduce raw material waste by nearly 90%. Instead of depositing chemical compounds on conductive substrates with conventional methods, inkjet printing could succeed in precise patterning with very limited waste of material, ultimately being a very low-cost way of producing solar energy cells. In this chapter, we will discuss the case of printed third-generation photovoltaic cells, mainly dye-sensitized and perovskite solar cells. In particular, we will describe the inkjet printing process in detail for all fabrication steps of dye-sensitized and perovskite solar cells and also present the structural properties of all materials deposited by this method. Finally, comparisons with conventional methods of material deposition will be discussed as well.

Keywords: Inkjet printing, dye-sensitized solar cells, perovskite solar cells, nanocrystalline materials, highly porous TiO₂, nanocomposite ink

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11.1 Introduction

Dye-sensitized solar cells (DSSCs) have attracted substantial interest as a low-cost alternative to conventional silicon-based solar cells owing to the simplicity of their fabrication procedures, practically under ambient conditions with mild chemical processes [1]. Their overall efficiency ~12% (for laboratory small-size cells) has placed DSSCs as potential inexpensive alternatives to solid-state devices. Alternatively, organometal halide perovskite, $\text{CH}_3\text{NH}_3\text{PbX}_3$, where X is a halogen atom (I, Cl, Br, or a combination of some of them) with polycrystalline structure, has been recently proposed as an alternative light-harvesting material for photovoltaic applications with promising results and obvious improvements to the DSSCs [2]. The overall conversion efficiency of these perovskite solar cells (PSCs) has been increased from 4% to almost 20% in only five years from their first demonstration. Both DSSCs and PSCs are placed in the category of third-generation photovoltaics where new trends and materials in photovoltaic technology are applied. Third-generation solar cells are based on nanostructured (mesoscopic) semiconductors and they are made of purely organic or a mixture of organic and inorganic components, thus allowing a vast and inexhaustible choice of materials. Because of their mesoscopic character, it is possible to make transparent solar cells which can be used as photovoltaic windows, while most of their components can be easily printed on glass using the inkjet printing process [3].

11.1.1 Dye-Sensitized Solar Cells

In conventional silicon-based photovoltaic cells, the perfect electric contact between two areas of different doped silicon with different Fermi levels is necessary. At least one of these materials must be excited by absorption of photons. This creates an electric potential step across the interface of the two materials. When a material is excited by absorption of photons, electron-hole pairs are generated. Under the influence of the potential step, the oppositely charged photogenerated species are forced to move in opposite directions. Thus, the charge carriers are separated and the photon energy is converted into electrical energy. In this case, the creation of electrons happens in the same material, while the biggest problem with the conventional approach is ultimately the cost, as extra pure materials are required. Silicon solar cells require a relatively thick layer of doped silicon in order to have reasonable photon capture rates but silicon processing is expensive. Third-generation mesoscopic solar cells are usually composed of nanostructured materials, while electron creation and diffusion happen in

different materials within the cell. Depending on the nature of these materials, we can divide third-generation mesoscopic solar cells into two major categories: purely organic solar cells and organic/inorganic solar cells, such as dye-sensitized solar cells, which finally exhibit the highest efficiency and longest stability. Indeed, the current world record for efficiency in this category, represented by the leading technology of dye-sensitized solar cells (DSSC), is $>12\%$ (versus about 9% for organic solar cells) and is theoretically put above 30% . In the case of DSSCs, one of the two active components is a nanostructured semiconductive transition metal oxide, typically, titanium dioxide (TiO_2), which is made of earth abundant elements and is the most stable, relatively nontoxic and easily fabricated nanostructured semiconductor. The second active material depends on each particular case, as will be later explained. However, in the most common cases, it is a liquid, dissolving a redox electrolyte with appropriate redox potential (electrochemical potential). Because most applicable wide-band-gap oxide semiconductors do not absorb visible light, the presence of a third component is necessary, that is, a sensitizer that absorbs visible light and injects the photogenerated electron into the conduction band of the oxide semiconductor.

For this function to be effective, the LUMO level (i.e., the lowest excitation level) of the sensitizer must be favorably located, i.e., higher (more electronegative) than the conduction band level of the semiconductor. These basic limitations set the fundamental principles of DSSC operation. For better understanding of these principles, the cell structure and operation diagram, along with a module, can be realized with DSSC stripes, as shown in Figure 11.1. The coexistence of different materials and the

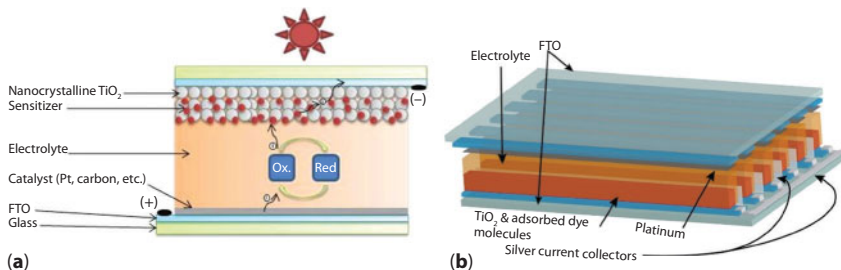


Figure 11.1 (a) Scheme of a DSSC: Photons are absorbed by the photosensitizer (S^0/S) (red spots). Excited electrons are injected (S^+/S^*) into the lower-lying conduction band of TiO_2 (grey cycles) and they are carried by means of the anode electrode (SnO_2 ; F, FTO glass) and the external circuit to the platinum functionalized cathode. Eventually, they are exchanged with the redox couple (I^-/I_3^-) which regenerates the oxidized sensitizer (S^+/S). (b) Scheme of a DSSC module with the presence of metal fingers to collect photogenerated electrons from each solar stripe.

necessity of a combination of energy levels limit the choice of materials applicable to the construction of DSSCs. Thus, among the oxides which have so far been used, only TiO_2 and ZnO , both with about the same energy band gap (3.2 eV) and of about the same conduction band level (-4.2 eV), have given DSSCs with acceptable efficiency and stability. Also, among all studied inorganic redox couples, only I^-/I_3^- has the appropriate redox level (about -4.8 eV) to be combined with the above oxides and the sensitizers employed so far. On the contrary, many more choices exist for sensitizers themselves, which can be organic dyes, organometallic complexes or even low-band-gap semiconductors such as CdS , CdSe and $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$. The nanostructured metal oxide is the acceptor and the conductor of the photogenerated electrons, as seen in Figure 11.1. The functionality of this basic cell component necessitates the coexistence of the following characteristics. It must be n-type semiconductor with well-defined conduction band level so as to accept and lead electrons to the anode electrode. The latter is usually made of a glass substrate bearing a transparent conductive fluorine doped- SnO_2 (FTO) layer or indium-tin-oxide (ITO) layer. It must be stable and must not be irreversibly oxidized during cell operation; it must be nanostructured so as to develop large specific surface area and its nanostructure must be such that the large active interface must not evolve at the expense of electric conductivity. The aforementioned TiO_2 and ZnO semiconductors can be synthesized and deposited in a variety of nanostructures, like nanoparticles, nanotubes, nanowires, etc. Nanotubes and nanowires ensure very large specific surface area and, because of their single-dimensional character, they provide conditions for better electron-hole separation. At the same time, the high probability of surface defects introduces more sites of electron-hole recombination. On the other hand, nanoparticles form percolation clusters and allow dense packing, thus securing several channels of electron conduction. The counter electrode (cathode) of a DSSC may also be made of a second transparent conductive electrode as the anode electrode, if making transparent or back-face excited cells is desired. If this is not necessary, carbon electrodes may have been employed. Some researchers have, for example, employed monolithic porous carbon electrodes and the liquid electrolyte was introduced through the pores of this back electrode. Electrodes and electrolytes do not form ohmic contacts. In order to facilitate transfer of electrons from the external circuit to the electrolyte an electrocatalyst must be deposited on the counter electrode. Even though platinum nanoparticles are repeatedly demonstrated to be the best electrocatalysts, their cost and scarcity make the search for other materials a valuable field of research [4]. Operation of a solar cell in a cyclic manner necessitates the transfer of holes from the

photoexcited sensitizer to the counter electrode, i.e., the cathode of the cell. Therefore, it is necessary to eliminate the remaining hole, otherwise it will oxidize the sensitizer. The transfer of holes is secured by the second major component of the cell, i.e., the electrolyte, which, according to its chemical structure, distinguishes DSSCs into the following major categories. In the first and so far most studied category belong cells bearing a liquid electrolyte composed of an organic solvent dissolving the I^-/I_3^- redox couple, which is made of an iodide salt and iodine. Since the iodide salt is hydrophilic but iodine is hydrophobic, it is necessary to employ appropriate systems that effectively accommodate both these redox reagents. Recent findings support organic iodide salts (ionic liquids), which are not only soluble in a large temperature range, but can also play the role of solvent themselves [5]. Many ionic liquids have very low volatility. Therefore, they better fit conditions where sealing problems arise, thus helping to prolong cell life. The second category of DSSCs employs a solid or a quasi-solid electrolyte [6]. This category is similar to the first one. Use of liquid electrolytes creates sealing problems, especially under high-temperature conditions. Therefore, researchers have devised electrolytes with lower sealing demands. Finally, the third category involves cells where the electrolyte is substituted by a hole-conducting conjugated polymer [7]. These interesting systems, known as hybrid solar cells, make completely solid-state constructions characterized by some advantages and some disadvantages. The employment of conjugated polymers in the construction of solar cells simplifies fabrication procedure, decreases cost, and allows construction of large area cells on flexible substrates, decreases weight and leads to novel architectural designs [8]. However, the efficiency of such cells is much lower than that of the liquid DSSCs, since hole conductivity is lower than ionic conductivity and since mixing of metal oxides with organic conjugated polymers is difficult, thus active interface is in that case limited.

11.1.2 Perovskite Solar Cells

In the last five years, organic/inorganic perovskites as new semiconducting materials replacing the dyes in DSSCs have boosted their cell efficiency from 5% up to 21% nowadays, much faster than any other photovoltaic technology [9]. This record makes the photovoltaic technology based on perovskites likely closer to the 26% performance of laboratory silicon cells, however, at an expected much lower cost. Besides, due to a foreseen increase in global energy usage, there is an emergency need to develop high efficiency solar cells in a cost-effective way. Unfortunately, DSSCs started with power conversion efficiency (PCE) of around 8% which was

improved to 12% using liquid electrolytes, but this threshold seems to have held constant for many years. However, the volatile character of the liquid electrolyte causes potential problems on sealing the device, especially at large scale where the stability of the cells is rather poor. For that reason, around 2010 several groups developed a solid-state solar cell with overall efficiency of 5% based on Sb_2S_3 inorganic sensitizer and organic hole conductors [10]. These activities took a major leap in 2012 when a lead halide perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$, was proposed, emerging as a light harvester in solid-state devices after the first presentation of the material in 2009 [11]. In particular, organometal halide perovskite material with the general formula of $\text{CH}_3\text{NH}_3\text{PbX}_3$, with polycrystalline structure, has been proposed as an alternative light-harvesting material for photovoltaic applications with promising results and obvious improvements to the third-generation solid-state photovoltaic cells. Organometal halide perovskite materials are direct band gap semiconductors with a nearly ideal band gap for solar radiation on the surface of the earth of around 1.55 eV and high absorption extinction coefficient [12]. Indeed, these organo-halide perovskites exhibit very high efficiency mainly due to their excellent optical properties, ambipolar charge transport and, finally, the very long and balanced electron-hole diffusion lengths. So far there are two structures that are most commonly implemented. The first one, which is of perovskite solar cell (PSC) consists of transparent conducting oxide (TCO)/very thin compact TiO_2 layer/a few hundred nanometer thick TiO_2 or alumina mesoporous scaffold/perovskite/hole-transporting layer (HTL)/evaporated metal [13]. The second one, which is commonly referred to as planar structure, consists of metal/hole-transporting layer (HTL)/perovskite/electron-transporting layer (ETL)/transparent conducting oxide (TCO), as perovskite materials can also act as highly efficient, ambipolar charge conductor [14]. Both structures are presented in Figure 11.2.

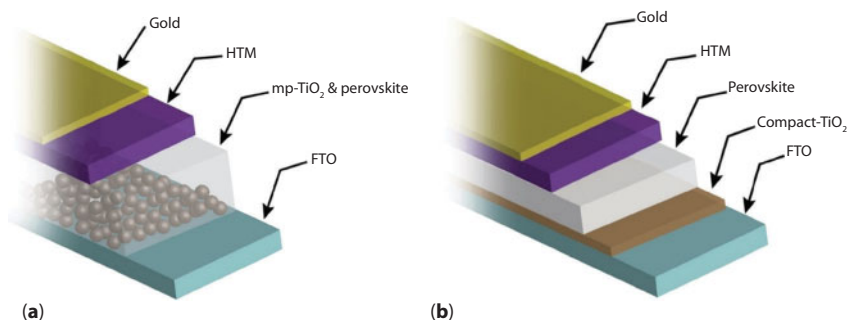


Figure 11.2 (a) Scheme of perovskite solar cell with perovskite growth on mesostructured oxides as scaffold and (b) planar structure of perovskite solar cell.

Devices based on mesoporous TiO_2 are generally fabricated on fluorine-doped tin oxide substrates (FTO) and a high annealing temperature (up to 500 °C) is necessary to form a well-connected nanostructure path for electron transport. In general, mesostructured solar cells with porous TiO_2 are of great interest because of the variety of TiO_2 morphologies and structure control that can be achieved in the presence of organic templates, while the remarkable particle interconnection may guarantee enhanced charge mobilities. Although other oxides as electron collection materials are also applied, TiO_2 is still the material of choice for high efficiency PSCs. However, the key factor towards high efficiency is the control and growth conditions of the materials but mostly the control of the interface between the perovskite and TiO_2 nanoparticles. Among the various deposition methods for the fabrication of PSCs, inkjet printing technology could also be selected for the fabrication of all-printed PSCs because of its capability to locally deposit small volumes of functional inks without a mask and with high positional accuracy and low cost. Inkjet printing has proven to be effective in fabrication of this type of solar cell, where the deposited materials exhibited similar nanoscale structure and excited state dynamics to spin-coated layers [15]. Besides, inkjet printing is an attractive digital printing technology for cost-effective, environmentally friendly integration of photovoltaic cells onto plastic substrates [16]. Finally, these printed solar harvesting devices could allow full integration into the manufacturing process of portable flexible electronic systems.

11.2 Inkjet Printing Process

In general, inkjet printing is a non-contact printing process with much higher resolution than commonly used in third-generation photovoltaic technology screen printing methods. Inkjet printheads are usually drop-on-demand dispensing devices with high accuracy. Inkjet printer nozzles of commercial products that are on the market are usually made of ceramic materials, which offer excellent corrosion resistance against organic solvents that are used in such kind of deposition materials and this type of solar cells. Common benchtop materials deposition systems are designed for micro-precision jetting of a variety of functional fluids onto any surface, including plastic, glass, ceramics and silicon, as well as flexible substrates from membranes, gels, and thin films to paper products. By employing usually inexpensive exchangeable cartridges, which researchers can fill with fluid materials prepared in laboratories, the inkjet printer system minimizes waste of sometimes expensive fluid materials, thereby eliminating the cost and complexity associated with traditional product

development and prototype fabrication. The cartridge is designed for high-resolution, non-contact jetting of functional fluids in a broad range of applications. Inkjet technology with Shaped Piezo Silicon MEMS fabrication process is used for depositing picoliter-sized droplets of functional fluids on all types of surfaces [17]. In general, the ink compositions used in these devices must meet various requirements concerning viscosity, surface tension, solubility, wettability of the substrate and rapid drying. For this reason, appropriate additives are added in to optimize droplet formation. The disadvantage of inkjet printing in most benchtop devices is probably the rather slow printing speed. This can be improved in much more expensive industrial-type inkjet printers where the number of nozzles is one hundred times larger. Thus, it is certain that inkjet printing could play an important role in large-scale production of organic/inorganic solar cells such as DSSCs and PSCs. Nevertheless, the high printing resolution enables inkjet printing to prepare complex patterned films.

11.2.1 Inkjet Printing in DSSC Technology

Nowadays, screen printing is the most common technique for applying most of the materials employed in a dye-sensitized solar cell. Namely, TiO_2 and platinum are both materials that are applied with screen printing technique even in long stripes of each material. For that purpose, a mesh is used to transfer the material onto the conductive substrate, except for some areas made impermeable to the ink by using blocking stencil. Then a squeegee is moved across the screen to fill the open mesh apertures with the material which is finally formed on the substrate [18]. For that purpose, special prepared pastes of the materials are used and the final film is achieved with only one pass of the squeegee. However, the major disadvantage of this method is the limited flexibility in patterning and the high amount of material waste, which is a serious drawback, especially in the case of expensive materials. Alternatively, the inkjet printing process could overcome the previous limitations, as it is easier to obtain freedom of design and succeed in the material's limited consumption, which is very important when the technology is transferred to production scale (Figure 11.3). In particular, to obtain full freedom of design, most of the functional layers need to be inkjet-printed without affecting the solar cells' performance. However, to move from lab-scale inkjet printing equipment (equipped for instance with 16 printing nozzles) towards industrial print-heads, allowing for instance the use of at least 1024 nozzles, substantial reoptimization in printing parameters, inks and substrate properties is required (Figure 11.4). The quality of jetting is determined by solid content



Figure 11.3 Freedom of patterning in DSSC technology by inkjet printing selective components.

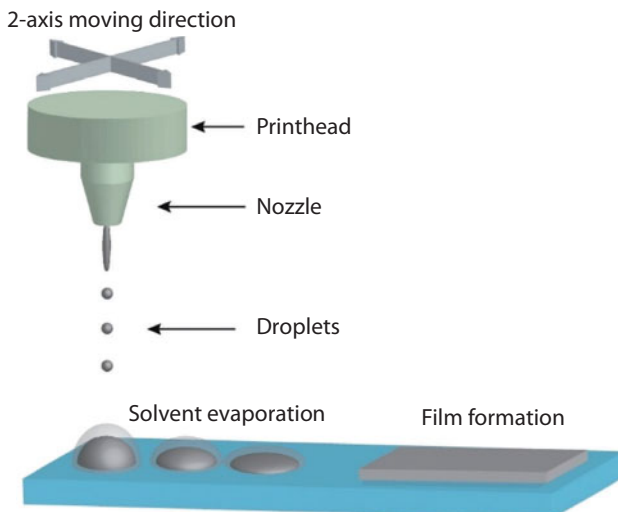


Figure 11.4 Procedure of film formation using inkjet printing technology.

and solvent composition in preparing the ink, viscosity, surface tension and vapor pressure of the ink prepared each time. Besides, the surface energy, the moisture of ambient air and the temperature of the substrate play an important role in most cases of fabricating a functional solar cell. Additionally, modifying the individual ejected droplets is also affected by the purpose for which the printhead was initially designed. When the drop size, which can be determined by nozzle diameter and the firing voltage, is 10 microliters for a lab-scale printhead it can be, for instance, three to five times more when an industrial printhead is used [19]. The spacing of the dot pitch determines the amount of deposited ink per surface area and thereby layer thickness and uniformity.

11.2.1.1 Inkjet Printing of Transition Metal Oxides

In DSSC technology the inkjet printing method can also be used as an alternative procedure to screen printing for patterning semiconducting oxide layers on conductive substrates. Common oxides that are used in dye-sensitized solar cells are titanium dioxide, zinc oxide, nickel oxide, tin oxide, etc. In the case of screen printing method, for instance, TiO_2 paste consisting of TiO_2 nanopowder with additives, such as solvent, binder and dispersants, is applied on the substrates by a squeegee to form a homogeneous layer usually a few micrometers in thickness. In order to be patterned, a mesh is used which raises obvious limitations to the variation of the desired shapes of TiO_2 films. However, in the case of large-scale applications the formulation of the paste is very important to get homogeneous crack-free films with the same thickness in the whole length of each stripe for making functional DSSCs.

Alternatively, solution-based inkjet printing of inorganic materials offers the challenge of depositing high quality thin films under ambient conditions that succeed in easy patterning, as it is controlled by computer software and made at very low cost. However, inkjet printing of inorganic materials is a more challenging procedure compared to the printing of organic small molecules or polymeric substances. Usually, metal salts or alkoxides are used to form a colloid in aprotic and average volatility solvents consisting of very small particles and, therefore, the solution that is commonly referred to as ink is completely pellucid. However, before the ink is transferred into the printer's tank and finally to the cartridge it is filtered in order to avoid any inhomogeneity of the film during the printing process and also to avoid clogging of the nozzles. This technique allows the printing process to follow a simple dissolution and drying mechanism. In some cases, the volatility of the solvent helps the drying process of the

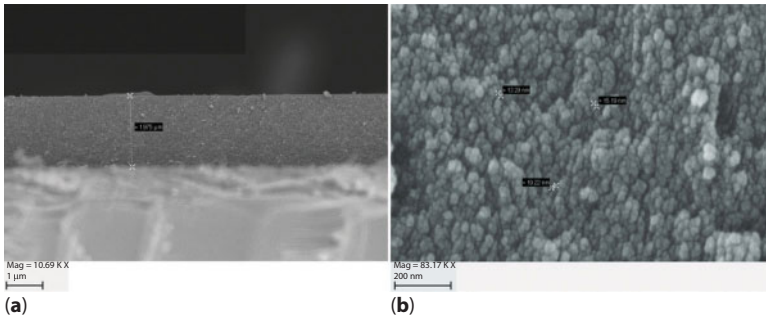


Figure 11.5 Thin TiO_2 nanocomposite films made with inkjet process: (a) cross-section image, (b) top view.

film to be a short time. Furthermore, the printing process demands the co-existence of organic materials in the metal-based inks to improve the printing process and also to modify the structural properties of the as-resulted films as it concerns the porosity and particle shape [20]. Usually, surfactants and small chain polymers can be used to achieve highly porous metal oxide films with fine nanostructure, namely, 4-(1,1,3,3-Tetramethylbutyl) phenyl-polyethylene glycol, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), etc. The desired thickness of the films can be achieved with multiple printings one up to the previous. In most cases, heating process at high temperature after film formation and drying is needed to remove the organic substances and get pure inorganic film with fine mesoporosity and controlled particle shape. An example of fine nanostructure is shown in Figure 11.5 where the metal oxide of choice is TiO_2 , which is commonly used in the majority of DSSC devices that appear in the literature.

11.2.1.2 Inkjet Printing of Dyes on Semiconducting Oxides

In the common fabrication method of dye-sensitized solar cell, a monolayer of dye molecules is attached to the nanocrystalline TiO_2 film by soaking the photoelectrode in a dye bath containing the sensitizer molecules for at least 14–24 hours depending on the solution's temperature. Usually this procedure concerns ruthenium complexes such as *Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)* (commonly abbreviated as N719), which is followed by rinsing off the excess dye from inorganic film surface. Although this method is suitable for small- and laboratory-scale experiments, and as a consequence is most popular in research labs, this process is too slow for a production line and high

throughput manufacturing, which should ideally consist of only fast deposition steps, each completed in the time frame from some seconds to minutes. For instance, the short time frame has already been demonstrated for roll-to-roll fabrication of organic solar cells [21]. Fortunately, research studies have shown that the time that is finally required for saturating the surface of the inorganic nanostructured photoelectrodes with the N719 dye can be shortened to a few minutes either by using a more concentrated dye solution for performing the sensitization at higher temperature, or supplying the dye molecules from the solution onto the mesoporous film by circulating the dye solution, or even by mixing the TiO_2 nanoparticles into the concentrated dye solution followed by spraying [22, 23]. For small area DSSCs, the fastest reported uptake of N719 through the soaking process can be completed in 5–10 minutes using drop-casting and pumping methods, which can give dye-sensitized TiO_2 photoelectrodes the capability of producing $11\text{--}18 \text{ mAcm}^{-2}$ short-circuit current density at the standard reporting conditions [24]. Since most of the active materials of DSSC can be deposited by inkjet printing and coating, it would be advantageous from the point-of-view of manufacturing if the dye could also be simply printed on the TiO_2 films. Early experiments have shown that just putting a concentrated solution of the dye on the surface of nanocrystalline TiO_2 by a pipette could help be an effective sensitization process. In particular, this process could take only three minutes at the most. Nevertheless, in some of these studies, the excess, non-adsorbed dye was washed away afterwards, which suggests that the control of the applied amount of dye was not sufficiently accurate to dispense just enough dye to saturate the film. However, the rapid sensitization could reach its full potential as a DSSC fabrication process only if it can be performed with a precise, automated and industrially scalable printing technique such as inkjet printing. Indeed, the printing parameter setup in the printer's software could affect different results concerning the sensitization process, which is obvious in Figure 11.6 where different printing analyses were applied and the quantity of the dye on TiO_2 surface was different.

In any case, the procedure of printing different dye molecules or a combination of them on the surface of inorganic semiconductors is challenging from a manufacturing point of view and several different colored solar windows could finally be produced with different aesthetic results, as shown in Figure 11.7.

11.2.1.3 Inkjet Printing of Ionic Liquid-Based Electrolytes

In DSSC technology, the type of electrolyte and its content is a very critical parameter to high efficiency solar cells. Besides this parameter, the

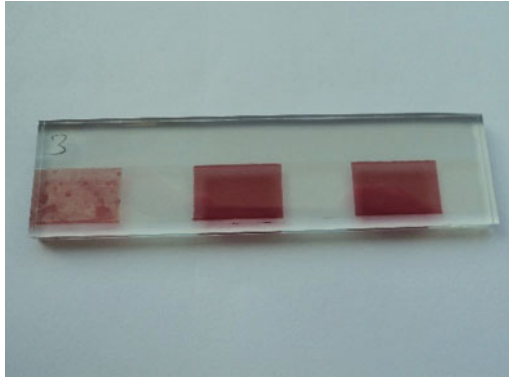


Figure 11.6 Inkjet-printed dye molecule on TiO_2 surface using various printing parameters such as the type of solvent (first image from the left).



Figure 11.7 Solar windows based on DSSC technology using dyes for fashioning different aesthetic results.

way that this electrolyte fills the space among the two electrodes is also very important. Volatile solvents, such as acetonitrile-, ethyl acetate- and propylene carbonate-based electrolytes, have been utilized in fabricating high efficiency cells but were not found suitable for long-term and stable operation mainly due to sealing problems. This issue was moderated by introducing relatively high boiling point solvent-based electrolytes that have shown good stability in aging tests. As an example, the combination of an ionic liquid with high boiling point solvent, such as sulfolane, is considered one of the best electrolyte formulations both in terms of performance and stability. Indeed, more than 80% of the initial solar cell performance was maintained over a 2230 h long light-soaking test

at 60 °C [25]. Compared to the optimization of electrolyte formulations, development of better electrolyte application methods has not received as much attention as the use of small laboratory devices does not necessitate it. For example, the common electrolyte filling step for small-sized DSSCs utilizes one drilled hole which is most often made on the counter electrode side. Usually in that process, a vacuum backfilling method is required. Two drilled holes can also be used for the same purpose where the filling is accomplished by capillary action. The one hole is for the electrolyte insertion and the other to release the trapped air within the cell. However, in both cases, the amount of electrolyte is difficult to be controlled because the entire cell space has to be larger than the active area to avoid overlap between the filling holes and the photoelectrode that would reduce the active area of the cell. This extra amount of electrolyte within the filling channel, which may cause an increase in the dark current of the cell, lowers the geometric filling factor and finally the efficiency of a DSSC module. In addition to these geometrical disadvantages, the filling procedure can be extremely difficult and somewhat problematic in the case of viscous ionic liquid or gel electrolytes and large-scale applications. In that case, the long distance gap of a large-area DSSC module cannot be safely filled at room temperature but additional heating is required. Furthermore, in the case of large-scale DSSCs, when the electrolyte flows through the gap between the two electrodes, capillary forces avoid homogeneous application of the viscous liquid. A recent theory describes the electrolyte's deposition directly over the photoelectrode or counter electrode followed by sealing of the device without holes in the substrates [26]. Introducing new materials in DSSC is always risky as it concerns the efficiency and long-term stability. However, the direct deposition of the electrolyte in a dye-sensitized solar cell without the need to make holes and finally free of sealing is possible using inkjet printing as a state-of-the-art method. In particular, ionic liquid in a solvent mixture electrolyte can be directly inkjet-printed on TiO_2 /dye electrodes. In fact, this hole free electrolyte filling method could give higher efficiency and equal stability with fewer preparation steps, while minimizing the amount of extra electrolyte in the cell. The precisely printed electrolyte could remain stable over the porous sensitized TiO_2 film during the printing step and does not spread around the active area of the electrode when it is contacted by the catalyst loaded surface of the counter electrode. The aforementioned procedure is described in Figure 11.8. Finally, depending on the requirements of the application and the porosity of the TiO_2 photoelectrodes, the electrolyte droplets can be produced in different sizes and velocities by adjusting the voltage and printing waveform.

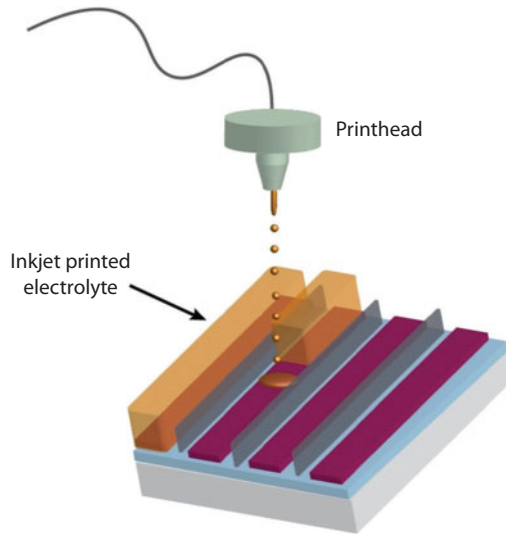


Figure 11.8 Printing method of electrolytes in DSSCs using an inkjet printer.

11.2.2 Inkjet Printing in Perovskite Solar Cell Technology

Perovskite solar cells can be generally considered as an improved version of DSSCs with the major difference being the use of hybrid organic/inorganic perovskite material as solar sensitizer instead of the dye commonly used. As in the case of DSSCs, most of the materials can be deposited on glass or plastic substrate with inkjet printing technique. At present, most of the perovskite layers were deposited on planar or mesoscopic metal oxide substrates by spin-coating technique with one-step or two-step approaches.

Alternatively, vacuum deposition technique was also employed to generate highly flat and uniform perovskite film, exhibiting a PCE of up to 15%. In the perovskite solar cells, photovoltaic performance is greatly dependent on the perovskite film morphology, which relies on the deposition method, annealing process and additives employed. Furthermore, inkjet printing can be easily used for controlled deposition of functional materials, such as small molecules and conductive polymers as main hole-transporting materials in PSC, and they can be easily facilitated and quickly deposited over a large area. In addition, inkjet printing is very promising because the polymer deposition can be easily fabricated, due to their compatibility with various substrates and complete patterning. Inkjet printing has been extensively used in the fields of polymer light-emitting diodes (LEDs) and thin film transistors (TFT) so there is already gained knowledge in the field.

11.2.2.1 Inkjet Printing of Perovskite Material

Both in planar or mesoscopic metal oxide PSC the inkjet printing of conductive polymers (e.g., P3HT) or small hole-transporting molecules (e.g., 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD)) is an easy and well-known method of material deposition where some critical parameters, including solvent formulation and inkjet printing temperature during the process, were studied to achieve high-quality inkjet-printed photoactive layers [27]. However, the printing process of perovskite material is a completely new perspective to the fabrication of inkjet-printed PSCs, which requires careful handling of the material since it is very sensitive to moisture. Furthermore, solvent choice is very critical to the final properties of the as-prepared perovskite films, while the printing temperature could support the crystallization of the material which is necessary for making functional solar cells. In the printing process, high boiling point (bp) solvents, such as γ -butyrolactone (bp = 206 °C), could be used in the ink. Besides, the high solubility of perovskite precursor also prevents nozzle clogging of the printhead due to the solvent evaporation during the printing [28]. In the conventional spin-coating process, most of the solvent can be rapidly removed by centrifugal force during the procedure. In contrast, the films made with inkjet printing are usually in a fluid state as they contain a large amount of solvent. As it is ultimately essential to speed up solvent evaporation from the wet film, heat treatment can be applied to the printer's plate where the FTO glasses are kept during the printing in order to accelerate solvent evaporation (Figure 11.9).

The influence of the plate temperature can be very critical on the morphology and structure of the perovskite film. The morphology of the films can be different from that made with the spin-coating process, as shown in Figure 11.10 for both procedures.

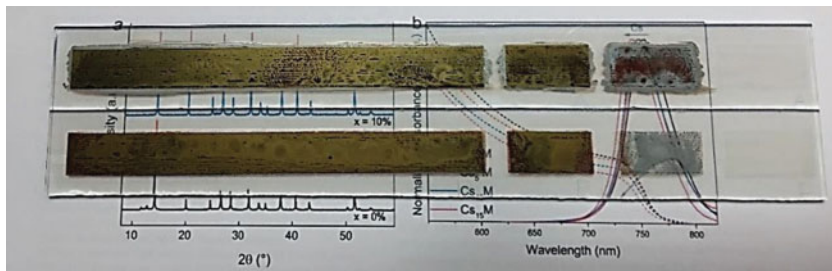


Figure 11.9 Inkjet-printed perovskite material on mesoporous TiO_2 film with various printing parameters.

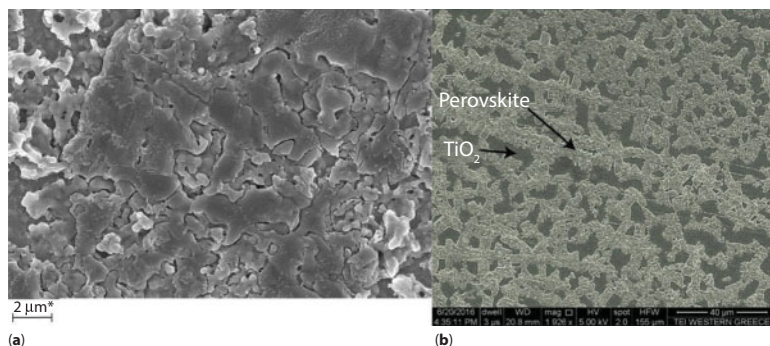


Figure 11.10 (a) Spin-coating and (b) inkjet deposition of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite on inkjet-printed TiO_2 film.

11.3 Conclusions

The recent development of dye-sensitized and perovskite solar cells is very promising technology in the field of third-generation photovoltaic cells. The relatively high efficiencies of DSSCs and the impressive progress of PSCs create the need for using new production technologies for the ultimate goal of making highly efficient, cost-effective solar cells. The freedom of design and flexibility in the choice of materials offered by inkjet printing of these types of solar cells make it a suitable technique, which is at the start-up phase of industrial-scale production. The obvious advantages of controlling the shape and size of solar cells and modules provide the necessary ability to adapt and grow with a developing market and offer a route to industrialization, allowing customizable production at high volumes. The substrates for the realization of solar cells and modules could be varied between glass and plastic. Consequently, plenty of applications for energy harvesting devices, from portable flexible cells to solar glass panels, could be accomplished.

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Part IV

INORGANIC MATERIALS AND PROCESS TECHNOLOGIES FOR PRINTABLE SOLAR CELLS

Solution-Processed Kesterite Solar Cells

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Abstract

Kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has recently attracted a great amount of interest as a potential absorber for next generation thin film solar cells, owing to its decent optical and electronic properties comparable to traditional $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGSe) and CdTe materials, and constituents of earth-abundant and low-toxic elements. Similar to CIGSe and CdTe , kesterite CZTSSe can be fabricated by both vacuum and solution based processes. Typical vacuum based processes such as evaporation and sputtering may suffer from scaling issues and high intrinsic costs. In this regard, solution based processes are desirable and are actively being developed. The solution processed approach permits the use of low-cost and high-throughput equipment and the deployment of large-scale production facilities with lower capital investment. This chapter discusses the fundamental aspects of kesterite thin film solar cells at first. Then, the deposition strategies of CZTSSe are reviewed. The last part of the text deals with solution processes including electrodeposition and direct solution coating used for the preparation of CZTSSe absorbers and solar cells. Today's state-of-the-art performance as well as challenges to achieve low-cost and environmentally friendly mass production are also discussed.

Keywords: Kesterite, thin film solar cells, deposition strategies, solution coating, electrodeposition

12.1 Introduction

Kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) semiconductor has attracted worldwide attention due to its excellent optical and electronic properties

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Nurdan Demirci Sankir and Mehmet Sankir (eds.) Printable Solar Cells, (385–422)
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comparable to traditional Cu(In,Ga)Se_2 (CIGSe) and CdTe materials for thin film solar cells, while consisting of earth-abundant and low-toxic constituent elements. Remarkable progress has been made in CZTSSe solar cells over the past few years and the highest efficiency (PCE) of 12.6% has been achieved by a group at IBM [1] which shows substantial commercial promise.

Similar to CIGSe, CZTSSe thin films can be fabricated by both vacuum and solution processes. Pioneering work has been reported by Katagiri *et al.* on sulfide $\text{Cu}_2\text{ZnSnS}_4$ with device conversion efficiency of 0.66% from the vacuum-based evaporation process [2]. Furthermore, the systematic development in this process has resulted in significant improvement in the conversion efficiency of up to 8.4% for sulfide $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) devices [3] and 11.6% for selenide $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) devices [4]. Sputtering technique has also been used and yielded 9.1% for CZTS devices [5], and over 10% for sulfoselenide CZTSSe devices [6, 7]. However, these vacuum-based techniques have some drawbacks such as high cost, low throughput, and, most notably, severe elemental losses during the deposition processes. Therefore, over the past few years, the quest for low-cost production has focused more and more on the non-vacuum solution-based deposition methods. Solution-based processes can be divided into two approaches: electrodeposition and direct solution coating (including particulate- and molecular-based solution coating). It is worth noting that a series of record-setting devices have been developed by the group at IBM using a hydrazine solution coating process [1, 8–10]. In this chapter, our main focus is dedicated to the current state-of-the-art fabrication routes for solution-processed kesterite. The challenges and future prospects of improving solution-processed kesterite solar cell performance are also presented.

12.2 Fundamental Aspects of Kesterite Solar Cells

12.2.1 Crystal Structure

Kesterite CZTS is the phase that is most commonly used in CZTS-based solar cells. Its crystal structure can be derived from the substitution of elements at the various lattice sites of two adjoining unit cells of the zinc blende crystal structure. First, Zn^{2+} ions in the zinc blende structure are replaced by Cu^+ and Fe^{3+} in a 1:1 ratio to form a chalcopyrite crystal structure that is characteristic of CIGSe. In the case of CIGSe, In^{3+} and Ga^{3+} are incorporated instead of Fe^{3+} . To form a kesterite crystal structure, the

Fe^{3+} ions are replaced by Fe^{2+} and Sn^{4+} . In the case of CZTS, Zn^{2+} ions are incorporated instead of Fe^{2+} . Their relationship can be clearly shown in Figure 12.1.

The structural models of two natural minerals are used to describe CZTS: kesterite and stannite crystal structures, as shown in Figure 12.2. These crystal structures are very close; in both structures the cations are located on tetrahedral sites but their distributions on planes perpendicular to the c -axis are not the same. In addition, the position of the chalcogen atom is slightly different in these structures [12]. When comparing the available data on X-ray diffraction on $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ from the International Council on Diffraction Data (ICDD), it appears that the sulphide compound tends to appear in kesterite structure, whereas the selenide compound occurs in stannite structure. However, because Cu^+

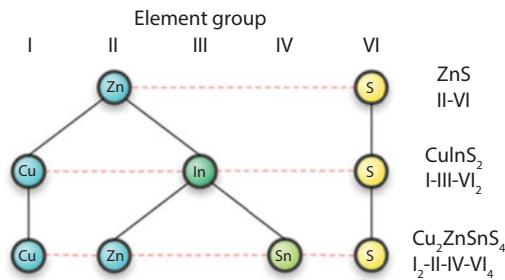


Figure 12.1 Relationship between binary, ternary, and quaternary semiconductors to produce $\text{Cu}_2\text{ZnSnS}_4$, starting from a II–VI parent compound. (Reprinted with permission from [11])

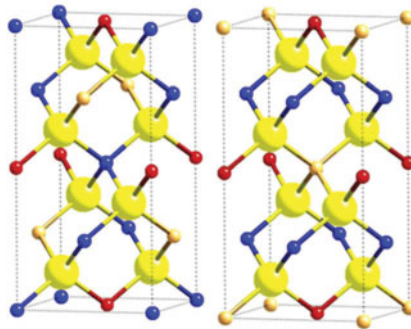


Figure 12.2 Kesterite (left) and stannite (right) structure; Large yellow spheres: S and Se; Small spheres: blue, Cu; yellow, Zn; red, Sn. (Reprinted with permission from [13])

and Zn^{2+} are isoelectronic, X-ray diffraction cannot distinguish between kesterite and stannite structure, because X-rays interact with the electron shell of the atoms. On the other hand, neutrons interact with the nuclei and can distinguish between Cu and Zn atoms [13]. In a comprehensive neutron diffraction study of various $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ compounds, it was shown that the sulfide as well as the selenide occur in the kesterite structure, not in the stannite structure. Both show a certain disorder in-between the Cu and Zn sites [13]. Thermodynamically, the kesterite structure has a lower energy and is more stable than the stannite structure, which was confirmed by the Madelung potentials [14].

Kesterite CZTS have XRD peaks very similar to those of secondary phases ZnS and Cu_2SnS_3 [15], and therefore in order to tell them apart, Raman spectroscopy is necessary [16]. However, it is not possible to make a quantitative determination of the secondary phases by Raman spectroscopy. For such a purpose, X-ray absorption near edge spectroscopy (XENAS) can be used [17].

12.2.2 Phase Space and Secondary Phases

Preliminary experimental work has been done to validate the calculated equilibrium phase space. Figure 12.3 (left) shows the experimentally determined pseudoternary $\text{Cu}_2\text{S}-\text{ZnS}-\text{SnS}_2$ system, with single-phase CZTS occupying a small region in the center [18], allowing only a few mol% absolute deviation of any of the constituent binaries [19, 20]. Therefore, it is very challenging to prepare single-phase kesterite materials with copper-poor and zinc-rich chemical composition, which is required for high efficiency solar cells [21], while avoiding the formation of secondary phases. This can be further supported by theoretical calculation, as seen in Figure 12.3 (right), which shows the chemical-potential stability diagram and the existence of other secondary phases along with the CZTS phase. As we can see, the volume of the stable region for CZTS is small. Compared to the stability region of CuInSe_2 , with the chemical potential window of In (μ_{In}) about 1.0 eV wide, the CZTSe quaternary compound shows a much narrower chemical potential range of Zn (μ_{Zn}) (less than 0.2 eV wide) and Sn (μ_{Sn}) (about 0.6 eV wide), which shows that more strict chemical potential control of Zn and Sn is required in the synthesis process. A deviation outside this space will cause the formation of CuS , ZnS , SnS , or Cu_2SnS_3 . The chemical potential domain also shows that under equilibrium conditions, a copper-rich ambient is required to produce the single-phase kesterite, contrary to the significantly Cu-poor, Zn-rich conditions associated with higher- efficiency devices. In other words, under equilibrium

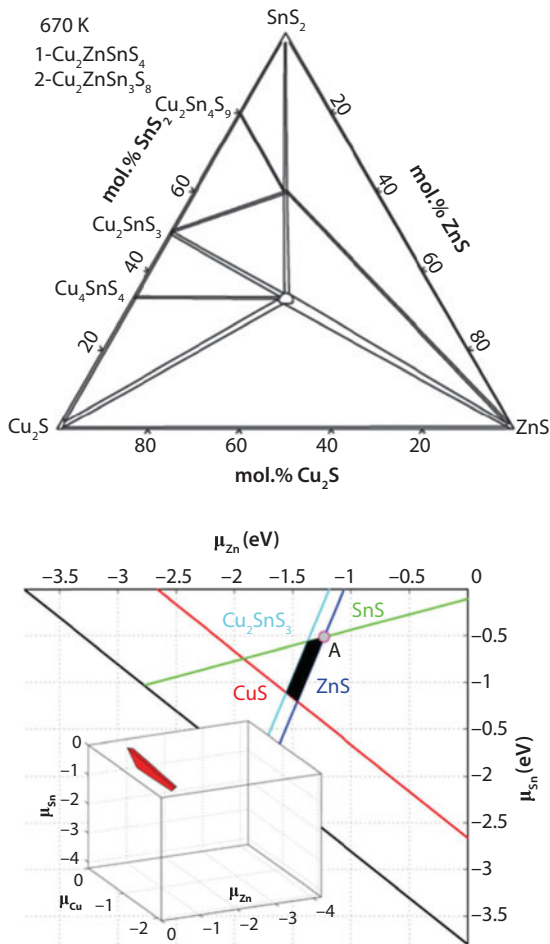


Figure 12.3 (left) Pseudoternary phase diagram showing a very small central area where CZTS forms (reprinted with permission from [18]). (right) The calculated chemical-potential stability diagram of $\text{Cu}_2\text{ZnSnS}_4$ in a 2D Cu-rich plane (stable 3D region in inset) (reprinted with permission from [22]).

conditions, the significantly Cu-poor, Zn-rich conditions used for high efficiency CZTSSe devices will likely produce secondary phases, specifically ZnS(e). Experimentally, ZnS and Cu_2SnS_3 have often been observed which can be explained according to the narrow accessible range of μ_{Zn} , i.e., Zn-rich leads to ZnS, while Zn-poor leads to Cu_2SnS_3 [11]. Besides, this narrow single-phase range is further complicated by Sn volatility during deposition. Therefore, composition and phase control is a major challenge for kesterite CZTSSe fabrication.

12.2.3 Optical and Electrical Properties

The kesterite $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ semiconductor offers wide-range absorption with a high absorption coefficient and tunable band gap energy. The absorption coefficients α of the CZTS-based kesterite semiconductor are as high as 10^4 – 10^5 cm^{-1} [2]. Taking a minimum of $\alpha = 10^4 \text{ cm}^{-1}$, a $2.5 \text{ }\mu\text{m}$ thick CZTS film is able to absorb more than 90% of the incident light in the absence of reflection losses.

The band gap of the kesterite can be adjusted from 1.0 eV at $x = 1$ to 1.5 eV at $x = 0$ [2, 23]. It can be experimentally determined by optical transmission measurements [24] or by quantum efficiency measurements in solar cells [21]. Calculation of the electronic band structure of CZTS reveals a direct band gap at the gamma point of the Brillouin zone [11]. The band gap has been theoretically estimated by density functional theory calculations in different approximations [25–29], hybrid functionals [25, 28, 30] and GW calculations [28]. All recent calculations for the kesterite structure agree quite well with the experimental band gaps, whereas the band gaps in stannite structure are about 100 meV lower [31].

The magnitude of the band gap of CZTS can be understood according to the chemical nature of the valence and conduction band states, and in particular, the low binding energy of the filled Cu 3d valence band [11]. For all Cu-based chalcogenides, including the quaternary kesterite and ternary chalcopyrite compounds, the valence band maximum (VBM) is an antibonding state of the anion p and Cu d orbitals [32]. Because the valence p level of S is lower in energy than Se, the VBM of the sulfide $\text{Cu}_2\text{ZnSnS}_4$ is lower than that of the selenide $\text{Cu}_2\text{ZnSnSe}_4$. But valence band offset (VBO) between the sulfide $\text{Cu}_2\text{ZnSnS}_4$ and selenide $\text{Cu}_2\text{ZnSnSe}_4$ is quite small ($<0.2 \text{ eV}$), lower than that between ZnS and ZnSe ($\sim 0.52 \text{ eV}$ [33]). This difference is from p-d hybridization in Cu-based chalcogenides, because the hybridization is stronger in the shorter Cu-S bond and pushes the antibonding VBM level of the sulfide up relative to that of the selenide. The conduction band maximum (CBM) is made up of a lone band originating from the Sn 5s and the S or Se p orbital [11]. The natural band alignments, calculated with reference to the energy difference of deep atomic-like core states across the kesterite/CdS heterojunction [33], are plotted in Figure 12.4.

Unlike silicon, where either atom of phosphorus or boron is intentionally doped to produce n-type and p-type semiconductors, respectively, CZTS-based materials are self-doped through the formation of intrinsic, interstitial and antisite defects during their growth [31]. The formation energies of most acceptor defects are lower than those of donor defects,

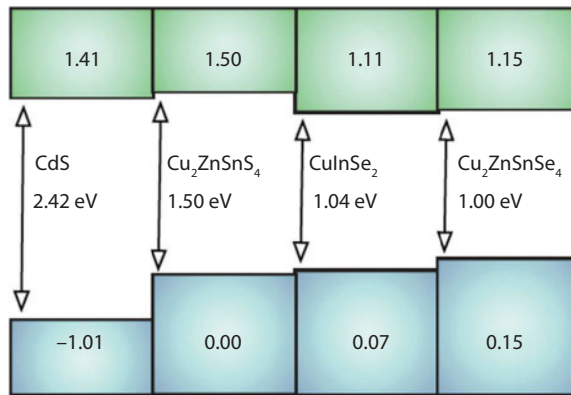


Figure 12.4 The calculated band alignment between CdS, $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$ and CuInSe_2 . CdS is a commonly used n-type window layer in thin-film solar cells. (Reprinted with permission from [34])

explaining the experimentally observed p-type conductivity and indicating that n-type doping will be difficult in these compounds. However, the lowest energy defect is Cu_{Zn} antisite, which is different from the case of CuInSe_2 where the dominant defect is the Cu vacancy (V_{Cu}) [35]. This Cu_{Zn} antisite defect produces a deeper donor level than V_{Cu} in the band gap of CZTS and causes significant band gap energy decrease, which is negative for CZTS solar cell efficiency. Therefore, it is necessary to decrease the formation energy and enhance the population of shallow V_{Cu} relative to Cu_{Zn} using Cu-poor and Zn-rich composition. The hole density of typical kesterite materials is around 10^{16} cm^{-3} [24, 36–38], which is characteristic of CIGSe in high efficiency CIGSe solar cells. Hole density of $10^{18} \sim 10^{19} \text{ cm}^{-3}$ also has been reported by some groups [39–41], due to the presence of $\text{Cu}_x\text{S}(\text{e})$ secondary phases leading to the films being useless degenerate semiconductor.

12.2.4 Device Architecture

The similarities in structural and electrical properties allow the device architecture that is optimized for chalcopyrite CIGSe to work just as well for kesterite CZTSSe absorber. These similarities also allow the knowledge gained from chalcopyrite research and development to aid in the understanding of kesterite materials and devices. Therefore, a comparison of kesterite CZTSSe and chalcopyrite CIGSe technologies is useful to realize higher efficiencies for kesterite solar cells. Figure 12.5 (left) shows the

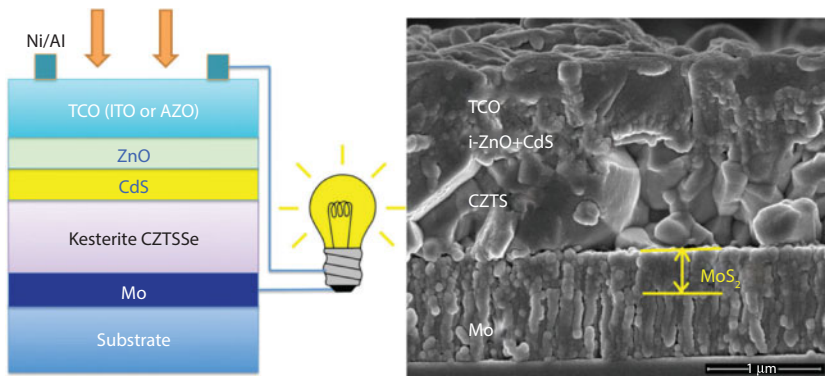


Figure 12.5 (left) Typical device architecture of kesterite CZTSSe solar cell device. (right) TEM cross-sectional image of a typical CZTS solar cell device. (Reprinted with permission from [42])

typical architecture of kesterite CZTSSe solar cell, which is based on a heterojunction cell structure which is completely the same as chalcopyrite CIGSe device architecture. For a typical kesterite solar cell, a 500 nm to 1000 nm thick Mo layer is first sputtered as back contact on a suitable substrate such as soda lime glass, polyimide (PI) or steel foil. Then kesterite CZTSSe absorber with a thickness of 700 nm to 2500 nm is deposited on the back contact by vacuum- or solution-based processes. An n-type buffer layer is grown next to form a p-n junction with the p-type CZTS absorber. For most CZTS-based solar cells, a 50 nm thick CdS by chemical bath deposition is used. Next, a 50 nm to 100 nm thick window layer, such as intrinsic ZnO (i-ZnO), is deposited by RF sputtering. The purpose of the i-ZnO layer is to minimize shunting pathways and prevent intermixing between the absorber and the transparent conductive oxide (TCO) when the thin CdS layer does not provide complete coverage of the underlying CZTS layer. Subsequently, a TCO layer, such as ITO or AZO, with a thickness of around 250 nm is sputtered. Finally, Ni/Al metal contacts, which serve as top electrode to collect the photogenerated electrons with minimal resistive losses, are deposited by evaporation on the TCO. A typical SEM cross-sectional image of the CZTS device fabricated by our group is shown in Figure 12.5 (right) [42].

The structure of a kesterite solar cell is quite complex because it contains several compounds as stacked films that may react with each other. Fortunately, no detrimental interface reactions occur at ambient temperatures. The formation of MoS(e)_2 at the back contact/CZTSSe interface during CZTSSe thin film growth is inevitable via reactions between

Mo and chalcogen at high chalcogen partial pressure or CZTSSe in the absence of chalcogen excess [43]{Scragg, 2011 #600}, which may facilitate an electrical quasi-ohmic contact and improve the adhesion of CZTSSe to Mo back contact, but leads to a high series resistance and accordingly deteriorates the device efficiency if not thin enough [44], similar to the case of CIGSe solar cells [45].

A moderate diffusion of Cd into kesterite has been observed by our group, and is believed to be beneficial to the cell performance [46]. This could be interpreted as the occupation of Cd for vacant Cu sites in the Cu-poor and Zn-rich CZTS matrix (which favors the formation of Cu vacancies [47]) according to the first-principles calculations [48] and Sardashti's report [49]. In CIGSe solar cells, a similar behavior at the CIGSe/CdS interface has been reported by many groups [50, 51] and is believed to be the key factor to the success of the CBD-CdS process [52]. Similar to the role of ordered vacancy compound $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ (OVC) in CIGSe, Cd on Cu sites would act as substitutional donors, and therefore can result in n-type absorber surface, facilitating a more effective buried homojunction [53].

12.3 Kesterite Absorber Deposition Strategies

Kesterite thin films can be prepared by a variety of deposition routes resulting in different material qualities and solar cell efficiencies. Most successful kesterite deposition routes have some common features. With the exception of some innovative examples, where pre-crystallized monograin powders are directly embedded into the device structure [54, 55], the formation routes of all device-quality absorber layer films have met the following conditions [56]:

1. The constituent elements are delivered to the substrate by vacuum or atmospheric pressure techniques. Regardless of the nature of the technique, a high degree of compositional and thickness uniformity must be achieved in order to obtain satisfactory large-area modules and devices. It must be noted that a single defect can shunt a solar cell, while the overall performance of a complete series connected module, especially its current, is limited by the lowest performance device. This fact is of particular relevance for the mass-production of monolithically integrated modules on large substrates, where cells cannot be individually replaced.

2. A high-temperature thermal treatment (400–600 °C) transforms the deposited elements into a crystalline material of the desired phase. High quality kesterite absorbers with excellent grain structure are generally demonstrated with heat treatment temperatures above the melting point of selected copper-chalcogen binaries (520–530 °C). This limits the choice of substrate and layer sequence (i.e., the p-n junction quality is deteriorated at temperatures above 300 °C, thereby making it difficult to deposit the kesterite absorber on top of the buffer layer).

Atmosphere control is also very crucial for kesterite absorber deposition to avoid element loss and secondary phases. The elements involved in kesterite deposition are prone to evaporation and sublimation. Zn sublimates at 430 °C [57]. Its loss can be prevented by using ZnS as a Zn source [58]. Continuous evaporation of Zn towards the substrate prevents the decomposition of CZTSe in a coevaporation process [59]. SnSe volatilizes at 350 °C [52], SnS at 370 °C and Sn at 460 °C [60, 61]. Moreover, high temperatures promote kesterite CZTSSe decomposition according to the equilibrium of Equation 12.1. According to the chemical equilibrium between CZTSSe and solid and gaseous binaries [63]:



where X represents S and/or Se. If this equilibrium is displaced towards the right members, ZnX, SnX and X formation and losses will occur, leading to a Cu₂X-rich layer with poor performance. Moderate loss in Sn is a universal problem especially seen in vapor deposition [59] as well as solution processing [62]. Mitzi *et al.* have suggested annealing under ambient pressure for short durations to reduce volatility [21]. Another route is pushing the equilibrium of Equation 12.1 towards kesterite CZTSSe by saturating the atmosphere in one of the right-side members of the equation to avoid element losses. For example, chalcogen has been widely added into annealing atmosphere. In addition, Redinger *et al.* have added SnS into annealing atmosphere [63] and Repins *et al.* have used a constant overpressure of Sn for coevaporation [59].

The techniques for synthesis of CZTS thin films can be classified into two types: vacuum- and solution-based processes. CZTSSe can only be a reasonable alternative to the established CIGSe technology if the cell efficiencies reach nearly the same values, i.e., in the range of 20% in the laboratory. Lower efficiencies are acceptable only if the overall cost per watt is

significantly lower. As the cost of the absorber material contributes only a minor part in today's vacuum-based CIGSe solar module manufacturing and system costs, the replacement of the expensive indium and gallium must also be accompanied by a cost-effective and simple production route. This means low-cost precursor materials and high throughput processing methods have to be combined for development of high efficiency CZTSSe solar module production. It is thereby very encouraging that the rapidly progressing CZTSSe technology has already achieved similar efficiencies for devices processed with both traditional vacuum- and solution-based processes [64]. The combination of a successful solution-based low-cost deposition process, as offered by the majority of non-vacuum approaches, and the abundant and/or readily available constituents of kesterite CZTSSe materials, offers the potential to bring unprecedented growth in photovoltaic manufacturing. Luckily and interestingly, the present world record for efficiency of kesterite CZTSSe devices is based on fabrication via non-vacuum solution coating process. One of the major issues is the more volatile mix of elements (e.g., Sn) in the kesterite CZTSSe system, causing a severe limitation for the vacuum-based techniques requiring post-annealing treatment at temperatures $> 400\text{ }^{\circ}\text{C}$ [65]. Although this problem is largely resolved by heat treatments under different chalcogen-containing (e.g., SnS) atmospheres [62], the device efficiencies are still below those prepared by solution coating processing. The solution-based processes for deposition of multicomponent inorganic absorber layers can be generally summarized under two main categories: electrodeposition and direct solution coating. Below we detail these processes that are being pursued to demonstrate high-performance solution-processed kesterite CZTSSe solar cell devices.

12.4 Electrodeposition

Electrodeposition is an attractive industrial approach for large-scale application and one that is well-established in the electronics industry (e.g., copper interconnection technology in microelectronics). It has been successfully employed in the large-scale production of CdTe- [66] and CIGSe- [67, 68] based thin film solar cells. Since the pioneering works of Scragg *et al.* [36, 69] and Araki *et al.* [70] in 2008, electrodeposition has attracted increasing attention as a low-cost route for the synthesis of kesterite CZTSSe thin films for solar cell applications. This process could provide: (a) a low-cost, high-rate process; (b) a large-area, continuous, multicomponent, low-temperature deposition method; (c) deposition of

films in a variety of shapes and forms (wires, tapes, coils and cylinders); (d) freedom from the requirement or need to use expensive equipment; (e) controlled deposition rates and effective material use; and (f) minimum waste generation (solution can be recycled) [71]. The preparation of kesterite CZTSSe films by electrodeposition is usually accomplished by chalcogenization of electrodeposited precursor films, including stacked metals Cu/Sn/Zn, binary alloys Cu-Sn and Cu-Zn, ternary metallic Cu-Zn-Sn, and quaternary Cu-Zn-Sn-(S, Se). On the basis of different strategies to electrodeposit a precursor film, electrodeposition of kesterite films can be divided into four subclassifications: (1) stacked elemental layer (SEL) electrodeposition; (2) metallic alloy co-electrodeposition; and (3) chalcogenide co-electrodeposition. The advantages, disadvantages and perspective remarks on the fabrication of kesterite thin films by using different electrodeposition approaches together with notable efficiency solar cells are shown in Table 12.1.

12.4.1 Stacked Elemental Layer (SEL) Electrodeposition

In this approach, copper, zinc and tin are subsequently deposited from the corresponding electrolyte solution. For copper film electrodeposition, the most commonly used electrolyte contains copper sulfate in acidic aqueous solution. In order to improve the uniformity of electrodeposited Cu film, additives such as tartrate, citric acid, sodium citrate and Empigen BB are used as complexing agents [77–79]. For thin film electrodeposition, it can be achieved in both acidic and alkaline solutions. In the acidic condition, Sn(II) is unstable and prone to oxidation to Sn(IV) compounds which form colloids and then precipitation. Complexing agents such as $\text{CH}_3\text{SO}_3\text{H}$ and sorbitol are applied to stabilize the Sn(II) in the electrolyte solution over a wide range of pH. Zinc sulfate is commonly used as the precursor salt in the zinc electrodeposition since sulfate allows high current densities. Acidic electrolyte is preferable for electrodeposition of zinc. Zn has a very negative standard reduction potential and hydrogen evolution is therefore competitive. In order to avoid changes of pH at the electrode surface (due to consumption of H^+ by the hydrogen evolution reaction), a pH buffer is often used [78–80].

Until now, the best power conversion efficiencies for electrodeposited kesterite (8.1% for $\text{Cu}_2\text{ZnSnS}_4$ [72] and 8.2% for $\text{Cu}_2\text{ZnSnSe}_4$ [73]) have been obtained from stacked elemental layers precursors. The most significant benefit of using the SEL approach is the ability to easily vary the composition by independently changing the deposition parameters of each layer. The precursor composition can be adjusted by varying the thickness

Table 12.1 Comparison of the different electrodeposition strategies.

Electrodeposition strategy	Advantages	Disadvantages	Achieves
Stacked elemental layer (SEL) electrodeposition	(1) easy control of composition (2) stable electrolytes (3) high quality of final CZTS absorbers (4) different stack orderings possible (5) more degrees of freedom (composition, stack ordering, density...)	(1) multiple electrolyte solutions and deposition steps (2) time-consuming (3) in-depth inhomogeneity (4) only one preferred stack (Cu/Sn/Zn) (5) difficult for chalcogen-incorporation	(1) 8.1% for $\text{Cu}_2\text{ZnSnS}_4$ device with V_{oc} of 705 mV, J_{sc} 18.0 mA/cm ² , and FF of 63.2% [72] (2) 8.2% for $\text{Cu}_2\text{ZnSnSe}_4$ device with V_{oc} of 425 mV, J_{sc} 30.8 mA/cm ² , and FF of 62.7% [73]
Metallic alloy co-electrodeposition	(1) time-saving (2) single bath with only one electrolyte (3) single step and short deposition time (4) minimum of equipment	(1) unstable electrolyte solution over a long period of time (2) difficult to control the alloy composition and microstructure (3) potential poor homogeneity on cm ² area from multiple diffusion coefficients and deposition potentials	(1) 3.87% $\text{Cu}_2\text{ZnSnS}_4$ device with V_{oc} of 512 mV, J_{sc} 15.6 mA/cm ² , and FF of 48% from co-electrodeposited Cu-Zn-Sn [74] (2) 5.8% $\text{Cu}_2\text{ZnSnSe}_4$ device with V_{oc} of 398 mV, J_{sc} 30 mA/cm ² , and FF of 49% [75]
Chalcogenide co-electrodeposition	(1) single bath with only one electrolyte (2) single step and short deposition time (3) minimum of equipment	(1) no stable or replenishable chalcogen source (2) long deposition time (3) difficult control of composition	(1) 6.6% $\text{Cu}_2\text{ZnSnS}_4$ device with V_{oc} of 581 mV, J_{sc} 19.9 mA/cm ² , and FF of 57.2% [76]

of each individual layer, controlling the charge flow in each step. Dense, homogenous layers can be obtained in this way. However, this technique does not provide complete precursor design freedom. Because of their different standard reduction potentials ($\text{Cu}^{2+}/\text{Cu} = 0.34\text{V} > \text{Sn}^{2+}/\text{Sn} = -0.14\text{V} > \text{Zn}^{2+}/\text{Zn} = -0.76\text{V}$ vs. NHE), only the (simplest) sequence Mo/Cu/Sn/Zn overcomes issues of metal exchange and layer stripping during the sequential electrodepositions [79, 81]. This sequence has also proven to be best in terms of device efficiencies [72, 73, 75, 78, 79, 82, 83]. Other reported stack ordering are Zn/Cu/Sn [84], Sn/Cu/Zn [85] and binary Cu-Zn/Sn [86], but no devices are reported from these alternative stacks. Besides, stacked binary alloys Cu-Zn and Cu-Sn on Mo/glass substrates by electro-deposition have also been explored by our group [87], which yield 3.67% efficient sulfide CZTS device.

12.4.2 Metallic Alloy Co-electrodeposition

In this approach, a Cu-Zn-Sn metallic precursor film can be co-electrodeposited from an electrolyte solution containing Cu, Zn and Sn cations. The kesterite CZTSSe films are then fabricated by the chalcogenization. The electrolytes employed are based either on sulfate and/or chloride metal divalent salts with concentrations in the range of 1–330 mM with an acidic pH ranging from 2.7 to 7. The depositions are carried out mainly in potentiostatic mode with potentials ranging from -1.1 to -1.62 V vs. Ag/AgCl, corresponding to deposition rates on the order of 20–60 nm/min [75, 88–96]. Compared to the SEL and stacked binary alloys, co-electrodeposition is simpler because the metallic film can be fabricated from an electrolyte solution at once. However, the co-electrodeposited approach still needs to overcome some difficulties. The electrolyte solution is unstable and precipitation may occur after a period of time due to the different chemistries of Cu(II), Sn(II), and Zn(II) aqueous solutions in which precipitation of oxides/hydroxides/basic salts occur at different pH values. In addition, the standard reduction potentials of Cu, Sn, and Zn are very different, as mentioned in the previous section, which implies that the composition of Cu-Zn-Sn metallic film is difficult to control. In many cases, much higher concentration of zinc salt [97–103] than copper and tin salt were used to obtain CZT film with a nearly stoichiometric composition. And the nucleation and growth regimes of the elements occur at different potentials, which would negatively impact on the morphological properties of the deposits if co-electrodeposition is performed from simple aqueous solutions of the divalent salts. Furthermore, due to the small free energy of the formation of Cu-Sn [104] and Cu-Zn [105] alloys

and to the absence of binary Sn–Zn and ternary Cu–Sn–Zn intermetallic phases [106], it is very hard to keep phase homogeneity and avoid metastable alloys. Only 3 ~ 4% efficiency CZTS [74, 98] and 5 ~ 6% CZTSe [75] devices have been reported up to now from this Cu–Zn–Sn co-electrodeposition approach. Besides, considering the stable Cu–Sn and Cu–Zn phases, recently we reported co-electrodeposited Cu–Zn and Cu–Sn stacked binary alloy layers for CZTS absorber fabrication, which yielded device efficiency of 3.67% [87].

12.4.3 Chalcogenide Co-electrodeposition

In this approach, the kesterite precursor thin films are directly electrodeposited on the conductive substrate from the electrolytic bath solution which contains Cu, Zn, and Sn cations as well as S-source such as $\text{Na}_2\text{S}_2\text{O}_3$ or Se-source such as H_2SeO_3 or NaSeO_3 . The as-deposited precursor films need to be further crystallized via post-annealing at temperature above 500 °C. A reactive atmosphere with a chalcogen partial pressure provided by chalcogen source (S, Se, H_2S or H_2Se , etc.) is still needed to fabricate high quality absorbers.

In 2010, Pawar *et al.* first reported the fabrication of $\text{Cu}_2\text{ZnSnS}_4$ precursors from an unstirred single aqueous bath consisting of Cu(II), Zn(II), and Sn(II) cations, SO_4^{2-} anions and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) with sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), and tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) as complexing agent [107]. The effects of complexing agent on the properties of electrodeposited precursors also has been revealed [108]. This electrolyte solution system was then further investigated/applied by many other groups [109–111]. Recently, Ge *et al.* have reported 5.5% efficient CZTS device based on this type of precursor [112], and the efficiency was then improved to 6.6% by optimizing the deposition times and employing sputtered CdS buffer [76]. Compared to the electrolyte used in the metallic alloy co-electrodeposition approach, the electrolyte system employed in one-step synthesis of CZTS is even more complex due to the presence of a sulfur source such as $\text{Na}_2\text{S}_2\text{O}_3$ with the metal species in the solution. Under moderately acidic conditions $\text{Na}_2\text{S}_2\text{O}_3$ is fundamentally unstable, as sulfur precipitates out of solution changing the available concentration of sulfur in the electrolyte. The direct electrodeposition of kesterite selenide precursors has scarcely been attempted. Septina *et al.* reported single-step electrodeposited $\text{Cu}_2\text{ZnSnSe}_4$ precursor from an acidic electrolyte containing 4 mM CuSO_4 , 80 mM ZnSO_4 , 20 mM SnCl_4 , 5 mM Na_2SeO_3 and 500 mM lactic acid [113]. Similar work was reported by Meng *et al.* except that tri-sodium citrate and SeO_2 were employed instead of lactic acid and Na_2SeO_3 [114].

Although many works have essentially shown that Cu, Sn, Zn and either S, or Se can be co-deposited, and that these precursors may be annealed to give absorber layers with some characteristics of the kesterite semiconductor, it is clear that the co-electrodeposition of four elements is extremely challenging by the fact that there have been very few reports on working solar cell devices, and at the moment there appears to be little benefit in terms of final material quality with this approach.

12.5 Direct Solution Coating

The direct solution coating approach virtually involves a group of methods by which a layer from particulate-based or molecular-based solution with a precursor is coated on the surface of a substrate, followed by the appropriate post-annealing (chalcogenization) process to yield the desired kesterite phase. The main processing steps in direct solution coating for kesterite fabrication, including both particulate-based and molecular-based processes is shown in Figure 12.6. The coating can be achieved by a variety of low-cost techniques, including spin coating, spray coating, doctor blading,

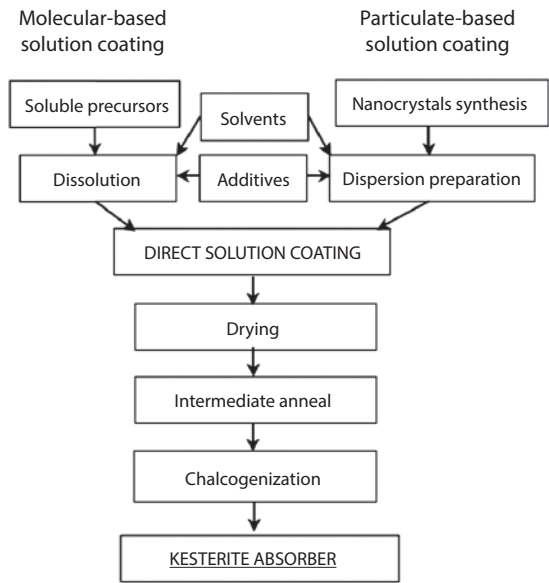


Figure 12.6 Main processing steps in direct solution coating for kesterite fabrication, including both particulate-based and molecular-based processes.

slit casting, and inkjet printing. The choice of particular coating technique is not crucial for the quality of the final film, provided that a uniform liquid layer of desired thickness can be formed. Much more important is the ability of the deposited materials to form a high-quality absorber upon subsequent chalcogenization treatment. The drying and intermediate annealing, depending on the nature of the precursor, can be done in air or inert atmosphere. While oxide coatings are often treated in air, in order to eliminate carbon contamination [115], air-sensitive samples are handled in inert atmosphere [8]. Even though drying can be considered as a primitive, standard step for solvent evaporation, it is also found to be important for the layer morphology, uniformity, and the presence of impurity elements and phases in the final kesterite CZTSSe absorber layer [64]. Chalcogenization (400–600 °C) is the last processing step under controlled atmosphere with the addition of chalcogen vapor or hydrogen chalcogenide. This step is decisive although chalcogen could be incorporated into the precursors and the effects of the reactive chalcogen-containing atmosphere is manifold. First, the reactive annealing can compensate the deficit of chalcogen in the dried precursor layer by increasing the S(Se)/metal ratio to slightly larger than 1:1. This condition is imperative for a phase-pure material with suitable electronic properties, since anion vacancies (V_s and V_{se}) can induce detrimental deep donor levels [47]. Second, the reaction with chalcogen can lead to volume expansion and densification during annealing, thus eliminating the layer porosity and increasing the grain size. Finally, the chalcogen vapor over pressure is essential for preventing a possible decomposition of the kesterite phase into binary copper and zinc chalcogenides, and volatile $SnS(Se)$ and $S(Se)$ [64]. Given the need for solvent evaporation and precursor decomposition, with resulting volume change of the film, each chalcogenization processing step often requires precise optimization in order to obtain adequate morphology and avoid film delamination, and crack and void formation [56].

According to the characteristics of the solution, direct solution coating can be divided into two subclassifications: both particulate-based solution coating and molecular-based solution coating. Considering the fact that the solution coating process from hydrazine solvent has yielded a series of record kesterite devices, the hydrazine solution coating process has been specially chosen as the third subclassification and overviewed first.

12.5.1 Hydrazine Solution Coating

Hydrazine (N_2H_4) is the carbon- and oxygen-free compound that can be considered as an ideal solvent because it dissolves metal chalcogenides and

elemental chalcogens (sulfur and selenium) and excludes the introduction of any detrimental impurity elements by decomposing cleanly into N_2 , NH_3 , and H_2 . Another important feature of hydrazine is its strong reducing action that prevents any metal oxidation [56].

The hydrazine route was developed by the group at IBM. In the early stage, a hybrid mixture of nanoparticles and a molecular solution, which involves undissolved Zn particles (in the form of $ZnSe(N_2H_4)$) and truly dissolved molecular solutions, was employed, and produced devices with several record efficiencies: 9.66% in 2010 [8], 10.1% in 2012 [9] and 11.1% in 2013 [10]. Then they further developed a purely molecular-based solution coating approach by using a zinc salt instead of elemental zinc [116], which yielded a 12.6% record efficiency in 2014 [1]. Currently, this performance holds the highest certified efficiency for kesterite solar cells. Another hydrazine solution coating approach was reported by Hsu *et al.* [117]. In this study, the hydrazine derivatives were designed to allow the effective incorporation of zinc compounds into hydrazine solution, forming a CZTS molecular-based solution. Based on a coating from this molecular-based solution and a subsequent selenization process, a solar cell with an efficiency of 8.08% was produced.

Although the hydrazine solution coating process has yielded kesterite solar cells with the highest efficiency, the explosivity and toxicity of hydrazine (all of its processing requires inert atmosphere and handling inside a glove box), are extremely limiting for its application in large-scale production [21]. It is hence essential to develop a relatively simple solution coating approach using less toxic solvents with comparable performance to those made from hydrazine-based approaches.

12.5.2 Particulate-Based Solution Coating

The particulate-based solution coating approach begins with the synthesis of chalcogenide nanocrystals (NCs) and the formulation of nanocrystal inks. These inks are coated onto substrate to form nanocrystal precursors which are subsequently annealed into dense kesterite CZTSSe absorbers under chalcogen-containing atmosphere at an elevated temperature. For example, Figure 12.7 shows a typical schematic illustration for one of the particulate-based solution coating approaches: the fabrication of CZTS device from blade-coated CZTS NCs ink and post-sulfurization by our group [118].

The synthesis of NCs has developed mainly using three approaches: the direct single-step synthesis of colloidal quaternary CZTS [63, 119–122], CZTSe [123, 124] or CZTSSe [125, 126] NCs; the formation of CZTSSe

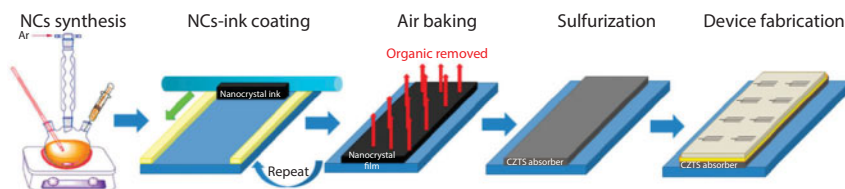


Figure 12.7 Schematic illustration for fabrication of CZTS device from CZTS NCs ink blade coating and post-sulfurization. (Reprinted with permission from [118])

absorbers from binary and ternary colloidal NCs [127]; and the synthesis of CZTSSe-based NCs using alloying with Ge [128, 129] or defect passivation with Na [130]. The most successful route for the synthesis of NCs is hot injection, which is based on a nonaqueous coprecipitation process. The general synthesis process starts with precursors, carefully chosen Cu, Zn, and/or Sn compounds, being dissolved in long-chain coordinating solvents followed by burst precipitation and controlled growth after injecting with a sulfur or a selenium source at the desired temperature. The metal chloride, acetate and acetylacetonate precursor compounds are effective as reported previously for hot-injection synthesis. The most widely used coordinating solvent is oleylamine (OLA) with high boiling point (364 °C) and high coordinating capability; meanwhile oleic acid (OA), trioctylphosphine oxide (TOPO) and octadecene (ODE) are also used occasionally. The elemental sulfur dissolved in OLA is used as a sulfur source; while thiourea, dodecanethiol (1-DDT) and tertdodecylmercaptan (t-DDT) can also be used to provide sulfur species, which also controls the crystal growth as well.

The direct single-step synthesis of colloidal quaternary CZTS NCs was first reported by Guo *et al.* in 2009 [119], and the CZTSSe solar cell with an efficiency of 0.8% using pre-synthesized CZTS nanocrystals coated on Mo substrates and post-selenization. By optimizing the Cu/(Zn+Sn) and Zn/Sn ratios, the same group improved the solar cell efficiency to 7.2% in 2010 [63]; and by further modification on NCs synthesis and selenization, the efficiency has been enhanced to 9.0% total-area power-conversion efficiencies [120]. Leidholm *et al.* from Solexant Corp. have reported a 10.2% CZTSSe device on flexible Mo-coated stainless steel foil substrates from CZTS NCs by hot injection and post-selenization, which is the highest efficiency for a particulate-based solution coating approach up to now. Cao *et al.* have reported CZTSSe absorbers from binary and ternary colloidal NCs [127], showing facile control of the final film composition with promising solar cell efficiencies of 8.5%. Many issues associated with phase stability and phase purity in quaternary NCs synthesis may be alleviated

in the synthesis of binary/ternary nanocrystals as these materials are often intermediate phases involved in the growth of quaternary NCs.

Although CZTSSe thin film solar cells from selenizing kesterite CZTS NCs have demonstrated efficiencies above 10%, when it comes to the sulfide CZTS solar cells from sulfurizing kesterite CZTS NCs, the demonstrated efficiencies are in the very low range of 2% [131]. The major reason for this poor device performance is postulated to be correlated with the difficulties in forming compact large grains (in micrometer scale) comparable to those achieved by selenizing CZTS NCs or sulfurizing metal sulfide precursors. Within this framework, by the sulfurization treatment of metastable wurtzite CZTS nanocrystals in several minutes, our group has recently overcome the grain-growth challenge of CZTS thin film from nanocrystals by demonstrating large-grained CZTS film and 4.8% efficient device [132]. Compared to thermodynamically stable kesterite phase CZTS nanocrystals, the driving energy for the significant grain-growth of metastable wurtzite CZTS nanocrystals upon sulfurization treatment may result from two aspects: (1) the high surface area of nanocrystals leading to a reduction in total energy; (2) free energy difference between the metastable wurtzite phase and the stable kesterite phase [132]. The efficiency has been further boosted to 6% recently by Na incorporation and sulfurization in SnS-containing atmosphere [133].

The incorporation of Ge is expected to be beneficial to device performance because it could adjust band gap of kesterite by substitution of Sn and avoid the presence of the Sn(II) oxidation state [134]. In 2011, Ford *et al.* reported for the first time the synthesis of $\text{Cu}_2\text{ZnGeS}_4$ (CZGS) and $\text{Cu}_2\text{Zn}_{(\text{Sn}1-x)}\text{Ge}_x\text{S}_4$ (CZTGS) NCs, and the device from CZTGS NCs with Ge/(Ge+Sn) of 0.7 and post-selenization has shown open circuit of 0.64 V (0.43 V for Ge/(Ge+Sn)=0) and efficiency of 6.8% [135]. The efficiency was further improved to 8.4% by the same group using CZTGS NCs with Ge/(Ge+Sn) of 0.25 in 2012 [128]. Kim *et al.* [136] have reported $\text{Cu}_2\text{Zn}_{(\text{Sn}1-x)}\text{Ge}_x\text{S}_4$ thin-film solar cells from CZTGS NCs and post-sulfurization, and they found that band grading of the CZTGS absorber by Ge/(Ge+Sn) could improve device efficiency from 4.6% for ungraded band gap to 6.0%. One of the routes for defect passivation is Na doping. Zhou *et al.* [130] introduced a new *in-situ* doping strategy to improve the device performance by the passivation of CZTSSe absorber film by the use of solution-processed CZTS:Na NCs precursors. The device efficiency has been improved from 3.89% using undoped CZTS NCs to 6.14% using Na-doped CZTS:Na NCs by enhancement of all electrical parameters for devices.

Despite all these promising reports, there are still some unsolved problems concerning the use of nanoparticles.

Firstly, one major issue is related to the carbon residues remaining in the final film after high temperature chalcogenization (selenization or sulfurization), promoting formation of the bilayer structure: a fine-grained interlayer in the film. This is a common feature of chalcogenized nanocrystal films, which leads to poor uniformity and adhesion and high series resistivity. The origin and composition of this fine grain layer can vary depending on the particular chalcogenization approach and processing conditions utilized. In efforts to minimize/eliminate the formation of the fine-grain layer, research has indicated that the fine-grain layer thickness is heavily dependent upon the selenization reaction conditions. Air annealing before chalcogenization also has been used to avoid fine grain in the final absorber layer.

However, complete removal of this fine-grain layer will most likely involve elimination of carbon from the pre-sintered nanocrystal films, which is an active research area in particulate-based solution coating processed devices.

Secondly, a deeper understanding of nanocrystals is still recommended. Further investigations are highly necessary to resolve the complexity in the synthetic chemistry, dissolution mechanisms, drying kinetics and phase formation of thin films and their relationship with various loss mechanisms in PV devices. And great efforts should be devoted to the mechanisms of phase evolution, elemental losses and grain growth, and the formation of phase pure CZTSSe without detrimental secondary phases.

Finally, since the fabricating costs of photovoltaic devices processed from nanocrystals are still relatively high, how to up-scale the production of NCs is a big challenge for researchers. As we have discussed above, colloidal syntheses of NCs are usually based on the decomposition and reaction of precursors in high boiling organic solvents, such as OLA, ODE, TOP and DDT, but the prices of these solvents are relatively high, e.g., 100 ml of technical grade OLA costs about 50 US dollars. Hence, using the alternative reaction media for green and sustainable synthesis needs further investigation. In addition, a typical reaction yields only about several tens or hundreds of milligrams of product. Therefore, non-injection synthesis of NCs is of great interest, and has also been studied extensively [137–139]. Given the promising future of a solar cell produced from “nanocrystal ink,” the cost and scalability of nanocrystal syntheses needs to be considered.

12.5.3 Molecular-Based Solution Coating

The molecular-based solution coating approach of kesterites involves several steps which include the preparation of molecular-based solution,

coating of a wet film, drying, and a final chalcogenization step for chemical reaction and crystallization. Coating and drying steps usually need to be repeated several times to obtain multilayer structures to build up desired thickness, which also can be used for improving layer homogeneity and creating intentional compositional gradients in the multilayer precursor coating. For example, Figure 12.8 shows a typical schematic illustration for one of the typical molecular-based solution coating approaches: the fabrication of CZTS device from solution (with 2-methoxyethanol as solvent and thiourea as chalcogen source) coating and post-sulfurization by our group [115].

This approach has all advantages of non-vacuum deposition such as the possibility to use low-cost and high-throughput equipment, low wastage of raw materials, high uniformity of layer properties over large area and, finally, potential deployment of large-scale production with low capital investment. In contrast to the other popular solution-based techniques for kesterites, such as electrodeposition (ED), chemical bath deposition (CBD) [140], successive ionic layer absorption and reaction (SILAR) [141], and spray pyrolysis [142], which imply a slow growth of the kesterite phase during the actual deposition step, the coating techniques such as spin-, spray-, dip-, blade-, and curtain-coating, as well as printing techniques like inkjet, flexography, and gravure, allow fast coating of the wet layer with low wastage of the precursor solution. As compared to nanoparticle-based inks, solutions offer the following benefits: (1) no need for pre-synthesized

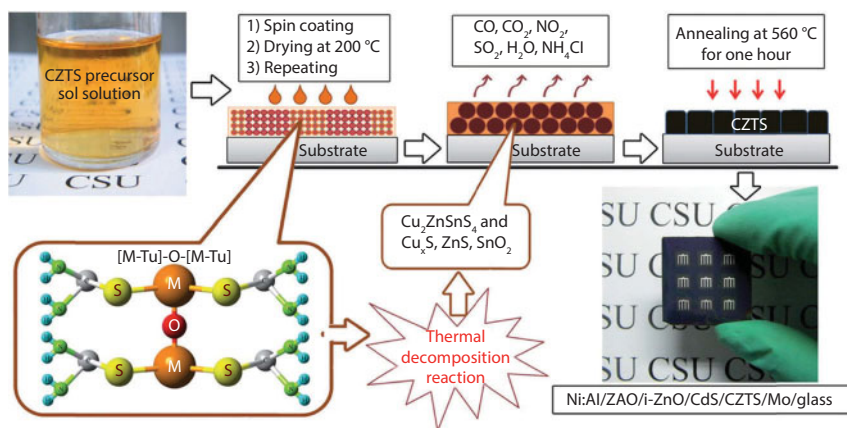


Figure 12.8 Schematic illustration for fabrication of CZTS device from solution (with 2-methoxyethanol as solvent and chalcogen-containing) coating and post-sulfurization. (Reprinted with permission from [115])

nanocrystals; (2) readily available, cheap metal salts with high purity and long storage time; and (3) reproducible processing with a homogeneous sinter mixing of constituent elements on the molecular level [64].

In order to obtain a high quality kesterite absorber and achieve greater efficiency, the selection of the solvent is extremely important. On the one hand, a good solvent should have a high solubility for metal sources (metal salts or oxides) and sulfur source (optionally, such as sulfur, thio-urea or thioacetamide, etc.), and low surface tension, allowing the solution to spread easily with full coverage and free of streaks or voids. On the other hand, it should have suitable boiling point and vapor pressure, allowing the solvent to readily evaporate with minimal residue yet not leading to instability during the coating and drying processes and the deterioration of the film microstructure due to a too rapid volatilization process. For sulfoselenide CZTSSe, some attractive power conversion efficiencies of 6.16% by water + ethanol [143], 6.52% by ethanol + 1-butylamine + 3-mercaptopropionic acid [144], 5.14% [145] and 6.62% [146] by water, 6.83% for 2-methoxyethanol + thioglycolic acid + monoethanolamine [147], 8.25% by 2-methoxyethanol [148], 8.32% [149] and 11.2% [150] by dimethyl sulfoxide (DMSO), and 11% by dimethyl formamide (DMF) [151], except for 12.6% by hydrazine (record efficiency) [1], have been achieved by several groups. For sulfide CZTS, however, efficiency of CZTS devices from purely solution-based processes is much lower and only very few groups have reported CZTS devices reaching efficiencies higher than 3%: 3.02% by ethanol [152], 5.29% by water + ethanol [153], 5.68% by DMF [154], and 5.1% [115] and 5.7% [155] by 2-methoxyethanol.

For solute, salts of Cu, Zn, and Sn, such as chlorides, nitrates, acetates, or iodides, are usually used as metal sources, which are readily available in high purity and have high solubility in a wide range of solvents. Since many salts are hygroscopic, hydrates are often employed to simplify the processing and to avoid uncertainties in weight. Copper(II) salts are preferred over copper(I) compounds because the latter are less soluble and can undergo oxidation or disproportionation, yielding insoluble precipitation. Regardless of the initial copper oxidation state, it takes the Cu(I) state in the kesterite phase after chalcogenization with chalcogen-containing atmosphere. Sn(II) and (IV) chlorides were chosen in most of the previous reports. In addition, metal dithio-carbamate precursors were explored as metal precursors because of their low thermal stability [156]. Concentrations of Cu, Zn, and Sn salts are typically chosen in the approximate molar ratio $\sim 1.8:1.2:1.0$ aiming at the Cu-poor and Zn-rich non-stoichiometric composition of the final CZTSSe layer. Loss of metals, e.g.,

Zn and Sn [157], may occur during the chalcogenization step and therefore the initial precursor concentrations have to be adjusted adequately.

The presence of a source of chalcogen (S or Se) in the initial precursor solution is beneficial to absorber quality and device performance. Either aqueous or nonaqueous molecular-based solution processes without chalcogen-containing entail forming metal-O-metal bonds in precursor solution so that metal oxides can be formed easily by this approach [158, 159]. As for the formation of sulfides, generally highly active but toxic H_2S is used in sulfurizing oxides into sulfides [160, 161], which results in prepared thin films that not only contain secondary phases, such as binary sulfides or oxides, but that also show poor surface morphology and weak adhesion with substrates. The formation of selenides meets a similar challenge, needing H_2Se for selenization. In order to induce the formation of kesterite during the chalcogenization step, chalcogen-contained solution is suggested. For example, in the process of depositing CZTS thin films, the content of sulfur in precursor thin films plays a very important role in forming high-quality thin films because sufficient sulfur in precursor thin film can avoid the deterioration of morphology (such as cracks and holes) caused by volume expansion during the sulfurization process [37, 162]. Moreover, sufficient sulfur can thermodynamically decrease the volatilization of Zn or Sn (or SnS) during the formation of CZTS thin film [62]. In order to incorporate enough sulfur into precursor thin films, recently some researchers have reported that excess thiourea (primary choice for chalcogen source being soluble in numerous polar solvents and able to coordinate metal ions in solution) was added into organic solvent to form M-S or M-S-M complexes with metal ions and then complexes were thermally decomposed into expected metal sulfides [115, 148, 163–166]. Besides, sulfur [167] and thioacetamide [168, 169] have also been employed as the chalcogen source. Elemental sulfur or selenium is certainly the simplest choice but their limited solubility in polar solvents somewhat limits their usage.

The conversion efficiency of devices has been beyond 11% for DMSO and DMF solution coating approaches, as mentioned above, with the exception of record efficiency from hydrazine solution coating, and it is highly possible for further improvements in conversion efficiency in the near future. From the aspect of efficiency, compared to vacuum-based and other solution coating approaches, the molecular-based solution coating approach seems more suitable to fabricate kesterite absorber for fundamental research of kesterite photovoltaics, such as absorber doping, defect and grain boundaries passivation, heterojunction interface, optimum back contact, Cd-free buffer layer, and others, that can be explored to further bolster the efficiency of kesterite solar cells.

12.6 Conclusion

Solution-processed kesterite solar cells have developed rapidly over the past few years. Tremendous progress has recently been achieved for both electrodeposition and direct solution coating processes. For electrodeposition, over 8% efficiency has been obtained for both CZTS and CZTSe from stacked elemental Cu/Sn/Zn layer and post-sulfurization and selenization, respectively. For direct solution coating processes, hydrazine solution coating approach has yielded CZTSSe device with 12.6% record efficiency, while particulate- and molecular-based solution coating produced beyond 10% and 11% efficient CZTSSe devices, respectively. To further improve the performance of solution-processed kesterite solar cells, efforts should be focused on two aspects: (1) real low-cost fabricated precursor with controlled composition and microstructure, and (2) post-chalcogenization with controlled phase evolution, element losses and grain growth to form phase pure CZTSSe without detrimental secondary phases. Also, research efforts need to be devoted into how to effectively incorporate the advanced experience of CIGSe photovoltaics and related nanotechnology into the research of CZTS photovoltaics technology, due to the great similarity between these two materials. Further improvement can be expected in understanding the fundamental knowledge using solution-processed kesterite absorbers and devices to overcome the performance gap between CZTSSe and CIGSe solar cells, making kesterite solar cells a truly competitive photovoltaics technology.

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Inorganic Hole Contacts for Perovskite Solar Cells: Towards High-Performance Printable Solar Cells

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Abstract

Organic-inorganic hybrid perovskites have been demonstrated to be efficient light absorbers for solar cells with a power conversion efficiency (PCE) exceeding 20%, and the low-temperature solution deposition process makes them very suitable for printable solar cells. For most perovskite solar cells, organic materials such as PEDOT:PSS and Spiro-OMeTAD are the most frequently employed hole transport material (HTM). However, the high acidity and hygroscopicity of PEDOT:PSS make it not good for the long-term stability of the device, and the high price of spiro-OMeTAD as well as its complicated doping process also make it not so attractive for device fabrication. Apart from the organic HTMs, many inorganic materials have also been employed as hole HTMs for perovskite films, such as CuI, CuSCN, NiO, and so on. Compared to the traditional organic HTMs, inorganic HTMs usually have higher mobility and stability, which probably promises a better device performance. In this chapter, we will present the recent results on preparation and characterization of inorganic hole HTMs together with their application in perovskite solar cells. Particularly, printed perovskite solar cells with inorganic hole HTMs will be reviewed and discussed.

Keywords: Inorganic hole transport materials, transition metal oxides, nickel oxide, organic-inorganic perovskite, printable

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13.1 Introduction

Organic-inorganic halide perovskite solar cell is a newcomer to the photovoltaic field, which was first reported by Miyasaka and coworkers in 2006. The initial organic-inorganic halide perovskite solar cell employed the same structure as that of dye-sensitized solar cells, in which perovskites were used as the sensitizer for the nanoporous TiO_2 film, and the device showed unstable power conversion efficiencies (PCE) of 2.2% ~ 3.8% [1, 2]. The breakthrough came in 2012 when Park and coworkers reported the first all-solid-state perovskite solar cell with relative long-term stability and high efficiency (>9%) [3]. They replaced the liquid electrolyte with the small-molecule organic material 2,2',7,7'-tetrakis(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD), which can transport holes efficiently and improve the device stability. Then the development of perovskite solar cells entered into the fast lane, and perovskite solar cells with different structures were reported. In 2013, an efficiency exceeding 15% was proved both on mesoscopic perovskite devices and planar heterojunction perovskite devices [4, 5]. Due to the simple fabrication process of perovskite solar cells, which is similar to that of DSSCs and organic thin film solar cells, many more researchers joined this field, resulting in a surge in the development of perovskite solar cells. As a result, the PCE record increased quickly and was already 22.1% at the beginning of 2016 [6].

Organic-inorganic halide perovskites have a 3D cubic structure with a general formula of ABX_3 , in which typically $\text{A} = \text{CH}_3\text{NH}_3^+$ or $\text{NH}_2\text{-CH-NH}_2^+$; $\text{B} = \text{Pb}^{2+}$ or Sn^{2+} ; and $\text{X} = \text{Cl}^-$, Br^- , or I^- . In most efficient photovoltaic devices, they are $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and $\text{NH}_2\text{-CH=NH}_2\text{PbI}_3$ (FAPbI₃). Generally speaking, organic-inorganic halide perovskites have many promising properties, such as excellent light harvesting, high charge carrier mobility, long carrier lifetime and low-cost solution deposition method [7, 8]. Perovskite solar cells can be mainly divided into two classes based on their structures: mesoscopic perovskite solar cells and planar perovskite solar cells, as shown in Figure 13.1. The first class evolved from solid-state dye-sensitized solar cells and contained a mesoporous film as the support layer of perovskite, for example, the TiO_2 and Al_2O_3 mesoporous films. While the other class has a similar structure to organic bulk heterojunction thin film solar cells, containing a perovskite absorber sandwiched between a p-type and n-type carrier transport layer. It can be further divided into two classes: normal n-i-p type devices and inverted p-i-n type devices.

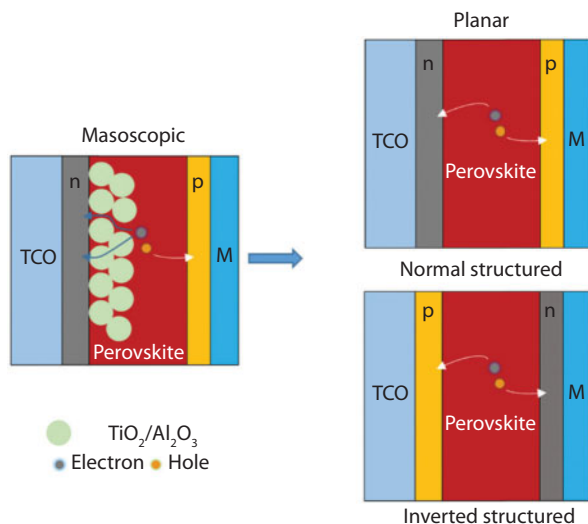


Figure 13.1 Classification of perovskite solar cells based on their structures.

In both planar and mesoscopic perovskite solar cells, compact TiO_2 films and organic spiro-OMeTAD films are the most frequent electron transport material (ETM) and hole transport material (HTM), respectively. Besides, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) is another common HTM that is frequently employed in p-i-n type inverted planar perovskite solar cells. The efficient hole extraction ability for spiro-OMeTAD and PEDOT:PSS has already been demonstrated on perovskite solar cells with different structures. However, spiro-OMeTAD not only has an extremely high price and poor stability against temperature and moisture, but also needs a complicated doping process to achieve efficient hole extraction ability [9]. While the high acidity and hygroscopicity of PEDOT:PSS also cause problems in the long-term stability of the device [10]. Compared with these organic HTMs, inorganic HTMs exhibit a promising application in perovskite solar cells due to their higher mobility and stability. Besides, some inorganic hole HTMs can be derived from low-temperature solution methods, making them very attractive for roll-to-roll printed techniques. In this chapter, we summarize the recent results on preparation and characterization of inorganic HTMs together with their application in perovskite solar cells. Particularly, printable perovskite solar cells will also be reviewed thoroughly, and special attention will be paid to the inorganic HTMs-based printed perovskite solar cells.

13.2 Transition Metal Oxides

The research of transition metal oxides as carrier transport materials in solar cells has a very long history, especially in organic electronic devices [11]. Considering the similar device structures, the application of these transition metal oxides can be easily transferred from organic solar cells to perovskite solar cells. However, their specific performances in perovskite solar cells are very different from those exhibited in organic solar cells.

13.2.1 Molybdenum Oxide (MoO_x , $x < 3$)

Molybdenum oxide (MoO_3) is an excellent hole extraction material with a wide band gap of more than 3.0 eV. There are usually a lot of oxygen deficiencies in the MoO_3 , therefore it is sometimes noted as MoO_x ($x < 3$). The conduction band of MoO_x is contributed by the unoccupied 4D band of molybdenum. It was once misidentified as a p-type semiconductor until the ultraviolet photoelectron spectroscopy demonstrated its n-type characteristics directly [12]. MoO_x films usually have a high work function of 5.3 ~ 6.9 eV, and the value is heavily dependent on the fabrication method and surface treatment [11]. The great success of MoO_x has not only been demonstrated in organic thin film solar cells [10], but also in various different types of solar cells, including silicon heterojunction solar cells [13, 14], PbS quantum dots heterojunction solar cells [15], CdS/CdTe thin film solar cells [16] and C60-based heterojunction solar cells [17].

In a typical normal-structured perovskite solar cell, the top metal electrode is usually made of noble metals such as Au and Ag. When low price metal Al is used as the anode electrode, a back diode will be created at the HTM/Al interface and the energy barrier will limit the hole extraction from the active layer. However, Zhu *et al.* [18] demonstrated that the back diode effect can be greatly reduced by inserting a thin layer of MoO_3 film between the HTM and Al electrode. Figure 13.2a shows the cross-sectional SEM image of their device, and the corresponding J-V curves and incident photon-to-electron conversion efficiency (IPCE) spectra for the devices are shown in Figure 13.2b,c. The PCE of device with MoO_3/Al electrode can be improved to the similar level with that of devices with Ag electrode (11.42 % vs. 12.36%). However, it should be mentioned that devices with only MoO_3 contact between perovskite and Ag showed almost no efficiency, which was probably caused by shorting associated with pinholes on the absorber layer. Thus, the use of organic HTM films is still crucial in the MoO_3 -based devices, because it can suppress shorting in perovskite cells. Therefore, MoO_3 films are mostly employed as the interfacial layer between

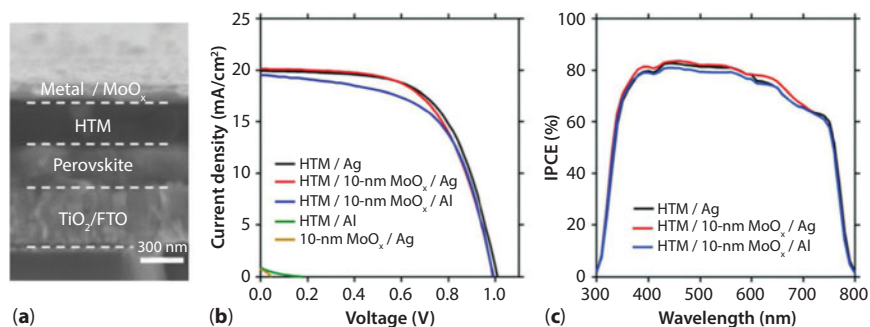


Figure 13.2 (a) Typical cross-sectional SEM image of a planar FTO/TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/MoO_x/metal (Ag or Al) solar cell. Comparison of J-V characteristics (b) and IPCE (c) of perovskite CH₃NH₃PbI₃ solar cells using different top-contact structures as indicated. (Reprinted from [18]; Copyright © 2014 API)

the organic HTM film and metal electrode, such as the diketopyrrolopyrrole-based copolymer/MoO₃/Ag, P3HT/MoO₃/Ag and so on [19].

Furthermore, MoO_x has also been applied in inverted planar perovskite solar cells, where it is usually employed to combine with some organic films to prepare a double-layer hole transport film. For example, Chu *et al.* [20] employed solution-derived MoO₃ film to modify the interface between ITO and PEDOT:PSS film in inverted planar perovskite solar cells. After incorporating the MoO₃ film, the PCE was increased from 9.81% to 12.78% for the optimized device, which should be ascribed to the increased hole collection efficiency of the PEDOT:PSS-MoO₃ double layer. Besides, the device stability was also improved to some extent. MoO₃ was also used as an interfacial layer between N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,10-biphenyl)-4,40-diamine (NPB) and ITO substrate, which improved the V_{oc} and PCE greatly [21].

In spite of all the above works, a successful perovskite cell with a solo MoO₃ hole transport film has yet to be reported. It seems that the direct contact of MoO₃ and perovskite is not favorable in perovskite cells. A detailed study of the CH₃NH₃PbI₃/MoO₃ interface by Gao *et al.* [22] demonstrated that a chemical reaction took place at the interface of CH₃NH₃PbI₃/MoO₃ when MoO₃ was evaporated directly onto CH₃NH₃PbI₃ surface, resulting in unfavorable interface energy level alignment for hole extraction. In their experiment, a potential barrier of ~1.36 eV was observed for holes, which impeded hole extraction from CH₃NH₃PbI₃ to MoO₃. This may explain why the attempt of MoO₃ application in perovskite solar cells is not as abundant and successful as that in organic solar cells.

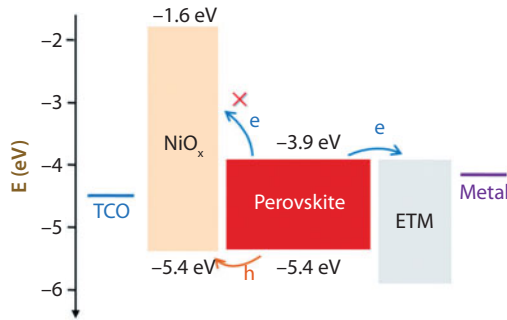


Figure 13.3 Band alignment of a typical NiO_x -based perovskite solar cell.

13.2.2 Nickel Oxide (NiO)

Nickel oxide is a p-type semiconductor which has also been well-studied in organic optoelectronic devices. It is believed that the p-type characteristics of NiO originates from positive charge compensation at the thermodynamically favored Ni^{2+} vacancies. Interestingly, the Ni 3d states contribute to both the valence band maximum and conduction band minimum. Its band gap is typically above 3.5 eV and is strongly dependent on the surface chemistry, crystal orientation and thin film deposition conditions [11].

Compared with MoO_3 , NiO has achieved great success in perovskite solar cells, partially due to its favorable band alignment [23]. As shown in Figure 13.3, the conduction band (CB) and valence band (VB) of NiO usually sit at -1.6 eV and -5.4 eV. Because of its high work function (usually above 5.0 eV), the energy barrier between the VB of NiO and perovskite is negligible, resulting in a fast transportation of holes from perovskite absorber to NiO. However, the energy barrier between the CB of NiO and perovskite is as high as 2.3 eV, which blocks the electrons transportation from the perovskite absorber to the NiO film. As a result, NiO is a very efficient hole selective transport material for perovskite.

13.2.2.1 Mesoscopic NiO Perovskite Solar Cells

In 2014, NiO was first introduced to mesoscopic perovskite solar cells by Guo *et al.* [24]. They prepared a compact NiO film by a sol-gel process using formate dihydrate as the nickel source. Then a mesoporous NiO film was deposited onto the compact NiO film by spin-coating a diluted slurry NiO solution. After that, a high-temperature annealing process at 400°C was conducted to remove the organic components. Perovskite films were deposited onto the NiO mesoporous films to fabricate perovskite solar cells

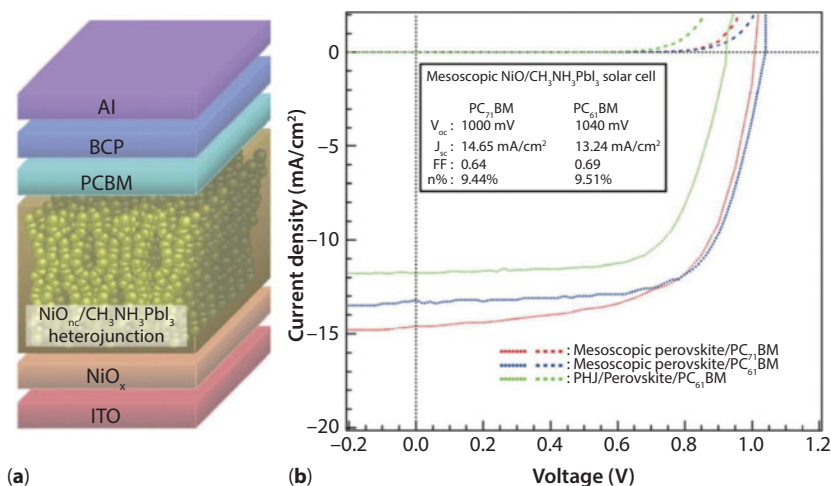


Figure 13.4 (a) The schematic of the NiO-based mesoscopic perovskite solar cell. (b) The current-voltage characteristics of photovoltaic devices made of mesoscopic NiO nc/perovskite/PCBM heterojunction solar cell and planar NiO/perovskite/PC61BM heterojunction solar cells (Reprinted from [24]; Copyright © 2014 NPG)

with a structure of ITO/NiO_x/NiO nc/CH₃NH₃PbI₃/PCBM/BCP/Al, as shown in Figure 13.4a. By using a PC61BM film as the ETM, the device achieved a highest PCE of 9.51% with a J_{sc} of 13.24 mA cm⁻², V_{oc} of 1.04 V, and FF of 0.69. Figure 13.4b presents the J-V curves of the optimized devices, where the J-V curve for a planar NiO-based perovskite solar cell is also presented. Later, the same group replaced the sol-gel-derived NiO film with a sputtered NiO film, and fabricated mesoscopic NiO perovskite solar cells with the same structure. After a careful optimization of the NiO thickness oxygen doping, the PCE was further improved to 11.6% with J_{sc} as high as 19.8 mA cm⁻² [25]. Besides, NiO mesoporous films can also be employed as the HTM on top of perovskite absorbers. This kind of structure is frequently employed to fabricate fully printed perovskite solar cells, which will be introduced in the latter part of this chapter.

13.2.2.2 Planar NiO Perovskite Solar Cells

Compared with the mesoscopic NiO perovskite solar cells, more researchers have focused their attention on the planar NiO perovskite solar cells, partially due to the possibility of a low temperature device fabrication process due to getting rid of the high temperature derived mesoporous film. Many methods have been developed to deposit NiO films for perovskite solar cells, including the vacuum-related methods such as evaporation,

sputtering, pulsed laser deposition (PLD), atomic layer deposition (ALD); and solution phase methods such as sol-gel route, spin coating from pre-synthesized nanocrystals, and electrodeposition [26–39].

13.2.2.2.1 Sputtering

Ahmadi *et al.* [28] deposited a double layer of NiO/Ni onto $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film by sputtering to fabricate a normal-structured perovskite solar cell with a structure of FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/NiO/Ni. The angular deposition of NiO layers resulted in a uniform and crack-free coverage of the perovskite layer without any damage. Although this process helps the devices get rid of the expensive noble metal electrode, the device PCE is relatively low (7.28%), making it unattractive to society. Wang *et al.* [29] employed magnetron sputtering to deposit NiO films on fluorine-doped tin oxide (FTO) substrate, which have a work function of 5.5 eV without UV-ozone treatment. The deposited films were employed to fabricate inverted planar perovskite solar cells with a structure of FTO/NiO/CH₃NH₃PbI₃/PCBM/BCP/Au, and a highest PCE of 9.83% was achieved.

13.2.2.2.2 Atomic Layer Deposition (ALD)

Compared with sputtering, atomic layer deposition is a more controllable method to deposit thin films with certain thickness, especially the ultrathin films. Shin *et al.* [31] prepared ultrathin NiO films on ITO substrates by ALD. The prepared NiO film with a thickness of 5 ~ 7.5 nm was crystalline and very transparent. It was found that the effective work function in ultrathin NiO apparently increased when the thickness was comparable to its Debye length. Besides, heat treatment can successfully control the surface NiOOH layer generated by surface hydroxylation. Both the above items contributed to the efficient hole extraction property of NiO film. Inverted planar perovskite solar cells exhibited a J_{sc} of 21.9 mA cm⁻², V_{oc} of 1.04 V, FF of 0.72 and an overall PCE of 16.4% with a negligible J-V hysteresis.

13.2.2.2.3 Pulsed Laser Deposition (PLD)

Seok *et al.* [30] reported a nanostructured NiO film prepared by pulsed laser deposition method. The NiO films were deposited on glass/ITO substrates with the post-annealing temperature of 200 °C, and the morphology and density of the deposited materials can be varied by adjusting the deposition parameters such as the oxygen partial pressure. It was found that oriented growth of NiO along the (111) plane direction was achieved when the oxygen pressure was low (200 mTorr, Figure 13.5a,b). Higher oxygen pressure (500–900 mTorr) decreased the crystallinity and degree of preferred orientation. Figure 13.5c shows the cross-sectional SEM image of the inverted planar perovskite solar cells based on the nanostructured NiO

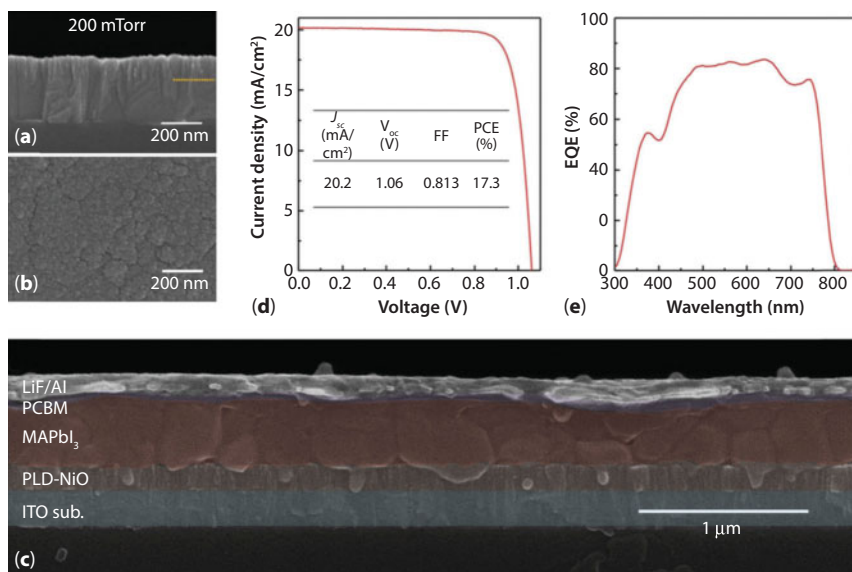


Figure 13.5 (a) Cross-sectional and (b) top-view SEM image of NiO films deposited by PLD at an oxygen pressure of 200 mTorr. (c) False color cross-sectional SEM image for the inverted planar perovskite solar cell based on nanostructured NiO hole transport film. (d) J-V curve and (e) EQE spectrum for the optimized perovskite cell based on nanostructured NiO hole transport film [30]. (Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA)

films. The device performance strongly depended on the deposition conditions of the NiO films. The transient photovoltage decay measurement revealed a longer recombination lifetime for the nanostructured NiO film than that for the disordered NiO thin film, indicating a faster hole extraction process in nanostructured NiO films. The best device performance was obtained on the nanostructured NiO film with a unique morphology and a preferred orientation. Figure 13.5d,e presents the J-V curve and external quantum efficiency (EQE) spectrum for the best device, which shows a PCE as high as 17.3% with a V_{oc} of 1.06 V, J_{sc} of 20.2 mA cm⁻², and FF of 0.813.

13.2.2.2.4 Sol-Gel Routes

Sol-gel routes may be the most frequently employed solution methods for NiO film deposition due to their simple process and good reliability. Typically, nickel salt is dissolved in an organic solvent to form a precursor sol, in which some stabilizers are usually added. The precursor sol is then used to prepare the NiO film by spin coating, followed by a

high temperature (usually above 300 °C) annealing process which aims to remove the organic components and crystalize the film. The thickness of the film can be adjusted by either changing the concentration of the precursor sol or varying the spin-coating speed and repeated times. Perovskite solar cells based on sol-gel-derived NiO films usually employ the similar inverted device structure, but the detail fabrication techniques, especially the absorber quality and interface control in the device, result in variations in performances. Yang *et al.* [38] introduced a uniform NiO film spin-coated from NiO nanocrystals sol using nickel(II) acetylacetonate and diethanolamine as the starting materials. The prepared crystalline NiO films, which had a good transmission in the visible region, were employed as the HTM for inverted planar perovskite solar cells, and a highest PCE of 9.11% was achieved for the optimized device. While in another work, a similar method was used to deposit NiO film, but a new approach was employed to deposit the perovskite films on the NiO layer which was believed to improve the quality of perovskite films greatly. As a result, the PCE was improved to 14.42% [32].

In order to further improve the device performance, doping the NiO films can be a good choice, because it is able to mitigate the losses in FF and J_{sc} through modulating conductivity. Fortunately, it is very convenient to dope the NiO film by sol-gel routes. Jen *et al.* [34] reported an efficient copper-doped NiO hole contact film by sol-gel method. As shown in Figure 13.6a, the conductivity examined by the conductive atomic force microscopy (AFM) was improved from $2.2 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ for pristine NiO to $8.4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for 5 at% Cu-doped NiO. The photoluminescence spectra shown in Figure 13.6b also proved the much more efficient hole extraction ability of the Cu:NiO film. Figure 13.6c,d presents the J-V curves and EQE spectra for the perovskite solar cells with different hole extraction layers. It was clear that copper doping benefited the device performance a lot. After the copper doping, the FF and J_{sc} increased from 0.59 and 14.42 mA cm^{-2} to 0.73 and 19.17 mA cm^{-2} , respectively, leading to an improvement of PCE from 8.94% to 15.40%. Later work from the same group decreased the heat treatment temperature for Cu:NiO film from 500 °C to 150 °C, at the same time further improved the device PCE to 17.8% [36]. The key point is using a so-called combustion route to prepare Cu:NiO film from $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ with the help of acetylacetone at a relatively low temperature.

Besides the element Cu, Mg and Li co-doped NiO films were also reported. Han *et al.* [40] successfully deposited NiMgLiO films by sol-gel routes using nickel(II) acetylacetonate, magnesium acetate tetrahydrate and lithium acetate as the metal ion sources. By using a double layer of PCBM/Ti(Nb)O_x as the electron transport film, they fabricated inverted planar

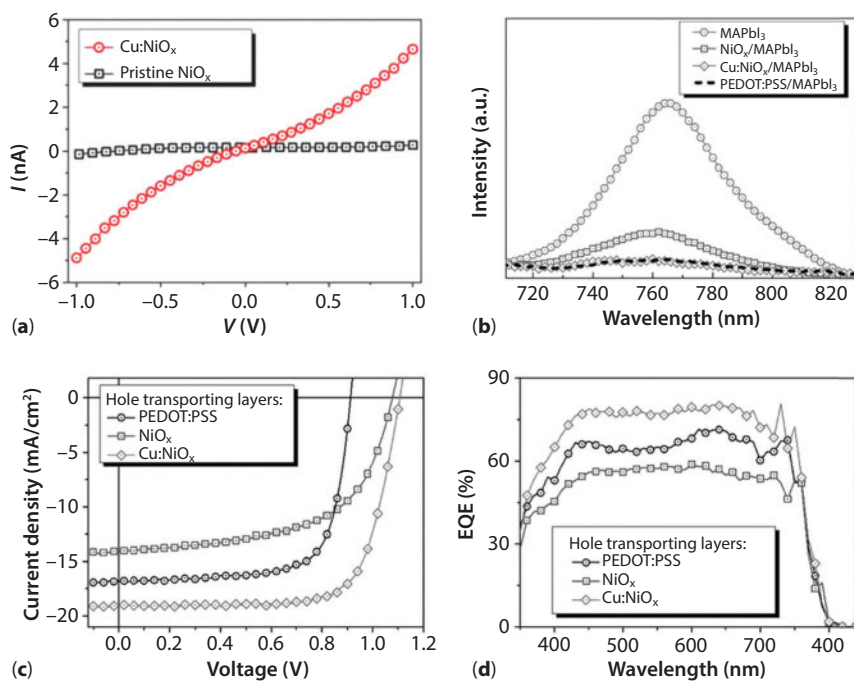


Figure 13.6 (a) I-V curves of pristine NiO_x and Cu:NiO_x measured by c-AFM. (b) Photoluminescence spectra (excitation at 600 nm) of perovskite (MAPbI₃) films on top of pristine NiO_x (squares), Cu:NiO_x (diamonds), and PEDOT:PSS (dotted line). J-V curves (c) and EQE spectra (d) of perovskite solar cells based on PEDOT:PSS (circles), NiO_x (squares), and Cu:NiO_x (diamonds) hole-transporting layers [34]. (Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA)

perovskite solar cells. Conductive AFM test demonstrated that the conductivity of NiO films can be increased by the Li-Mg doping process. The robust inorganic nature of the layers allowed improvement on the PCE to 18.40% on small devices (0.09 cm²). For the device with a large active area (1.02 cm²), a PCE of 16.2% was achieved, on which a PCE of 15% was also certified by a public test center (Calibration, Standards and Measurement Team at the AIST Research Center for Photovoltaics). Besides, the hysteresis effect of J-V curves was also eliminated. More importantly, the sealed device showed very good stability with > 90% of the initial PCE remaining after 1000 hours of light soaking.

One advantage of inorganic carrier transport materials is their higher stability than the organic materials. Therefore, the perovskite cell using both inorganic ETMs and HTMs can maximize this merit. Yang *et al.* [35] reported a perovskite solar cell using a sol-gel-derived NiO film as the hole

transport layer and a ZnO nanoparticles film as the electron transport layer. The device with a structure of glass/ITO/NiO/perovskite/ZnO/Al showed an improved stability against water and oxygen degradation when compared with the devices based on organic charge transport layers. After 60 days storage in air at room temperature, the all-metal-oxide devices retain about 90% of their original efficiency.

13.2.2.2.5 Spin Coating from Pre-Synthesized Nanocrystals

Another solution method to prepare NiO films involves synthesizing crystalline NiO nanocrystals first, and then spin-coating NiO films from the nanocrystal dispersion. The merit of this method is that it gets rid of the high-temperature annealing process after the film deposition, so that it is very suitable for flexible substrates which can not afford high-temperature process above 150 °C. Also, pre-synthesized NiO nanocrystals are beneficial to deposit NiO films on flexible substrates by a roll-to-roll printing method.

Our group has reported a NiO film deposited from pre-synthesized NiO nanocrystals which were prepared by a chemical precipitation method. The $\text{Ni}(\text{OH})_2$ nanoparticles, which were first prepared by the reaction of NiCl_2 and NaOH, were then annealed at 270 °C for 2 h to get NiO nanoparticles from the decomposition of $\text{Ni}(\text{OH})_2$. Figure 13.7a shows the prepared NiO nanocrystals, which have an average size of 10 nm. The NiO films were deposited by spin coating from the NiO nanocrystal colloids which were prepared by dispersing the NiO nanocrystals in water. The prepared NiO films were crystalline even without annealing, providing an excellent hole transport ability. Figure 13.7b,c presents the top-view and cross-sectional SEM images of the deposited NiO films, which are very rough but continuous without voids. Perovskite films were deposited onto the NiO film by a modified one-step spin-coating method. As illustrated by the cross-sectional SEM image shown in Figure 13.7d, the prepared inverted planar perovskite solar cell had a structure of glass/ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Ag. The J-V curve for the device on a rigid substrate showed a highest efficiency of 16.47% (Figure 13.7e). Because the whole device fabrication process was conducted at a low temperature of 130 °C, it can be easily transferred to a polyethylene naphthalate (PEN) flexible substrate, and a highest PCE of 13.43% was demonstrated for the fabricated NiO-based flexible perovskite solar cells.

13.2.2.2.6 Electrodeposition

The electrodeposition method is also an easy solution process to prepare NiO films. Sarkar *et al.* [37] prepared $\text{Ni}(\text{OH})_2$ films on FTO substrate by galvanostatic electrodeposition in a three-electrode system using an

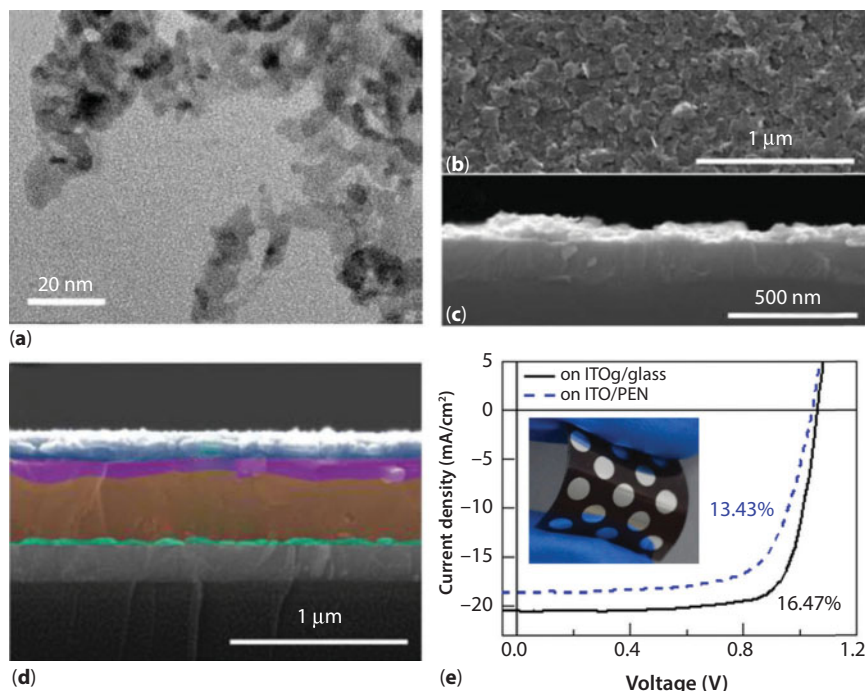


Figure 13.7 (a) TEM image of the NiO_x nanoparticles. (b) Top-view and (c) cross-sectional SEM images of the NiO_x film on ITO substrate. (d) False color cross-sectional SEM image of the NiO_x-based perovskite solar cell. (e) J-V curves for NiO_x-based perovskite solar cells on ITO-glass and ITO-PEN substrates [33]. The inset presents a digital photograph of a flexible inverted planar perovskite solar cell in a PEN substrate. (Copyright © 2016 American Chemical Society)

aqueous NiNO₃ solution as the electrolyte. The prepared Ni(OH)₂ was then converted to NiO by annealing at 350 °C for 1 h. Inverted planar perovskite solar cells were fabricated on a FTO-glass substrate with a structure of glass/FTO/NiO/CH₃NH₃PbI_{3-x}Cl_x/PCBM/Ag, on which a highest PCE of 7.26% was obtained.

Above all, NiO has been successfully employed in both mesoscopic and planar perovskite solar cells. The excellent performance in PCE, stability and hysteresis behavior allows it a promising future in the field of perovskite solar cells. Table 13.1 summarizes the performances of some represented NiO-based perovskite solar cells that have been reported so far. It is clear that the highest PCE has reached 18.40% for small devices and 16.1% for square centimeter devices. It should be mentioned here that this is also the first large-area perovskite solar cell with relative high PCE and stability.

Table 13.1 Summary of the performances of the reported NiO_x-based organic-inorganic hybrid perovskite solar cells. The word “non” means the parameter was not presented in the paper.

Device configuration	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)	Steady-state PCE (%)	Area (cm ²)	Method/temperature	Ref.
FTO/NiMgLiO/CH ₃ NH ₃ PbI ₃ /PCBM/Ti(Bb)Ox/Ag	1.096 1.072	20.39 20.62	0.823 0.748	18.40 16.2	18.28 Non	0.09 1.02	Spray pyrolysis/500 °C	[40]
ITO/NiO/CH ₃ NH ₃ PbI ₃ /C60/Bis-C60/Ag	1.03 1.00	21.8 20.66	0.784 0.705	17.6 (glass) 14.53 (PET)	17.50 14.50	0.06	Spin coating/RT	[41]
ITO/Cu:NiO/CH ₃ NH ₃ PbI ₃ /C60/Bis-C60/Ag	1.05	21.60	0.77	17.46	17.80	Non	Spin coating/150 °C	[36]
ITO/PLD-NiO/CH ₃ NH ₃ PbI ₃ /PCBM/LiF/Al	1.06	20.2	0.813	17.3	17.2	Non	PLD/ 200 °C	[30]
ITO/NiO/CH ₃ NH ₃ PbI ₃ /PCBM/Ag	1.07 1.04	20.58 18.74	0.748 0.689	16.47 (glass) 13.43 (PEN)	16.22 13.29	0.07	Spin coating/130 °C	[33]
ITO/NiO/CH ₃ NH ₃ PbI ₃ /PCBM/Ag	1.04	21.87	0.72	16.40	Non	0.24	ALD/300 °C	[31]
ITO/NiOx/CH ₃ NH ₃ PbI ₃ /ZnO/Al	1.01	21.0	0.76	16.1	Non	0.1	Spin coating/300 °C	[35]
FTO/Cu:NiO/CH ₃ NH ₃ PbI ₃ /PCBM/Ag	1.11	18.75	0.72	15.40	Non	Non	Spin coating/550 °C	[34]

FTO/TiO ₂ /Al ₂ O ₃ / (CH ₃ NH ₃ PbI ₃)/NiO/ Carbon	0.915	21.62	0.76	15.03	Non	0.16	Spin coating/500 °C	[42]
FTO/TiO ₂ /ZrO ₂ /NiO/ Carbon-(CH ₃ NH ₃ PbI ₃)	0.917	21.36	0.76	14.9	Non	Non	Doctor blade/500 °C	[43]
FTO/NiO _x /CH ₃ NH ₃ PbI ₃ / PCBM/Ag	1.09	17.93	0.738	14.42	14.18	0.07	Spin coating/500 °C	[32]
FTO/TiO ₂ /Meso-TiO ₂ /Meso- ZrO ₂ /NiO nanosheets	0.965	20.4	0.72	14.2	13.9	0.6	Screen printing/500 °C	[44]
FTO/NiO/Meso-Al ₂ O ₃ / CH ₃ NH ₃ PbI ₃ /PCBM/BCP/ Ag	1.036	17.989	0.724	13.49	13.61	0.09	Spray pyrolysis/500 °C	[45]
ITO/NiO/meso-NiO/ CH ₃ NH ₃ PbI ₃ /BCP/Al	0.96	19.8	0.61	11.6	Non	Non	Sputtering/400 °C	[25]
FTO/TiO ₂ / NiO(CH ₃ NH ₃ PbI ₃)/Carbon	0.89	18.2	0.71	11.4	Non	0.6	Screen-printing/500 °C	[46]
FTO/NiO NCs/CH ₃ NH ₃ PbCl _{3-x} I _x /PCBM (PS)/Al	1.07	15.62	0.64	10.68	Non	Non	Spin coating/500 °C	[47]
Au/NiO/CH ₃ NH ₃ PbI ₃ /C60/ Bis-C60/Al	1.02	13.04	0.77	10.24	Non	Non	Evaporated/500 °C	[27]
FTO/NiO/CH ₃ NH ₃ PbI ₃ / PCBM/Ag	1.10	15.17	0.59	9.84	Non	Non	Sputtering/Not heated	[29]
FTO/NiO NCs/CH ₃ NH ₃ PbI ₃ / PCBM/Au	0.882	16.27	0.635	9.11	Non	Non	Spin coating/500 °C	[38]

(Continued)

Table 13.1 Cont.

Device configuration	V_{oc} (V)	J_{sc} (mA/ cm ²)	FF	PCE (%)	Steady-state PCE (%)	Area (cm ²)	Method/ temperature	Ref.
ITO/NiO/meso-NiO/ CH ₃ NH ₃ PbI ₃ /BCP/Al	1.04	13.24	0.69	9.51	Non	0.06	Spin coating/400 °C	[24]
ITO/NiO/CH ₃ NH ₃ PbI _{3-x} Cl _x / PCBM/BCP/Al	0.92	12.43	0.68	7.8	Non	0.06	Spun-cast/300 °C	[39]
ITO/NiO/CH ₃ NH ₃ PbI ₃ / PCBM/Al	1.05	15.4	0.48	7.6	Non	0.0725	Spin coating/350 °C	[48]
ITO/NiO/CH ₃ NH ₃ PbI ₃ / PCBM/BCP/Al	0.901	13.16	0.6538	7.75	Non	0.06	Evaporation/450 °C	[26]
ITO/NiO/CH ₃ NH ₃ PbI ₃ / PCBM/BCP/Al	0.920	11.77	0.68	7.40	Non	0.06	Spin coating/300 °C	[24]
FTO/NiO/CH ₃ NH ₃ PbI _{3-x} Cl _x / PCBM/Ag	0.786	14.2	0.65	7.26	Non	0.07	Electrodeposited/350 °C	[37]
FTO/TiO ₂ /CH ₃ NH ₃ PbI _{3-x} Cl _x / NiOx/Ni	0.77	17.88	0.53	7.28	Non	0.1	Sputtering/90 °C	[28]

13.2.3 Binary Copper Oxide (CuO and Cu₂O)

Copper oxides have two well-known forms, cuprous oxide (Cu₂O) and cupric oxide (CuO), both of which are p-type semiconductors with unique properties like low cost and environmental friendliness. The band gap for CuO and Cu₂O was reported to be 1.9–2.1 eV and 2.1–2.6 eV, respectively [49]. And both of them have a low-lying valence band around 5.4 eV, which matches well with CH₃NH₃PbI₃ and can be good hole extraction materials for perovskite absorbers [50].

Zuo and Ding [50] prepared Cu₂O films by immersing a spin-coated CuI film in NaOH solution. The Cu₂O films can be transformed to CuO by annealing in air at 250 °C. The prepared Cu₂O and CuO films were employed as the HTMs to fabricate inverted planar perovskite solar cells with a structure of glass/ITO/HTM/CH₃NH₃PbI₃/PCBM/Ca/Al, and highest PCEs of 13.35% and 12.16% were obtained for Cu₂O and CuO cells, respectively. Pal and Chatterjee [52] synthesized Cu₂O films on ITO substrates by a successive ionic layer adsorption and reaction (SILAR) method and reported a PCE of 8.23% for the Cu₂O-based inverted planar perovskite solar cell with a structure of glass/ITO/Cu₂O/CH₃NH₃PbI₃/PCBM/Al. Wu *et al.* [53] demonstrated that thermally oxidized ultrathin Cu films can also served as efficient HTM for perovskite solar cells. They prepared Cu₂O films by thermal oxidizing ultrathin Cu film which was deposited by sputtering. The resultant Cu₂O-based perovskite solar cells achieved a highest PCE of 11.0% when the thickness of Cu₂O film was optimized to be 5 nm. Chen *et al.* [54] prepared CuO_x films by spin-coating a copper acetylacetonate-based aqueous solution which contained a certain amount of H₂O₂. UV-O₃ post-treatment was employed to obtain a fully oxidized state of copper oxide, which was able to improve the device performance significantly. A highest PCE of 8.68% was achieved for inverted planar perovskite using such CuO_x film as HTM.

More recently, Huang and coworkers [51] introduced a simple method to prepare CuO_x films for perovskite solar cells. In their experiment, high quality CuO_x films were deposited by spin-coating a diluted acetylacetonate solution followed by a low-temperature annealing and UV-O₃ treatment. The prepared CuO_x was homogeneous and smooth, as demonstrated by the SEM image shown in Figure 13.8a,b. X-ray photoelectron spectroscopy (XPS) results revealed the ratio of Cu⁺/Cu²⁺ in CuO_x was about 2:1, and this value can be decreased by increasing the UV-O₃ treatment time. The fabricated perovskite devices, whose cross-sectional SEM image is shown in Figure 13.8c, showed hysteresis-less J-V curves with a high PCE of 17.1%. Besides, the device exhibited a better stability than the PEDOT:PSS device.

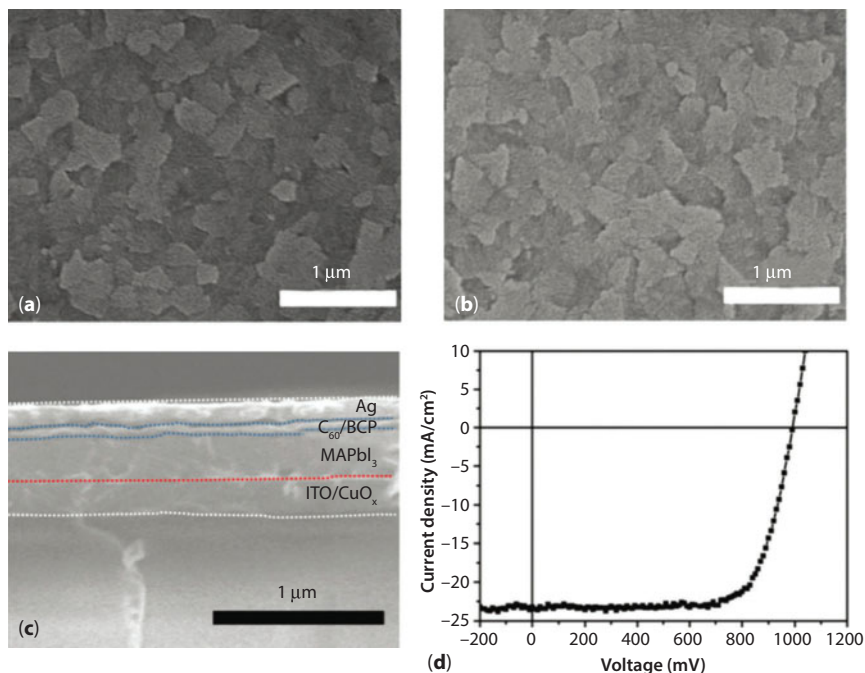


Figure 13.8 SEM images for an ITO substrate (a) and a CuO_x film on ITO substrate (b). Cross-sectional SEM image (c) and J-V curve (d) for the fabricated CuO_x -based perovskite solar cell [51]. (Copyright © 2016 The Royal Society of Chemistry)

By replacing the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film, the device PCE was further improved to 19% [55].

13.2.4 Other Transition Metal Oxides

Although other transition metal oxides such as V_2O_5 and WO_3 have been demonstrated to be potential HTMs in organic solar cells, their application in perovskite solar cells is rare. As far as I know, there is only one report about the WO_3 -based planar perovskite solar cell with a structure of glass/ITO/ WO_3 / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al. However, the WO_3 -based device showed an unattractive low PCE of 7.68% [56].

13.3 Non-Oxide Copper Compounds

In addition to copper oxides, there are various other p-type copper-related compounds which have the potential to be used as HTMs in perovskite solar cells.

13.3.1 Cuprous Iodide (CuI)

Cuprous iodide is a p-type semiconductor with a band gap of 3.1 eV. Its valence band is located around -5.2 eV. Kamat *et al.* [57] employed CuI as the HTM for mesoscopic perovskite solar cells and reported a PCE of 6.0%. Later, Spiccia *et al.* [58] deposited CuI films on perovskite films by a doctor blading method, and then fabricated planar perovskite solar cells with a structure of glass/FTO/TiO₂/perovskite/CuI/Au(or graphite). The device exhibited a highest PCE of 7.5% with significantly diminished J-V hysteretic behavior.

13.3.2 Cuprous Rhodanide (CuSCN)

Cuprous rhodanide is a highly transparent intrinsically p-type semiconductor with a wide band gap of 3.6 eV. It possesses a high hole mobility of $0.01 \sim 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and adequate energy levels with a valence band of -5.4 eV and a conduction band of -1.8 eV, enabling it to be an excellent HTM. Ito *et al.* [59] first introduced doctor-bladed CuSCN films into mesoscopic perovskite solar cells and got a PCE of 4.85%. By optimizing the thickness of CuSCN to 600 nm, the PCE of CuSCN-based mesoscopic perovskite solar cells can be further improved to 12.4% [60]. Later, they reported a normal-structured CuSCN-based planar perovskite solar cell with a PCE of 7.19% [61]. Mora-Sero *et al.* [62] also fabricated normal-structured planar perovskite solar cells based on CuSCN films which were deposited by drop-casting a saturated solution of CuSCN in propylsulfide, and a highest PCE of 6.4% was obtained on the optimized device.

Besides the normal-structured planar perovskite, CuSCN films were also employed to fabricate inverted planar perovskite devices. Sarkar *et al.* [37] prepared CuSCN films on FTO substrates by electrodeposition and fabricated inverted planar perovskite solar cells with a structure of glass/FTO/CuSCN/perovskite/PCBM/Ag. Unfortunately, the device PCE was only 3.8%. Amassian *et al.* [63] deposited CuSNC films by a simple spin-coating process followed by a low temperature baking at 60°C , and the resultant CuSCN-based inverted planar perovskite device showed hysteresis-less J-V curves with a PCE of 10.8%. Huang *et al.* [64] deposited CuSCN films on ITO substrates by potentiostatical electrodeposition in an aqueous solution, and then fabricated inverted planar perovskite solar cells with a structure of glass/ITO/CuSCN/CH₃NH₃PbI₃/C60/BCP/Ag. An average PCE of 15.6% with the highest record of 16.6% was demonstrated on the resultant devices. Almost at the same time, Jen *et al.* [65] succeeded in depositing thin and compact CuSCN films by spin-coating method through optimizing the solvent for CuSCN in the precursor sol.

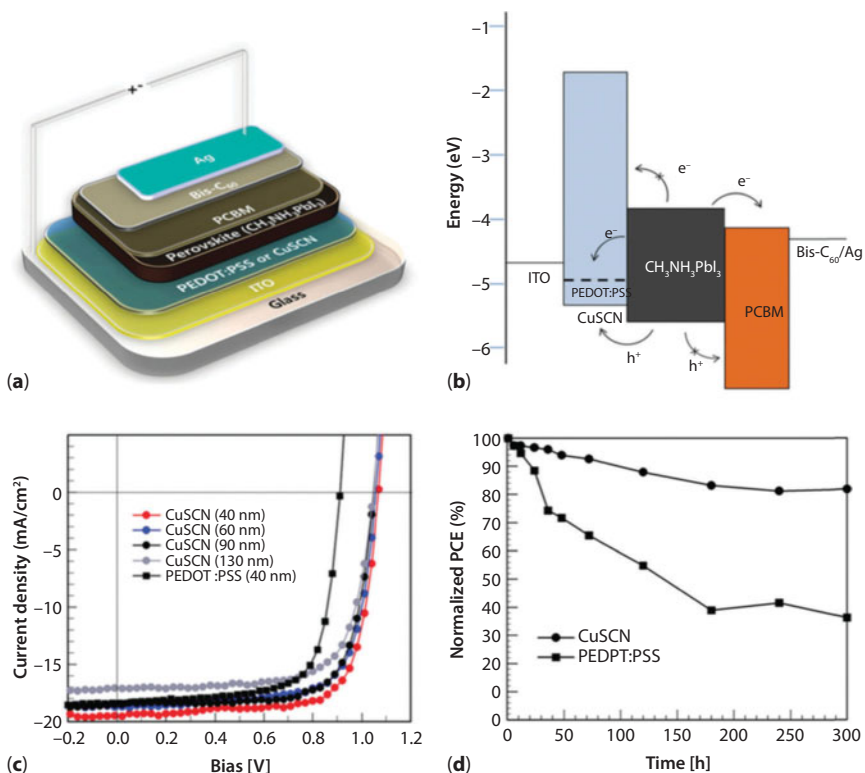


Figure 13.9 (a) Device architecture and (b) corresponding energy band diagram relative to vacuum level of the perovskite solar cell. (c) J-V curves of devices with different HTMs. (d) the ambient device stability of the optimized devices with CuSCN or PEDOT:PSS [65]. (Copyright © 2015 Wiley-VCH Verlag GmbH & Co. KGaA)

The structure and band alignment of the fabricated device are shown in Figure 13.9a,b. The favorable band alignment enabled it to transport holes and block electrons from perovskite efficiently. As a result, the CuSCN-based devices exhibited an optimized PCE of 16% with more enhanced stability than the PEDOT:PSS-based devices (Figure 13.9c,d).

13.3.3 Copper Sulfide (CuS)

Copper sulfide has also been used to modify the surface of TCO to prepare planar perovskite solar cells. Huang *et al.* [66] demonstrated that the work function of ITO substrates can be increased from 4.9 eV to 5.1 eV by spin coating pre-synthesized CuS nanoparticles. The inverted planar perovskite

solar cells with a structure of glass/ITO/CuS/CH₃NH₃PbI₃/C60/BCP/Ag showed a highest PCE of 16% with low J-V hysteresis and excellent stability.

13.3.4 CuAlO₂

CuAlO₂ is a p-type semiconductor possessing decent optical transparency, and chemical and thermal stability. It has a wide band gap of 3.8 eV and its conductivity could be as high as 1 Scm⁻¹, making it a potential candidate for transparent conductive oxide. Liao *et al.* [67] deposited amorphous CuAlO₂ (a:CuAlO₂) thin films by a direct current magnetron sputtering technique and employed double layers of a:CuAlO₂/PEDOT:PSS as the HTM for inverted planar perovskite solar cells. The device occupied a structure as shown in Figure 13.10a, in which the work function of a:CuAlO₂ can be tuned by the thickness of the film (Figure 13.10b). By

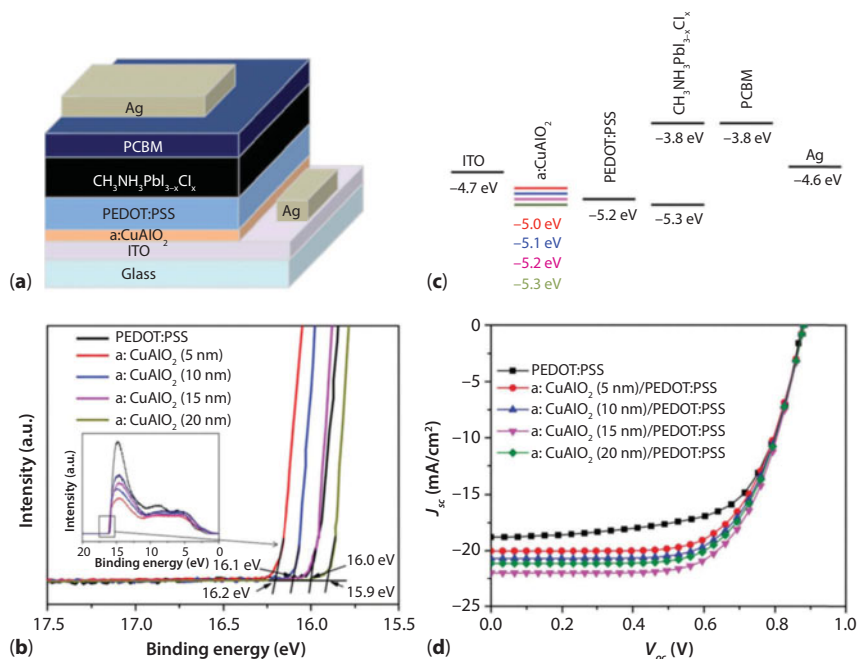


Figure 13.10 (a) Device structure of the fabricated device with the a:CuAlO₂ buffer layer. (b) UPS spectra revealing the secondary cut-off regions for PEDOT:PSS (40 nm) and 5, 10, 15 and 20 nm a:CuAlO₂ films. (c) Energy level diagram of the device components along with various thicknesses of a:CuAlO₂. (d) J-V characteristics of the devices with different configurations of a:CuAlO₂/PEDOT:PSS and pristine PEDOT:PSS hole conductors [67]. (Copyright © 2016 The Royal Society of Chemistry)

tuning the thickness and work function of the a:CuAlO₂ film, as shown in Figure 13.8c, a favorable band alignment can be formed between a:CuAlO₂ and perovskite, enabling an efficient hole extraction from the perovskite absorber. The optimized device exhibited a J_{sc} of 21.98 mA cm⁻², V_{oc} of 0.88 V, FF of 0.75 and an overall PCE of 14.52%. A better stability was also demonstrated for the devices based on a:CuAlO₂/PEDOT:PSS film than those based on PEDOT:PSS film.

13.3.5 CuInS₂ and Cu₂ZnSnS₄

Both CuInS₂ and Cu₂ZnSnS₄ are p-type semiconductors with a bulk band gap of around 1.5 eV, and they are commonly used as the absorber in thin film solar cells. Dai *et al.* [68] tried to employ CuInS₂ quantum dots (QDs) as hole HTM in a mesoscopic perovskite solar cell with a structure of glass/FTO/c-TiO₂/meso-TiO₂/CH₃NH₃PbI₃/CuInS₂ QDs/Au, and reported a PCE of 8.38% for the optimized device. Besides, they also fabricated planar perovskite solar cells with a structure of glass/FTO/CH₃NH₃PbI₃/Cu₂ZnSnS₄/Au, in which the Cu₂ZnSnS₄ film was deposited from a pre-synthesized Cu₂ZnSnS₄ nanoparticles dispersion [69]. The Cu₂ZnSnS₄-based devices showed a highest PCE of 12.75%, which is slightly lower than the spiro-OMeTAD control device.

13.4 Other Inorganic HTMs

13.4.1 PdS Quantum Dots (QDs)

Although PbS is a p-type semiconductor with a narrow band gap of 0.41 eV, the band gap of PbS QDs can be widely tuned from 0.7 to 2.1 eV by facial size-tuning in dot synthesis due to its big Bohr radius of 18 nm. Therefore, PbS QDs may have the potential to be applied as HMT in perovskite solar cells. Ma *et al.* [70] reported an inverted planar perovskite solar cell with a structure of glass/ITO/PbS QDs/Perovskite/PCBM/Al shown in Figure 13.11a,b. By tuning the size of the PbS QDs, as shown in Figure 13.11c, the energy alignment between the PbS QDs HTM and the perovskite absorber can be adjusted, and a highest PCE of 7.5% was achieved for the resultant devices. Considering that the band gap of PbS QDs is relatively small, more researchers would like to incorporate them into perovskite films as absorbers in solar cell research. But this is beyond the topic of this chapter and will not be discussed further here.

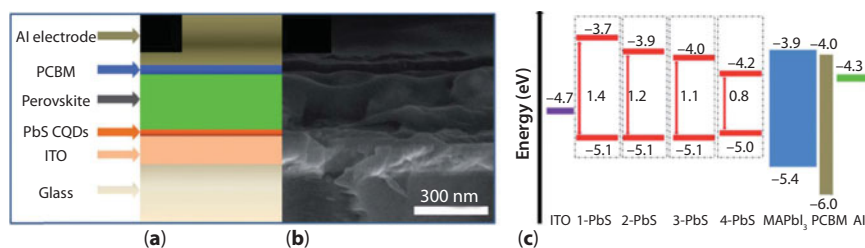


Figure 13.11 (a) Schematic of device architecture. (b) Cross-sectional SEM image of the device. (c) Energy level diagram of the corresponding materials used in our devices employing different PbS QDs [70]. (Copyright © 2015 The Royal Society of Chemistry)

13.4.2 Two-Dimensional (2D) Materials

Two-dimensional materials are a class of interesting materials that exhibit some unique properties. Because of the excellent charge transport properties of 2D materials, such as graphene, graphene oxide (GO), MoS and WS, they have been used as both ETMs and HTMs in solar cells. GO was more frequently employed as HTM in perovskite solar cells. Perovskite films grown on GO show enhanced crystallization, high surface area and preferred in-plane orientation of the (110) plane. Sun *et al.* [71] first reported the application of GO as HTM in perovskite solar cells. They employed spin-coated GO films as the HTMs for inverted planar perovskite solar cells, and achieved a PCE of over 12%. Jang *et al.* [72] employed silver trifluoro-methanesulfonate (AgOTf) to dope GO and prepared (PEDOT:PSS):AgOTf-doped GO films as the HTMs for perovskite solar cells. They obtained a highest PCE of 11.90% on a rigid substrate with a device structure of glass/ITO/(PEDOT:PSS):AgOTf-doped GO/CH₃NH₃PbI_{3-x}Cl_x/PCBM/Au. Using the same structure, a PCE of 9.76% was achieved on a polyethylene terephthalate (PET)/ITO substrate. Later, the same group deposited a nitrogen-doped GO nanoribbons hole transport layer on FTO substrate, on which planar perovskite solar cells with a structure of glass/FTO/NGONR/CH₃NH₃PbI₃/ZnO NP/Al were fabricated. The device showed an optimized PCE of 12.94%, which is higher than that of the PEDOT:PSS control device. Gao *et al.* [73] reported an ammonia modified GO film for perovskite solar cells, and fabricated inverted planar perovskite solar cells according to the process shown in Figure 13.12a. The prepared PEDOT:PSS-GO:NH₃ film showed higher work function than that of PEDOT:PSS-GO film and PEDOT:PSS film, as demonstrated by Figure 13.12b. With the favorable band alignment shown in Figure 13.12c, a highest PCE of 16.11% was achieved on the optimized device.

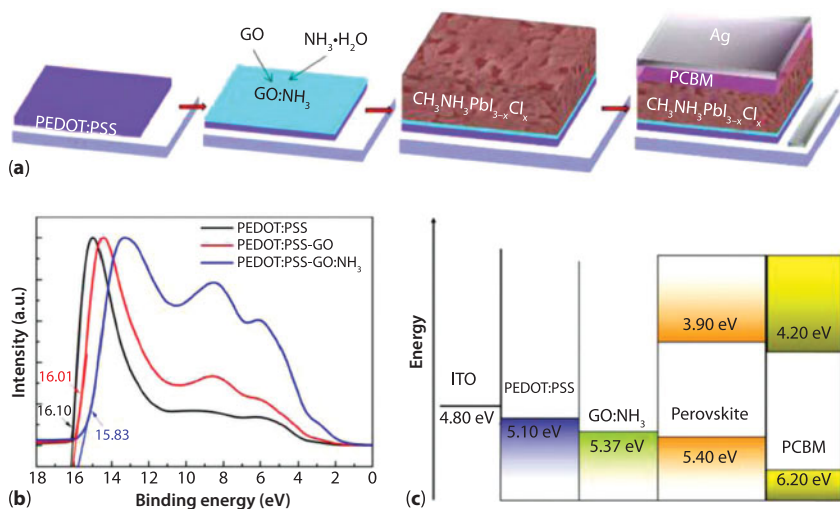


Figure 13.12 (a) Flowchart of fabrication process for the present PSCs with the PEDOT:PSS-GO:NH₃ layer. (b) UPS spectra of three films. The numbers indicate the second-electron cutoffs of these films. (c) The energy level diagram of the devices using the PEDOT:PSS-GO:NH₃ layer [73]. (Copyright © 2016 American Chemical Society)

Besides GO, MoS₂ and WS₂ were also used as the HTMs for inverted planar perovskite solar cells, and PCE of 9.53% and 8.02% have been reported for the MoS₂- and WS₂-based perovskite solar cells, respectively [74]. Loh *et al.* [75] studied the interface between perovskite and MoS₂ and revealed that a pristine MoS₂ monolayer and CH₃NH₃PbI₃ formed a type I heterojunction which hampered the extraction of holes from perovskite. They further found that creating S vacancies in MoS₂ through mild O₂ plasma treatment could improve the hole transfer rate greatly.

13.5 Towards Printable Solar Cells

Since high-quality perovskite films can be easily deposited by several low-cost and low-temperature solution processes, they are very suitable for printed solar cells. Several large area device processing techniques have been developed for organic solar cells, such as spray coating, inkjet printing, blade coating, screen printing, and roll-to-roll printing. Some of the above methods have also been used to prepare printed perovskite solar cells.

Han *et al.* [76] first reported a fully printed mesoscopic perovskite solar cell with a carbon counter electrode in 2013, and the device output had a

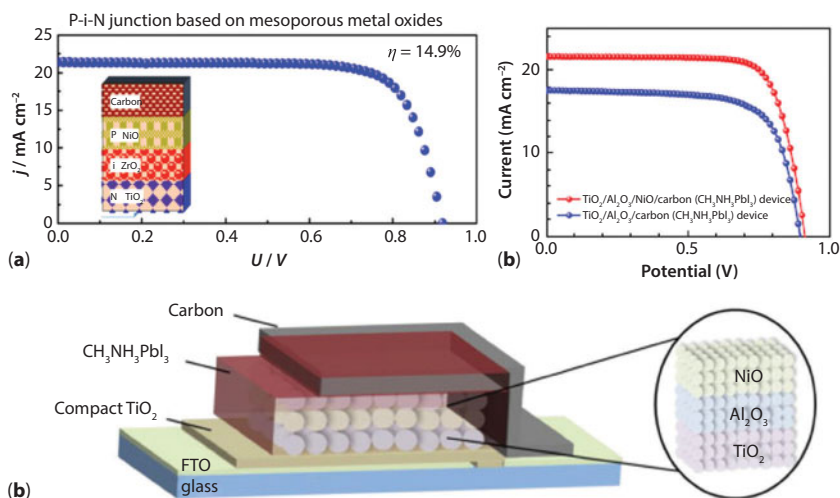


Figure 13.13 (a) Schematic and J-V curve characterization of a screen-printed perovskite solar cell with NiO hole transport film [43] (Copyright © 2015 American Chemical Society). (b) Schematic of a fully printed perovskite solar cell with Al₂O₃ separator layer and NiO hole transport film. (c) J-V curves characterization of printed perovskite solar cells with and without NiO layer [42]. (Copyright © 2015 Elsevier)

PCE of 6.64%. Shortly after, they improved the PCE record to 12.8% through optimizing the composition of perovskite film [77]. The porous TiO₂ and ZrO₂ scaffold layers with a thickness of 1 μm and 2 μm were deposited onto a spray-pyrolyzed compact TiO₂ film successively by screen printing, and annealing was conducted for each layer after the screen printing. Then a 10 μm thick mesoscopic carbon film was also screen-printed onto the ZrO₂ layer. After an annealing process at 400 °C, the perovskite absorber was introduced by infiltrating perovskite precursor into the mesoporous film. To further improve the device performance, they focused a lot of attention on the optimization of perovskite composition. By replacing the common CH₃NH₃PbI₃ with an optimized CH₃NH₃PbI_{3-x}(BF₄)_x, they were able to further increase the PCE to 13.24% [78]. Wang *et al.* also did excellent work on printed mesoscopic perovskite solar cells [42, 43]. They made some modification on Han's device structure, as shown in Figure 13.13a, where a meso-NiO film was deposited between the ZrO₂ layer and the carbon electrode. Therefore, the TiO₂ layer and NiO layer worked as electron transport film and hole transport film, respectively. The incorporation of NiO HTM greatly improved the device PCE to 14.9% even using the common CH₃NH₃PbI₃ as absorber. Later, the same group replaced the ZrO₂ with Al₂O₃ in the device while maintaining the other parts unchanged, as

shown in Figure 13.13b. Compared with the device without NiO film, NiO-based device showed a much higher current density (Figure 13.13c). As a result, an optimized PCE of 15.03% was obtained on the $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{NiO}$ devices [42]. These results suggest that NiO mesoscopic film has the capability as a hole selective contact in printed mesoscopic perovskite solar cells with perfect performance. The robust and abundant NiO material promises the reality of commercial applications of printed perovskite solar cells.

Besides the mesoscopic structure, fully printed planar perovskite solar cells have also been reported by several groups. Yang *et al.* [79] employed an inkjet printing technique to fabricate planar perovskite solar cells with a nanocarbon hole-extraction electrode, and Figure 13.14a shows the fabrication process of their devices. By optimizing the deposition process, a PCE of 11.6% was achieved on their best device. Vak *et al.* [80] reported a slot-die coating method to prepare printed planar perovskite solar cells for the first time, and a highest PCE of 11.96% was demonstrated. In their experiment, all the functional layers except for the Ag electrode were deposited by the slot-die method. Apart from the normal-structured planar perovskite solar cells, inverted planar perovskite solar cells have also been fabricated by printing methods. Jen *et al.* [81] used a blading method to prepare perovskite solar cells, and Figure 13.14b shows the schematic illustration of a fully printed perovskite solar cell with a structure of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Bis-C60/Ag. Figure 13.14c presents the blade-coating equipment used in their experiment as well as an as-prepared

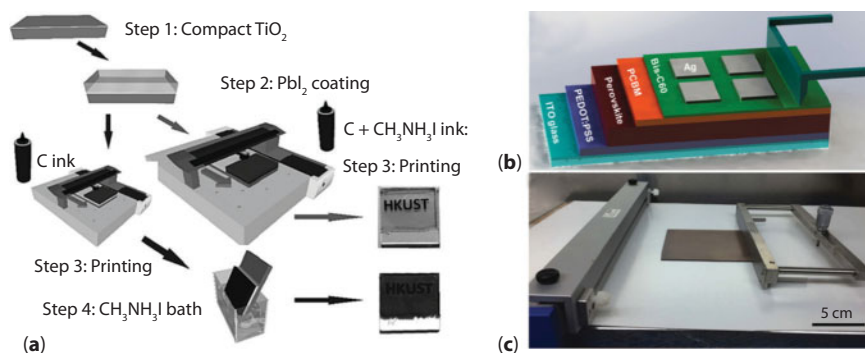


Figure 13.14 (a) Fabrication process flow for the instant inkjet printing of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ planar perovskite solar cells. For comparison, a different strategy was used to convert PbI_2 into $\text{CH}_3\text{NH}_3\text{PbI}_3$ using a separate step 3 and step 4 [79] (Copyright © 2014 Wiley-VCH Verlag GmbH & Co. KGaA). (b) Schematic illustration of a fully printable perovskite solar cell. (c) Blade-coating equipment with as-prepared 10 cm $\times$ 10 cm perovskite film [81]. (Copyright © 2015 Wiley-VCH Verlag GmbH & Co. KGaA)

10 cm × 10 cm perovskite film. After an optimization of the fabrication technique, PCEs of 10.44% and 7.14% were obtained on ITO-glass and ITO-PET substrates, respectively. However, it should be mentioned here that the Ag counter electrode used in their devices was deposited by vacuum evaporation. To achieve fully printed devices, other deposition methods such as screen printing should be adopted for the counter electrode.

13.6 Conclusions and Perspectives

A detailed review of inorganic HTMs for perovskite solar cells was presented. Material physics, film deposition methods and device structures were discussed, along with their device performances. Generally speaking, transition metal oxides are the most important class of HTMs to be investigated in perovskite solar cells. The study of NiO-based devices especially contributes to the major part of this research. Many different methods have been explored to deposit NiO films for perovskite devices, including sputtering, ALD, PLD, sol-gel routes, spin coating from pre-synthesized nanocrystals and electrodeposition. A doping process is usually employed to improve the conductivity of NiO films, resulting in an increased FF and efficiency. It was on a Mg-Li co-doped NiO film-based perovskite device that the highest PCE of inorganic HTM-based perovskite solar cell was obtained. In addition to NiO, copper-related compounds are another big class of inorganic HTMs for perovskite solar cells, including Cu_2O , CuO, CuI, CuSCN, CuS, CuAlO_2 , CuInS_2 and $\text{Cu}_2\text{ZnSnS}_4$. Among these materials, Cu_2O and CuSCN exhibited the most promising properties for device application. Besides, other attempts, such as PbS QDs and 2D materials, have also been introduced.

The research on printed perovskite solar cells was introduced in the last part of this chapter. Both mesoscopic and planar structures have been employed in printed perovskite solar cells and low-cost carbon films are often used as the counter electrodes. Although such investigations are not very abundant at present, the existing results point to a bright future for them. Particularly, the best printed perovskite solar cell was achieved by using a NiO nanoparticles film as the hole transport layer in the mesoscopic device. Considering that efficient hole transport films can be easily deposited from nanoparticle (e.g., NiO, Cu_2O , CuSCN) inks by several large-area device processing techniques, including blade coating, screen printing, and roll-to-roll printing, it is very convenient to incorporate them into the fabrication process of printed perovskite solar cells. In addition to their unique properties, such as high carrier mobility and good stability, it is worth developing inorganic HTMs-based printed perovskite solar cells.

Acknowledgment

This work was funded by the National Natural Science Foundation of China under Grant No. 51502239, China Postdoctoral Science Foundation under grant No. 2015M582659, Natural Science Basic Research Plan in Shaanxi Province of China under Grant No. 2016JQ6058, and partially by the Science and Technology Developing Project of Shaanxi Province under Grant No. 2015KW-001.

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Electrode Materials for Printable Solar Cells

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Abstract

Printable solar cells hold promise for fabricating lightweight and flexible photovoltaic devices via low-cost and high-throughput non-vacuum production process. Typically, printable solar cells are integrated on flexible substrates in a layer-by-layer fashion, in which the photoactive layer is sandwiched between two electrodes, i.e., a transparent front electrode and a back electrode. To ensure good photovoltaic performance as well as compatibility with substrate materials and printing techniques, it is required that the electrode materials should exhibit high conductivity, good mechanical properties, reasonable physical and chemical stability, be compatible with solution-processing techniques, and preferably low-cost. In addition, transparent electrode also requires high optical transparency besides the above-mentioned properties. In this chapter, progress in the development of materials suitable for either transparent front electrodes or back electrodes of printable solar cells is highlighted. The factors influencing the performance of these electrode materials, such as chemical structure, intrinsic physical property,

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Nuridan Demirci Sankir and Mehmet Sankir (eds.) Printable Solar Cells, (457–512)
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thin film morphology, processing techniques and treatment methods, will be discussed extensively, in the hope of providing guidance for material design and mechanistic study. The chapter concludes with an outlook of possible R&D directions of electrode materials for printable solar cells.

Keywords: Electrode materials, printable solar cells, flexible transparent electrode, printable back electrode

14.1 Introduction

Photovoltaic cells, also commonly known as solar cells, are devices that can convert photons directly into electrons. Their presence readily bridges the most abundant, clean and sustainable solar energy to the most widely used secondary energy source, electricity. Therefore, development of photovoltaic technology is extremely meaningful to tackle both the energy crisis and environmental problems that human beings are facing. Currently the photovoltaic market is dominated by silicon solar cells. But the high fabrication cost reduces its competitiveness. Printable solar cells, which utilize soluble functional materials and printing technologies, represent the next-generation photovoltaic technology. They share many merits like low fabrication cost, light weight, high mechanical flexibility, tunable chemical and physical properties via material design, good performance in low light intensity, and fast module installation. Two representatives of printable solar cells are organic photovoltaics (OPVs) and perovskite solar cells (PSCs). These two types of printable solar cells share very similar cell architecture, i.e., the photoactive layer is sandwiched between a transparent electrode and a back electrode. In research laboratories, the transparent electrode is usually indium tin oxide (ITO) and the back electrode is formed by depositing metals in high vacuum. However, the costly and brittle ITO, as well as the vacuum deposition of metal electrodes, are incompatible with low-cost and high-throughput printing technology, thus hindering the commercialization of this technology.

To ensure good photovoltaic performance as well as compatibility with substrate materials and printing techniques, it is required that the electrode materials should exhibit high conductivity, good mechanical properties, reasonable physical and chemical stability, be compatible with solution-processing techniques, and preferably low-cost. In addition, transparent electrode also requires high optical transparency besides the above-mentioned properties. In fact, many new materials have been developed to replace ITO and evaporated metals. This chapter reviews six types of the most promising electrode materials, including transparent conjugated

polymers, carbon-based nanomaterials, metallic nanostructures, multi-layer thin films, printable metal back electrodes and carbon-based back electrodes. Materials suitable for transparent electrode application will be introduced first, followed by materials for back electrode. The chapter concludes with an outlook of possible R&D directions of electrode materials for printable solar cells.

14.2 Transparent Conjugated Polymers

Conjugated polymers possess a large number of delocalized π electrons when doped, giving rise to electrical conductivity and optical band gap. When the band gap is wide enough, some conjugated polymers show both good conductivity at room temperature and extraordinary transmittance in visible range, making them important for transparent electrode application. Among hundreds of thousands of conjugated polymers developed so far, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, whose chemical structure is shown in Figure 14.1) is the most successful one in terms of practical application [1]. PEDOT:PSS films have a high transparency in visible range, a stable tensile strain, and an excellent thermal stability. It is commercially available as aqueous dispersions or solid pellets from companies such as Heraeus and Agfa. But the pristine PEDOT:PSS films often suffer from low conductivity. The key to truly employing PEDOT:PSS films as transparent electrode for printable solar cells lies in how to greatly improve the film conductivity.

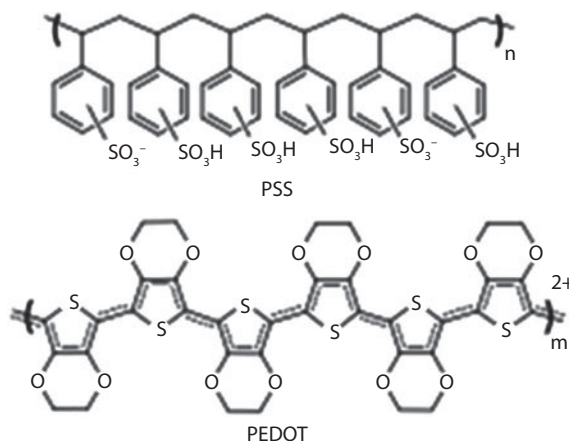


Figure 14.1 Chemical structure of PEDOT:PSS.

14.2.1 Solvent Additive Method

The conductivity of PEDOT:PSS films can be enhanced by orders of magnitude by addition of poly-alcohols or high-dielectric solvents, such as dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) [2–6]. Zhang *et al.* first introduced this method in 2002 [3]. After mixing with glycerol or sorbitol, the conductivity of the PEDOT:PSS (Baytron P) increased by two orders of magnitude (to ~ 10 S/cm). The optimum conductivity occurs when 85 wt% glycerol or 65 wt% sorbitol was introduced to the pristine PEDOT:PSS solution. The maximum power conversion efficiency (PCE) of the OPVs employed poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) as the active layer could reach 0.36%. Nardes *et al.* found that sorbitol-induced enhancement of conductivity was due to a reduction in the thickness of the insulating PSS barrier that separates the conducting PEDOT rich grains as well as a rearrangement of PEDOT-rich clusters into elongated domains [7].

Kim *et al.* proposed that polar solvents with a high dielectric constant were able to induce strong screening effects between the positively charged PEDOT and the negatively charged PSS, so it reduced the Coulombic interactions between the counterions and the charge carrier [4]. Ouyang *et al.* improved the conductivity of the films by adding meso-erythritol into PEDOT:PSS (Baytron P, V4071). The conductivity of the spin-cast films was 155 S/cm after thermal annealing. They were able to obtain the PCE 1.5% in OPVs with MEH-PPV as active layer [8]. Polar compounds such as diethylene glycol (DEG), DMSO or sorbitol were added to PEDOT:PSS (Baytron PH500) by Ahlswede *et al.* The films exhibited a conductivity of 300 S/cm and a maximum transmittance of 74%. Average value of PCEs was around a remarkable 2.6% [9]. The conductivity of the PEDOT:PSS (PH 750) film was enhanced from 1.3 S/cm to 570 S/cm after addition of 5 vol% DMSO and 13 vol% isopropanol [10]. Na *et al.* also enhanced the conductivity through optimizing the concentration of DMSO and they further explored the influence of annealing temperature to the films. The conductivity of PEDOT:PSS (PH510) increased to 464 S/cm by adding 11% DMSO [11].

Solvent additives can sometimes induce aggregation of PEDOT:PSS in solution and thus lead to poor wettability on substrate. To remedy this problem, this method is often used in combination with surfactant. Colsmann *et al.* enhanced the conductivity of PEDOT:PSS (Baytron PH500) films to 316 S/cm by adding 5% DMSO, 5% isopropanol (IPA) and 5% Surfynol, while the maximum value was up (treated with 5% DMSO and 5% isopropanol) [12]. Zhou *et al.* added DMSO and Zonyl surfactant to PEDOT:PSS

solution and the resulting films exhibited a maximum conductivity of 220 S/cm. The OPV with an APFO3:PCBM photoactive layer and the modified PEDOT:PSS transparent electrode could reach a PCE of 2.23%, which was 80% of the PCE of the ITO-based control OPV [13]. Vosgueritchian *et al.* reported PEDOT:PSS (PH1000) films with a sheet resistance (R_s) of 46 Ω /sq and a transmittance (T) of 82% T at 550 nm after addition of DMSO and a fluorosurfactant Zonyl-FS300. The fluorosurfactant improved the wetting properties of the PEDOT:PSS solution, which enabled the facile deposition of highly conducting PEDOT:PSS films on a variety of hydrophobic substrates that would otherwise not be possible. The PCE could reach 2.16% in a poly(3-hexylthiophene) (P3HT):PC₆₁BM-based OPV [14].

14.2.2 Post-Treatment of PEDOT:PSS Films

In recent years, apart from adding solvents into the PEDOT:PSS aqueous solution to enhance the conductivity of PEDOT:PSS films, post-treatment has proved to be an effective way to improve their conductivity. Kim and coworkers prepared PEDOT:PSS (PH 1000) by dipping the annealed film in EG for 30 min, the conductivity of the PEDOT:PSS films was significantly increased from 735 to 1418 S/cm [15]. Xia *et al.* found when a PEDOT:PSS film was treated with water or a common organic solvent like ethanol, iso-propyl alcohol (IPA), acetonitrile (ACN), acetone, or tetrahydrofuran (THF), its conductivity did not change remarkably; while the conductivity could be significantly enhanced when the PEDOT:PSS film was treated with a cosolvent of water and one of these common organic solvents. The conductivity of PEDOT:PSS (Clevios P) increased from 0.2 S/cm to 79 and 73 S/cm after treatment with a cosolvent of 80% ACN and 20% water or 80% ethanol and 20% water, respectively. They were able to obtain a PCE of 2.87% in OPVs with P3HT:PCBM active layer [16]. Sun *et al.* showed that the conductivity of another PEDOT:PSS grade (Clevios P VP Al 4083) could also be enhanced from 10^{-3} to 10^0 S/cm through a treatment with a cosolvent of hydrophilic methanol and hydrophobic 1,2-dichlorobenzene (DCB) [17]. Xia *et al.* further enhanced the conductivity of PEDOT:PSS (PH1000) film using an amphiphilic fluoro-compound, i.e., hexafluoroacetone (HFA) [18]. By dropping 100 mL pure HFA or an aqueous solution of HFA on a PEDOT:PSS film on a hot plate at 140 °C, the conductivity was increased from 0.3 S/cm to 1164 S/cm, leading to a R_s of 172 Ω /sq and a transmittance (T) of 94% at 550 nm. It could be further increased to 1325 S/cm after treatment with HFA for four times. The mechanism for the conductivity enhancement goes like this: HFA hydrolyzes into

1,1,1,3,3,3-hexafluoropropane-2,2-diol (HFP2OH) with water. HFP2OH acts as a surfactant with two $-OH$ groups on one side and two $-CF_3$ groups on the other side. So the two functional groups can preferentially interact with the hydrophobic PEDOT and the hydrophilic PSS chains of PEDOT:PSS, resulting in the phase separation between PEDOT and PSS and the eventual removal of insulating PSS component.

Acid treatment of PEDOT:PSS films started to gain popularity after the pioneering work done by Ouyang and his coworkers in 2002 [19]. The conductivity of PEDOT:PSS (PH1000) films was increased to more than 1000 S/cm, 2000 S/cm and 2400 S/cm after an acid treatment using 0.05 M, 1 M and 1.5 M H_2SO_4 , respectively. In addition, they observed a conductivity of 3065 S/cm after the films were treated with 1 M H_2SO_4 at 160 °C for three times, producing a 66 nm-thick PEDOT:PSS film with a sheet resistance of 67 Ω /sq. Mengistie *et al.* used almost 100% concentrated acid to enhance the conductivity of PEDOT:PSS (PH1000). The conductivity was 625, 1900 and 2050 S/cm by dropping 2, 10 and 26 M formic acid (98% v/v concentration) on annealed PEDOT:PSS film at 140 °C [20]. Although the strong acid treatment can enhance PEDOT:PSS film conductivity, its corrosive properties hinder industrial application. Ouyang systematically studied a number of mild organic acids [21]. He found that boiling point, acid dissociation constant and melting point all played a role in the post-treatment process. The highest conductivity value was 3300 S/cm, achieved by treating with 8 M methanesulfonic acid (MSA). Sun *et al.* used MSA-treated PEDOT:PSS films as a transparent electrode for perovskite solar cells [22]. The optimal PCE was close to 11% for the rigid PSCs, and it was more than 8% for the flexible PSCs with a MSA-treated PEDOT:PSS film as the transparent electrode on polyethylene terephthalate (PET). Fan *et al.* enhanced the conductivity of the films by a combination of alcohol and acid treatment [23]. The conductivity of PEDOT:PSS (PH1000) films reached a record 4800 S/cm after a pretreatment of 6 vol% methanol followed by a post-treatment of 8 M MSA.

Besides dipping or post-annealing with solvents, other post-treatment methods for PEDOT:PSS films have been invented. Yeo and coworkers applied polar solvent vapor annealing to PEDOT:PSS (PH 1000) films and induced significant segregation of the excess PSS on the top surface of the PEDOT:PSS film [24]. Then the PEDOT:PSS films were subsequently immersed in a DMSO bath for various times, resulting in the highest conductivity of 1475 S/cm. Zhang proposed a post-spin-rinsing method to prepare highly conductive PEDOT:PSS films [25]. 0.1 vol% Zonyl FS-300 and 5 wt% DMSO were first mixed with the PEDOT:PSS (PH1000) solution. After film formation using the modified PEDOT:PSS solution,

100 μL DMSO was dropped onto the as-prepared PEDOT:PSS films and waiting for different time. Finally, the DMSO was removed by spinning. The highest conductivity of 1335 S/cm and an optimal PCE of 4.82% in PCDTBT:PC₇₁BM-based OPV were obtained.

The physical properties of the PEDOT:PSS transparent electrode and the detailed photovoltaic parameters for the above-mentioned works and other relevant studies are summarized in Table 14.1 for reference. We regret that many more excellent works in this area are not listed due to limited space.

14.2.3 Printing PEDOT:PSS Inks

Because PEDOT:PSS is usually in the form of dispersed aqueous solution, in addition to the spin coating frequently used in laboratories, PEDOT:PSS is fully compatible with different industrial printing techniques. Eom *et al.* coated smooth PEDOT:PSS (Baytron P AI 4083) films by using a commercial inkjet printer (UJ2100, UniJet, Korea). The film conductivity was increased to 164 S/cm when 6 wt% glycerol and 0.2 wt% ethylene glycol butyl ether were added in PEDOT:PSS ink [26]. This group further demonstrated inkjet-printed OPV devices in which both the PEDOT:PSS layer and the P3HT:PCBM photoactive layer were printed. The best solar cell had a PCE of around 3.7% [27]. Cho *et al.* investigated gravure printing method to coat PEDOT:PSS films onto a flexible PET substrate [28]. Gravure-printed PEDOT:PSS (mixed with 7% DMSO) exhibited a R_s of 359 Ω/sq and a T of 88.92% at a wavelength of 550 nm. The flexible OPVs employing a printed PEDOT:PSS anode on PET delivered a 2% efficiency. More recently, electrospray (e-spray) was introduced to enable high deposition efficiency without a heated substrate. Kim *et al.* studied the e-spray deposition of highly conductive PEDOT:PSS (PH1000) films by independently varying the process parameters, such as the solvent dilution ratio, the amount of DMSO additive, and the substrate temperature. The optimal conductivity of the e-sprayed PEDOT:PSS film reached 800 S/cm at 2.5 vol% DMSO additive. The OPV with a P3HT:PCBM active layer had a PCE of 1.25% [29].

14.3 Carbon-Based Nanomaterials

Carbon-based nanomaterials, such as graphene and carbon nanotubes (CNTs), are allotropes of carbon. In the last decades, they have emerged as potential transparent electrode materials due to their high conductivity,

Table 14.1 Summary of optoelectronic properties of PEDOT:PSS transparent electrode and its application in solar cells.

Transparent Electrode	Treatment chemical	σ (S/cm)	R_s (Ω /sq)	T (%)	Active layer	J_{sc} (mA/cm ²)	Voc (V)	FF	PCE (%)	Year	Ref.
Glass/Baytron P (sorbitol)	—	—	1300	—	MEH:PPV:PC ₆₁ BM	0.021	0.47	0.4	3.4	2002	[3]
Glass/PV4071 (meso-erythritol)	—	155	—	—	MEH:PPV:PC ₆₁ BM	5.1	0.72	—	1.5	2005	[8]
Glass/PH500 (①)	—	300	80	74	P3HT:PCBM	—	—	0.6	2.6	2008	[9]
Glass/P V4071	EG	—	—	93	P3HT:PC ₆₁ BM	8.99	0.59	0.64	3.39	2008	[30]
PET/PH500 (5% DMSO, zonyl)	—	220	230	90	APFO3:PC ₆₁ BM	4.06	0.98	0.56	2.23	2008	[13]
Glass/PH500 (②)	—	316	132	84	P3HT:PC ₆₁ BM	—	—	—	2.2	2009	[12]
Glass/P Al 4083 (③)	—	164	—	—	P3HT:PC ₆₁ BM	10.68	0.63	0.55	3.71	2010	[27]
Glass/PH510 (11% DMSO)	—	464	63	88	P3HT:PC ₆₁ BM	9.47	0.57	0.64	3.48	2009	[11]
Glass/PH500	PAH-D	220	—	75	P3HT:PC ₆₁ BM	6.68	0.59	0.47	1.86	2010	[31]
Glass/PH750 (5% DMSO)	—	570	—	—	P3HT:PC ₆₁ BM	—	0.57	0.4	0.6	2010	[32]
PET/PH510 (7% DMSO)	—	—	359	88.9	P3HT:PC ₆₁ BM	9.1	0.50	0.45	2.0	2011	[28]
Glass/PH1000 (6 vol% EG)	—	1418	470	90	ZnPc:C60	7.98	0.55	0.58	2.54	2011	[15]
Glass/Clevios P	80% ACN	79	—	—	P3HT:PC ₆₁ BM	8.99	0.61	0.52	2.87	2011	[16]
Glass/PH 1000	ethanol	1362	147	90	P3HT:PC ₆₁ BM	9.41	0.58	0.66	3.62	2012	[33]
Glass/PH1000 (④)	—	—	46	82	P3HT:PC ₆₁ BM	6.69	0.58	0.55	2.16	2012	[14]
Glass/PH1000	H ₂ SO ₄	3065	67	87	P3HT:PCBM	9.29	0.59	0.65	3.56	2012	[19]
Glass/PH1000	HFA	1319	46	83	P3HT:PC ₆₁ BM	9.44	0.59	0.64	3.57	2012	[18]

Glass/PH 1000	DMSO	1475	131	—	P3HT:PC ₆₁ BM	7.29	0.58	0.65	2.74	2013	[24]
Glass/PH1000 (⑤)	—	1070±50	24~259	71~95	P3HT:PC ₆₁ BM	8.8	0.59	0.58	3.2	2013	[34]
Glass/PH1000	Formic Acid	2050	23	80	P3HT:PC ₆₁ BM	11.7	0.57	0.61	4.1	2014	[20]
Glass/PH 1000	⑥	3500	74.9	93.8	DSSC	11.62	0.714	0.6	5.00	2014	[35]
Glass/PH1000 (⑦)	EG	4800	32	89.5	P3HT:PCBM	10.18	0.595	0.65	3.92	2015	[23]
Glass/PH1000 (⑧)	H ₂ SO ₄	807	188	—	P3HT:ICBA	7.38	0.83	0.62	3.80	2015	[36]
Glass/PH1000	MSA	2540	50	92	CH ₃ NH ₃ PBI-Cl _{3.3x}	17.43	0.97	0.65	11.0	2015	[22]
Glass/PH1000	DMSO	1335	100	92.3	PCDTBT:PC ₇₁ BM	8.89	0.85	0.64	4.82	2016	[25]
PET/PH 1000	Au	—	20.9	82.6	—	—	—	—	—	2016	[37]
Glass/PH1000	⑨	3300	43	80	PTB7:PC ₇₁ BM	15.98	0.78	0.613	7.9	2016	[38]
Glass/PH1000	⑩	1660	—	—	P3HT:PC ₆₁ BM	8.71	0.58	0.65	3.51	2016	[39]

Note: ① Diethylene glycol, dimethyl sulfoxide, sorbitol and Surfynol. ② 5% DMSO, 5% isopropanol. ③ glycerol, ethylene glycol butyl ether. ④ 5% DMSO, 1 wt% Zonyl. ⑤ 73.0 vol% IPA, 1.3 vol% ethylene glycol. ⑥ 0.9 M p-toluenesulfonic acid in DMSO. ⑦ 6 vol% Methanol, 8 M methane sulfonic acid, 0.5 vol% Zonyl FS-300 fluorosurfactant. ⑧ 4-chlorobenzoic acid, methanol. ⑨ 0.1 M methylammonium iodide, dimethylformamide, DI water or IPA.

excellent transmittance in visible range, good flexibility, superior chemical and physical stability, etc.

14.3.1 Graphene

Graphene is a single atomic layer of carbon atoms that arrange themselves in an extended honeycomb pattern. It possesses many unparalleled properties, such as high conductivity, excellent optical transmittance and noticeable mechanical properties, making graphene an important flexible optoelectronic material. For example, due to its large network of π conjugated system, the predicted mobility of graphene is in the order of $10^6 \text{ cm}^2/\text{V}\cdot\text{s}$ and an intrinsic charge carrier concentration, n_i , is around 10^{12} cm^{-2} [40]. Since the first successful acquisition and characterization of graphene by Andre Geim and Konstantin Novoselov in 2004 [41], it has garnered great attention worldwide. Application of graphene as transparent electrode in solar cells started in 2008. A few representative works are summarized in Table 14.2. It is worth noting that this table is not a complete list of published work in this area, but only serves as a guideline to reflect the trends of technological development.

In the past decade, two major fabrication routes have been developed to synthesize graphene films for transparent electrode application, one of them is solution-processible reduced graphene oxide (rGO) [42–45]. In 2008, Wu *et al.* demonstrated that very thin films of graphene can be obtained through reducing functional graphene oxide prepared by Hummers' method. Such graphene films were smooth enough to be used as anode in solid-state OPVs [42]. Even though the PCE was only 0.40%, it represented the first demonstration that graphene could serve as a transparent electrode in solar cells. About two year later, Yin *et al.* transferred chemically reduced graphene oxide onto polyethylene terephthalate (PET) substrates, which enabled the fabrication of flexible OPVs [43]. Unfortunately, probably due to too many defects generated during the oxidization and film transfer steps, rGO transparent electrodes usually showed poor electrical conductivity. Making thicker rGO films could ease the conductivity problem, but transparency was largely reduced. As a result, the PCE of solar cells based on rGO electrodes was normally below 1%. The turning point occurred in 2013, when Zhang *et al.* ingeniously introduced graphene mesh electrodes (GMEs) by standard industrial photolithography technique and O_2 plasma etching process. The new graphene-based transparent electrode overcame the intrinsic trade-off between conductivity and transmittance associated with rGO films, leading to a dramatic improvement of PCE to 2.04% [45].

Table 14.2 Photovoltaic performance of solar cells with graphene or rGO as transparent electrode.

Device architecture	Processing method	Rs (Ω/sq)	T (%)	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)	Year	Ref.
Quartz/graphene/P3HT/PC ₆₁ BM/Ag	–	18k	85	0.36	0.38	0.25	0.29	2008	[56]
Quartz/rGO/CuPc/C ₆₀ /BCP/Ag	Redox	100–500	85–95	2.10	0.48	0.34	0.40	2008	[42]
Glass/graphene/PEDOT:PSS/P3HT:PC ₆₁ BM/LiF/Al	CVD	210–1350	72–91	6.05	0.55	0.51	1.71	2009	[47]
Glass/graphene/PEDOT:PSS/P3HT:PC ₆₁ BM/TiO ₂ /Al	CVD	606	87	9.02	0.63	0.67	2.60	2010	[48]
PET/graphene/PEDOT:PSS/CuPc/C ₆₀ /BCP/Al	CVD	230	72	4.73	0.48	0.52	1.18	2010	[46]
Quartz/graphene/PEDOT:PSS/P3HT:PC ₆₁ BM/Al	CVD	1.645 k	81	4.82	0.54	0.26	0.68	2010	[49]
Quartz/graphene/PEDOT:PSS/CuPc/C ₆₀ /BCP/Ag	CVD	300–500	91–97	9.15	0.43	0.42	1.63	2010	[50]
PET/rGO/PEDOT:PSS/P3HT:PC ₆₁ BM/TiO ₂ /Al	Redox	3.2 k	65	4.39	0.56	0.32	0.78	2010	[43]
Glass/graphene/PEDOT:PSS/P3HT:PC ₆₁ BM/Al	Redox	2 k	75	1.84	0.44	0.25	0.20	2011	[44]
Glass/graphene/PEDOT:PSS/P3HT:PC ₆₁ BM/Al	CVD	400	98.77	10.19	0.62	0.25	3.98	2011	[51]
Glass/graphene/Au/PEDOT:PSS/P3HT:PC ₆₁ BM/LiF/Al	CVD	1.2–2.2 k	75–82	5.20	0.54	0.44	1.24	2011	[52]

(Continued)

Table 14.2 Cont.

Device architecture	Processing method	Rs (Ω/sq)	T (%)	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)	Year	Ref.
Glass/graphene/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	CVD	374 $\pm$ 3	84.2	6.91	0.52	0.33	1.17	2012	[53]
Glass/graphene/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	CVD	278	92.2	8.90	0.57	0.48	2.58	2012	[54]
Glass/graphene/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	CVD	119 $\pm$ 1	92.1	8.26	0.60	0.58	2.86	2012	[65]
Quartz/rGO grid/PEDOT:PSS/ P3HT:PC ₆₁ BM/LiF/Al	Redox	608	55	6.35	0.54	0.58	2.04	2013	[45]
Quartz/graphene/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	Carbonization	1.46 k	52.1	5.43	0.58	0.55	1.73	2013	[58]
Quartz/graphene/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	Carbonization	2.5 k	$\sim$ 60	6.33	0.58	0.48	1.76	2013	[57]
PET/graphene/GraHEL/ PCDTBT:PC ₇₀ BM/Ca/Al	CVD	72.9	92.1	8.83	0.90	0.55	4.33	2014	[60]
PEN/graphene/PEDOT:PSS-IPA/MoO ₃ / PTB7:PC ₇₁ BM/ Ca/Al	CVD	$\sim$ 300	$\sim$ 92	14.40	0.72	0.59	6.10	2014	[61]
PEN/graphene/ZnO/PTB7:PC ₇₁ BM/ MoO ₃ /Ag	CVD	$\sim$ 300	$\sim$ 92	14.10	0.72	0.66	7.10	2014	[61]
Quartz/graphene/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	CVD	600–800	–	8.96	0.57	0.54	2.76	2015	[55]

PET/rGO/PEDOT:PSS/ PCDTBT:PC ₇₁ BM/TiO _x /Al	Redox	565	59.1	7.81	0.85	0.46	3.05	2015	[59]
Glass/FTO/TiO ₂ /perovskite/Spiro- OMETAD/ PEDOT:PSS/graphene	CVD	140 ± 35	> 90	17.75	0.95	0.72	12.03	2015	[62]
Glass/rGO/PEDOT:PSS/P3HT:PC ₆₁ BM/ Ca/Al	Redox	~ 1–10 k	57–87	2.26	0.56	0.26	0.33	2015	[66]
Glass/rGO/compact TiO ₂ /mesoporous TiO ₂ /perovskite/ spiro-OMETAD/Au	Redox	3.08 k	55	3.05	0.69	0.38	0.81	2016	[63]
Glass/graphene/MoO ₃ /PEDOT:PSS/ perovskite/C ₆₀ /BCP/LiF/Al	CVD	~ 500	~ 97	21.90	1.03	0.72	17.10	2016	[64]

An alternative and popular way to prepare graphene film is by chemical vapor deposition (CVD) method. This method requires a metal foil, typically copper foil, as the substrate and a high reaction temperature above 500 °C. Therefore, a complicated transferring technology, which is illustrated in Figure 14.2, is often needed after the CVD growth of graphene films [46]. In 2009, Wang *et al.* first obtained graphene film with large size, low resistance, and high optical transparency by employing CVD method. They further solved the hydrophobic problem of graphene tactfully by using noncovalent functionalization with pyrene buanoic acid succidymidyl ester (PBASE). Subsequently, a PCE of 1.71% was achieved on an OPV based on P3HT:PC₆₁BM [47].

Based on this method, tremendous works were contributed by various groups to enhance the quality of graphene film and the device performance [48–55]. Park *et al.* found depositing a thin layer of AuCl₃ on top of the graphene could improve the solar cell efficiency by enhancing the surface wetting of graphene transparent electrode [50]. In 2011, Wang *et al.* fabricated organic hybrid solar cells utilizing CVD-grown single-layer graphene films that has an optical absorbance of only 1.23% at the wavelength of 532 nm. Single-layer graphene-based OPV displayed a PCE of up to 3.98%, higher than that of the ITO-based device (3.86%) [51]. Zhang *et al.* proposed a simple yet effective method to decorate interfacial properties of graphene by depositing a thin layer of Au, assisted by a separate UV ozone process, to solve the issues of large hole injection barrier between graphene anode and the donor material P3HT and hydrophobicity of graphene. After optimization, they realized a P3HT:PC₆₁BM-based OPV with a PCE of 1.24% [52].

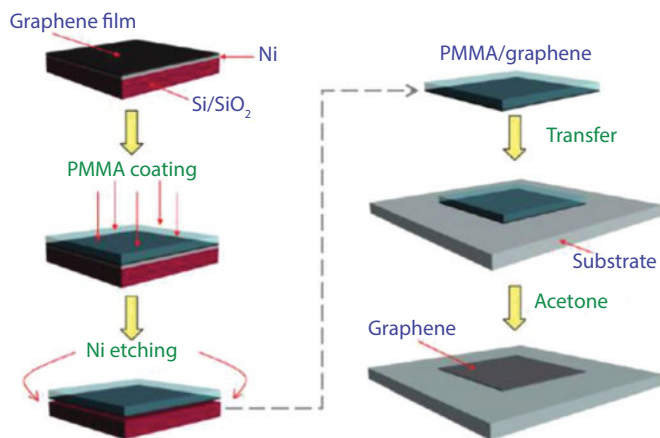


Figure 14.2 Schematic of the transfer process of CVD-prepared graphene onto transparent substrates. (Reproduced with permission from [46])

Hsu *et al.* reported an attractive idea to promote the PCE of polymer solar cells via a layer-by-layer molecular doping process, i.e., thermal evaporating tetracyanoquinodimethane (TCNQ) on graphene to form sandwiched graphene/TCNQ/graphene stacked films. The anode structure with two TCNQ layers sandwiched by three CVD graphene layers showed a sheet resistance of $278 \Omega/\text{sq}$, a transmittance of 92.2% at 550 nm and an optimum PCE of 2.58% [54]. In the research done by Kim *et al.*, they used a simple, solvent-free, and efficient electron beam (EB) irradiation-based modification of CVD-prepared graphene as a transparent anode of OPVs, and obtained a PCE of 2.76% [55].

Besides the two major fabrication routes mentioned above, there have been other techniques developed by chemists. In 2008, Wang *et al.* adopted a bottom-up chemical approach to obtain transparent graphene constructed films (TGFS) by thermal reaction of synthetic nanographene molecules, e.g., polycyclic aromatic hydrocarbons (PAHs) [56]. Furthermore, Na *et al.* investigated a catalyst- and transfer-free solution-processed carbon sheet through a cyclization reaction and a carbonization process [57, 58]. These two graphene-based photovoltaic cells exhibited PCEs of around 1.7%.

Due to the robust mechanical properties of graphene, flexible solar cells with graphene electrode demonstrated outstanding capability to operate under bending angles up to 138° , whereas the ITO-based devices displayed cracks and irreversible failure when bent to 60° [46]. Konios *et al.* refreshed the PCE record for flexible OPV devices, which showed 3.05% PCE after incorporating a reduced graphene oxide micromesh (rGOMM) that was precisely patterned by a laser-based patterning technique [59]. In one report, Kim *et al.* added perfluorinated ionomers (PFI) to pristine PEDOT:PSS to overcome the poor film-coating problem of PEDOT:PSS on unmodified CVD-grown graphene films. Accordingly, flexible OPVs based on poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4';7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl-C71-butyric acid methyl ester (PC_{71}BM) exhibited a relatively high PCE of 4.33% on PET substrate [60]. Further improvement was achieved by Park *et al.*, who reported flexible OPVs by employing low pressure CVD-grown graphene anode or cathode which displayed record-high PCEs of 6.1 and 7.1%, respectively [61].

Recently, graphene transparent electrode has been used in perovskite solar cells as well. You *et al.* are pioneers in fabricating semitransparent perovskite solar cells by laminating two layers of CVD-produced graphene as top transparent electrode [62]. A 12.03% efficiency was recorded when the cells were illuminated from the graphene side. Batmunkh *et al.* made the first trial to utilize solution-processed rGO film as transparent cathode

in perovskite solar cells, but PCE was below 1% due to the dilemma between transparency and conductivity [63]. On the other hand, Sung *et al.* presented the first perovskite solar cells adopting CVD-grown graphene as a transparent anode. After evaporating a few nanometer thick MoO_3 layer between graphene and perovskite film, the solar cells achieved over 17% efficiency [64].

14.3.2 Carbon Nanotubes

Carbon nanotube (CNT) is a one-dimensional cylindrical nanostructure composed entirely of sp^2 -hybridized carbon atoms. It resembles a roll of graphene, with length-to-diameter ratio of up to $1.32 \times 10^8:1$ [67]. Due to the large aspect ratio and widely connected conjugated system, CNTs exhibit a so-called “ballistic conduction,” i.e., electrons can propagate rapidly along the axis of the nanotubes. In other words, CNTs can be considered as conducting wires with diameters in nanometer scale. So an ultrathin CNT network is potentially electrically conductive and also transparent. Depending on the number of layers, CNT can be classified into single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs).

Since its first discovery by Japanese microscopist Sumio Iijima in 1991 [68], scientists took a long time to improve the quality of CNT and found applications for it. The first successful attempt to employ CNT as transparent anode in OPVs was demonstrated by Ago *et al.* in 1999 [69]. The cell has a structure of glass substrate/MWNTs/poly(phenylene vinylene) (PPV)/Al, leading to a J_{sc} of 0.56 uA/cm^2 , V_{oc} of 0.90 V, FF of 0.23, and PCE of 0.081%. Compared with ITO-based devices, the low photovoltaic performance was attributed to the high sheet resistance of functionalized MWNT films. Six years later, Pasquier *et al.* described the application of SWNT thin film as transparent anode of OPVs. Due to the three-dimensional contact between the SWNT network and P3HT:PC₆₁BM photoactive layer, efficiency close to 1% was obtained, comparable to that of an ITO-based OPV with the same cell architecture [70]. Table 14.3 summarizes works focused on CNT-based transparent electrode after 2005.

One of the main issues for the CNT-based transparent electrode is its high surface roughness that can easily lead to short circuit of photovoltaic devices. In a report by Rowell, SWNT produced by arc discharge was dissolved in solution with surfactants, and then after the dispersed solution was sonicated it was vacuum filtered. The dried SWNT film was eventually transferred onto PET substrate by PDMS stamp. Such an operation could produce relatively smooth films with root mean square roughness

Table 14.3 Photovoltaic performance of solar cells with CNT as transparent electrode.

Device architecture	Processing method	R_s (Ω/sq)	T (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	Year	Ref.
Quartz/SWNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ga/In	–	282	45	6.65	0.5	0.3	0.99	2005	[70]
PET/SWNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Al	Arc discharge	200	85	7.8	0.61	0.52	2.5	2006	[71]
Glass/CNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Al	–	717	> 80	5.47	0.49	0.49	1.32	2006	[80]
Glass/SWNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Al	–	50	70	9.24	0.56	0.29	1.5	2006	[81]
Glass/FWNT/P3HT:PC ₆₁ BM/Al	–	86	70	4.46	0.36	0.38	0.61	2009	[75]
Glass/SWNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ga/Al	Laser ablation	60	> 70	11.5	0.58	0.48	3.1	2009	[72]
Glass/SWNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	–	56	70	13.78	0.57	0.53	4.13	2010	[82]
Glass/SWNT/P3HT:PC ₆₁ BM/Ca/Al	–	60	–	11.18	0.52	0.46	2.65	2010	[82]
Glass/SWCNT/PEDOT:PSS/Au NPs/ P3HT:PC ₆₁ BM/LiF/Al	–	820	78	4.6	0.58	0.58	1.54	2011	[77]
Glass/SWCNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/LiF/Al	Arc discharge	51	69	11.1	0.59	0.54	3.6	2012	[73]

(Continued)

Table 14.2 Cont.

Device architecture	Processing method	R_s (Ω/sq)	T (%)	J_{sc} (mA/cm^2)	Voc (V)	FF	PCE (%)	Year	Ref.
Glass/CNT web/PEDOT:PSS/ P3HT:PC ₆₁ BM/Ca/Al	–	327	58	6.37	0.55	0.47	1.66	2013	[83]
Glass/FTO/compact TiO ₂ /mosoporous TiO ₂ /CH ₃ NH ₃ PbI ₃ /CNT	CVD	–	–	15.46	0.88	0.51	6.87	2014	[78]
Glass/FTO/compact TiO ₂ /mosoporous TiO ₂ /CH ₃ NH ₃ PbI ₃ /CNT	CVD	–	–	18.1	1.00	0.55	9.90	2014	[78]
Glass/SWNT/PEDOT:PSS/ P3HT:PC ₆₁ BM/Al	CVD	311	93	9.6	0.50	0.45	2.2	2014	[74]
Glass/SWNTs/PEDOT:PSS(EtOH)/ PTB7:PC ₇₀ BM/BCP/Al	–	187	73	12.32	0.68	0.52	4.37	2015	[84]
Glass/SWNT/PEDOT:PSS/ CH ₃ NH ₃ PbI ₃ /PC ₆₁ BM/Al	CVD	25.6	65	14.9	0.79	0.54	6.32	2015	[76]
PET/SWNT/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ / PC ₆₁ BM/Al	CVD	25.6	65	11.8	0.71	0.56	5.38	2015	[76]
CNTs:spiro-OMeTAD/TiO ₂ NTs:CH ₃ NH ₃ PbI ₃ /Ti foil	CVD	–	–	14.36	0.99	0.68	8.31	2015	[79]

(R_{rms}) of less than 10 nm over a surface area of $25 \mu\text{m}^2$. Besides, this SWNT electrode exhibits a transmittance of 85% at 550 nm and a sheet resistance (R_s) of $200 \Omega/\text{sq}$, resulting in a 2.50% OPV cell [71]. In 2009, Tenent *et al.* employed ultrasonic spray technique to produce uniform SWMT electrode. Through ultrasonic spraying of sodium carboxymethyl cellulose (CMC) dispersed CNT solution followed by a nitric acid treatment, smooth SWNT films with R_{rms} as low as 3 nm could be quickly obtained. Accordingly, an OPV fabricated on this SWNT film displayed 3.1% PCE under AM 1.5 illumination [72]. After this work, using the spraying method to prepare CNT films became more and more popular. Kim *et al.* prepared patterned SWNT electrodes by pressure-driven spray-coating approach, in which the P3HT:PC₆₁BM bulk heterojunction solar cells yielded PCEs of 3.6% and 2.6% on glass and plastic substrates, respectively [73]. Ostfeld *et al.* prepared CVD-grown SWNT solution by reductive dissolution process, then transparent conductive films deposited on glass were formed through spray coating; the resulting CNT films showed dramatic improvement in electrical conductivity and optical transmittance. As a result, P3HT:PC₆₁BM OPVs utilizing these transparent electrodes achieved PCEs of up to 2.3% [74].

Another serious problem pertaining to CNT transparent electrode is the trade-off between sheet resistance (R_s) and transmittance (T). Feng *et al.* tried to optimize the device performance using spray-coated few-walled carbon nanotube (FWNT) film with different thicknesses, but the maximum efficiency was only 0.61% [75]. In fact, the electrical properties of CNT films are often enhanced via doping. Jeon *et al.* illustrated that when equipped with 35 vol% dilute HNO_3 -doped SWNT transparent electrodes, the inverted perovskite photovoltaic devices could deliver PCEs of 6.32% and 5.38% on glass and PET substrates, respectively [76]. As for tuning the optical properties, Kymakis *et al.* incorporated plasmonic Au nanoparticles into OPVs with SWNT as transparent anode, leading to a 70% improvement in PCE [77].

The CNT films can not only be used as bottom transparent electrode, but can also serve as top transparent electrode. Recently, Li *et al.* transferred CVD-produced CNT films onto $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cells to replace both the hole transport layers (HTLs) and the metal top electrode. The best value of PCE was 6.87%, which was further enhanced to 9.90% after inserting the HTL, 2,2',7,7'-tetrakis(N,N-p-dimethoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) [78]. Wang *et al.* even demonstrated flexible perovskite photovoltaic devices consisting of a cathode of titanium foil/ TiO_2 nanotubes and a laminated CNT anode [79].

In summary, because of the good combination of outstanding optical, electrical, chemical and mechanical properties, carbon-based materials, especially graphene and CNT, hold great promise to substitute the costly and brittle ITO or energy-consuming thermally evaporated metal electrodes. In the aspect of application, they also share advantages such as abundant supply, decreased cost and compatibility with roll-to-roll technique. But to become next-generation transparent electrode, more effort to further increase the conductivity and transparency simultaneously of these carbon-based thin films, to easily manipulate the surface properties and to develop robust transferring technology is needed.

14.4 Metallic Nanostructures

Transparent electrode based on metallic nanostructure is a promising candidate for substituting commonly used ITO electrode due to its admirable properties, such as high conductivity, acceptable optical transmittance and good mechanical flexibility. For non-transparent materials such as metals, high transparency could be achieved at ultrathin thickness; but at the expense of conductivity loss due to surface scattering and defects. In the past several years, tremendous work has been carried out to realize a better coexistence of these two properties. Accordingly, metallic nanostructures were classified into metal nanomeshes, metal nanowire networks and ultra-thin metal films, which will be discussed in detail in the following sections.

14.4.1 Metal Nanomeshes

Some highly conducting materials, such as silver and copper, can be imprinted on the substrate to form conducting metal mesh/pattern. And it is demonstrated that such a mesh or grated structure is helpful for improving the light absorption of active layer due to resonance effects and surface plasmon polaritons [85]. Furthermore, absorption could be further enhanced by an additional capping layer on the Ag grating, e.g., WO_3 . A few methods to fabricate such metal nanomeshes are reviewed below and summarized in Table 14.4.

Early in 2007, Tvingstedt and Inganäs reported a silver grid structure through a facile and cheap soft lithographic metal deposition method [86]. As depicted in Figure 14.3, the silver solution flowed from the open end of the channels to the other end driven by capillary force and the lower pressure originating from the syringe at the end of the channels. After conductive silver stripes were formed, the samples were thoroughly washed

Table 14.4 Photovoltaic performance of OPVs with metal grids as the transparent electrode.

Grids material	Width (μm)	Height (nm)	Spacing (μm)	R _s (Ω/sq)	T (%)	Active layer	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)	Year	Ref.
Ag	20 ~ 40	100	100 ~ 800	0.5	–	APFO-Green 5:PC ₆₀ BM	3.67	0.58	0.47	1.00	2007	[86]
Au	0.4	40	10 and 0.7	24	84	P3HT:PCBM	5.50	0.57	0.62	1.96	2008	[87]
Cu	0.4	40	10 and 0.7	28	83	P3HT:PCBM	5.71	0.57	0.63	2.06	2008	[87]
Ag	0.4	40	10 and 0.7	23	78	P3HT:PCBM	5.34	0.58	0.65	2.00	2008	[87]
Ag ¹	15	1000	2000	–	–	P3HT:PCBM	7.06	0.5	0.545	1.92	2012	[88]
Ag ²	132	300	2000	–	–	P3HT:PCBM	4.27	0.5	0.351	0.75	2012	[88]
Ag ³	133	700	2000	–	–	P3HT:PCBM	7.02	0.51	0.512	1.82	2012	[88]
Ag	2	55	20 ~ 60	10	86	PBDTPD:PC ₇₀ BM	7.2	0.57	0.518	2.14	2014	[89]
Pt	–	–	–	170	94	TNAR based DSSCs	10.99	0.66	53	3.82	2015	[92]
Ag	15	4700	> 300	1.49	86	PCDTBT: PC ₇₀ BM	8.20	0.61	0.423	2.12	2016	[91]
Cu	–	–	–	28.7	83.5	P3HT:PCBM	7.8	0.57	0.458	2.04	2016	[93]

Note: ¹Roll-to-roll thermal imprinting.²Roll-to-roll inkjet printing.³Roll-to-roll flexographic printing

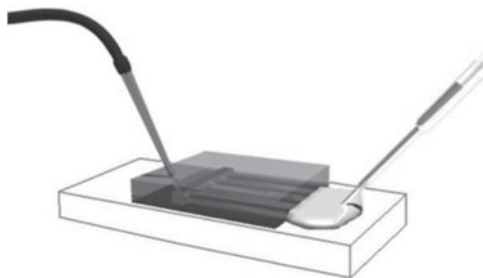


Figure 14.3 Drawing of the fluidic deposition method exploiting PDMS stamps. Air is extracted through the left syringe, generating a lower pressure that speeds up the capillary flow of the deposited electroless silvering solution. (Reproduced with permission from [86])

in DI water and blown dried with nitrogen gas. The resultant silver grids consisted of lines with widths of $20 \sim 40 \mu\text{m}$ separated by a distance of $100 \sim 800 \mu\text{m}$ and with a height of 100 nm . Four-point probe measurement showed the sheet resistance was around $0.5 \Omega/\text{sq}$. After being spin-coated with diethylene glycol-doped PEDOT:PSS (DEG-PEDOT) for the purpose of getting a smoother surface, the Ag grid electrodes were incorporated into OPVs with a cell architecture of substrate/Ag grid/DEG-PEDOT/APFO-Green 5:PC₆₁BM/Al, resulting in 1.00% efficiency. The control cell with an ITO transparent electrode showed a PCE of 0.83%.

Kang *et al.* fabricated metal grid electrode with high transparency and low sheet resistance by nanoimprint lithography (NIL) [87]. Metal grid was formed by depositing 40 nm-thick Au, Cu, or Ag on the poly(dimethylsiloxane) (PDMS) stamp, resulting in sheet resistance of $24 \Omega/\text{sq}$, $28 \Omega/\text{sq}$, and $23 \Omega/\text{sq}$, and transmittance of 84%, 83%, 78%, respectively. The P3HT:PCBM-based OPVs using nanopatterned Au, Cu, Ag and ITO showed PCEs of 1.96%, 2.06%, 2.00% and 2.00%, respectively. This work demonstrated the possibility of fabricating such metal grid electrodes on flexible substrate using roll-to-roll technique.

In 2012, Yu *et al.* fabricated all-printed polymer solar cells employing three kinds of Ag grid electrode, i.e., embedded silver grid (embedding the grid structure into the substrate) by roll-to-roll thermal imprinting and Ag filling; raised silver grid (printing thin grid structure with a raised topography) by roll-to-roll inkjet printing; and raised silver grid by roll-to-roll flexographic printing [88]. The embedded Ag grids with a nominal width of $15 \mu\text{m}$ and a height of $10 \mu\text{m}$ buried in substrates are of high conductivity but low processing speed (no faster than 6 m/min) due to thermal imprinting, Ag filling and drying. The P3HT:PCBM OPVs based on such

an electrode showed 1.92% efficiency. And the raised Ag grids processed by inkjet or flexographic printing showed high processing speed, i.e., 75 m/min for inkjet printing and 200 m/min for flexographic printing, but with greater optical shadow loss. The same OPVs based on the former electrode showed a PCE of 0.75% and the latter of 1.82%. It should be noted that all the fabrication and encapsulation steps were roll-to-roll processed in this study.

Rao *et al.* fabricated Ag network innovatively by using a cracked template produced by drying an acrylic-based colloidal dispersion on a glass substrate [89]. In this method, 55 nm of Ag was deposited by vacuum evaporation and the template was subsequently dissolved in chloroform. The OPVs with such a silver network displayed a PCE of 2.14%, comparable to 2.27% of ITO-based cells.

Oh *et al.* developed high-performance metal grid transparent conductors (TCs) by direct imprinting of thermally reduced Ag nanoparticles via deformation-driven ink injection, as illustrated in Figure 14.4 [90]. By designing a “reservoir” in grid patterned PDMS mold, the reservoir could capture outgoing ink and then inject ink into the grid pattern mold, thus removing the residue ink between the mold and the substrate, and also improving the ink filling in the mold cavity. In a separate report, they incorporated Ag nanowire networks into the microscale Ag grid structures fabricated by the same method, achieving a $R_s < 1.5 \Omega/\text{sq}$ and a T of 86% at 550 nm, superior to the corresponding values of Ag NW networks without Ag grid (R_s of $15.6 \Omega/\text{sq}$ at a similar T) [91].

Besides commonly used Ag, metallic Pt network was also demonstrated as transparent electrode for highly flexible dye-sensitized solar cell [92]. And high-quality Cu mesh with ordered pore arrays was prepared

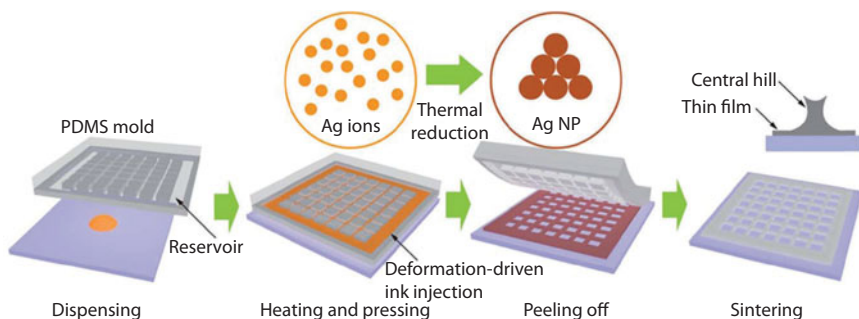


Figure 14.4 Schematic illustration of the direct imprinting of thermally reduced Ag NPs via deformation-driven ink injection using the PDMS mold with a “reservoir” design. (Reproduced with permission from [90])

as transparent electrodes using polymer films with ordered pore arrays as template [93].

14.4.2 Metal Nanowire Networks

In general, conducting and transparent films made from Ag nanowires could be obtained by depositing Ag nanowires on the flexible or glass substrate and then depicting them in a grid pattern by photolithography. Compared to ITO, transparent electrode based on Ag nanowire is estimated to be less energy-demanding and more cost-efficient, as seen in Table 14.5. The slot-die coating and the drying of the layer account for ~55% of the embodied energy in the film, and the fabrication of Ag nanowire makes up 30% ~ 65% of the total costs of the film [94]. The range is based on different chemical prices from different suppliers.

Early in 2008, Lee *et al.* fabricated transparent electrode using solution-processed Ag nanowires [95]. The initial sheet resistance was > 1 kΩ/sq, and it was reduced by more than one order of magnitude due to the partial decomposition of the insulating capping agent, poly(vinyl pyrrolidone) (PVP), at 200 °C. Finally, the Ag nanowire electrodes with sheet resistance of 16 Ω/sq and transparency of 86% were achieved and incorporated into the organic photovoltaics employing CuPc:PTCBI as active layer. The devices showed 0.38% PCE, which was close to that of ITO-based devices (0.42%).

Later, De *et al.* prepared flexible conducting film using aqueous dispersions of silver nanowires by vacuum filtration using porous mixed cellulose ester filter membranes [96]. Under optimal thickness, conducting films with optical transmittance and sheet resistance of 85% and 13 Ω/sq as well as superior flexibility were achieved on PET substrate. Similar results using the same fabrication method were obtained by Madaria *et al.* [97].

Kang *et al.* tried to fabricate Ag nanowire electrode using nanoimprint lithography (NIL) method for OPVs [98]. The designed nanowire

Table 14.5 Comparison of life circle analysis and cost analysis between ITO and Ag nanowire. Note that these values do not contain the embodied energy or cost of the PET substrate with the exception of the cost of ITO film, which contains the cost of PET [94].

Transparent electrode	Embodied energy (MJ EPE ¹ /m ²)		Cost (Euro/m ²)	
	Min	Max	Min	Max
ITO	71.98	271.19	14.64	65.50
Ag nanowire	47.84	53.78	5.31	17.87

period was set to 220 nm so that the enhanced absorption range due to surface plasmon resonance coincides with the peak solar spectrum. The device efficiency was 1.32%, higher than that of the ITO control device (0.96%).

The PCE of P3HT:PCBM-based organic solar cell using spin-coated Ag nanowire as transparent electrode was refreshed to 3.45% by Leem *et al.* [99]. In this work, PEDOT:PSS capping layer was proposed to realize full coverage and smooth surface. ZnO nanoparticle was also demonstrated to be a good buffer layer [100, 101]. A similar spin-coating technique was also adopted by other groups [102, 103].

Lim *et al.* reported a simple brush-painting technology to fabricate Ag nanowire network electrode [104]. They found the electrical and optical properties of the obtained electrode as a function of the brushing times. The optical transparency decreased from 87.62% to 81.89% and the sheet resistance decreased from 38.7 Ω/sq to 14.0 Ω/sq with brushing times increased from 1 to 3. The best P3HT:PCBM OPVs with brushed Ag nanowires as transparent electrode displayed a best PCE of 3.23%, comparable to that of ITO-based cells (3.34%). Similarly, Kiran Kumar *et al.* coated Ag nanowire ink on PET substrates using Mayer rod appliances followed by drying at 100 °C for 5 min and 130 °C for 10 min, resulting in high transmittance beyond 90%, sheet resistance below 300 Ω/sq and haze about 2% [105]. Kang *et al.* presented brush-painted Ag nanowire network for flexible organic solar cell showing sheet resistance of 26.4 Ω/sq and transmittance of 81.8% [106].

Park *et al.* prepared patterned Ag nanowire electrodes with a pattern mask by electrohydrodynamic (EHD) spraying for organic solar cell, achieving a PCE of 5.27%, which was another step forward to high efficiency [107]. A similar method was tried to fabricate Ag nanowire transparent electrode by other groups [108–110]. The Ag nanowire electrode was also successfully fabricated by other methods, including dip-coating technique [111], *in-situ* fabrication technique (as illustrated in Figure 14.5) [112] and inkjet printing technique [113].

Besides the above-mentioned Ag nanowires, other metals were also explored. For example, Cu nanofiber film was presented as transparent electrode fabricated by electrospinning and electroplating technique, as illustrated in Figure 14.5. Ultra-low sheet resistance (0.359 Ω/sq , 0.371 Ω/sq , 0.420 Ω/sq) and high transmittance (92%, 93%, 97%) was achieved while also possessing excellent flexibility and robustness. Also reported were ultrathin gold nanowires fabricated at the air/water interface by a bottom-up self-assembly approach in which a sheet resistance of 130.1 Ω/sq and transmittance of ~ 92% were obtained [114].

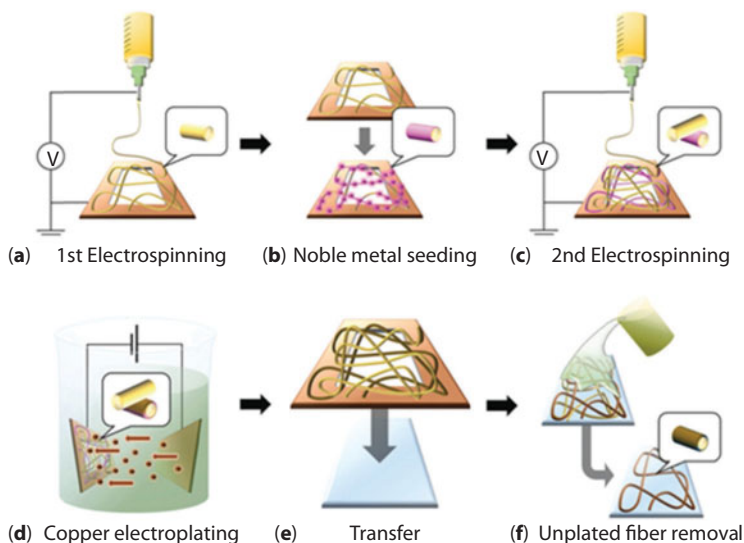


Figure 14.5 Schematic of the fabrication process for Cu electroplated nanowire meshes for transparent conducting electrodes. (a) A layer of electrospun polymer nanofibers is deposited onto a copper frame. (b) The nanofibers are made conductive by noble metal seeding. (c) The second layer of electrospun polymer nanofibers is deposited above the platinum-seeded nanofibers. (d) Only the metal-seeded nanofibers are electroplated by copper. (The second layer of electrospun nanofibers is not electroplated because they are nonconductive without metal seeding.) (e) The electroplated and non-electroplated nanofibers are transferred to a transparent substrate. (f) The nonelectroplated nanofibers are removed by dissolution. (Reprinted with permission from [115])

14.4.3 Ultrathin Metal Films

One way to fabricate high-performance transparent electrode is to deposit ultrathin metal films on glass or PET/PEN substrates. A desirable metal film electrode should be thin enough to ensure high transmittance without sacrificing conductivity. Therefore, much effort has been made to create ultrathin metal films that are smooth and uniform.

Usually, the ultrathin metal film is fabricated by vacuum thermal evaporation. Meiss *et al.* reported thin metal Ag films as transparent electrode for OPVs taking $\text{ZnPc}:\text{C}_{60}$ as active layer, resulting in PCE of 2.09% [116]. The introduction of 1 nm-thick Al beneath the 14 nm-thick Ag film was helpful to film morphology, as evidenced by the decreased number of Ag clusters and smaller root mean square roughness R_{rms} of 2.3 ~ 2.6 nm, as compared to that of Ag film without Al layer (3.6 ~ 5 nm). Formica *et al.* proposed 1 nm Ni capping layer that increased the work function and the stability of the underlying Ag film, achieving a PCE of 2.48% for

Table 14.6 Photovoltaic performance of solar cells with metal nanowire networks as the transparent electrode.

Material	Length (μm)	Diameter (nm)	R_s (Ω/sq)	T (%)	Active layer	J_{sc} (mA/ cm^2)	V_{oc} (V)	FF	PCE (%)	Year	Ref.
Ag	8.7 ± 3.7	107 ± 17	16	86	CuPc:PTCBI	1.83	–	–	0.38	2008	[95]
Ag	–	–	–	77	CuPc:C ₆₀	5.21	0.5	0.5	1.32	2010	[98]
Ag	–	–	29	88	P3HT:PCBM	10.1	0.56	0.611	3.45	2011	[99]
Ag	Tens of micrometers	> 100	4.2	80	P3HT:PCBM	8.6	0.59	0.46	2.4	2011	[100]
Ag	6.5	80	15	–	P3HT:PCBM	9.51	0.6	0.68	3.85	2012	[101]
Ag	–	–	38.7	87.62	P3HT:PCBM	8.933	0.588	0.615	3.23	2012	[104]
Ag	20	40	11	~ 80	PBDTTT-C:PCBM	15.84	0.69	0.482	5.27	2013	[107]
Ag	7/15	90/60	15	85	ZnPc:PCBM	7.1	0.56	0.588	2.31	2013	[111]
Ag	Tens of micrometers	25 ± 5	10	95	PTB7-F20:PC ₇₁ BM	14.4	0.67	0.598	5.8	2013	[102]
Ag	10 ~ 20	$25 \sim 30$	26.4	81.8	P3HT:PCBM	7.276	0.574	0.492	2.055	2014	[106]
Ag	–	–	16	95	P3HT:PCBM	8.89	0.61	0.596	3.25	2014	[103]
Ag	110 (thick) 80 (thin)	200 50	20.2	94.7	P3HT:PCBM	6.67	–	–	1.81	2015	[108]
Ag	–	–	44.9	86.4	P3HT:PCBM	8.44	0.6	0.54	2.71	2015	[113]
Ag	25	90	10.0	80	ZnPc:C ₆₀	7.14	0.46	0.372	1.23	2015	[109]
Ag	10	30	–	~ 80	Perovskite	16.48	0.918	0.49	7.45	2016	[110]
Ag	20 ~ 50	115	3.5	86	PCDTBT:PC ₇₁ BM	8.20	0.61	0.423	2.12	2016	[91]

F4-ZnPc:C₆₀ OPVs [117]. Other than thermal evaporation, the ultrathin metal films could also be fabricated by sputtering [118–121].

The growth of Ag film on the substrate obeys the Volmer-Weber mode [122], and it is important to select a suitable seed layer underneath the Ag film to obtain a smooth morphology. Salinas *et al.* introduced 40 nm TeO₂ as seed layer to fabricate smooth, highly conductive and transparent Ag ultrathin films ($R_s = 7.02 \text{ } \Omega/\text{sq}$, $T = 54.89\%$) [123]. Applying such electrode to PIDT-phanQ:PC₇₁BM OPVs resulted in PCEs of 6.56% on PET substrates and 5.78% on glass substrates. Schubert *et al.* introduced ultrathin seed layer of high surface energy, such as Ca, Al or Au, to fabricate Ag films as transparent electrode for organic solar cells [124]. The continuous and smooth Au/Ag film showed a sheet resistance of $19 \text{ } \Omega/\text{sq}$ and a transmittance of 83% at 530 nm wavelength. F4ZnPc:C₆₀ OPV using Au/Ag electrode achieved a PCE of 4.7%, which was similar to 4.6% of ITO-based devices. Xu *et al.* deposited nanoporous Ag film on the MoO_x seed layer by thermal evaporation [125]. By controlling the thickness to 10 nm and the evaporating rate to 0.5 nm/s, nanoporous Ag films with average aperture size of 60 nm and density of pores of $\sim 200 \text{ per } \mu\text{m}^2$ were obtained. Uniform and smooth (with $R_{\text{rms}} = 1.86 \text{ nm}$) MoO_x/Ag/MoO_x films achieved high conductivity of $11 \text{ } \Omega/\text{sq}$ at transmittance of 70%.

Doping method has been reported to enhance conductivity and transparency. Wang *et al.* reported an ultrathin Ag transparent electrode with a ZnO/AgO_x/ZnO (ZAOZ) structure using minimal oxidation [118]. Both ZnO and Ag were deposited on PET substrate by magnetron multi-gun sputtering at room temperature. The oxygen-doped Ag (O/Ag = 3.4 at%) film exhibited continuous and much smoother morphology when the thickness was beyond 6 nm. Better average transmittance of 91% and sheet resistance of $20 \text{ } \Omega/\text{sq}$ were achieved compared to the undoped film (ZAZ, $T = 77\%$ transparency at similar resistance). The sheet resistance for both electrodes showed negligible change, i.e., 1.52% for ZAZ and 1.33% for ZAOZ, after being bent to a bending radius of 2.8 mm. Efficiency of PTB7-F20:PC₇₁BM inverted OPVs was improved from 5.65% for ZAZ electrode to 6.34% for ZAOZ electrode. Zhang *et al.* presented Al-doped Ag ultrathin film as an effective alternative to replace ITO for organic solar cells [119]. Doping of Al into Ag was realized by a simple co-sputtering process. Such a method allowed the film to be formed without seed layer as the Al dopant could greatly reduce the roughness of Ag (R_{rms} is less than 1 nm). Such a 7 nm-thick Al-doped Ag film showed a sheet resistance of $23.4 \text{ } \Omega/\text{sq}$ with transmittance of more than 80%. Incorporating such electrode into PBDTTTC-T:PC₇₁BM OPVs resulted in a 7.44% efficiency, which was superior to 6.87% of an ITO-based device.

Table 14.7 Photovoltaic performance of OPVs with ultrathin metal film as the transparent electrode.

Material	Thickness (nm)	Roughness (nm)	R_s (Ω/sq)	T (%)	Active layer	J_{sc} (mA/ cm^2)	V_{oc} (V)	FF	PCE (%)	Year	Ref.
Ag	14	2.3 ~ 2.6	–	–	ZnPc:C ₆₀	7.02	0.529	0.56	2.09	2009	[116]
Ag	9	–	11	75	F4-ZnPc:C ₆₀	6.53	0.76	0.5	2.48	2012	[117]
Ag	12	–	7.02	54.89	PIDT-phanQ:PC ₇₁ BM	11.57	0.87	0.65	6.56	2012	[123]
Ag	7	–	19	83	F4-ZnPc:C ₆₀	11.7	0.67	0.60	4.7	2013	[124]
Ag	10	–	11	70	SubPc:C ₆₀	5.15	1.03	0.65	3.45	2013	[125]
Ag	6	~ 5	20	91	PTB7-F20:PC ₇₁ BM	16.39	0.68	0.58	6.34	2014	[118]
Ag	7	0.78	23.4	> 80	PBDTTTC-T:PC ₇₁ BM	14.76	0.80	0.63	7.44	2014	[119]
Ag	10	0.95	8.6	90	PIDT-PhanQ:PC ₇₁ BM	12.0	0.87	0.63	6.59	2014	[127]
Cu	15	1.08	6.4	79.7	PCDTBT:PC ₇₁ BM	7.4	0.93	0.52	3.6	2014	[126]
Ag	8	0.9	6.2	87.7	PTB7:PC ₇₁ BM	14.66	0.75	0.76	8.34	2015	[120]
Ag	12	–	–	–	Perovskite	9.5	0.889	0.73	6.15	2015	[128]
Ag	8	2.0 ± 0.3	9.7	80	PTB7:PC ₇₁ BM	10.92	0.65	0.51	3.65	2016	[129]
Ag	8	2.0 ± 0.3	9.7	80	PCDTBT:PC ₇₁ BM	6.56	0.86	0.59	3.33	2016	[129]
Cu	6.5	< 0.3	18.8	82.8	PTB7:PC ₇₁ BM	15.4	0.74	0.62	7.1	2016	[121]
Ag	8	~ 1.6	6	78	Perovskite	22.84	1.01	0.70	16.23	2016	[130]

Copper has also attracted significant interest due to its low cost and high conductivity. Luo *et al.* explored ultrathin Cu film by thermal evaporation as transparent electrode for inverted polymer solar cells [126]. A poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyl fluorene)] (PFN) interlayer was employed between Cu and photoactive layer to obtain smooth Cu film and ohmic contact. The 15 nm-thick Cu film had a R_{rms} of 1.08 nm, and a high conductivity of 6.4 Ω/sq , with average transmittance of 79.7%. As a result, the inverted polymer solar cells based on PCDTBT:PC₇₁BM achieved 3.6% PCE. Zhao *et al.* reported a continuous and smooth copper ultrathin film fabricated by reactive sputtering process at room temperature [121]. Less than 1% nitrogen doping dramatically improved the wetting ability of copper on zinc oxide surface. The electrode based on the N-doped Cu film exhibited an optimized average transmittance of 84% and a sheet resistance lower than 20 Ω/sq , without electrical degradation after exposure to a strong oxidation condition for 760 h.

To briefly summarize, metal nanostructures are a promising ITO replacement in consideration of their excellent electrical conductivity, good mechanical flexibility and compatibility with printing techniques. Nevertheless, metal is opaque to light. Thanks to the metal nanostructures with holes or small thickness or even surface plasmonic effect that can enhance light transmission. There are metal nanostructures achieving high conductivity and transmittance that are comparable to or even a little better than ITO. One remaining concern is their stability against oxidation.

14.5 Multilayer Thin Films

Multilayer thin films (MTFs), built via an advisable combination of distinctive layers, present an excellent comprehensive performance, including low sheet resistance, high transparency in the visible range, admirable chemical stability and mechanical flexibility. Over the past five years, there has been tremendous work committed to excavating the suitable materials for MTFs and optimizing the structure. The constructing materials of MTF are mainly classified into conducting oxide, metal nanostructure and graphene-based nanomaterial.

The idea of MTF configuration originated from ITO modifications. In the hope of elevating the overall electrical conductivity of ITO, Jeong and Kim sandwiched a metal conductor, such as silver, between two ITO electrodes [131]. Subsequently, the ITO layer was further replaced by other dielectric material with a high refractive index and moderate electrical conductivity in consideration of the scarcity and high cost of indium. In

general, the dielectric material in the dielectric/metal/dielectric (DMD) multilayer transparent electrode usually acts as an antireflection layer to promote the transmittance of metal thin film electrodes, and the in-plane conductivity is mainly contributed by the metal layer, which must be thick enough to overcome its percolation threshold.

Recent works about photovoltaic properties of DMD transparent electrode are summarized in Table 14.8. Jeong and Kim successfully synthesized ITO/Ag/ITO multilayer transparent electrodes via a linear facing target sputtering at room temperature [131]. They observed that the ITO/Ag/ITO MTF showed an obvious decrease in sheet resistance from $34 \text{ } \Omega/\text{sq}$ of ITO to $4.4 \text{ } \Omega/\text{sq}$ without sacrificing optical transmittance. This was attributed to the excellent conductivity and strong surface plasmon resonance of metallic silver. Beyond the ITO/Ag/ITO system, other materials were also exploited to construct DMD transparent electrode. Sahu and Huang achieved ZnO/Cu/ZnO MTF via simultaneous DC magnetron sputtering of Cu and RF magnetron sputtering of ZnO [132]. The as-prepared MTF could maintain a transmittance over 85% with sheet resistance of $9.46 \text{ } \Omega/\text{sq}$ after a post-growth annealing at 200°C in vacuum. By optimizing the thickness of each layer, Bou *et al.* obtained a sheet resistance of $6.7 \text{ } \Omega/\text{sq}$ and a transmittance of 78.5% at 550 nm for $\text{SnO}_x/\text{Ag}/\text{SnO}_x$ MTF [133]. Shen *et al.* declared that the metal-mirror-microcavity (MMC) structure construct in the DMD transparent electrode should also be responsible for improving optical properties [134]. They observed the efficiency of the polymer solar cells device was improved by 27.4% compared to a device with an ITO transparent electrode when the thickness of active layer was 70 nm; but for the device with a 150 nm-thick active layer, the efficiency was reduced by 19.9%. The diversity of efficiency was attributed to the MMC induced by microcavity resonance effect, as illustrated in Figure 14.6. Besides, the MTF electrode can also serve directly as cathode for electron extraction or anode for hole extraction, depending on the choice of oxide layer. Chen *et al.* designed MoO_3 as a buffer layer with an excellent property for hole extraction; while Han *et al.* used TiO_x with low work function as an electron extraction layer to form good ohmic contact with the PC_{61}BM acceptor [135, 136].

Hybrid metal nanowire/graphene electrode is often equipped with high conductivity, excellent durability and remarkable transparency simultaneously due to the synergistic effect of metal nanowire and graphene. On one hand, graphene can greatly reduce the roughness of metal nanowire and enhance the efficiency of charge carrier collection [150]. On the other hand, metal nanowire can also boost the electrical conductivity of the composite film. Lee *et al.* fabricated graphene-Ag nanowire hybrid structures

Table 14.8 Photovoltaic performance of solar cells with dielectric/metal/dielectric MTFs as the transparent electrode.

MTF (Thickness in nm)	R _s (Ω/sq)	T (%)	Active layer	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)	Year	Ref.
ITO(40)/Ag(16)/ITO(40)	4.4	86.54	P3HT:PCBM	9.22	0.54	0.65	3.25	2009	[131]
WO ₃ (40)/Ag(15)/WO ₃ (20)	–	–	P3HT:PCBM	5.85	0.59	0.58	2	2012	[134]
ZTO(20)/Ag(8)/ZTO(39)	9	82	P3HT:PCBM	7.3	0.54	0.51	2	2012	[137]
MoO ₃ (2)/Ag(6)/MoO ₃ (10)	6.2	80	PCDTBT:PC ₇₁ BM	8.4	0.85	0.62	4.44	2012	[138]
ITO/AgOx/ITO	4.2	88	PTB7-F20:PC ₇₁ BM	14.62	0.67	0.6	5.88	2013	[139]
MoO ₃ (10)/Ag(9)/ZnO(20)	5	70	P3HT:PCBM	7	0.59	0.62	2.3	2013	[140]
WO ₃ (40)/Ag(10)/Ta ₂ O ₅ (35)	11	90	P3HT:PC ₆₁ BM	7.4	0.63	0.61	2.9	2013	[141]
TiO _x (5)/Ag(15)/ZnS(25)	–	–	PCDTBT:PC ₇₁ BM	9.8	0.9	0.58	5.1	2013	[136]
ZnO(20)/Ag(9)/MoOx(10)	18	61.48	P3HT:PCBM	7.62	0.59	0.42	1.92	2014	[142]
AZO(50)/AgNW/AZO(50)/ZnO	11.3	93.4	Cu(In _{1-x} Ga _x)S ₂	36.43	0.54	0.56	11.03	2014	[143]
NiO/Ag/NiO	7.6	82	PBDT ^{TT} -C: PC ₇₁ BM	13.37	0.71	0.64	6.07	2014	[144]
FZTO(40)/Ag(9)/FZTO(40)	9.06	88.15	PTB7: PC ₇₁ BM	12.28	0.72	0.54	4.84	2015	[145]
ZnO(40)/Ag(19)/ZnO(40)	3.6	95	P3HT:PCBM	7.07	0.67	0.55	2.63	2015	[146]
MTO(40)/Ag(11)/MTO(40)	10.1	85.4	P3HT:PCBM	7.12	0.62	0.62	2.73	2015	[147]
GTO(35)/Ag(9)/GTO(35)	9.51	86.48	P3HT:PCBM	6.46	0.61	0.66	2.6	2015	[148]
ITO/Ag(8)/ITO	–	–	PV-D4610:PC ₇₁ BM	0.72	0.78	0.51	2.87	2016	[149]

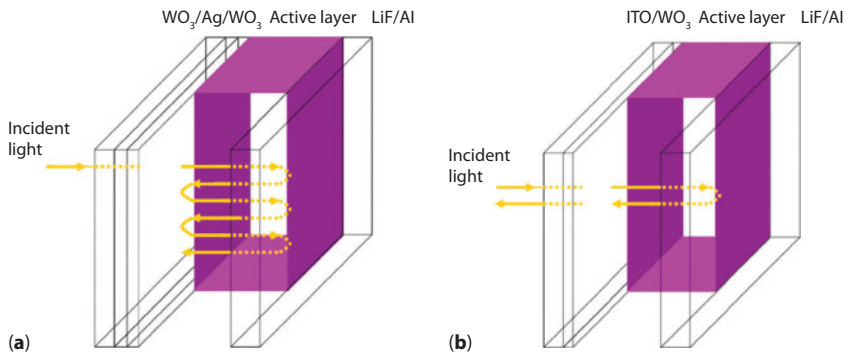


Figure 14.6 (a) Structure of the ITO-free OPV is glass/ WO_3 (40 nm)/Ag (15 nm)/ WO_3 (20 nm)/P3HT:PCBM/LiF/Al. (b) The structure is ITO/ WO_3 (20 nm)/P3HT:PCBM/LiF/Al. (Reproduced with permission from [134])

via spinning a suspension of Ag nanowires onto a CVD prepared graphene layer. Such hybrid structures not only showed a 94% transmittance in the visible range and a low sheet resistance of 33 Ω/sq , but also exhibited a superb stretchability and flexibility [151].

Recent trends show that the unfavorable geometry of metal nanowires in the graphene-based MTF is being replaced by metal grid with precisely controlled distribution of nanowire via nanolithography technology. Compared with the random distribution of metal nanowires, well-ordered metal grid can greatly reduce the contact resistance at interwire junctions. Tour *et al.* fabricated a hybrid transparent electrode using Au grid obtained by photolithography with wet etching and CVD-synthesized graphene, which showed a sheet resistance as low as 3 Ω/sq and the transmittance at $\sim 80\%$ [155]. Besides, it also suggests that the transmittance of the hybrid film can be adjusted by modulating the metal grid size and grid line width. Cha *et al.* studied the influence of metal grid size on the properties of transparent anodes and investigated their application in flexible OPVs [156]. The devices equipped with PET/Ag grid/single-layer graphene substrates yielded PCEs in the range of 3.4–3.9%; the optimal performance of 3.9% was achieved when the Ag grid size of 200 μm (length) $\times$ 200 μm (width) $\times$ 50 nm (height) $\times$ 2 μm (linewidth) was used. To simplify the process and retrench in expenditure, Lee *et al.* employed an ink-jet printing method that is mask-free to fabricate Ag grid. Furthermore, the CVD-grown graphene was substituted by a low-cost and easily up-scalable hydrogen reduced graphene oxide by Zhi and coworkers [158]. Some recent publications on metal nanowire or grid/graphene MTFs are listed in Table 14.9.

Table 14.9 Photovoltaic performance of OPVs with graphene-based MTFs as the transparent electrode.

Cell architecture	R _s (Ω/sq)	T (%)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)	Year	Ref.
Au grid/graphene/PEDOT:PSS/P3HT:PCBM/TiO ₂ /ITO/glass	22	81.4	9.3	0.63	0.53	3.11	2013	[152]
Ag grid/graphene/PEDOT:PSS/P3HT:PCBM/CPE/Al	28	87	8.05	0.58	0.51	2.38	2013	[153]
Ag grid/graphene/PEDOT:PSS/P3HT:ICBA/TiO _x /Al	12	73	6.8	0.8	0.53	2.9	2014	[154]
Ag grid/graphene/PEDOT:PSS/P3HT:PC ₆₀ BM/CPE/Al	27.3	–	10.9	0.58	0.61	3.9	2015	[156]
Cu nanowire/graphene/PEDOT:PSS/PTB7:PC ₇₁ BM(1:1.5)/LiF/Al	36	79	8.2	0.73	0.68	4.04	2015	[157]
Au nanogrates/graphene/PEDOT:PSS/PTB7:PC ₇₁ BM/ZnO NPs/Al	8	90	14.82	0.73	0.59	6.3	2016	[150]

Most recently, there have been reports showing that the dielectric inorganic layers in MTF can be replaced by solution-processed organic materials. Kang *et al.* presented an innovative way to create uniform, strong metallization nuclei on plastic substrates by coating polyetherimide (PEI) so that amine groups on PEI can act as evenly distributed atomic-scale nucleation centers [159]. Their MTF had a structure of substrate/PEI/Ag/PEDOT:PSS. Over the visible range, i.e., between 400 and 600 nm, the MTF exhibited high T of 96% at 550 nm and a maximum T of 98% at 485 nm. The OPVs employed such a transparent electrode yielded high PCE values of 9.9% on PEN and 10.1% on glass. Those performances were even superior to those of conventional ITO-based OPVs, for which PCEs were 9.5% on PEN and 9.7% on glass. In another report, Aleksandrova *et al.* introduced PEDOT:PSS(35 nm)/Au(15 nm)/PEDOT: PSS(35 nm) MTF, which exhibited a sheet resistance of 20.9 Ω/sq and a maximum optical transmission of 82.6% in the visible region. Its sheet resistance variation was 3.8% after applying 2000 bending cycles at a radius of 6 mm [37].

In summary, MTF is a promising candidate to be an ideal transparent electrode because well-structured MTF can integrate various merits of each component, often accompanied by excellent conductivity, high transparency and even admirable flexibility at the same time. The properties of MTF are greatly improved, but even after tremendous efforts and devotion, the number of drawbacks still remains remarkable, such as its poor mechanical stability, high manufacturing cost and cumbersome fabrication process. To meet the requirements of commercial application, much effort is still needed in material selection, structure innovation and process optimization.

14.6 Printable Metal Back Electrodes

The role of back electrode in a solar cell is to collect the charges generated by the photoactive layer, either holes or electrons, and plunge them into the external circuit to do electrical work. Thus a highly conductive back electrode is desirable to minimize the resistive loss in the solar cell. Because metals are the best known conductors, they are widely used as back electrodes in solar cells. To be fully compatible with the printing technology, metal nanomaterials are formulated into inks or pastes to replace vacuum-deposited metal thin films.

Even though other metals, such as copper, have the potential to form high-quality back electrode by printing [160], up till now, silver is still the dominant metal material for such an application [161–164]. Many

silver-based printable electrodes have been investigated, including silver pastes [165], silver inks [166, 167] and silver/conducting polymer composites [168]. Currently, silver inks are frequently used to form a back electrode through R2R printing. The most commonly used silver inks are based on highly concentrated dispersions of silver flakes or nanoparticles [169]. Many silver inks are commercially available. Different formulations can lead to vastly different device performances for a particular photovoltaic system. Krebs *et al.* tested ten different kinds of commercial inks in parallel [170]. The inks were all screen printed to complete the cell architecture of ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag. Table 14.10 lists the maximum PCE and average photovoltaic performance parameters of 150 modules with 16 serially connected cells and a module length of 60 mm.

Since the deposition of the silver back electrode is performed as the last step for the multilayer stack manufacturing of a printable solar cell, solvent selection becomes particularly important to prevent dissolution of the underlying layers [170]. Krebs *et al.* investigated three different types of printable silver inks, i.e., organic solvent-based heat curable (PV410 from Dupont), UV curable and water-based heat curable, on P3HT:PCBM-based solar cells. The result showed that current extraction fell to almost zero for PV410 but not for the other two inks. With the aid of light beam-induced current (LBIC) technique, it was revealed that the organic solvent(s) in PV410 could diffuse into and then partly dissolve the active layer, and

Table 14.10 Average OPV module performance of 10 different kinds of commercial inks. (Reproduced with permission from [170])

Silver ink	Max PCE (%)	Mean PCE (%)	Mean Isc (mA)	Mean Voc (V)	Mean FF
Toyo UV	2.2	1.95	61.8	7.75	39.0
Toyo Solvent	0.77	0.65	40.7	5.38	28.6
Spraylat XCMS-016	1.00	0.86	44.8	6.12	30.1
Spraylat XCMD-022	0.83	1.05	44.8	6.87	32.7
Spraylat XCMS-031	1.17	1.11	53.7	6.23	31.9
Spraylat XPVS-145	0.70	0.60	41.0	4.77	29.8
DuPont 410	1.73	1.64	54.7	7.78	37.1
DuPont 5000	1.01	0.96	40.6	7.18	31.8
DuPont 5007E	1.29	1.13	52.2	6.53	31.9
DuPont 5025	1.59	0.93	45.6	5.96	31.7

thereby destroy the morphology of the bulk heterojunction before heat curing is completed [171].

The drying and thermal annealing processes after printing can also be crucial to some inks. Hösel and Krebs studied a commercial water-based flexo silver ink PFI-722 (PChem Associates) and a homemade silver ink, which was a dispersion of Ag nanoparticles (40–70 nm) in a 1:1 mixture of triethylene glycol monomethyl ether and o-xylene, with a final concentration of 25 wt% and filtered through a 2.7 mm filter prior to printing. Sheet resistance of the commercial ink was measured to be 1.55 Ω/sq . In contrast, the homemade ink showed no conductivity after printing and drying. And after an additional drying process at 140 °C for 4 min, the sheet resistance finally reached 271 Ω/sq [172].

After ink was printed on substrate, a “coffee-ring effect” might occur during the solvent drying process [173, 174]. A “coffee ring” is a pattern left by a puddle of particle-laden liquid after it evaporates. It is generated by the migration of particles from the center to the edge of a drying drop, leading to irregular printed structures. Consequently, the coffee-ring patterns destroy the dispersion characteristics and thus decrease the conductivity of the printed electrode. To tackle this issue, Hu and Larson proposed that the elimination of coffee-ring effect not only requires a pinned contact line, but also suppression of Marangoni flow [175]. In 2013, Friederich *et al.* revealed that in an inkjet printing process, the coffee-ring effect could be suppressed by a rapid viscosity increase during drying [176].

In silver paste formulations, functional powders are usually mixed with organic vehicles that are composed of polymeric binder (e.g., ethyl cellulose), surfactant (e.g., stearic acid) and solvent, such as the commonly used solvent α -terpineol, to provide suitable rheological properties and dispersion state for processing and quality control purposes. Jiang *et al.* found that the size and shape of the spherical silver nanoparticles could also influence the rheological properties of silver paste [177, 178].

With the employment of the above-mentioned silver inks or pastes, the photovoltaic performance of the printed solar cells was constantly improved throughout the years. Four examples are listed in Table 14.11. In 2009, Krebs fabricated inverted OPV cells (Ag-grid/PEDOT/P3HT:PCBM/ZnO/Ag-solid/PEN) using the slot-die method. Silver ink was formulated by mixing silver nanoparticles (100 ± 15 nm) with a cosolvent of triethylene glycol monomethyl ether and ortho-xylene (1:1 volume ratio) to obtain a concentration of 25% (w/v). Although the sheet resistance was as low as 0.01 Ω/sq , a low PCE of only 0.27% was obtained [179]. In 2013, Angmo *et al.* used the inkjet printing method to fabricate an inverted device with the structure of ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag.

Table 14.11 Photovoltaic performance of P3HT:PCBM-based OPVs with printed silver electrode.

Printing techniques	Rs (Ω/sq)	Voc (V)	Jsc (mA/cm^2)	FF	PCE (%)	Year	Ref.
Slot die	0.01	–	–	–	0.27	2009	[179]
Inkjet	1	0.51	8.39	45.45	1.96	2013	[180]
Spin coat	2.3	0.61	6.3	55	2.1	2014	[181]
Inkjet	0.63	0.564	7.11	62.6	2.4	2015	[182]

They used a commercial ink (Suntronic U571) that had a high loading (40% concentration) of silver nanoparticles (10–50 nm in size) to obtain 1.7 μm -thick silver back electrode. Its sheet resistance was close to 1 Ω/sq and PCE reached 1.96% [180]. One year later, Betancur and Jaramillo used the spin-coating method to produce a silver electrode with a commercial silver paint from SPI, dispersed in toluene to an approximate concentration of 20%. With the same cell structure as Angmo’s, a sheet resistance of 2.3 Ω/sq and a PCE of 2.1% were obtained [181]. Recently, Patil *et al.* used opaque bottom electrode and semitransparent top electrode to fabricate an all-solution-processed top-illuminated OPV, whose architecture was Ag-grid/PEDOT:PSS/P3HT:PCBM/ZnO/Ag/Glass. A nanoparticle-based silver ink (Suntronic U5603) was inkjet-printed with a commercial printer (DMP-2800, Dimatix-Fujifilm Inc.) to deposit the bottom Ag electrode. It had a thickness of ~135 nm and a sheet resistance of 0.63 Ω/sq , resulting in a PCE of 2.4% [182].

14.7 Carbon-Based Back Electrodes

With the emergence of perovskite solar cells, carbon electrode has gained much attention due to its many merits, including low cost, solution processability, chemical and physical stability, resistance to water and oxygen diffusion into the device, and reasonable electrical conductivity, etc. It has become a promising alternative back electrode material to replace evaporated metal electrode or printable metal inks. The commonly used carbon materials in carbon back electrode include carbon black, graphite and/or carbon nanotube (CNTs).

Carbon black is one type of amorphous carbon, which has a high specific surface area (10 ~ 3000 m^2/g) [183]. It is produced from incomplete burning of carbonaceous materials (coal, natural gas, heavy oil, fuel oil,

etc.), so carbon black usually shares low cost. Due to its naturally formed porous structure and large surface area, it is able to absorb large amounts of water or oxygen molecules. In other words, it can slow down the diffusion rate of moisture and oxygen, providing protection for the solar cells.

Graphite is one of the allotropes of carbon, which has a layered planar structure. In each layer, the carbon atoms are arranged in a honeycomb lattice. Atoms in the plane are bonded covalently in sp^2 configuration, with only three of the four potential bonding sites satisfied. The fourth electron is free to migrate in the plane, making graphite electrically conductive. The radius of the benzene rings in graphite sheets is ca. 5 Å, smaller than the size of water clusters (ca. 30 Å) [184], and comparable to the size of an oxygen molecule (ca. 3 Å). Therefore, graphite is believed to be resistive to moisture and oxygen.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, similar to those of graphite. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

“Perovskites” is the nomenclature for any materials that adopt the same crystal structure as calcium titanate, namely, ABX_3 [185], and a perovskite solar cell is a type of solar cell which includes a perovskite compound as its photoactive layer [186, 187].

The first attempt to use carbon material as back electrode for perovskite solar cells was reported by Han *et al.* in 2014 [188]. They printed the carbon black/graphite composite slurry on the ZrO_2/TiO_2 scaffold of a PSC and sintered it at 400 °C for 30 min to produce a 10 µm-thick carbon back electrode. Consequently, the PSC afforded a certified power conversion efficiency of 12.8% and was stable for >1000 hours in ambient air under full sunlight. After this work, more research on carbon back electrode for perovskite solar cells has been done.

Yang *et al.* reported a simple and low-temperature process to fabricate an all-carbon back electrode [189]. Their carbon electrode consisted of two parts: a mesoscopic carbon layer for good contact with the perovskite layer, and a piece of flexible graphite sheet as the conducting electrode. They first mixed pure graphite with different mesh sizes or different compositions of the smallest graphite and carbon black with 2.5 wt% butadiene-styrene rubber and 2.5 wt% ethyl cellulose that acted as binder to make carbon paste. Then they formed the mesoscopic carbon layer above the $CH_3NH_3PbI_3$ perovskite layer by screen-printing technique. After this, a piece of commercial flexible graphite sheet was pressed onto the mesoscopic carbon layer to fabricate the conducting electrode. The best composition was 75 wt% graphite and 20 wt% carbon black to form the

mesoscopic carbon layer, whose resistivity could reach $0.802 \Omega\cdot\text{cm}$. The PSC with such a carbon back electrode exhibited a J_{sc} of $18.73 \text{ mA}/\text{cm}^2$, a V_{oc} of 0.95 V , an FF of 0.572 and a PCE of 10.20% .

Wei *et al.* improved the back electrode by optimizing the composition of carbon films and hot-pressing pressure [190]. The components they used to fabricate the back electrode were carbon black, graphite and polyvinyl acetate (PVAc). The weight content of PVAc is 20% in the carbon film, thus the total weight ratio of carbon materials is 80% . At first, the carbon materials were dispersed into an ethyl acetate solution of PVAc and ball-milled to make carbon paste. Then a carbon film was formed on Teflon film by doctor-blading. Subsequently the carbon film was hot-pressed onto the surface of perovskite. Finally, an Al foil was pressed above the carbon film to form a conducting electrode. The optimal weight ratio between graphite flake and carbon black powder was $2:1$, at which the resistivity of the carbon film could reach $0.86 \Omega\cdot\text{cm}$ before hot-press. The PSC showed a remarkable photovoltaic performance, with J_{sc} of $21.30 \text{ mA}/\text{cm}^2$, V_{oc} of 1.002 V , FF of 0.634 and PCE of 13.53% .

Zhang *et al.* conducted research on the effect of carbon back electrodes on perovskite solar cells [191]. The carbon paste was made from carbon black and graphite with different sizes. The specific operation was as follows: 2 g carbon black powders (particle size: 30 nm) was mixed with 6 g graphite powders in 30 mL terpeneol, and then 1 g of 20 nm ZrO_2 nanopowders and 1 g of hydroxypropyl cellulose were added into solution, followed by stirring vigorously using ball milling for 2 h . Then back electrodes were fabricated by screen-printing technique. From the experiment, they found when the size of graphite was $8 \mu\text{m}$, the back electrode had the lowest sheet resistance of $11.47 \Omega/\text{sq}$. And perovskite solar cells based on such carbon electrode presented a V_{oc} of 0.882 V , a J_{sc} of $18.30 \text{ mA}/\text{cm}^2$ and a FF of 0.72 , corresponding to a PCE of 11.65% . They came to a conclusion that graphite size has a huge influence on the porosity and conductivity of carbon back electrode. Changes in the size of graphite will induce differences in the filling of PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursors and also the resistance of back electrode, which will eventually result in PCE variations.

Despite that carbon back electrode based on graphite and carbon black was gaining popularity, its high resistivity resulted in low FF. So new carbon materials such as MWNT or SWNT were used to improve the performance. Wei *et al.* dispersed MWNTs into chlorobenzene at a concentration of $10 \text{ mg}/\text{mL}$ with a probe ultrasonic processor, then the carbon solution was drop casted on the top of the $\text{TiO}_2/\text{PbI}_2$ substrates and heated [192]. With one MWNT layer, the FF could reach 0.75 . With two MWCNT layers, the FF of the device improved to 0.80 , while other photovoltaic parameters

were V_{OC} of 0.88 V, J_{SC} of 18.00 mA/cm² and PCE of 12.67%. They arrived at two reasons for the good performance of the MWNT-based PSCs. The first one was that MWNT has the proper size and 1D chain structure, which allowed the carbon material to be embedded into the perovskite film and form a highly conductive network. The second one was there was an interpenetrating bi-continuous charge transfer highway at the interface between the CH₃NH₃PbI₃ perovskite and the MWNT network.

Up to now, the highest PCE reached 14.7% recorded by Li *et al.* [193]. A mixture of SWNT, carbon black and graphite was used as carbon paste by them. The specific formulation was as follows: 1 g of SWNTs was dispersed in 20 mL ethyl alcohol and then sonicated in a bath sonicator for 30 min, and then 0.588 g ZrO₂, 4 g graphite and 1 g carbon black were added. This solution was treated with an ultrasonic probe for 5 min, followed by magnetic stirring for 10 min, and the agitation steps were repeated three times. The mixture was subsequently centrifuged for 5 min at 4500 rpm to remove non-functionalized SWNTs and other carbonaceous particles. Then the mixture was dispersed in ethyl alcohol, to which 17.6 mL terpinol was added. The mixture was then treated by an ultrasonic probe for 5 min, followed by magnetic stirring for 10 min, and ball-milling for 16 h. 2.94 g ethyl cellulose was added to the mixture. In the last step, the ethyl alcohol was removed with rotary evaporation. The obtained carbon paste could be printed to fabricate the back electrode. When the weight ratio of graphite and carbon black was 4:1 and the content of SWNT was 0.05%, they could achieve the best PSC performance, a V_{OC} of 1.01 V, a J_{SC} of 21.26 mA/cm² and a FF of 0.69, corresponding to a PCE of 14.7%.

To briefly summarize, it has only been two years since carbon material has been used as back electrode for perovskite solar cells. However, the power conversion efficiency has already reached 14.7%. Besides the high efficiency, carbon-based back electrode also provided good protection for a long lifetime of PSCs. But most of the carbon pastes need high-temperature sintering, which is incompatible with flexible plastic substrates. And the low-temperature processed carbon back electrode requires complicated material systems and preparation processes. Developing low-temperature carbon electrode with simplified formulation and processing steps will bring a bright future to printable solar cells.

14.8 Summary and Outlook

This chapter has representatively focused on the most prominent electrode materials for printable solar cells. Although there is a vast array of

materials and structures suitable for use as electrode in flexible and printable electronics, depending on the photovoltaic cells application, electrode selection will typically be rationalized and guided by overall device performance, ease of use and low cost. Three major material parameters, including mechanical compliance, optical transparency and electrical conductivity, are critical to meet the requirements. It is quite encouraging to see a few novel materials have out-performed traditional electrode materials such as ITO or vapor-deposited metal back electrodes.

In addition to those materials mentioned above, some noteworthy advances in 2D materials, e.g., N-doped graphene, graphyne and MoS_2 , or nano-conductive composites, will further expand the boundaries of our knowledge and enable us to develop more advanced electrode materials in the future. On the other hand, the fast development of wearable devices and other consumable electronics will impose additional criteria on the electrode materials, including stretchability and self-healing properties. Therefore, more research work on electrode materials will be definitely needed to explore new materials and to engineer novel and better properties.

Acknowledgment

This work was supported by research grants from Chongqing University under the “One Hundred Talents” programme (0212001104431), the Key Laboratory of Low-grade Energy Utilization Technologies and Systems (LLEUTS-2017004) and Natural Science Foundation of China (61504015, 51203077).

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Photonic Crystals for Photon Management in Solar Cells

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Abstract

Tailoring optical properties of a device always accompanies the development of solar cells and results in the enhancement of power conversion efficiencies. Coupling photonic crystals (PCs) to photovoltaics is regarded to be an effective method for photon management. This chapter summarizes recent progress in this field, including fabrication strategies and applications of PCs for printable solar cells or solar cells with potential possibility for printable fabrication. The future perspectives of PC-based photovoltaics are also discussed.

Keywords: Photonic crystals, solar cells, photon management, fabrication strategies, photonic-crystal functionalities

15.1 Introduction

The energy scarcity is undoubtedly one of the greatest challenges of the 21st century. The U.S. Energy Information Administration predicts that total world energy consumption will rapidly grow from 505 quadrillion Btu in 2008 to 619 quadrillion Btu in 2020 and 770 quadrillion Btu in 2035 [1]. More seriously, the worldwide demand for energy is predicted to double

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by 2050 and triple by 2100 [2]. To overcome this crisis, various renewable energies, such as hydroelectric, wind, biomass, geothermal, marine tidal and solar energy, provide us with a great opportunity to meet the world-wide energy demand. Among these energies, solar energy is a key component and it has by far the highest potential of all renewable energy sources because solar radiation has the potential to provide our planet with about 10000 times more energy than our global daily consumption [1], and some other renewable energies may be restricted (e.g., wind and geothermal) [3].

The harvested solar light can be transformed to heat, chemical fuels, and electricity. Typical devices exemplifying these concepts are solar heat collectors, artificial photosynthesis systems, and photovoltaic systems, respectively. When solar energy is purposefully converted to electricity, attention must be paid to the different steps in the transforming process, including initial photon absorption, generation of charge carries as well as their separation, transport, and collection [3], to achieve better efficiency and reduced cost. Coupling as much light as possible into solar cells (i.e., enhancing photon absorption) is important in achieving both goals [4]. Besides, there is a trend across many solar cell technologies towards thinner devices. The reasons for reducing the dimensions of the active layer vary by technology, for instance, to reduce the cost of devices, to improve charge collection efficiency in organic devices, to benefit fabrication of printable solar cells, and so on. Although thinner solar cells offer numerous advantages, they present new challenges to cell designers. A decrease in thickness may also be accompanied by incomplete absorption of photons and a corresponding decrease in efficiency [4]. Therefore, incorporating photon management elements into current solar cells has emerged as a hot research topic in an effort to enhance light harvesting in photovoltaics. Nanostructured materials, such as photonic crystals (PCs) [5, 6], scattering layers with randomly textured surfaces or large particles [7, 8], and plasmonic nanometals [9], have opened unprecedented opportunities for light management, notably in thin-film solar cells.

In this chapter, we provide a comprehensive review with a focus on the new and promising developments of photon management in solar cells based on PCs, and those PC coupled solar cells which are roughly printable or of potential possibility for printable fabrication. Firstly, a brief introduction about the fundamentals of PCs will be given. Secondly, a general review of PC fabrication methods that are applicable to different solar cells will be provided. Thirdly, we will lay emphasis on the understanding of the different functionalities of PCs in solar cells. Finally, we will summarize the chapter and point out future research directions for further exploration of PC coupled solar cells.

15.2 Fundamentals of PCs

Coupling PCs with spatially ordered lattices are one kind of well-known photonic nanomaterials. PCs enable control of light propagation just as atomic crystals enable control of electron conduction [4]. In an atomic crystal, the periodic arrangement of atoms results in a spatially periodic electrical potential on the scale of electron waves. Electrons with certain energies and momenta will be able to pass through the crystal without scattering while other combinations of energies and momenta will be forbidden [4]. Similarly, the periodic arrangement of the dielectric materials endows a PC with an amazing property known as the photonic band gap (PBG). The light propagation in PCs can be described by an electromagnetic wave equation, derived from Maxwell's equations [10],

$$\nabla \times \left[\frac{1}{\varepsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right] = \left(\frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}) \quad (15.1)$$

where $\mathbf{H}$ and ε represent the magnetic field and the relative dielectric constant of the media, respectively. The optical response of PCs can be derived by the eigenvalues on the right-hand side after the introduction of the spatial dependence of ε corresponding to the periodic structure of PCs. When the dielectric contrast and scaling of features in a PC are properly selected, an opening of a gap in the photonic band structure, known as the PBG, just like Bragg conditions for X-ray diffraction, but in optical wavelengths, is generated. Photons with certain frequencies in the PBG are forbidden for propagating either in any direction or in certain directions; as a result, the unique band structure of PCs will strongly influence the light propagation in PCs. Optical reflection and transmission spectra are employed as tools to characterize the PBG of PCs, in which light with certain frequencies is reflected, leading to a peak in reflectance spectrum and a dip in transmittance spectrum.

With periodicity in one, two, and three directions, PCs can be roughly classified as one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D), respectively (Figure 15.1a) [11]. Among them, 1D PCs, also known as Bragg stacks or Bragg reflectors, consist of alternating layers of two different materials, where the refractive index is periodically varied in only one dimension but homogeneous in the other two dimensions [12]. For 2D PCs (with columns arranged in a crystal lattice structure in the plane), the refractive index is varied in two spatial dimensions and constant in the third. For 3D PCs, the most complicated structures

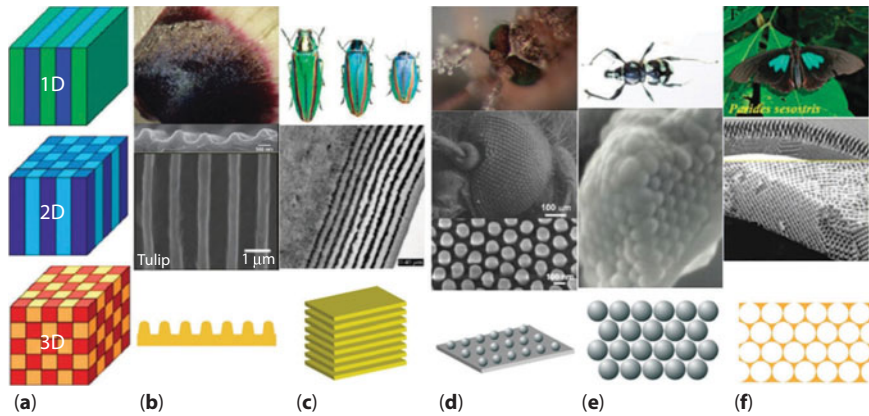


Figure 15.1 (a) Schematic illustration of three kinds of PCs (adapted from [11]; Published by The Royal Society of Chemistry). (b) A *Hibiscus trionum* petal showing iridescence overlying red pigment and its 1D grating structure (adapted from [15]). (c) Dorsal views of the Japanese jewel beetle, *Chrysochroa fulgidissima*, at various viewing angles and its 1D periodicity in the form of multilayers (adapted with permission from [16]; Copyright © 2005 Wiley-VCH). (d) A photograph of antifogging mosquito eyes and 2D grating structure covering an ommatidial surface (adapted with permission from [18]; Copyright © 2007 Wiley-VCH). (e) A dorsal view of the beetle, *Pachyrhynchus argus*, and its opal analogue structure (adapted with permission from [19]; Copyright © 2003 Nature Publishing Group). (f) Inverse opal analogous nanostructures generating the iridescence of several species of exotic butterflies such as the *Parides sesostris* (adapted with permission from [14]; Copyright © 2012 The Royal Society of Chemistry).

among all three types of PCs, the refractive index is varied in all three dimensions [12, 13].

Before artificial PCs were created, throughout four and a half billion years of evolution and natural selection, nature's creatures had already developed many kinds of photonic nanostructures that can form structural colors (Figure 15.1b–f). These colorations are used as an adaptation by living creatures to their surrounding environment and as signals to ward off their enemies through mimicry or mislead them through camouflage, or to transmit information [14]. Compared with pigment color, which mainly relies on the selective absorption of light by chemical chromophores to achieve coloration, the structural color, which is generated by geometric structures, is much more efficient in energy consumption and also in the use of light.

The natural photonic nanostructures also cover various periodic structures with periodicity in one, two, and three directions. Generally, the 1D photonic nanostructures with grating or multilayers can be found in some insects, birds, fish, plant leaves, berries and algae [15, 16]. The design of

these photonic nanostructures is quite smart and usually superior to the artificial ones. For instance, the multilayers of some butterflies are intercalated with layers of air in order to generate efficient interference colors; with the same trick, the platelets of solid guanine in some aquatic vertebrates are separated by cytoplasmic fluid. Compared to 1D photonic nanostructures, 2D and 3D photonic periodic structures within natural creatures are rather uncommon. Generally, natural surfaces with 2D gratings are not designed for the generation of bright structural colors. They may be used for antireflection and thus for increasing the efficiency of the animal's vision and reducing unwanted reflection that might attract predators [17]. Besides, the 2D gratings may exhibit self-cleaning capability due to the high fraction of air trapped in the trough area between arrays. [18]. The 3D photonic nanostructures were first investigated in detail in the 1960s, which were responsible for the iridescence of natural gem opals. A similar gem opal structure was recently discovered in a beetle, *Pachyrhynchus argus*, by Andrew Parker and colleagues. This structure forms a metallic structural coloration visible from any direction of the beetle [19]. In contrast to the gem opal structure, the inverse opal structure was also found in some butterflies, which was composed of lattices of hollow air-filled voids within a network of interconnecting cuticle materials. This 3D photonic nanostructure could offer excellent reflectivity over a broad angle range [20].

Because of the distinct function of PCs, the PC materials have found important applications in optical fibers, switches, sensors, display devices, solar cells, and so on [21–26]. However, due to the lack of the inspirational designs of photonic structures and efficient generation technologies of three-dimensional nanoarchitectures, the development of the artificial photonic materials is slow even with the assistance of powerful computers and advanced nanotechnologies. In contrast, the above-mentioned natural photonic structures offer an ideal school for artificial PC materials design, fabrication and associated disciplines such as chemistry, biology, and physics [27, 28]. Inspired by natural creatures, researchers have already achieved great progress in developing photonic materials in recent years. One very famous example is mimicking the compound eyes of moths and some butterflies, which have hexagonal arrays of non-close-packed cylindrical nipples with sub-300 nm size on the cornea. These 2D arrays of PCs with tapered profiles exhibit a gradient in refractive index between the air and the surface of the cornea. They can dramatically suppress the reflection losses and increase transmission of light at the interface simultaneously over a wide range of wavelengths and a large field of view [17]. By fabricating the similar structure on glass surface, antireflection and even

self-cleaning capability can be achieved, which has become a promising technology to enhance light-harvesting of solar cells.

15.3 Fabrication Strategies of PCs for Photovoltaics

The spike in the interest and research on PCs over the last decade has been boosted by various factors, including the significant advances in computational design tools and their accessibility, the emergence of new nanofabrication techniques, as well as the realization of new optical and structural characterization methods. Undoubtedly, the most important factor is the progress in the area of fabricating photonic nanostructures [29]. Fabrication of artificial PCs can be generally categorized by one of two approaches: top-down or bottom-up. Top-down fabrication produces increasingly smaller elements using precise macroscopic tools, such as lithography with photons, electrons, atoms and ions, as well as with embossing and scanning tips methodologies. The drawback of top-down fabrication is its generally serial nature that makes it progressively slower and costlier to produce smaller periodically arranged features over large areas with increasingly high precision [10]. In contrast, bottom-up approaches rely on the self-driven assembly of basic building blocks into ordered periodic structures that are generally faster, cheaper and on a larger scale than top-down approaches, although the control and precision in fabricating the structures may pale slightly when compared with top-down approaches. Nonetheless, the lower cost and ease of fabrication make bottom-up approaches a viable and practical alternative that could rival top-down approaches. Especially considering the cost control in the photovoltaic industry, top-down approaches could be futureless in spite of some prototyping in research labs.

When applied in photovoltaics, PCs are basically engineered to manipulate electromagnetic radiation in the wavelength range from ultraviolet to visible to near-IR (ca. 300 to 2000 nm). Consequently, PC periodicity should be on the order of a fraction of the wavelength of the band gap, which defines a size range of PC building blocks from ca. 50 to 1000 nm. Considering that PCs can in turn be assembled out of smaller subcomponents, a more broad range of sizes of PC building blocks from ca. 10 to 1000 nm is reasonable. This range is appreciably larger than molecular dimensions (and that of regular structures produced by molecular self-assembly) and is in the realm of colloid science [10]. As a matter of fact, spherical beads are the most commonly used building blocks for photonic colloidal crystals fabricated by bottom-up assembly. Typically, these

particles are usually silica, polystyrene (PS), or poly(methyl methacrylate) (PMMA) latex particles because of their ease of synthesis. Besides, nonspherical nanoparticles, metal or semiconductor nanocrystals, or thin films may also act as building blocks of PCs.

The bottom-up assembly of a colloidal crystal is self-driven, implying that there are colloidal forces at work that bring the tiny building blocks together. In colloidal assembly, these forces are crucial and there are three types of forces that should be highlighted. The first type is the presence of intrinsic driving forces for ordering, which could be the entropically favorable packing of monodisperse colloids into ordered arrays. For this, the monodispersity of the particles (i.e., size and shape homogeneity) is crucial. The second type to consider is the long-range external forces, such as gravity or centrifugation, which act to bring the particles together. The third type is the repulsion forces between particles to prevent premature aggregation that could arise from van der Waals forces. Electrostatic repulsions [30] by charge stabilization in polar solvents and steric repulsions [31] by solvated adsorbed layers are two examples of these kinds of repulsion forces.

Since the publication of the pioneering theoretical work by Yablonovitch and John in the late 1980s [32, 33], there has been much interest in exploring new strategies to fabricate artificial PCs. Some of the typical fabrication techniques, such as evaporation, sputtering, dip/spin-coating, anodic etching, lithography, atomic layer deposition (ALD), chemical vapor deposition (CVD), microfluidics and so on, can be found in several excellent reviews [10, 12, 14, 21]. Herein, we only focus on those PCs that are applicable to solar cells: (1) 1D multilayer PCs, (2) 2D PCs, and (3) 3D PCs. The recent development of techniques to integrate these PCs into different solar cells will also be highlighted.

15.3.1 1D Multilayer PCs

One-dimensional (1D) PCs, dubbed Bragg stacks, Bragg reflectors/mirrors or dielectric mirrors, are rarely fabricated by spontaneous, free energy driven self-assembly. Bottom-up processed periodic multilayer structures are usually assembled sequentially by layer-by-layer deposition of alternating materials on a planar substrate, such as spin coating, dip coating, and so on. In such processes the directed assembly of nanoparticles, sol-gel precursors or polymer solutions onto a wettable substrate is driven by the action of centrifugal forces or capillary forces during solvent evaporation. The deposition of multilayer structures is a multistep process often requiring drying and annealing steps between each subsequent layer, but

it is very robust and compatible with other established technologies. An insuperable drawback of most deposition methods, especially spin and dip coating, is the lack of precise control over the layer thickness, which may vary by as much as 20% because of variations in solution concentration, aggregation/condensation state of the solution constituents, and solvent evaporation or drying processes during fabrication of subsequent layers [10]. This will lead to deviations of the optical properties from those for the ideal configuration, but the functionality approaching the desired one may still be achieved.

So far, the most general and widely applied method to prepare periodic multilayer stacks is spin coating, in which centripetal forces are responsible for spreading of a uniform film of a precursor solution, a polymer solution, or a nanoparticle dispersion on a substrate and together with gravitational forces, particle compaction (for spin coating nanoparticle dispersions) (Figure 15.2a). For colloidal assembly by spin coating, capillary forces are also a nonnegligible factor to final stages of particle ordering during solvent evaporation from spin-coated films [21]. Large-area uniform films with thicknesses on the order of 10 to 500 nm can be deposited by spin coating.

A successful application of 1D multilayer PCs to dye-sensitized solar cells (DSCs) by spin coating was reported by Míguez and coworkers [34]. The 1D multilayer PCs consist of 1D $\text{SiO}_2/\text{TiO}_2$ multilayer (Figure 15.2b), which is coupled to a conventional mesoporous TiO_2 photoanode. SiO_2 and TiO_2 are chosen due to easy fabrication of thin films and their very different refractive indices for attaining intense and wide reflection peak. The typical fabrication procedure is as follows: (1) a mesoporous TiO_2 transparent electrode is prepared by the conventional doctor-blade method; (2) a very thin TiO_2 overlayer is first spin-coated on the mesoporous TiO_2 film; (3 and 4) alternate layers of SiO_2 and TiO_2 colloidal particles are spin-coated on the top surface of the electrode; (5) the prepared photoanode is calcined after steps 3 and 4 are repeated for desired times. To form high-quality 1D $\text{SiO}_2/\text{TiO}_2$ multilayer, a flat TiO_2 substrate is necessary. However, the doctor-blade fabricated TiO_2 mesoporous layer cannot meet the demand. Therefore, step 2 is used to smooth the surface of the TiO_2 mesoporous layer and obtain a flat film [1].

By a similar technique, Míguez *et al.* successfully enlarged average pore size of 1D $\text{SiO}_2/\text{TiO}_2$ PC for better electrolyte/photoanode contact, in which polymeric porogenes were incorporated into the TiO_2 colloidal suspension to create larger pores after calcination [35]. A 1D $\text{SiO}_2/\text{TiO}_2$ PC with multi-periodicity has also been integrated into the TiO_2 mesoporous layer (Figure 15.2c) [36]. This PC, consisting of three secondary 1D

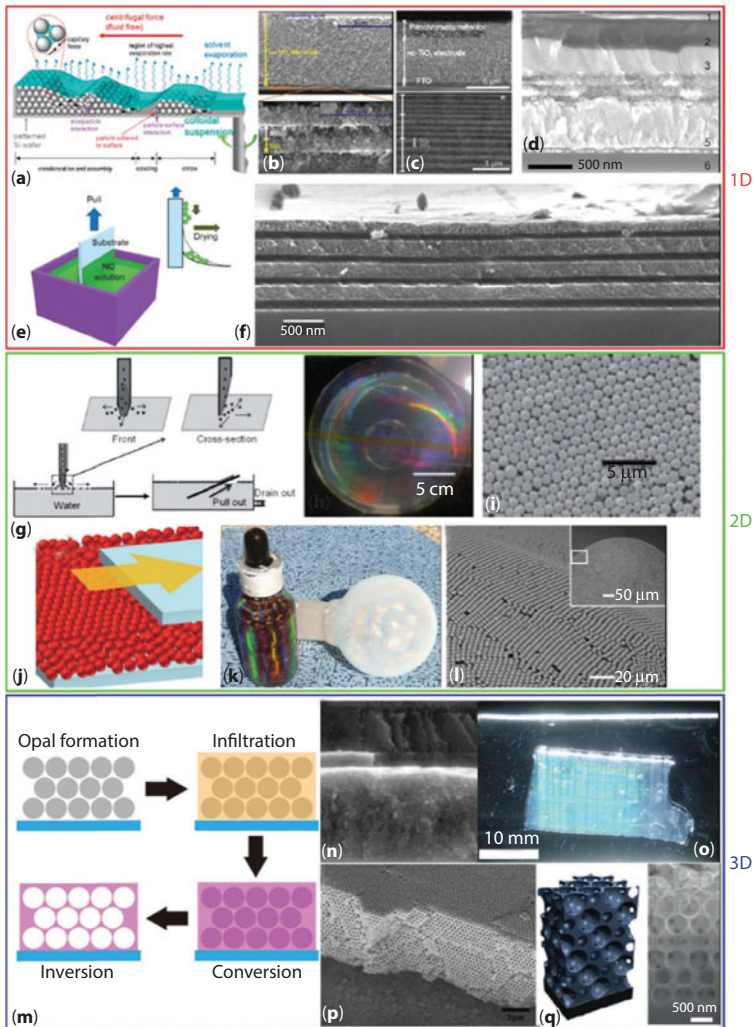


Figure 15.2 (a–d) Schematic illustration of spin coating and the 1D PCs prepared by it. (e,f) Schematic illustration of dip coating and the 1D PC prepared by it. (g–i) Schematic illustration of self-assembly at the gas/liquid interface and the 2D PCs prepared by it. (j–l) Schematic illustration of rubbing and the 2D PCs prepared by it. (m–q) Schematic illustration for IO fabrication and different Ios. (Figures (a,b) from [29, 34], Copyright © 2009 Wiley-VCH; Figure (c) from [36], Published by the PCCP Owner Societies; and Figure (d) from [38], Copyright © 2015 American Chemical Society. Figure (e) from [40], Copyright © 2015 Wiley-VCH; and Figure (f) from [41], Copyright © 2007 Wiley-VCH. Figures (g–i) from [51], Copyright © 2012 Wiley-VCH. Figures (j–l) from [54], Copyright © 2014 Wiley-VCH. Figure (n) from [61], Copyright © 2003 American Chemical Society; Figure (o) from [62], Copyright © 2014 Elsevier B.V.; Figure (p) from [6], Copyright © 2010 American Chemical Society; Figure (q) from [67], Copyright © 2011 Nature Publishing Group. All figures adapted with permission.)

$\text{SiO}_2/\text{TiO}_2$ PCs of different periodicities (Figure 15.2), can be fabricated by modulating the concentration of each colloidal suspension and the processing parameters of spin coating. In addition, the layer-by-layer spin-coating method has also been successfully introduced to couple the 1D multilayer PC to DSC counter electrode [37] and other solar cells, such as organic-inorganic halide perovskite solar cells (Figure 15.2d) [38], silicon solar cells [39], and so on.

As an alternative to the spin-coating procedure, dip coating of 1D multilayer PCs has not yet been demonstrated for a large variety of materials, and its potential has been primarily revealed in the realm of sol-gel-based oxides. Dip coating of metal oxide sols containing porogens typically requires a high degree of environmental control, ambient relative humidity in particular, to induce controlled evaporation-induced self-assembly at the organic-inorganic interface while the substrate is withdrawn vertically from solution (Figure 15.2e). However, a delicate balance of factors like solution aging, solvent evaporation, substrate withdrawal speed and temperature is also a prerequisite for the achievement of highly ordered mesoporous films with controlled thickness. Dedicated aging, thermal stabilization treatments and template removal steps after deposition of each layer, render dip-coating assembly of mesostructured materials a rather laborious and time-consuming procedure. Nevertheless, highly ordered multilayered films with high and controlled porosity could be produced by this technique [10, 40]. For instance, as pioneered by Míguez and coworkers, mesoporous metal oxide multilayer with controlled nanoporosity (Figure 15.2f) and subsequent tailoring of the optical properties were fabricated by structure-directing agents in assisted dip-coating technique [41].

Layer-by-layer electrostatic self-assembly is another tool to fabricate optical-quality conformal multilayer heterostructures with very low interfacial roughness, high compositional control, and good stability. This self-assembly involves the sequential deposition of polyelectrolytes or nanoparticles carrying surface charge usually from aqueous solutions. The first generation of optical-quality multilayer structure assembled from poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) and PAA/poly(sodium 4-styrenesulfonate) (SPS) layers was reported by Cohen and coworkers [42]. Properly assembled PAH/PAA regions exhibit a reversible, pH-gated nanoporosity transition while PAH/SPS regions remain unchanged upon treatment at low pH. These structures can be applied as one-dimensional dielectric mirrors and vapor sensors. Subsequently, Rubner and coworkers further prepared multilayers containing $\text{TiO}_2/\text{SiO}_2$ nanoparticles by polyelectrolyte-assisted layer-by-layer deposition, followed by calcination to remove the polyelectrolytes. The structural color

characteristics of the resultant nanoporous Bragg stacks could be precisely tuned in the visible region by varying the number of stacks and the thickness of the high- and low-refractive-index stacks [43]. Layer-by-layer electrostatic self-assembly bodes well for applications as antifogging, anti-reflection, self-cleaning, or structural color coatings.

The above-mentioned techniques of spin coating, dip coating, and layer-by-layer electrostatic self-assembly applied in research labs have the potential to be adapted for printable fabrication. However, compared to spin-coating and dip-coating methods, layer-by-layer electrostatic self-assembly is fairly time-consuming for depositing because the layer assembly relies on sequentially immersing the substrates into the deposition and rinsing solutions, and hundreds of adsorbed layers may be necessary to achieve the desired optical properties owing to each layer's small size. Therefore, additional faster deposition schemes are required. Using robotic coaters is a possible solution to this problem. Besides, automated spray-layer-by-layer assembly of polyelectrolyte- TiO_2 and $-\text{SiO}_2$ multilayer structures with more than 800 individual deposition steps has recently proven to be 20 times faster than the immersion layer-by-layer assembly [44]. By precisely controlling variables, such as the spraying time, Bragg mirrors with reflectivities in excess of 90% and uniform optical quality were deposited on centimeter-large substrates.

Anodization is another powerful tool to fabricate PCs with given texture. Although the method falls into the top-down category, it still offers multi-degrees of freedom in the design of nanostructures and is low cost. An impressive example is the TiO_2 nanotube (NT) PC that was developed by Huang *et al.* which acts as a dielectric mirror in DSCs [45, 46]. The structure is actually TiO_2 NT with periodicities along the axial direction of NTs fabricated by a periodic current-pulse anodization process, in which alternating high current and low current was adopted to obtain TiO_2 NTs with different periodicities. The number of periods and the lattice constant are determined by the number of pulses and the pulse duration, respectively. Therefore, the PBG of the TiO_2 NT PCs is freely tunable, and the PC membranes of various colors covering the whole visible spectrum can be obtained.

Nevertheless, the strong light reflection of a normal PC with a changeless periodic structure usually lies in a relatively narrow range, which is unfavorable to maximize the light harvesting for DSCs. To achieve a strong light reflection over a broader range, a spatial variation of the PC periodicity is one of the solutions [47]. Based on this consideration, the successful fabrication of TiO_2 NT aperiodic PC (APC) has also been demonstrated by Huang *et al.* using a time-diminishing current-pulse anodization

process [48]. During the anodization process, the time duration of the current-pulse is decreased gradually, following an arithmetic sequence. As a result, the TiO_2 NT APC with a gradually decreasing lattice constant from ~ 230 nm on the top to ~ 180 nm in the middle and ~ 110 nm on the bottom, respectively, is fabricated.

15.3.2 2D PCs

The self-assembly of 2D PCs basically draws on two techniques. The most prominent one is to fabricate opal monolayers by modified colloidal crystal assembly protocols and subsequently using the monolayers as template to prepare the desired 2D PC structures. The second fabrication scheme relies on the microphase separation of specifically tailored block copolymers into planar 2D periodic arrays of polymers that can be suitably translated into hybrid or inorganic structures. However, the application examples based on the second technique are few, probably due to the lack of the degrees of freedom to design and synthesize block copolymers with suitable domain size that exhibit photonic properties.

Hexagonal-close-packed (hcp) monolayer colloidal crystals (MCCs) are the most commonly obtained and the most easily self-assembled MCCs since the hcp structure is the thermodynamically stable 2D arrangement of monodisperse isotropic colloidal spheres. The self-assembly methods of hcp MCCs are diverse, including the above-mentioned spin coating and dip coating with optimized conditions, but there are few methods capable of fabricating MCCs with high quality and productivity. Self-assembly at the gas/liquid interface is a facile and efficient route towards large-area MCCs since nanospheres at the interface are able to exclusively form a monolayer without variation in the layer thickness, which is hardly realized in the evaporation-induced self-assembly on solid substrates [49]. In a typical self-assembly at the gas/liquid interface, monodisperse colloidal particles, dispersed in a lower alkanol-water suspension, are spread onto a water surface by various tools and spontaneously form close-packed 2D arrays at the interface through attractive interactions between the particles. Controlled aggregation, ordering and consolidation of the monolayer may be facilitated by the addition of a surfactant lowering the surface tension, such as sodium dodecyl sulfonate [50]. Spreading of the particles is a consequence of the Gibbs-Marangoni effect, which describes the movement of a fluid due to a gradient in surface tension (induced by surfactant addition or using ethanol-water PS dispersions), resulting in mass transfer along the fluid-fluid interface away from the regions of low surface tension [10].

How to spread colloidal dispersions onto a water surface rather than slipping them into water is critical to obtain MCCs with high quality, and requires skillful operation and sometimes ingenious devices [51–53]. For instance, Asher and coworkers designed a needle-tip flow method in which the tip of a sharpened injection needle was positioned to be just in contact with the water surface (Figure 15.2g–i) [51]. Ye and coworkers developed a micro-propulsive injection method for a high-throughput surface texturing process based on large-area MCCs. A large-area PS monolayer, even beyond the size of a few square meters, can be readily achieved through fine control of several key parameters, including contact states between the injectors and the water surface, injection speeds, injector numbers, and so on [52].

The transfer of the as-obtained MCCs onto a substrate is straightforward and can be done by several methods. The substrate may be immersed in the liquid before or after the addition of the particle suspension, placed below the monolayer and lifted off while the MCCs are deposited on the substrate surface (Figure 15.2). Besides, the substrate can be inserted into the water across the particle film and lifted up vertically at a steady speed, as in Langmuir-Blodgett-type deposition, leaving colloidal arrays on both sides of the substrate. Otherwise, water can be dropped onto the substrate to form a water film on which MCCs are formed. The MCCs are deposited on the substrate surface after evaporation of the liquid.

In addition to the above strategies about self-assembly of MCCs, there is a unique method utilizing dry powders of particles and unidirectional rubbing to fabricate a single-crystal colloidal monolayer on a flat or curved substrate (Figure 15.2j) [54]. This technique is quick, inexpensive and reproducible, and the assembly conditions are readily accessible, although it requires a particle size larger than 100 nm and a particle-substrate adhesion stronger than the particle-particle interaction to separate a particle from an aggregate (Figure 15.2k,l).

The MCCs deposited on specific substrates can be the template to prepare different variations of 2D PC structures of the substrates. Dry or wet etching assisted by MCCs has been employed to fabricate various nanostructure arrays for the advantage of high controllability, high selectivity, and the realization of anisotropic etching, including nanopillar, nanocone, nanopencil, inverted-nanopyramid arrays, and so on [49, 52]. Taking Si nanopillar arrays as an example: first, MCCs of silica spheres were deposited on a silicon substrate (e.g., a cleaned silicon wafer); second, the silica spheres were used as a mask and the area of substrate uncovered by silica spheres was etched by applying reactive ion etching with SF_6 ; finally, uniform periodic nanowire arrays of silicon were formed after removing

the silica spheres [55]. The diameter and the length of the Si nanowire arrays can be determined by the diameter of silica spheres and changing the etching time, respectively. This type of “hybrid” lithography interfaces bottom-up and top-down deposition schemes by using self-assembled opal monolayers as masks through which large-scale nanoscale features can be deposited rather efficiently. These various nanostructure arrays may function as absorber, light-trapping element, and/or antireflection layers in solar cells.

The MCCs can also be extended further towards replicating these structures in inverse MCCs, essentially the 2D counterparts of 3D inverse opals (IOs). Due to the analogy between the replication strategies of 2D and 3D IOs, an outline of the replication strategies will be reviewed in the next section (15.3.3), and two examples will be highlighted. One example was demonstrated by Yao and coworkers, in which light management by forming whispering-gallery resonant modes inside a spherical nanoshell structure of nanocrystalline silicon (nc-Si) was achieved by using silica MCCs as template, and subsequently removing it after formation of nc-Si nanoshells. The geometry of the structure gives rise to a low quality-factor, facilitating the coupling of light into the resonant modes and substantial enhancement of the light path in the active material, thus dramatically improving absorption. The absorption of a single layer of 50 nm-thick spherical nanoshells is equivalent to a 1 μm -thick planar nc-Si film [56]. The other example is preparation of 2D incomplete IO perovskite photonic films reported by Chen and coworkers [57]. The perovskite nanostructure also utilized the template of PS MCCs and resulted in colorful devices with respectable power conversion efficiency.

A materials class apt to self-assemble into 1D, 2D as well as 3D periodic structures directly without going through mask and etching steps, is the class of block copolymers (BPCs). Linear diblock copolymers consist of two chemically distinct polymer segments joined together at their end-points, which tend to phase segregate into domains with sizes similar to the dimensions of the respective blocks (i.e., from a few nanometers up to about a hundred nanometers).

Microphase separation of the two chemically distinct polymer segments can be induced by either annealing or solvent vapor treatment, and generates various structures, including lamellar structures, body-centered cubic lattices composed of spheres, hexagonal-packed cylinders, and so on. The optical properties of the periodic structures consisting of block copolymers often suffer from a normally low refractive-index contrast between the two microdomains, although they can be improved by selective loading of one domain with high index nanoparticles or selective etching of one of

the microdomains. One example of a 2D PC was fabricated by Thomas and coworkers via microphase separation of a high molecular weight PS-*block*-polyisoprene copolymer. The phase separation generated cylindrical domains forming a regular hexagonal lattice with the adjacent cylinder-cylinder spacing around 130–160 nm. The BCP film exhibited blue light reflection visible to the naked eye, but the bandwidth was small due to the small dielectric contrast between the microdomains [58].

15.3.3 3D PCs

Artificial opals composed of colloidal crystals and their replicas, IOs, composed of a suitable high refractive index material and air spheres with an *fcc* lattice, are the most important 3D PCs that can be fabricated by bottom-up methods, and IOs can be obtained based on a more diverse range of materials than artificial opals. In principle, IOs provide high enough porosity as well as suitable lattice topology and symmetry to facilitate solar cell design and exhibit a full PBG in the visible regime if the refractive index contrast is large enough [59]. These properties have led to IOs becoming the most widely used 3D PCs in solar cells.

The fabrication strategies for IOs basically centers on one common motif, the inversion of a self-assembled colloidal-crystal template using the selected material. The most important colloidal-crystal building blocks and colloidal-crystal assembly processes have been summarized in some reviews [10, 14, 29, 60]. Suffice it to say that at this point almost all IOs are derived from three types of colloidal-crystal building blocks with variable sizes, namely SiO₂, PS, and PMMA spheres, and colloidal-crystal templates can be fabricated by spin coating, dip coating, natural sedimentation, vertical deposition, centrifugation, shear ordering, and so on. These building blocks lend themselves particularly well to IO fabrication because their fabrication is reproducible, well controlled, and of large scale. The general fabrication scheme for IOs can be summarized in four steps: (1) Opal formation, (2) infiltration, (3) conversion, and (4) inversion (Figure 15.2m).

Infiltration proceeds, in which infilling the pores of the opal is typically performed by capillary action with a fluid (liquid, vapor) that is subsequently consolidated by physical or chemical conversion. The conversion step depends on the target material and the type of precursor used, as well as the specific fabrication procedure. For example, chemical conversion into the target polymer or inorganic solid induced by heating or reactive deposition may become necessary if a monomeric precursor is used in the infiltration step. The inversion procedure for the composite material is predetermined by the choice of the initial opal template and can

either be chemical etching, calcination or solvent extraction. For SiO_2 templates, wet chemical etching with aqueous or nonaqueous HF or NH_4F , or strongly basic etchants, such as concentrated KOH solution, are used; the fluoride-based etchants, which are specifically for SiO_2 , typically allow for a better control of the etching process. Polymeric templates are more easily removed either thermally by calcination at temperatures above 300°C , or chemically by solvent extraction using, e.g., toluene or chloroform, or by air/oxygen plasma treatment.

There are three major protocols (i.e., impregnation, gas-phase infiltration, and electrochemical deposition) for IO fabrication from colloidal-crystal templates according to the reported data, which are distinguishable largely by the nature of the infiltration step. Regardless of the details of the fabrication process, a prerequisite requirement in all colloidal-crystal templating protocols for IO fabrication is the tailoring of the precursor-to-solid transformation taking place in the interstitials of the colloidal-crystal template, as will be discussed below.

Impregnation is an infiltration method that has proven invaluable especially for inorganic oxide dielectrics with a wide variety of compositions, including TiO_2 . TiO_2 is an important wide-band-gap semiconductor being transparent at optical wavelengths and at the same time having a high refractive index, and it has already become a critical element of many solar cells. Therefore, it is not surprising that impregnation is utilized to prepare TiO_2 IOs of solar cells. Mallouk and coworkers demonstrated the first TiO_2 IO coupled sensitized solar cell. An impregnation deposition method was used to infiltrate TiO_2 into voids of the colloidal template, in which the colloidal crystal films were first reacted with a solution containing titanium isopropoxide, dried vertically in air, and then soaked in an aqueous solution of ammonium hexafluorotitanate and boric acid. Uniform TiO_2 filled the void volume of the template completely, and no shrinkage was observed during the process (Figure 15.2n) [61]. In addition to TiO_2 IOs, polymer gel IOs fabricated via impregnation were also reported by Zhang and coworkers, which acted as quasi-solid-state electrolytes of DSCs. The polymer gel IOs (Figure 15.2o) were fabricated by filling voids of SiO_2 colloidal crystals with polymer monomer solution, then carrying out polymerization, and finally etching the SiO_2 template [62, 63].

The above impregnation method can be further classified into sol-gel route according to the precursors used. The sol-gel route allows the synthesization of a wide range of transition metal oxide IOs in high oxidation states, but is not suitable for the too reactive precursors of selected materials, such as low-valence transition metal oxides and alkaline earth metal oxides. To solve this problem, other impregnation methods, including salt

precipitation and nanocrystal sintering, may replace the sol-gel route. In a typical procedure of salt precipitation, a template is impregnated with a metal salt dissolved in ethanol or acetic acid. Subsequently, the metal salt/template composite is impregnated with oxalic acid, leading to the precipitation of the respective insoluble, non-melting metal oxalates. Chemical conversion into the macroporous metal oxides is induced by calcination, which proceeds under liberation of CO and CO₂ [64]. The key point of nanocrystal sintering is to use preformed nanocrystals for building up the IO architecture, which at the same time is dense and less reactive than monomeric precursors, thus significantly reducing the distortion of the optical lattice by chemical transformations [65].

Gas-phase deposition is another powerful tool for the IO fabrication. The most widely used gas-phase deposition techniques involve chemical vapor deposition (CVD) and atomic layer deposition (ALD). The basic policy of this method requires suitable mixtures of reactive gaseous precursors that are injected at reduced pressure into temperature-adjusted reactors, and the nucleation and growth can be more finely adjusted and affected, allowing for a high level of precision and layer-by-layer deposition of uniform shell coatings around the microspheres. Therefore, this method is chosen for IO fabrication where wet impregnation fails because of a lack of suitable liquid precursors. Besides, gas-phase deposition may become a competitor with wet impregnation because it can in principle be a much more controllable process than solution-phase impregnation.

From a photovoltaic materials point of view, the most important IO structure grown by CVD should be that of silicon, the hallmark material of today's photovoltaic industry. The first prototype Si IO was fabricated by growing silicon inside the voids of the SiO₂ opal template by means of CVD using disilane gas as a precursor, then heating the samples in order to improve the semiconductor crystallization and to allow diffusion of silicon inside the void structure; and finally removing silica template using a fluoride-based etching procedure. The Si IO was designed for allowing coherent localization of light with wavelengths of around 1.5 μm , in an important telecommunication frequency range [66]. Yao and coworkers demonstrated a new approach to light management by forming Si IO structure and dramatically improved absorption of a 50 nm-thick nc-Si nanoshell. The Si IO was also fabricated by CVD except for using silane as the precursor vapor [56]. In addition to the IOs of silicon, it is also possible to prepare IOs of TiO₂ by CVD. One example was reported by T  treault and coworkers. The TiO₂ IOs were prepared by a binary atmospheric pressure CVD technique, in which the template was heated to 80 $^{\circ}\text{C}$ before being subjected to water vapor and then to titanium tetrachloride vapor in

alternating cycles to form amorphous TiO_2 (Figure 15.2p) [6]. The sample was then heated to 500 °C (3 h, heat ramp 1 °C/min) to burn off the organic material and to crystallize the TiO_2 .

Although IOs deposited by CVD are mostly polycrystalline structures with random crystallite orientation within the walls, deposition needs to be taken to an even higher level of perfection since single-crystalline semiconductor IOs are expected to perfectly qualify as high-performance optoelectronic materials owing to their reduced charge recombination, high charge carrier mobilities, and long carrier lifetimes. To achieve this goal, Braun and coworkers demonstrated the epitaxial growth of group III-IV semiconductor, GaAs, IOs by selective area epitaxy through a 3D silica template. By fine-tuning the growth of metal-organic precursors through a delicately patterned 3D mask under well-defined metal-organic CVD conditions, homogeneous nucleation of the vapor species arsine and trimethylgallium in and around the template was achieved (Figure 15.2q), resulting in the bottom-up growth of single-crystalline GaAs confined by the template [67].

Atomic layer deposition (ALD) is another excellent means to deposit a variety of materials into the porous template. It has the superiority of retaining the topology of the scaffold as well as the smoothness of the conformal layers to CVD methods because of its layer-by-layer growth characteristics. Furthermore, ALD qualifies for integrating higher levels of complexity into the IO structure. For example, non-close packed IO structures can be created by ALD backfilling an IO replica of the initial structure with additional layers and subsequently reducing the air-sphere radius [10].

15.4 Different Functionalities of PCs in Solar Cells

PCs used in solar cells can be classified into three types by the relative positions of the PCs and the active layer of a solar cell: PCs placed on the shadow side of the active layer, the active layer itself structured as PCs, and PCs placed at the front side of the active layer (Figure 15.3) [4, 59]. The aims of these PCs may be to enhance the photogenerated current by reducing light loss from reflection off the front surface of solar cells and/or prolonging the light-photovoltaic material interaction time and hence efficiently utilizing the solar spectrum. Besides, they may also be used to meet a host of other requirements for photon management in real applications. For instance, solar cells in building-integrated photovoltaics (BIPV) may need to be partially transparent and colorful; those in concentrator systems may require directional selectivity; and those in thermophotovoltaic

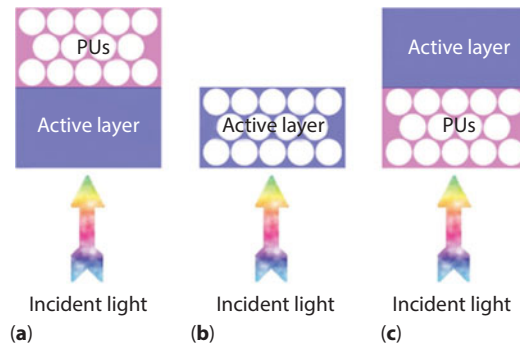


Figure 15.3 Schematic illustration of the relative positions of the PCs and the active layer of a solar cell: (a) PCs placed on the shadow side of the active layer, (b) the active layer itself structured as PCs, and (c) PCs placed at the front side of the active layer.

systems require optical layers with specifically tuned absorption and emission spectra.

In the following sections, we will review a number of functionalities of PCs useful to photon management. First, PCs placed on the shadow side of the active layer, mainly provide wavelength-dependent reflection, scattering, and so on. Second, when absorbers themselves are structured as PCs, they may demonstrate field localization for enhanced absorption or endow solar cells with colorful appearance. Third, PCs placed at the front side of the active layer, may be used for antireflection, directional selectivity, and coupling of incident light to interfacial modes. Finally, PCs with functionalities other than the above-described will also be listed.

15.4.1 PC Reflectors

A reflector is a conventional optical design for solar cells to increase the optical path length, for example, a back-side metal mirror placed on the shadow side of the active layer. This reflector almost equally reflects the light of different wavelengths back to the active layer. On the other hand, PCs are another kind of reflector. Compared to the mirror reflectors, PC reflectors have a key advantage of tunable spectral selectivity which ensures the reflection or diffraction of unabsorbed photons inside the band gap and high transmissivity outside the band gap. One useful application for wavelength-selective PC reflectors is for semitransparent BIPV. BIPV are used for roofs, skylights, windows, or facades in place of traditional building materials to generate electricity while simultaneously providing thermal management and tinting/shading. In addition, PCs may

be designed to diffract the incident light into highly oblique angles, which further lengthens the optical path in cells. When the angle of the diffracted light is larger than the critical angle, even the totally internal reflection is possible.

The structure of PC, consisting of an alternating periodic stack of layers with different dielectric permittivity, is perhaps the simplest PC reflector. Assuming negligible absorption and proper scaling of the layers, light propagation through the layers is forbidden, and they become a near perfect reflector to the light frequencies within the PBG. Kherani and coworkers demonstrated rear Bragg reflectors composed of alternating layers of sputtered ITO and spin-coated silica nanoparticles, which were adjacent to a 100 nm-thick amorphous silicon (a-Si) absorber. Although the solar cells with optimized rear ZnO/Ag contact achieved similar efficiency to that of the rear Bragg reflector contact, no solar power was transmitted through the former cells, and 430 W/m² were transmitted through the latter [68]. Their results indicate the superiority of PC reflectors in BIPV, which can be available for building heating and cooling. A full a-Si cell coupled with a stack of three TiO₂/SiO₂ Bragg reflectors with different stop bands was reported by Shih and coworkers. By adjusting the position of the Bragg reflector stop bands to further utilize visible light and to allow the transmission of certain parts of light through the solar cells, the cell efficiency could be enhanced from 3.68% to 4.66%, and the transmission of blue light (430 ~ 500 nm) was also achieved (Figure 15.4a) [69].

Organic photovoltaic solar cells with Bragg reflectors composed of seven alternating layers of TiO₂ and SiO₂ were reported by Lunt and Bulovic. The solar cells were fabricated by using near-infrared absorbing organic semiconductors (i.e., chloroaluminum phthalocyanine and C₆₀), and the Bragg reflectors were designed to form a stop band around $\lambda = 800$ nm. Therefore, the Bragg reflectors led to an increase in the efficiency from 1.3% to 1.7%, while maintaining high visible transparency of > 55% (Figure 15.4b). Furthermore, due to the near-infrared reflection of the Bragg reflectors, the devices could be used for architectural cooling applications [70].

These 1D Bragg reflectors have also been utilized in DSCs with a bilayer architecture. Compared to the above similar structures used in silicon and organic photovoltaics, the reflectors in DSCs must be permeable to the electrolyte, so the porosity of Bragg reflectors is nonnegligible. Míguez and coworkers demonstrated several examples of light harvesting and efficiency enhancement in DSCs by coupling porous Braggreflectors, composed of alternating layers of spin-cast SiO₂ and TiO₂ particles (Figure 15.4c), to a thin nanocrystalline TiO₂ (nc-TiO₂) film. In addition to the photovoltaic effects, the integration of the Bragg reflectors had the effects on the cell appearance both in reflection and transmission modes. It was demonstrated

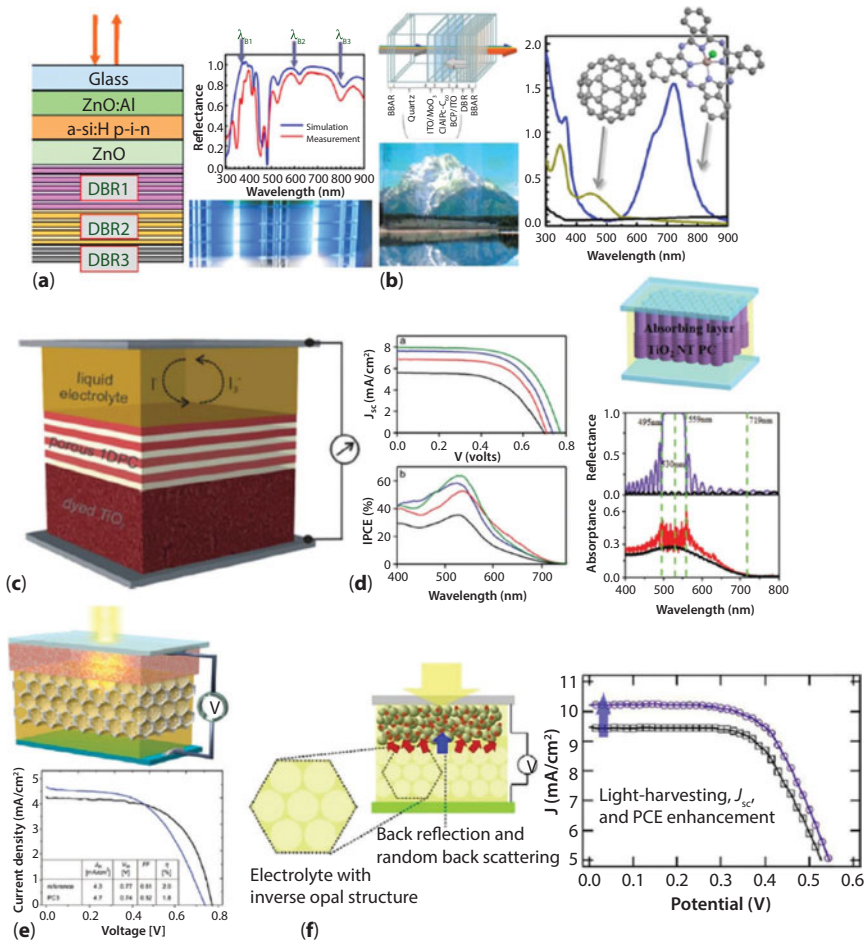


Figure 15.4 Different PC reflectors: (a) Selectively transparent silicon thin film solar cell with 1D Bragg reflectors (adapted from [69]). (b) Transparent, near-infrared organic photovoltaic solar cells with 1D Bragg reflectors. (c) A DSC with porous Bragg reflectors. (d) A DSC with TiO₂ NT PCs and the simulation for its optical properties. (e) A DSC with a 3D TiO₂ IO structure on the top of nc-TiO₂ film. (f) A DSC based on gel electrolytes with a 3D IO structure. (Figure (b) from [70], Copyright © 2011 American Institute of Physics. Figure (c) from [71], Copyright © 2012 The Royal Society of Chemistry. Figure (d) from [1], Copyright © 2015 The Royal Society of Chemistry. Figure (e) from [6], Copyright © 2010 American Chemical Society. Figure (f) from [62]; Copyright © 2014 Elsevier B.V. All figures adapted with permission)

that both the transparency is preserved after integrating the Bragg reflectors and that the color reflected by the device can be tailored to measure by means of the parameters of the photonic nanostructure, which can be of major interest for applications in BIPV systems [34, 71, 72].

A very special TiO_2 NT PC structure with periodicities along the axial direction of the NTs (Figure 15.4d) was reported by Huang and coworkers [45, 46, 48]. In a related theoretical study of the TiO_2 NT PC structure, the simulated reflectance of the TiO_2 NT PC, the absorbance of the PC coupled DSSC and the wavelength-dependent electric field distribution in the integrated photoanode showed that the NT PC could result in strong localization of the electric field in the absorbing film caused by back reflection from the PC in the stop band (Figure 15.4d). Besides, a Fabry-Perot-cavity-like behavior of the PC, resulting in a huge field envelope in the NT PC layer at two band edges, was also responsible for the efficiency and photocurrent enhancement [73].

Inverse TiO_2 opals with interconnected cavities have been heavily investigated for DSCs, and they become most effective when coupled to an nc- TiO_2 thin film and forming a bilayer structure. Halaoui and coworkers showed an improvement in the incident photon-to-electron conversion efficiency in a bilayer DSC structure over either the planar layer of nanocrystalline TiO_2 or a photonic crystal TiO_2 backbone alone [74]. Similarly, Guldin *et al.* observed improved short-circuit current density in a non-optimized bilayer DSC (Figure 15.4e) [6]. Lee and coworkers improved the power conversion efficiency of a bilayer DSC device to 8.3% compared to 6.5% for a comparable reference cell with the same dye loading. They found the improvement to be highly dependent on the optical coupling between the photonic crystal and the thin film [75]. Li and his colleagues found similar levels of improvement in relative efficiency in a recent study (an improvement of 2.76% to 3.59%) [76]. When 3D IOs are placed on the shadow side of the dye-sensitized layer, different mechanisms may be responsible for absorption enhancement except for backreflection from the PBG that also was owned by 1D Bragg reflectors, including the localization of heavy photons at the edges of the photonic gap (a narrow-band effect which enhances light absorption in the red regime), enhanced backscattering due to disordered regions in the crystal, and, significantly, because of the localization of light in the absorber film due to multiple resonant modes at the interface between the crystal and the absorber [4].

Porous 1D Bragg reflectors and 3D TiO_2 IOs may still face electrolyte diffusion difficulties when solid-state or quasi-solid-state electrolytes are used to replace the conventional liquid electrolytes. Furthermore, the PC structures may induce adverse effects on charge transport and recombination, even resulting in a penalty in the cell efficiencies. Therefore, it is essential to develop innovative PC reflectors to achieve light-harvesting enhancement for DSCs. Based on the above consideration, Zhang and coworkers first developed a polymer gel electrolyte with IO structure fabricated by

using SiO_2 opal films as templates and subsequent template etching. The DSCs based on the electrolyte showed enhanced photocurrent and efficiencies compared to the reference cells without the IO structure. More detailed characterizations of action spectra revealed the significance of the electrolyte IO structure for light harvesting and efficiency enhancement by back scattering and reflection of incident light (Figure 15.4f). In addition, the electrochemical impedance spectra further demonstrate that the gel electrolytes with IO had a lower impedance value than the reference gel electrolyte, which could also contribute to the observed PCE enhancement [62, 63].

15.4.2 PC Absorbers

When the active layer itself is structured as PCs, another functionality (i.e., localization of light within the PC itself) of PCs appears. This effectively tailors the absorption spectrum of a material by enhancing the path length or residence time of light at certain frequencies. Forming absorbers which are themselves structured as PCs has thus been an area of active interest, whereas it seems particularly important for organic solar cells. Organic photovoltaics usually suffer from the conflict between the relatively short exciton diffusion length (e.g., 10 nm) and the relatively long absorption length (e.g., 100 nm) [77], so strong light absorption in thinner layers of the active material is desired.

The early study about PC absorbers of organic solar cells mainly concentrated on theoretical simulation. Duché and coworkers theoretically studied a P3HT/PCBM thin film with a periodical nanostructure (Figure 15.5a), which allowed “slow Bloch modes” (group velocity close to zero) to be coupled inside the material. The P3HT/PCBM photonic crystal parameters could be adjusted (i.e., optimizing the periodicity [500 nm], wire diameter [400 nm], and slab thickness [150 nm]) to maximize the density of Bloch modes and obtain flat dispersion curves, based on which the light-matter interaction was thus strongly enhanced, and a 35.6% increase of absorption in the 600–700 nm spectral range was obtained by Finite-Difference Time-Domain simulations [78]. However, while absorption could be effectively enhanced in such a bilayer structure, the donor and acceptor were separated on a length scale unsuitable for efficient exciton diffusion.

To solve the problem that donor and acceptor are separated on a too large length when they act as two periodic elements with different refractive indices, a low-index PC, for example, nanocrystalline ZnO or titanium dioxide ridges, pillars, or cones, is impressed into a bulk-heterojunction matrix, in which donor and acceptor polymers phase-separated into an

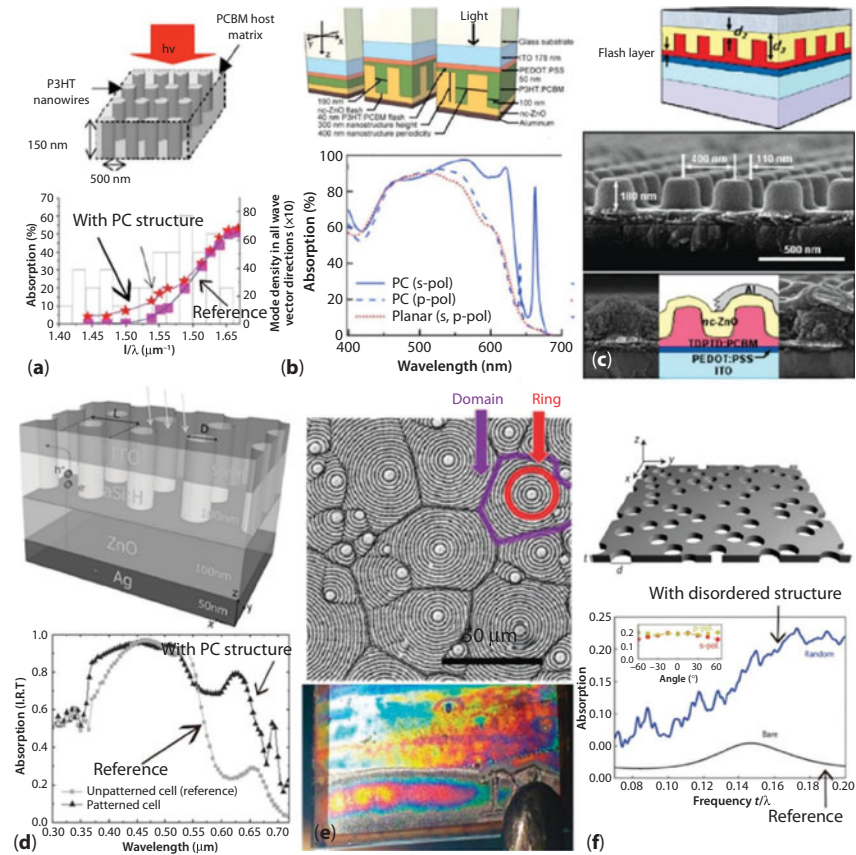


Figure 15.5 (a) The P3HT/PCBM PC structure and its enhanced absorption. (b) The P3HT:PCBM/ZnO PC structure and its enhanced absorption. (c) TDPTD:PCBM/ZnO PC structure fabricated by the PRINT method. (d) Silicon PC structure and its enhanced absorption. (e) A perovskite film with a concentric ring photonic structure and its appearance. (f) Photon management in two-dimensional disorder media. (Figure (a) from [78], Copyright © 2008 American Institute of Physics. Figure (b) from [79], Copyright © 2009 American Institute of Physics. Figure (c) from [82], Copyright © 2009 American Chemical Society. Figure (d) from [87], Copyright © 2010 Elsevier B.V. Figure (e) from [88], Copyright © 2015 The Royal Society of Chemistry. Figure (f) from [91], Copyright © 2012 Nature Publishing Group. All figures adapted with permission)

intimately intermixed nanostructure. An additional advantage of this design is that it offers higher index contrast than that of the PCs composed of the donor and acceptor polymers alone. A theoretical study, reported by Tumbleston and coworkers, presented 1D and 2D periodic nanostructured designs for organic photovoltaics where a PC was formed between

blend P3HT:PCBM and nanocrystalline ZnO (Figure 15.5b). Absorption enhancements over the full absorption range of P3HT:PCBM of 20% (one polarization) and 14% were shown for the 1D and 2D structures, respectively. These improvements resulted in part from band edge excitation of quasiguided modes. The geometries were also shown to create excitons 26% (1D) and 11% (2D) closer to P3HT:PCBM exit interfaces, indicating further photovoltaic improvement [79]. Other simulations also revealed a reduction of the distance between exciton creation and separation, suggesting favorable electrical properties in addition to higher absorption [80]. Besides, the morphology of the low-index layer may have an influence over the device performance. It was predicted that tapered structures of the low-index layer, such as cones and pyramids, could be superior to rectangular structures because of antireflection effects and perhaps higher exciton generation [81].

In addition to the theoretical simulations, Samulski and coworkers reported the fabrication of organic solar cells with a PC active layer by the PRINT method, in which the TDPTD:PCBM layer was patterned with a perfluoropolyether mold under pressure at 200 °C, and then the mold was peeled off to give highly ordered and regular nanopatterns (i.e., columns with a height of 180 nm and a periodicity of 400 nm) (Figure 15.5c). After that, the columns were back-filled with 5 nm ZnO nanoparticles to complete the PC structure. The devices exhibited a 3-fold enhancement of the absorption in specific regions of the solar spectrum in part through multiple excitation resonances and efficiency improvements of <70%, that resulted not only from greater absorption, but also from electrical enhancements according to the improved incident photon-to-electron conversion efficiency over the entire spectrum, not merely in the region of enhanced absorption [82]. This methodology is theoretically applicable to organic solar cells and the experimental findings also corroborate the above predictions. Later, the same group further fabricated standard and inverted organic solar cells with a PC active layer also by the PRINT method, but nanopatterns with more shapes, dimensions, periodicities, and material composition. The optical interference in PC cells was strongly affected by not only physical dimensions, such as height and periodicity of the nanopatterned layer, but also by the device architecture, standard versus inverted [83].

Crystalline silicon and amorphous silicon photonic crystal slabs consisting of various nanopatterns have been investigated theoretically and experimentally for solar cell applications [56, 84–87]. All of these studies found large improvements in absorption (Figure 15.5d) and/or short-circuit current density as a result of coupling to quasiguided modes in the slab. However, there is still a lack of examples using patterned silicon

photonic crystal slabs in practice, probably due to the challenges of passivation of the structures and other electrical problems [4] as well as increased fabrication cost.

For organic-inorganic hybrid perovskite solar cells, there are several examples related to perovskite PC structures. A unique example was reported by Huang and coworkers. In this research, the perovskites films, having a combination of a hundred micrometer-size large domain structure and a concentric ring photonics structure in each domain (Figure 15.5e), were fabricated during doctor-blade coating. Furthermore, the PC periodicity could be well tuned by the substrate temperature and the precursor solution concentration, generating very colorful perovskite films (Figure 15.5e) and the finished devices [88]. Another example was about 2D IO perovskite photonic films that were fabricated by using colloidal monolayer as template. The 2D IO films exhibited vivid structural colors and could modify the intrinsic electronic states of perovskites due to spatial confinement on crystal grains [89]. However, it is regrettable that these studies do not involve the subject of light trapping of the perovskite PC absorber.

It is noteworthy that an absorber layer with quasiperiodic PC structures or disordered systems may also be used as a photon management approach. For example, Oskooi and coworkers theoretically described a design principle for enhancing both light trapping and robustness using a 2D PC slab of silicon with controlled degrees of disorder. It was found that an optimal amount of disorder (a mean value of 20% of the lattice spacing) controllably introduced into a multi-lattice photonic crystal causes the characteristic narrow-band resonant peaks to be broadened, resulting in a device with enhanced and robust performance ideal for typical operating conditions of photovoltaic applications [90]. Vynck and his colleagues proposed a new strategy for photon management in thin films that combines both advantages of an efficient trapping due to coherent optical effects and broadband/wide-angle properties due to disorder. By numerical calculations, the spectral and angular responses of thin films containing disordered photonic patterns (Figure 15.5f) were intimately related to the in-plane light transport process and could be tuned through structural correlations. Their findings were particularly suited for improving the absorption efficiency of thin-film solar cells [91].

15.4.3 Front-Side PCs

Front-side PCs can also be used for light management in some types of solar cells. The most common applications may be those antireflection

Míguez and coworkers also reported perovskite solar cells with Bragg reflectors within the perovskite active layer (Figure 15.6b), but we were more inclined to argue that the PC structure was in the front of the active layer due to the low porosity of the TiO_2 layer (*vide infra*). The Bragg reflectors were composed of sol-gel prepared TiO_2 layers and spin-coating prepared SiO_2 nanoparticle layers. The refractive index contrast between the layers in the PC was maximized by grossly varying the porosity of each layer, in which the relatively dense (4% open porosity) layers of TiO_2 were formed alternately onto the porous (50% open porosity) layers of SiO_2 . The photovoltaic devices showed tunable color across the visible spectrum due to the PC structure (Figure 15.6b). However, there were no light trapping effects of the PC structure emphasized in this report; in contrast, the research focused on the perovskite solar cells with highly desirable properties for cladding in the built environment and encouraged design of sustainable colorful buildings and iridescent electric vehicles as future power generation sources [94].

15.4.4 PCs for Other Functionalities

Although a number of PC applications have been summarized according to the relative positions of the PCs and the active layer of a solar cell as well as their functionalities, there are still some examples beyond the above classifications that are from the wonderful ideas of researchers. One example is a PC concentrator for efficient output of DSCs. Figure 15.7a shows a schematic illustration of the photovoltaic system containing a PC concentrator. The PC concentrators were fabricated by self-assembly of latex spheres on concave watch glasses (Figure 15.7b) based on the vertical deposition method, and they were used as a light-harvesting module to concentrate light for DSCs to generate electricity. The light corresponding to the absorbance of N719 dye can be converged when the stopband of the PC concentrator just overlaps the absorbance of the dye (Figure 15.7c), and the IR and UV light could be filtered out simultaneously. The biggest enhancement of the maximum output power reached more than 5 times when using the optimized concentrator with a stopband of 530 nm (Figure 15.7d) [95].

15.5 Summary and Outlook

Tailoring optical properties of a device always accompanies the development of solar cells and results in the enhancement of power conversion efficiencies. Coupling PCs to photovoltaics is regarded to be an effective

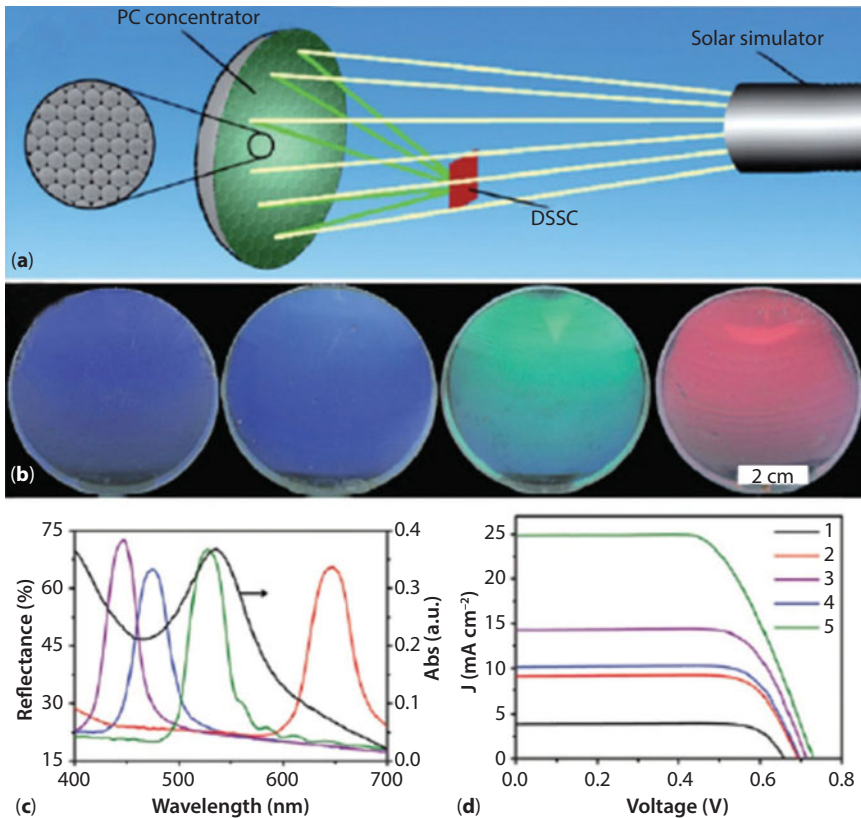


Figure 15.7 (a) Schematic illustration of the photovoltaic system with a PC concentrator. (b) Typical photographs of the PC concentrators with different colors. (c) The absorbance spectrum of the N719 dye (black) and the reflectance spectra of the PC concentrators. (d) The I-V characteristics of the DSCs with different concentrators. (Adapted with permission from [95]; Copyright © 2008 The Royal Society of Chemistry)

method for photon management. This chapter has summarized recent progress in this field, including fabrication strategies and applications of PCs for printable solar cells or solar cells with potential possibility for printable fabrication.

In the PC biological world, there is a class of animals that can reversibly change their PC structure and structural colors in response to their surrounding environment. One famous example is *Paracheirodon innesi*. These fish normally display a structural color of cyan, from the interference of light on periodically stacked microstructures of reflecting platelets in skin cells. They can change their blue coloration rapidly to yellow by simultaneously varying the spacing of the reflecting platelets under

stressful conditions. Although numerous theoretical, experimental, or practical PC structures have been developed to enable excellent antireflection, large absorption enhancement, and the possibility to tailor the optical response of solar cells for various applications in unprecedented ways, all of these artificial structures lack the flexibility to respond to the natural environment, unlike *Paracheiroduon innesi*. Therefore, future continued effort must concentrate on refining PC nanostructure designs and qualifying them to respond to temperature, incident angle of light, light intensity, and so on.

Acknowledgment

This work was partly supported by the Natural Science Foundation of Jiangsu Province (Grant No. BK20140256), Project Funded by China Postdoctoral Science Foundation (Grant No. 2015M571633), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 16KJB430002), and the National Natural Science Foundation of China (Grant No. 51602031).

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Index

- [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), 240–244, 253–257
- [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM), 240, 248–252, 256–257
- Absorption, 166, 168–171, 293–294, 305
- Absorption coefficient of perovskites, 316
- Acceptor, 6–7
- Additives, 305
- Adhesion, 235, 254–257
- Airbrush spray coating introduction, 206–209
- Annealing, 238, 244, 253
- Back contact, 392, 393, 408
- Back PEDOT cell concept, 14
- Band gap, 168, 169, 171, 390, 391, 404
- Bilayer heterojunction, 7, 12
- Blade coating, 176, 177
- Blocking layer, 97, 98, 102
- Buffer layer, 15–16
- Bulk heterojunction, 5–8, 67–68, 70–71
- Bulk heterojunction polymer solar cells (BHJ-PSCs), 236–237, 240–241, 248–254, 256–257
- Carbon black, 494–495
- Carbon nanotube (CNT), 472–476, 495
- Carrier/exciton ratio, 300
- Casting, 174
- Charge
 - charge collection, 237–238, 240, 254
 - charge separation, 237
 - charge transport, 235–239, 241, 246, 248, 250, 252, 257
- Charge carrier diffusion length of perovskites, 316
- Coffee-ring effect, 493
- Conjugated polymers, 459
- Copper oxide (CuO , Cu_2O), 439–440
- Copper sulfide (CuS), 443
- Crystallite orientation, 235, 237–238, 240, 246–252, 257
- $\text{Cu}_2\text{ZnSnS}_4$, 444
- CuAlO_2 , 443–444
- CuInS_2 , 444
- Cuprous iodide (CuI), 441
- Cuprous rhodanide (CuSCN), 441–442
- Degradation, 302–304, 306
- Device architecture
 - inverted, 239–240, 250, 252–254, 256–257
 - regular, 239, 246, 250, 252
- Device performances, 235–257
- Diffusion length, 294–295
- Direct solution coating, 386, 395, 400, 401, 409
- DNA based OFETs, 225
- Donor, 6–7
- Donor/acceptor interface, 67
- Doping (molecular), 102, 106, 108, 124, 131–135, 139

- Dye, 18
- Dye-sensitized solar cells, 16, 17, 364–367
- Edge-on/face-on crystallites, 237–239, 247–252, 257
- Efficiency, 165, 166, 168–170, 181
- Electrode
 - Ag, 239, 252–256
 - Au, 235, 239, 252–257
 - evaporation, 235, 239, 240, 252–253
 - laminated metal foils, 235, 239–240, 252–257
- Electrode materials, 457–459, 498
- Electrodeposition, 386, 395–400, 406, 409
- Electrolyte, 18
- Electron transport materials (ETM), 292, 295, 425, 429, 433, 445
- Electronic
 - band structure, 390
 - industry, 395
 - properties, 385, 401
- Electrospray coating introduction, 211–212
- Energy dispersive X-ray spectroscopy (EDS), 244–245, 247
- Exciton, 7
- Exciton binding energy of perovskites, 316
- Exciton diffusion length, 67
- Exciton dissociation, 7
- Extrinsic degradation, 15
- Fermi level pinning, 100
- Fill factor, 68–69, 192, 193
- Fill factor (FF), 277
- Flexible PeSCs, 325, 333
- Flexographic printing, 184, 185
- Formamidinium lead triiodide, 322
- Graphene, 466
 - bottom-up chemical synthesis, 471
 - chemical vapor deposition (CVD), 470
 - doping, 471
 - reduced graphene oxide (rGO), 466–469
- Graphene oxide (GO), 445–446
- Graphite, 495
- Gravure printing, 182–184
- Heterojunction, 167, 170–173
- Hole transport material (HTM), 295–296, 423, 425–427, 429, 432–433, 439–447, 449
 - carbon nanotubes, 116, 141
 - graphene, 116–117, 142
 - metal, 112
 - metal oxide, 112, 118, 139
 - metal salts, 116, 140
 - polymers, 104, 126, 137
 - self-assembled monolayers, 119
 - small molecules, 109, 123, 128
- Hole-transporting materials (HTM), 273–280
- HOMO, 7
- Hysteresis, 300–301
- Indium tin oxide (ITO), 458, 480
- Indium-tin-oxide, 325
- Inkjet printing, 185–188, 446, 448
- Inkjet printing process, 369–379
 - DSSC technology, 370–372
 - inkjet printing in perovskite solar cell technology, 377–379
 - inkjet printing of dyes on semiconducting oxides, 373–374
 - inkjet printing of ionic liquid-based electrolytes, 374–377
 - inkjet printing of perovskite material, 378–379
 - inkjet printing of transition metal oxides, 372–373

- Integer charge-transfer model, 99–101
- Interface
 - active layer interface, 238–247, 249–252
 - donor-acceptor interface, 236–237, 240–247, 257
 - hole/electron conducting layer-metal interface, 239–240, 254–257
 - PEDOT:PSS/metal foil, 254–257
- Interfacial layer, 96, 97
- Interpenetrating network, 67, 76, 81
- Intrinsic degradation, 15
- Inverted
 - BHJ, 252–257
 - device architecture, 239, 240, 252
 - PSC, 240, 250, 252, 256
- Inverted structure of PeSCs, 319
- Inverted type solar cells, 15
- ITO-free transparent electrodes, 325–326
- Lamination, 235, 239, 240, 252–257
- Lead-free perovskite, 323
- Leak current, 237
- Light absorbance, 297
- Low cost, 236, 252, 257
- LUMO, 7
- Meniscus guide, 336–337
- Mesoscopic perovskite solar cells, 424–425, 428, 441, 447–448
- Meso-superstructured solar cells, 318
- Metal
 - bonds, 408
 - chloride, 403
 - contacts, 392
 - divalent salts, 398
 - exchange, 398
 - ions, 408
 - oxidation, 402
 - oxides, 408
 - ratio, 401
 - salts, 407
 - sources, 407
 - species, 399
 - sulfides, 404, 408
- Metal leaves, 235, 253, 255
- Metal nanomesh, 476–480
- Metal nanowire network, 480–482
- Metal nanowires, 220–221
- Metal oxide and nanoparticles for spray coating, 220–222
- Methylammonium lead trihalides, 322
- Microcavity, 487, 489
- Mixed halide formulations, 322
- Mixed-organic-cation (MOC)
 - perovskite-based solar cells
 - fill factor, 277
 - photoluminescence spectra, 275, 276
 - photovoltaic performance, 275, 276
- Mix--metal nanowires, 221–222
- Molybdenum oxide (MoOx, MoO₃), 426–428
- Multilayer thin film (MTF), 486–491
- Nanostructured active layers, 240–242, 257
- Naphthobisthiadiazole-based polymer (PNTz4T), 240, 248–252, 256–257
- Nickel oxide (NiO, NiOx), 423, 428–438, 447–449
- N-i-p structure, 319
- Nonconjugated zwitterions, 16
- Non-corrosive metals, 15
- n-type, 6–7
- Ohmic contact, 69, 101
- Open circuit voltage, 191, 192
- Open-circuit voltage, 68
- Optical spacer, 103, 106
- Organic-inorganic halide perovskite solar cell, 424
- Organic materials for spray coating, 216–220

- Other high efficiency materials, 219
- Other spray coating applications, 224–226
- P3HT:PCBM active layer, 217–218
- PdS quantum dots (PdS QDs), 444
- PEDOT:PSS, 104–109, 126–127, 138
- PEDOT:PSS HTL, 219
- Perovski, Lev, 317
- Perovskite, 495
 - solar cell, 495
- Perovskite absorber, 291–292, 296
- Perovskite solar cells, 21–23, 367–369
- Perovskite solar cells by spray coating, 222–224
- Perovskite stability, 302–303, 305
- Perovskite-based solar cells, 291–292
- Photogenerated charges, 238, 241
- Photogenerating carriers, 66
- Photonic crystals
 - fabrication, 513–514, 517–521, 523–524, 527–529, 537–538, 541
 - functionalities, 513–514, 530–531, 540
 - fundamentals, 514–515
 - natural photonic nanostructures, 516
- Photonic sintering, 340
- Photovoltaic cells, 458
- Photovoltaic performance, 300, 304
- Physical principles of film formation
 - by solution processes, 38
- Pillow effect, 98
- P-i-n structure, 319
- PL quenching, 244
- Planar perovskite solar cells, 424–425, 427, 430, 432, 435, 439, 441–446, 448
- Poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS) thin films
 - as hole-transporting material, 273–280
 - benzoid and quinoid forms, 265–267
 - chemical structure, 265–267
 - electrical conductivity, 281–282
 - electronic characteristics, 270–271
 - highly conductive, 271–273
 - intrinsic (local) conductivity, 281
 - molecular structure, 264–265
 - optical and electrical characteristics, 267–270
 - Raman fingerprint, 266
 - spin rate effect, 275–277
 - surface roughness, 279–280
 - theoretical carrier concentration, 281
 - thermal annealing temperature effect, 277–278
 - transparent conductive electrode, 264
 - viscosity effect, 278–280
 - water droplet contact angle, 279–280
 - work function, 274–275
- Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), 459
 - additive, 460–461
 - ink, 463
 - post-treatment, 461–463
- Poly(3-hexylthiophene) (P3HT), 236, 240–248, 253–257
- Polymer-based solar cells, 77
- Precursors, 396, 399–405, 407
- Pre-metered technique, 336
- Printable solar cells, 457–459
- Printed electronics, 164, 165
- Properties and characterization of thin films, 46
- p-type, 6–7
- Quantum dots, 66, 77

- Raman fingerprint, 266
- Regiorandom poly(3-hexylthiophene) (RRa-P3HT), 242–246
- Roll-to-roll (R2R), 314, 331, 347, 425, 434, 446, 449
- Rubbing, 246–248, 257
- Scalable method, 328, 337
- Screen printing, 180–182, 437, 446–447, 449
- Secondary phases, 388, 389, 391, 394, 405, 408, 409
- Selenization, 402–405, 408, 409
- Semiconductor, 385, 387, 390, 391, 400
- Semiconductor oxide, 17
- Sequentially deposited diffusive bilayer polymer solar cells (SD-PSCs), 237–238, 240–248, 257
- Series resistance, 70
- Short circuit current, 191, 192
- Short-circuit current, 68
- Shunt resistance, 70
- Silver ink, 491–494
- Slot die coating, 177, 178
- Solar cells
 - dye-sensitized, 121
 - organic, 97
 - perovskite, 127
 - photon management, 513–514, 530–531, 536, 538, 541
- Solar cells:
 - CIGS, 165–167, 169, 173
 - organic, 164, 165, 170–173
 - perovskite, 165, 167–170, 173
- Solid state dye sensitized solar cells, 19–21
- Solution processing techniques for thin film deposition
 - doctor blade, 43
 - slot-die coating, 44
 - spin coating, 42
 - spray coating, 46
- Solvent treatments, 214–216
- Spin coating, 174–176
- Spin rate effect, 275–277
- Spiro-MeOTAD, 123–137, 141, 142
- Spray coated OFETs, 225
- Spray coated OPDs, 226
- Spray coating history, 206
- Spray coating mechanism, 208–209
- Spray-coated PMMA, 225
- Sulfonated poly(imide) (SPI) polymer, 282
- Sulfurization, 402–406, 408, 409
- Surface free energy, 250, 255
- Theoretical carrier concentration, 281
- Thermal annealing, 213–214
- Thermal annealing temperature effect, 277–278
- Thin films, 163–165, 167, 173, 174, 176
- TiO₂, 220
- Traditional structure of PeSCs, 319
- Transition metal oxides, 423, 426, 440, 449
- Transparent conductive electrode (TCE), 264
- Trap-state density of perovskites, 316
- Treatment used during spray coating, 212–216
- Two-dimensional materials, 445
- Two-dimensional technique, 350
- Ultrasonic spray coating introduction, 209–210
- Ultrathin metal film, 482–486
- Understanding the crystallization processes in hybrid semiconductor films
 - effect of the annealing process on morphology and crystalline properties of perovskite films, 55
 - heat transfer processes in a meso-structured perovskite solar cell, 53

- role of precursor composition in the crystallinity of perovskite films, 56
 - thermal transitions revealed by DSC, 50
- Vapor-based techniques, 333
- Vertical donor-acceptor concentration gradient, 237–238, 241–247, 257
- Viscosity effect, 278–280
- Work function, 274–275
- X-ray
 - absorption, 388
 - diffraction, 387, 388
- XRD
 - 2D-XRD, 247–249
 - GIWAXD, 250, 251
 - GI-XRD, 247
- ZnO, 220

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