

Investigating Low Cost Hole Transporting Materials for Perovskite Solar Cells



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A thesis submitted for the degree of

Doctor of Philosophy

2016

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Abstract

Organic-inorganic halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have attracted strong attention of photovoltaic research community since 2012, benefiting from the low cost of organometal halide perovskite precursors and their simple solution processability. However, the chemical instability of this material, especially in high humidity environment, restricts its photovoltaic application in industry. This thesis is focusing on employing novel hole transporting materials (HTMs) for perovskite solar cells (PSCs). Besides their main responsibility acting as a hole selective layer increasing the photovoltaic performance, HTMs can also play an additional role serving as moisture blocking layers, enhancing the stability of PSCs.

Chapter 2 presents the general background knowledge of the physics of solar cells, delving deeper into the working principle of PSCs and related researches about the HTMs and stability of the devices. In chapter 3, the device fabrication techniques and the characterization methods used are presented in details. Commencing from chapter 4, the application of two kinds of HTMs and related studies are discussed. Chapter 4 demonstrates the use of a p-type organic material, PEDOT, on ‘regular’ structured PSCs, achieving devices with decent power conversion efficiency (PCE) but relatively huge hysteresis and low stabilized power output (SPO). Stability analysis shows this organic material provides a better protection of the perovskite film comparing to that of doped Spiro-OMeTAD, which is the most generally used HTM. Chapter 5 presents a study about CuSCN, an inorganic p-type semiconductor, being applied in PSCs as HTM. The CuSCN based devices show comparable performance to that of Spiro-OMeTAD based devices, but an interfacial degradation mechanism is found to facilitate the perovskite degradation even in inert atmosphere. A facile sealing protocol is established to deal with this problem, leading to super stable photovoltaic devices under thermal stressing. The following chapter 6 demonstrates a CuI doping technique to improve the hole transporting effectiveness of CuSCN layer. This doping technique modifies the morphology of CuSCN film and leads to a substantial improvement in the photovoltaic performance.

Acknowledgments

First, I would like to thank Professor Henry Snaith for giving me the opportunity to carry out my research in his group. Professor Snaith is a brilliant scientist with marvellous novel scientific ideas. He inspired me a lot on how to conduct a meaningful scientific research during my DPhil period. I would also like to thank my friendly and supportive colleagues, who together create an awesome working atmosphere for the group. I would especially mention Dr. Sandeep Pathak, who provides me so much guidance whenever I had some problems with my research.

I would like to thank China Scholarship Council (CSC) for full financial support during my DPhil period.

I also thank my family for supporting me finish my DPhil. Thank you for motivating me to overcome the difficulties during these four years.

Finally, I must express my gratitude to my dearest girlfriend Yimeng. During my hardest time, your encouragement shined light to my world. No word can describe how important you are to my life. Love you forever.

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Nomenclature

Fundamental Constants

h	Planck's constant
c	Speed of light in vacuum
k	Boltzmann constant
q	Charge of the electron

Symbols

$\mathcal{E}_G$	band gap energy
$\mathcal{E}_C$	conduction band lower edge
$\mathcal{E}_V$	valence band upper edge
n_e	density of electrons
n_h	density of holes
b_i	mobility of the particles of type i
σ_i	conductivity of the particles of type i
D_i	diffusion coefficient
L_{eh}	electron-hole diffusion length
E_{bi}	built-in electric field
V_{bi}	built-in potential
J	current density
J_s	reverse saturation current
V	voltage

V_{oc}	open-circuit voltage
J_{sc}	short-circuit current
t	tolerance factor
P_{in}	light intensity
R_{rec}	recombination resistance

Acronyms

Quad	quadrillion British thermal unit
hrs	hours
PV	photovoltaic
VB	valence band
CB	conduction band
LUMO	lowest unoccupied molecular orbital
HOMO	highest occupied molecular orbital
FB-SC	forward bias to short circuit
SC-FB	short circuit to forward bias
Si	silicon
GaAs	gallium arsenide
CdTe	cadmium telluride
CIGS	copper indium gallium selenide
FTO	fluorine-doped tin oxide
Spiro-OMeTAD	(2,2',7,7'-tetrakis (N, N-di-p-methoxyphenyl-amine) 9, 9'-Spirobifluorene
LiTFSI	bis(trifluoromethanesulfonyl)imide salt
<i>t</i> BP	4-tert-butylpyridine
P3HT	poly(3-hexylthiophene-2,5-diyl)
PTAA	poly(terephthalic anhydride)

PEDOT	poly(3,4-ethylenedioxythiophene)
PSS	polystyrene sulfonic
PCPDTBT	Poly [2,6-(4,4-bis-(2-ethylhexyl) -4 <i>H</i> -cyclopenta [2,1- <i>b</i> ;3,4- <i>b'</i>]dithiophene)- <i>alt</i> -4,7(2,1,3-benzothiadiazole)]
IPFB	iodopentafluorobenzene
HPA	hypophosphorous acid
CuSCN	copper(I) thiocyanate
CuI	copper iodide
PMMA	poly(methyl methacrylate)
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
IPA	iso-propanol
ACN	acetonitrile
MAI	methylammonium iodide
TiO ₂	titanium dioxide
MA ⁺	CH ₃ NH ₃ ⁺
Al ₂ O ₃	aluminium oxide
HCl	hydrochloric acid
PbCl ₂	lead chloride
N ₂	nitrogen
DSSC	dye-sensitized solar cell
PSC	perovskite solar cell
HTM	hole-transporting material
HTL	hole-transporting layer
ETL	electron transporting layer
LED	light emitting diode
FET	field effect transistor
PCE	power conversion efficiency

SPO	stabilized power output
FF	fill factor
PL	photoluminescence
EIS	electronic impedance spectroscopy
XRD	X-ray diffraction
SEM	scanning electron microscopy
EBIC	electron beam-induced current
UPS	ultraviolet photoelectron spectroscopy
OCVD	open-circuit voltage decay
TCSPC	time-correlated single photon counting

Chapter 1. Introduction

1.1 Background and Motivation

With the rapid increase in the global population and the evolution of the industrial economy, world energy consumption is increasing at an alarming rate. The total world primary energy consumption reached 523.9 quadrillion British thermal units (quads, 1 quad= 1.055×10^{18} joules) in 2010; renewable energy consumption is 56.2 quads, constituting only 10.7% of world demand.¹ It is projected that world energy consumption will increase to 819.6 quads by 2040 with an average annual growth rate of 1.5%, when the majority of energy supply will still come from the combustion of traditional fossil fuels, such as liquid fuels, natural gas and coal.¹ This combustion will lead to unavoidable emissions of carbon dioxide, which is a major contributor to anthropogenic greenhouse gas emissions worldwide, resulting in rising global temperatures.² If the current trend continues, it will lead to disastrous consequences in terms of weather patterns, frequency of coastal flooding, natural ecosystems, and the future of human society as it is now.^{2,3} To prevent these adverse effects, carbon dioxide emissions must be reduced significantly within the next 20-30 years.²

In order to meet the energy demand and the environmental protection challenges, intensive research has been conducted on developing renewable, cheap and clean energy sources. Of all the available alternative energy sources, solar energy is the most abundant.⁴ However, the global installed solar generating capacity is only 37 gigawatts in 2010.¹ With intensive research and development into solar techniques, this number is projected to be increased to 266 gigawatts by 2040.¹

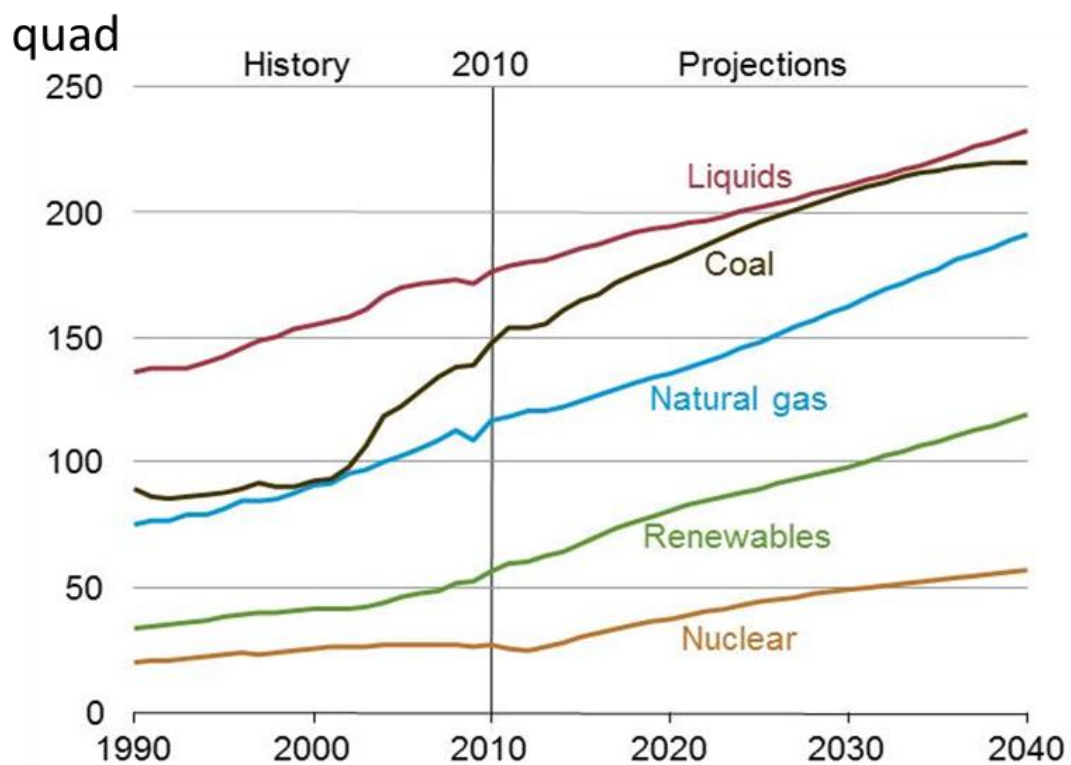


Figure 1.1 World energy consumption by fuel type, 1990-2040. Figure was reprinted from ref.¹.

Amongst the various categories of solar technologies used to convert solar irradiation to usable energy, photovoltaic devices are some of the most promising, due to their ability to directly convert absorbed sunlight into electrical power. To date, the best performing photovoltaic devices are based on inorganic crystalline semiconductors,

such as silicon (Si) and gallium arsenide (GaAs). Si-based solar cells have already been widely commercialized and employed in residential and industrial applications, with power conversion efficiencies (PCEs) approaching 25% (single crystal).⁵ However, due to the indirect bandgap characteristics of Si, the thickness of the absorbing layer required to form an efficient solar cell needs to be in the order of hundreds of micrometers to ensure enough light absorption. This significantly increases the complexity and cost of the fabrication process, consequently limiting the material's usage in energy industry. On the other hand, although thin film solar cells with PCEs reaching 28.8% can be obtained using the direct bandgap material GaAs⁵, the production cost of this material is too high for widespread commercialization⁶. Several other alternative materials have also been studied for the fabrication of thin film solar cells, such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), reaching PCEs of 22.1% and 22.3% respectively⁵. However, the former suffers from the toxicity of the cadmium, which may cause environmental hazards,^{7,8} while the large-scale production of the latter is limited by the complexity of the fabrication and the unavailability of indium as a rare element.⁹ As a result, long financial and energy payback times are currently limiting the widespread use of such photovoltaic devices.

Solution processed semiconductors have emerged as promising materials to apply in a variety of optoelectronic devices, such as light-emitting diodes (LEDs), field effect transistors (FETs) and photovoltaic devices. This category of devices benefit from tunable, cheap and easily accessible materials, allowing for low-cost, simple solution processing techniques such as spin-coating, spray-coating and reel-to-reel printing. Therefore, solar cells based on these materials should benefit from lower financial and energetic costs, compared with conventional crystalline inorganic semiconductors.

In 1991, O'Regan and Grätzel developed a solar cell with a combination of nanostructured electrodes and efficient charge injection dyes, called a dye-sensitized solar cell (DSSC).¹⁰ This kind of solution processed photovoltaic devices separate material components, offering the possibility of separately studying and tailoring the fundamental processes of solar energy conversion. Inspired by the structure of DSSCs, Miyasaka *et al.* proposed a perovskite sensitized solar cell in 2009, achieving a moderate PCE of 3.81%.¹¹ Later in 2012, Snaith *et al.* proposed a successful replacement of the TiO₂ mesoporous with an insulating Al₂O₃ scaffold, boosting the PCE to over 10%.¹² Since then, perovskite solar cells (PSCs) have become the most promising photovoltaic materials and a focus of intensive research, with the record PCE rapidly increasing to 22.1% by the beginning of 2016.^{5,12-14} However, besides the success of obtaining high efficiency, PSCs still face two major problems that hindering the widespread application of such materials in the energy industry. First, the most commonly used hole-transporting material (HTM) for PSCs (2,2',7,7'-tetrakis (N, N-di-p-methoxyphenyl-amine) 9, 9'-Spirobifluorene, Spiro-OMeTAD) is too expensive for industrialization¹⁵. Second, organic-inorganic halide perovskite as an ionic solid is very sensitive to moisture from the atmosphere, which can cause a rapid degradation if the perovskite film is not properly protected¹⁶. Therefore, the research into alternative effective HTMs that offer low cost and perfect stability is one of the major topics in perovskite photovoltaic research.

1.2 Goals of the Thesis

The aim of this thesis is to search for alternative HTMs for low-cost, efficient and stable PSCs. In regular structured PSCs where the hole-transporting layer (HTL) is placed on top of the perovskite layer, the HTL has two functions: (i) selectively extracting holes from absorber layer, and effectively transporting free carriers to the

electrode¹⁷, and (ii) acting as a blocking layer to defend the perovskite layer against moisture ingress from the environment¹⁶. Although the PSCs based on commonly used Spiro-OMeTAD HTM have achieved acceptable PCEs, the property of this material is not ideal to meet the aforementioned criteria. First, Spiro-OMeTAD has relatively low hole mobility in its pristine form, and thus additives such as lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) and 4-tert-butylpyridine (tBP) need to be routinely incorporated into the Spiro-OMeTAD solution to enhance the hole conductivity^{17,18}. Second, these additives have a hygroscopic nature, which makes perovskite film sensitive to moisture from the environment¹⁹. Furthermore, the high cost of Spiro-OMeTAD limits the industrialization potential of PSCs based on this material. In this thesis, two kinds of alternative HTMs are intensively studied for use in PSCs: one is the conductive polymer Poly(3,4-ethylenedioxythiophene) (PEDOT), and the other is the inorganic semiconductor copper(I) thiocyanate (CuSCN). Both were reported to be highly conductive and thermally stable p-type hole conducting material with low fabrication cost.²⁰⁻²² Different deposition techniques are tested and optimized for better solar cell performance. The effectiveness of charge extraction and the transport of different HTMs are assessed with various characterization methods, including conductivity measurement, photoluminescence (PL), and electronic impedance spectroscopy (EIS), etc. The stability test of perovskite devices or films is conducted in an ambient environment at 85 °C, characterized by X-ray diffraction (XRD), UV-vis absorption, and degradation of solar cell performance.

Beginning with Chapter 2, the background knowledge about the basic physics of solar cells is first reviewed, followed by the introduction of the structure and working principles of PSCs. Related researches about HTM and the stability issue of PSCs from the community are also reviewed in this chapter.

Chapter 3 presents the experimental methods, including precursor preparation, device assembly, and characterization techniques.

The scientific chapters commence from Chapter 4, where the use of a dispersion of PEDOT in toluene as HTM is first demonstrated. Devices with PCEs comparable to that of Spiro-OMeTAD based cells (up to 14.5%) are achieved by employing this much cheaper material. However, it is found that the steady-state stabilized power output (SPO) is much lower for the PEDOT-based cells than for the Spiro-OMeTAD-based cells. The origin of this reduced stabilized power output is investigated by EIS, which indicates an enhanced recombination rate at the perovskite/HTM interface. Stability tests on the perovskite films covered with different HTMs suggest that PEDOT provides better protection comparing to doped Spiro-OMeTAD, but not so good as neat Spiro-OMeTAD (without doping).

Chapter 5 demonstrates a smooth CuSCN HTL obtained with spray-coating method, achieving PCEs of up to 13.3% and the highest SPO of 10.9%. The film quality, which is checked using scanning electron microscopy (SEM), is much better comparing to the previously reported films deposited by the doctor-blading method²³. PL quenching measurement suggests that the charge extraction of as fabricated CuSCN layer is as effective as the doped Spiro-OMeTAD. The thermal stability test, however, shows an accelerated perovskite degradation induced by CuSCN coverage. This phenomenon is different from normal perovskite degradation accelerated by moisture, since it takes place regardless of environmental conditions. Careful investigation of the degradation mechanism is conducted with XRD measurement of samples placed in either an ambient or inert (nitrogen filled glovebox) atmosphere, and a reaction between CuSCN and perovskite at elevated temperature (85 °C) is proposed to be responsible for the accelerated degradation. To overcome this issue, a

multi-component hole-transport layer is demonstrated; this is composed of mesoporous Al_2O_3 infiltrated with CuSCN and subsequently coated in a thin layer of Poly(methyl methacrylate) (PMMA). This structure prevents the reaction from progressing, and the resultant devices exhibit tremendously improved ambient stability at 85 °C that survives for over 1000 hrs.

Taking a step forward, Chapter 6 shows a successful combination of the two most commonly used inorganic HTMs, copper iodide (CuI) and CuSCN. This chapter presents a simple route to improve the electronic property of spray-coated CuSCN film by adding a small amount of CuI solution into the CuSCN precursor. The SEM images suggest that this doping technique can affect the morphology of the as fabricated CuSCN film, leading to a better electronic connection between CuSCN crystals. Improvement of the charge collection and transport of the as fabricated film is then certified with PL and conductivity measurement. As a consequence, PSCs with modified CuSCN HTM achieved a PCE of 14.4% and a stabilized power output (SPO) of 12.3%, compared with 11.5% (PCE) and 9.9% (SPO) for PSC with non-doped CuSCN as HTM.

To summarize, this thesis aims at applying novel low-cost HTMs in PSCs, achieving devices with high efficiency and excellent stability. The study on PEDOT successfully employed this material in regular structured PSCs, where the problem of insufficient charge extraction effectiveness limits the device performance. The study of CuSCN reveals a serious instability problem induced by the reaction between CuSCN and perovskite. And this problem can be solved simply with a facile sealing technique, leading to super stable PSCs. The performance of CuSCN-based PSCs can be further improved with CuI doping, achieving better HTL film morphology as well as charge collection effectiveness.

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Chapter 2. Background

Further information about semiconductor properties and solar cells physics can be referred to standard text by Würfel *et al*¹ and Hook *et al*². All the equations in this chapter were taken from ref¹.

2.1 Semiconductors

In isolated atoms, the discrete energy values are separated by large gaps on the energy scale. When the distances between the atoms are decreased to a few Å (in solid), strong interaction among the atoms causes the previously identical energy values split into energy ranges, in which the energy values lie closely to form a continuum energy bands. In a solid material with metallic conductivity, a partly occupied band allows the electrons to be given additional velocity required for charge current to flow. This partly occupied band is called conduction band. Conversely, pure semiconductors and insulators are non-conductive, because the highest occupied energy band (valence band, VB) is completely occupied (at $T=0K$), and the next higher band (conduction band, CB), separated by energy gap ϵ_G with VB, is unoccupied (at $T=0K$). In this case the fermi energy ϵ_F , which is defined as the energy at which there is a 50% probability

of occupation, lies in the gap between VB and CB (Figure 2.1).

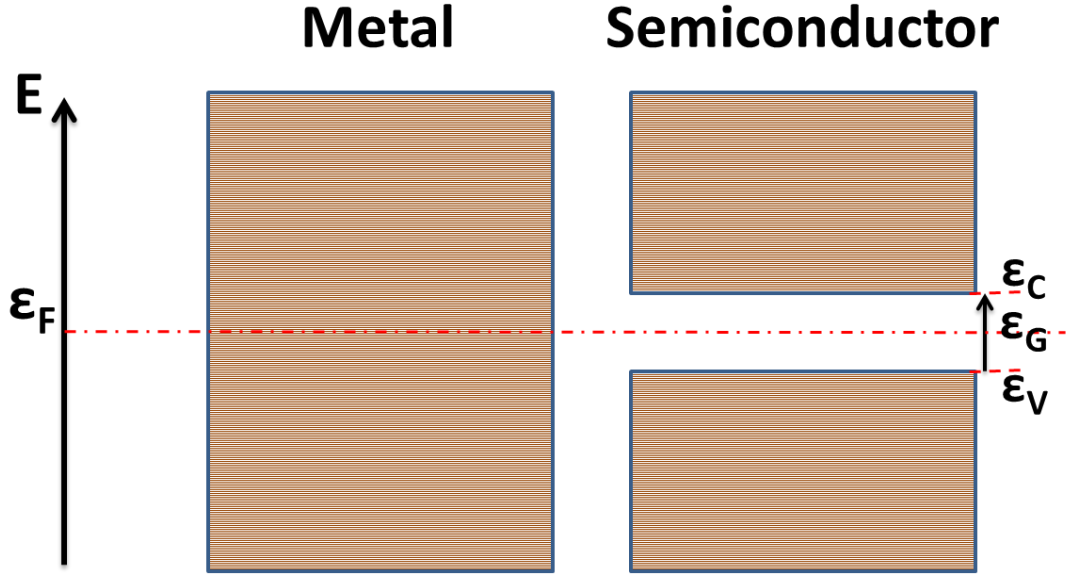


Figure 2.1 Illustration of energy band structure for metal and semiconductor. At $T=0K$, all the electronic states below Fermi energy level ϵ_F are occupied and all the states above ϵ_F are unoccupied.

For temperatures $T>0 K$, we can obtain the distribution of electrons considering three conditions: (i) According to Pauli Exclusion Principle for particles with non-integral spin, the same quantum state can only be occupied by no more than one particle. (ii) The occupation of the states depends only on the energy. (iii) The occupation of the states lead to a minimum of the free energy $F=E-TS$, where S is the entropy. The distribution function which satisfies all of the above conditions can be expressed as below

$$f_e(\epsilon_e) = \frac{1}{\exp\left(\frac{\epsilon_e - \epsilon_F}{kT}\right) + 1} \quad (2.1)$$

The equation (2.1) is called Fermi distribution, which contains Fermi energy ϵ_F as a

characteristic energy.

The density of electrons can be calculated with equation

$$n_e = \int_{\varepsilon_C}^{\infty} D_e(\varepsilon_e) f_e(\varepsilon_e) d\varepsilon_e , \quad (2.2)$$

where $D_e(\varepsilon_e)$ is the density of states for electrons. From the above equation the density of electrons can be obtained as

$$n_e = 2 \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2} \exp \left(-\frac{\varepsilon_C - \varepsilon_F}{kT} \right) = N_C \exp \left(-\frac{\varepsilon_C - \varepsilon_F}{kT} \right) . \quad (2.3)$$

N_C is called the effective density of states in conduction band. m_e^* is the effective mass of electrons given by $\varepsilon_e - \varepsilon_C = p^2/(2m_e^*)$.

The unoccupied states in the valence band, knowns as holes, can also permit charge transport with a positive charge. Using the same approximation for electrons, the density of holes is

$$n_h = \int_{-\infty}^{\varepsilon_V} D_e(\varepsilon_e) [1 - f_e(\varepsilon_e)] d\varepsilon_e = N_V \exp \left(-\frac{\varepsilon_F - \varepsilon_V}{kT} \right) , \quad (2.4)$$

where $N_V = 2(2\pi m_e^* kT/h^2)^{3/2}$ is the effective density of states of the valence band.

Combing equation (2.3) and (2.4), we can obtain an important relationship

$$n_i^2 = n_e n_h = N_C N_V \exp \left(-\frac{\varepsilon_C - \varepsilon_F}{kT} \right) \exp \left(-\frac{\varepsilon_F - \varepsilon_V}{kT} \right) = N_C N_V \exp \left(-\frac{\varepsilon_G}{kT} \right) . \quad (2.5)$$

Here n_i is called intrinsic density, which only depends on the band gap ε_G and does not depend on the position of Fermi energy or individual densities of the electrons or holes.

The individual densities of electrons and holes can be changed by doping the semiconductor with impurity atoms. In the simplest picture, the impurity atoms replace the semiconductor atoms at their lattice positions. The impurity atoms with one valence electron more than is needed for chemical bonding with neighbouring

atoms are called donors (D). In semiconductor, the binding energy of this electron reduce drastically due to the polarization of the neighbouring atoms, which cause the electron energy ϵ_D only slightly smaller than the conduction band lower edge ϵ_C . Therefore, the donors donate their electrons easily to the conduction band. On the other hand, acceptors (A) are impurity atoms which have one valence electron less than is needed for chemical bonding with neighbouring atoms. Since the energy of an electron ϵ_A at the acceptor only slightly higher than the upper edge ϵ_V of the valence band, the acceptors can accept electrons easily, creating holes in the valence band. With the incorporation of donors, a semiconductor becomes an electron conductor or n-type semiconductor, and with the incorporation of acceptors it becomes a hole conductor or p-type conductor. Combining equation (2.1) and (2.5), we can infer that with n-type doping the electron density increases, causing Fermi level moves close to lower edge ϵ_C of conduction band. On the contrary, with p-type doping the hole density increases, causing the Fermi level move towards to the valence band upper edge ϵ_V .

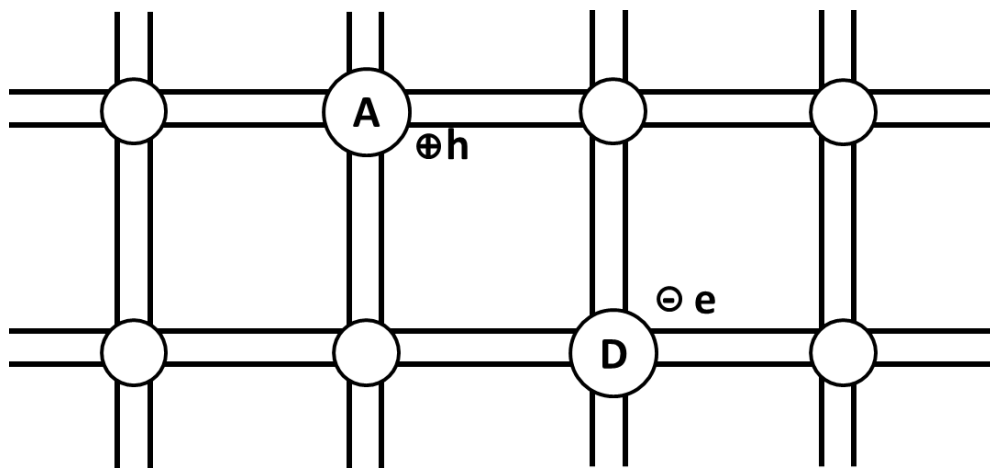


Figure 2.2 Impurity atoms with higher (D) or lower (A) valency replace lattice atoms by doping.

2.2 Working Principles of p-n Junction Solar Cells

2.2.1 Transport of Electrons and Holes

Current flow of electrons and holes can be divided into two types of current depending on different types of driving forces. The first one, field current, is driven by electric field E on the charge. Since the charge carriers may collide with obstacles while moving in the lattice, we use the collision time $\tau_{c,i}$ to indicate the mean time between two collision. Therefore, the mean velocity of particles of type i can be expressed as

$$\langle v_i \rangle = z_i \frac{e}{m_i^*} \tau_{c,i} E = z_i b_i E . \quad (2.6)$$

$b_i = e\tau_{c,i}/m_i^*$ is called mobility of the particles of type i . Then density of field current is then

$$j_{f,i} = z_i^2 e n_i b_i E = \sigma_i E . \quad (2.7)$$

Here $\sigma_i = z_i^2 e n_i b_i$ is the conductivity of the particles of type i .

The second type of current is called diffusion current, which flows when the charge concentration is non-uniform. The diffusion current of particles of type i is given by

$$j_{d,i} = z_i e (-D_i \text{grad} n_i) = -\frac{z_i e n_i D_i}{kT} \text{grad} \mu_i , \quad (2.8)$$

where D_i is called diffusion coefficient, μ_i is the chemical potential originated from free energy of electron-hole pairs. Using the Einstein Relation $b_i/D_i = e/kT$, (2.8) can be written as

$$j_{d,i} = -\frac{z_i e n_i b_i}{e} \text{grad} \mu_i = -\frac{\sigma_i}{z_i e} \text{grad} \mu_i . \quad (2.9)$$

Since the electrons and holes recombine after a time, the minority carriers travel by

diffusion vanish by recombination after certain distance. This process can be expressed with equation

$$\Delta n_e(x) = \Delta n_e(0) \exp(-x/\sqrt{D_e\tau_e}) = \Delta n_e(0) \exp(-x/L_e) , \quad (2.10)$$

where $L_e = \sqrt{D_e\tau_e}$ is called diffusion length, τ_e is the lifetime of the minority carriers for radiative recombination. The diffusion length is the mean path length for the diffusion of a charge carrier during its lifetime.

2.2.2 p-n Junction

A p-n junction is formed by joining p-type and n-type semiconductors in a planar heterojunction. Since the semiconductors have different types of majority carriers, electrons from n region near the interface tend to diffuse to the p region where they recombine with holes, leaving positively charged dopant atoms in n region. Similarly, holes from p region near the interface diffuse to n region and recombine with electrons, leaving behind negatively charged ions in p region. This process leads to the alignment of Fermi energy level and the formation of an intrinsic built-in potential V_{bi} across the junction, where the built-in electric field E_{bi} point from n region to p region (Figure 2.3).

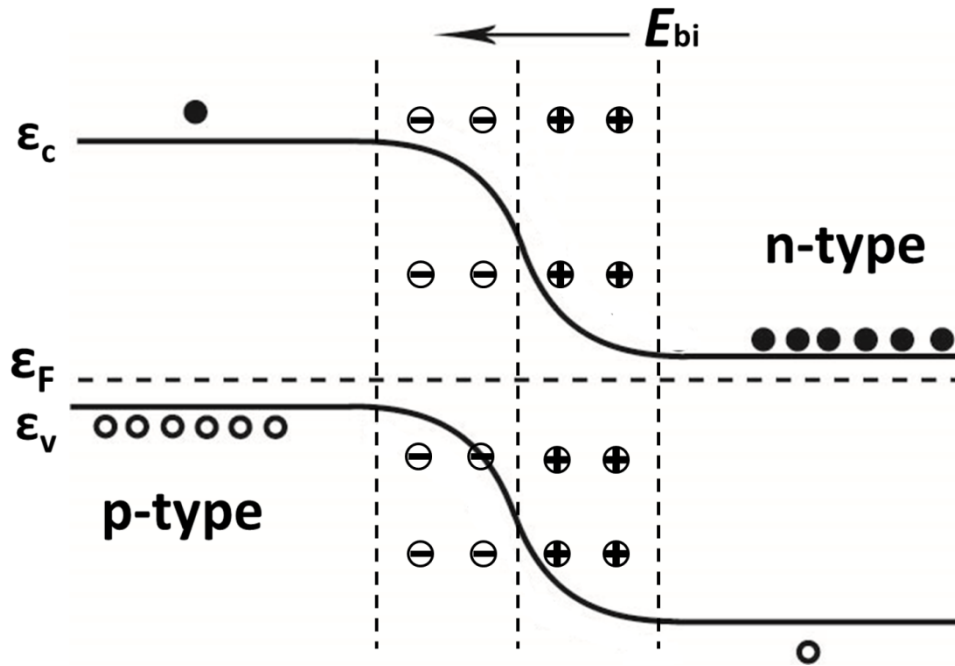


Figure 2.3 Schematic representation of a p-n junction with zero-bias voltage applied.

2.2.3 Current-voltage Characteristic of the p-n Junction Solar Cells

When the p-type region is connected with the positive terminal and n-type region is connected with the negative terminal, the p-n junction is applied with forward bias. In this case, holes from p region and electrons from n region are forced to junction area where they recombine. With increasing forward-bias voltage, the built-in electric field cannot counteract charge carrier motion across the p–n junction. Thus the electrons from n region continue to travel as minority carriers in p region within diffusion length L_e , similar as for holes travel in n region. Beyond the diffusion length, the majority carriers begin to flow in opposite direction. On the contrary, reverse bias is applied when connecting p-type to the negative terminal and n-type to the positive terminal. Here, holes in p-type material and electrons in n-type material are pulled away from junction, causing the barrier voltage to increase and a high resistance to the flow of charge carriers, and thus minimizing the current flow across p-n junction.

The current-voltage characteristic of p-n junction under bias voltage can be described with

$$j = j_s \left[\exp\left(\frac{eV}{kT}\right) - 1 \right], \quad (2.11)$$

where j_s is called the reverse saturation current.

Electron-hole pairs can be generated with absorption of photons with sufficient energy $h\nu$. The photo-induced electron-hole pairs will significantly increase the population of minority carriers in semiconductors (holes for n-type and electrons for p-type), leading to a separation of Fermi levels, where we use ϵ_{FC} for electrons in CB and ϵ_{FV} for holes in VB. In a homogenous semiconductor, the electron-hole pairs will finally recombine within lifetime τ . While in p-n junction, electrons and holes can separate under the driving force from E_{bi} , resulting in an accumulation of positive charge in p region and negative charge in n region (Figure 2.4).

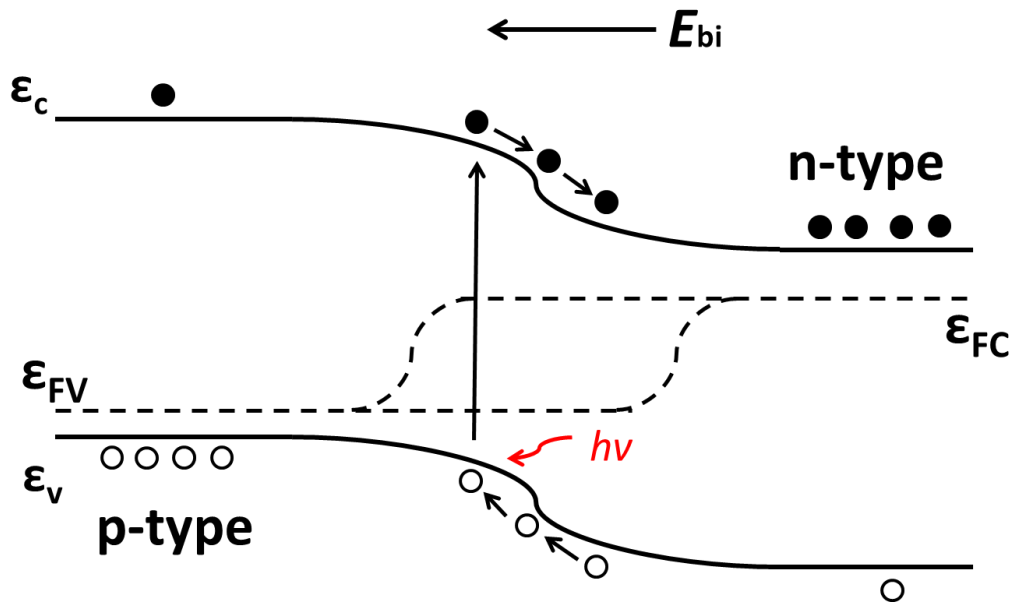


Figure 2.4 Schematic representation of a p-n junction absorbing incident photons.

Connecting the p-n junction to external circuit, the light generated carriers will then be able to flow through the circuit. Considering the distribution of light generated current, equation (2.11) now has the form

$$j = j_s \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] + j_{sc} , \quad (2.12)$$

where j_{sc} is the short-circuit current. This is the current-voltage (J - V) characteristic of the p-n junction solar cells. For $j=0$, we obtain the open circuit voltage V_{OC} as

$$V_{oc} = \frac{kT}{e} \ln \left(1 - \frac{j_{sc}}{j_s} \right) . \quad (2.13)$$

The maximum energy delivered by solar cell is given by the largest rectangle fitting under the J - V characteristic, which defines the maximum power point for the current density j_m and the voltage V_m . We define the fill factor (FF) as

$$FF = \frac{j_m V_m}{j_{sc} V_{oc}} . \quad (2.14)$$

2.3 Dye-sensitized Solar Cells

Dye sensitized solar cell (DSSC) was inspired by the energy and electron transfer mechanisms in natural photosynthesis and in dye sensitized silver halide emulsion used for photography³. The first breakthrough of using dye-sensitization in photovoltaics was in 1991, when O'Regan and Grätzel developed a solar cell with the combination of nanostructured electrodes and efficient charge injection dyes, pushing DSSC efficiency (η) from 1% to 7%⁴. In standard DSSC, a solution processed mesoporous titanium dioxide (TiO_2) with suitable electron mobility and CB position act as electron acceptor and transporter⁵. The surface of the nanocrystalline metal oxide film is attached with a monolayer of charge transfer dye, of which the photo excitation results in the injection of electrons into the conduction band of TiO_2 ^{6,7}. The dye is subsequently regenerated with electrons from hole-transporting

material (HTM), usually a liquid redox electrolyte or a solid state p-type semiconductor^{4,8}. An illustration of DSSCs structure and operation principle is shown in Figure 2.5.

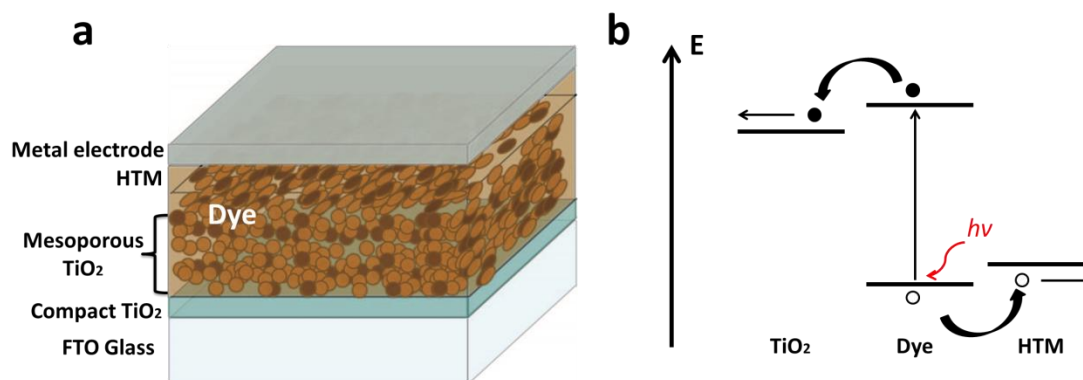


Figure 2.5 Schematic of DSSCs (a) structure and (b) operation principles.

There are three factors limiting the performance of DSSCs. First, the solution processed mesoporous TiO₂ nanoparticle network exhibit very large trap densities, which are primarily due to surface defects such as grain boundaries, oxygen vacancies, and poor electronic contact between nanoparticles^{5,9,10}. As a result, the density of electronic states in the TiO₂ is dominated by an exponential tail of sub gap states, and deviates far from that of an ideal semiconductor¹¹. The second limitation is from the HTM. Although DSSCs employing liquid electrolytes such as the $3I^- \leftrightarrow I_3^-$ redox couple or Co^(II/III)tris(bipyridyl)-based redox couple have reached photo conversion efficiencies (PCEs) over 12%¹², they suffer from the corrosive nature of electrolytes and the susceptibility to leakage. The application of solid state HTMs such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-Spirobifluorene (Spiro-OMeTAD) seeks to allow more stable devices. However, the low hole mobility of such small molecule HTMs limits the performance of DSSCs to only 7.2%^{8,13–15}. Thirdly, the optimized device thickness is only ~2 μm, far less than the absorption

depth when using dye sensitizers with low extinction coefficients^{16–18}. Therefore, sensitizer with high extinction coefficient, such as organometal halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$)^{19–21}, is a necessary solution for this problem.

2.4 Organometal Halide Perovskite Solar Cells

2.4.1 Organometal Halide Perovskite

Perovskite originally refers to a calcium titanium oxide mineral species with the chemical formula of CaTiO_3 , which was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after the Russian mineralogist Lev Perovski.²² Later on, the word perovskite was borrowed to describe materials with the same crystal structure as CaTiO_3 , known as perovskite structure.²³ The general chemical formula of perovskite crystals is ABX_3 , where the larger A cation occupies a cubo-octahedral site shared with twelve X anions while the smaller B cation is stabilized in an octahedral site shared with six X anions (Figure 2.6).²⁴ In $\text{CH}_3\text{NH}_3\text{PbI}_3$, the A-site cation is CH_3NH_3^+ (MA^+), the B-site cation is Pb^{2+} and the anion X is I^- .

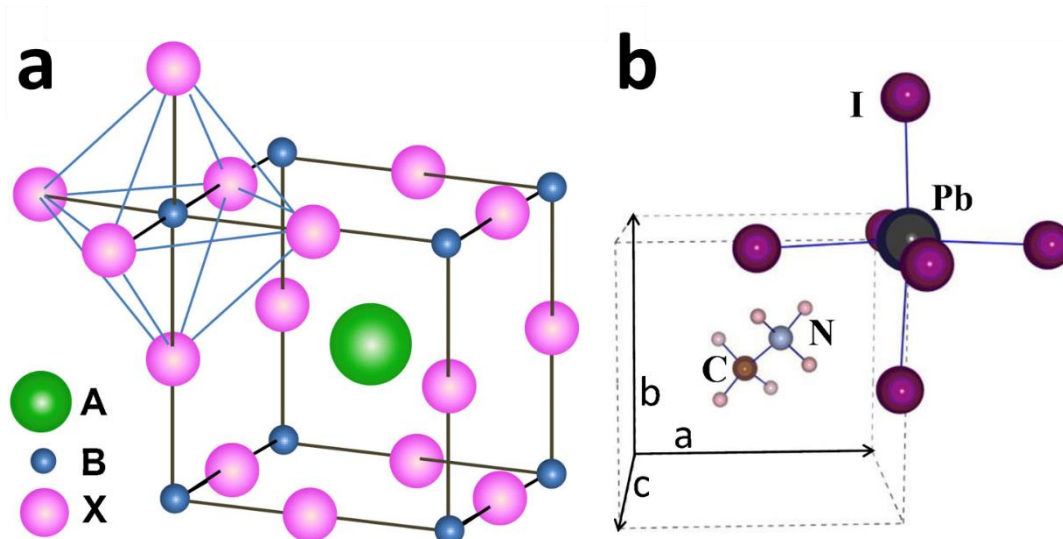


Figure 2.6 (a) ABX₃ perovskite structure showing BX₆ octahedral and larger A cation occupied in cubo-octahedral site. (b) Unit cell of cubic CH₃NH₃PbI₃ perovskite. Figures (a) and (b) were reprinted from Ref.²⁴.

There are strict requirements for relative ion size to maintain the stability of the cubic structure. In fact, slight buckling and distortion can lead to several lower-symmetry distorted versions, in which the coordination numbers of ‘A’ cations or ‘B’ cations are reduced. Many important physical properties of perovskites depend crucially on the details of these distortions, including the electronic, dielectric and magnetic properties. The formability of perovskite is estimated based on its geometric tolerance factor (t)²⁵, $t = (r_A + r_x)/\sqrt{2}(r_B + r_x)$, where r_A , r_B and r_x are the effective ionic radii for A, B and X ions, respectively. An ideal cubic perovskite is expected when $t = 1$. For alkali metal halide perovskite, formability is expected for $0.813 < t < 1.107$ ²⁶. Therefore, A cations with radii between ~ 1.60 Å and ~ 2.50 Å were found to form perovskite structures²⁷. Methylammonium cation, with ionic radius of 1.8 Å, results in the tolerance factor of CH₃NH₃PbI₃ to be 0.83. This indicates a deviation from an ideal cubic structure with octahedral distortion²⁸.

From ultraviolet photoelectron spectroscopy (UPS) and the Tauc plot obtained with UV-vis spectral data, the VB maximum ε_v , CB minimum ε_c , and the band gap for $\text{CH}_3\text{NH}_3\text{PbI}_3$ were estimated to be -5.43 eV, 1.5 eV and -3.93 eV, respectively²¹. Based on band gap energy, the absorption onset wavelength is expected to be around 826 nm²⁴. The extinction coefficient was estimated to be 1.5×10^4 cm⁻¹ at 550 nm, indicating that the penetration depth for 550 nm light is only 0.66 μm . At 700 nm, the extinction coefficient was 0.5×10^4 cm⁻¹, suggesting a penetration depth of 2 μm ²⁴. The short penetration depth suggests that most incident light is absorbed by a thin perovskite film of 2 μm , which is a perfect sensitizer for high efficiency solid-state sensitized solar cells.

2.4.2 The Development of Perovskite Solar Cell

In 2009, Miyasaka *et al.* pioneered the first perovskite solar cells (PSCs) based on mesoporous TiO_2 photoanodes that were sensitized with $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{I}, \text{Br}$)²⁰. However, the resulting PCEs were only moderate (3.81% for the triiodide and 3.13% for the tribromide), and the cells with a liquid electrolyte configuration degraded rapidly within a few minutes. The next breakthrough came in late 2012, when Snaith in collaboration with Miyasaka demonstrated “meso-superstructured” solar cells in which n-type mesoporous oxide can be replaced by an inert scaffold, such as Al_2O_3 , onto which $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and spiro-OMeTAD were coated. This non-sensitization type PSC generates increased V_{OC} values as high as 1.13 V and a PCE of 10.9% .¹⁹ Later from the middle of 2013, the efficiency of organometal halide perovskite based solar cells was rapidly pushed to over 15% with innovation of the cell fabrication technique. Liu *et al.* demonstrated the planar heterojunction PSC fabricated by vapor deposition, giving a PCE of 15.4% .²⁹ Basically at the same time, sequential deposition method is demonstrated by Grätzel *et al.* for the fabrication of perovskite on the

m-TiO₂ film, which gave a PCE of 15%.³⁰ As of March 2016, the certified record PCE of 22.1% was achieved by the Korean Research Institute of Chemical Technology (KRICT), which was certified by the National Renewable Energy Laboratory (NREL)³¹.

2.4.3 Perovskite Solar Cell Structures and Operation Principles

PSCs with structure similar to the classical DSSCs were fabricated with the organometal halide being deposited in a nanostructured TiO₂ layer, followed by spiro-OMeTAD being deposited as HTM on top (Figure 2.7a). In this structure, weakly bound excitons were generated by light illumination³² and accumulation of photo-generated charges takes place in perovskite³³, followed by charge separation with electrons injected into nanostructured TiO₂ and holes injected to HTM. An important alteration of the above architecture was the replacement of the TiO₂ mesoporous by an insulating Al₂O₃ scaffold achieving efficiencies of 10.9%¹⁹. Since alumina's has a conduction band far higher than the absorber's LUMO, no electron injection from perovskite to mesoporous metal oxide takes place, and this indicates that the electron transport occurs within the perovskite layer. Furthermore, this result implies that the sensitization concept is not necessary for PSC design. Similar results have been obtained with non-injecting ZrO₂ scaffolds³⁴. Since an electron accepting oxide nanostructured layer is not required, PSCs can be fabricated with the planar *pin* junction concept, in which a planar perovskite layer is located at the middle between the *n*-type thin TiO₂ film and the *p*-type HTM film (Figure 2.7b). This structure can be realized by both vapor deposition and solution deposition, achieving PCE over 15%.^{29,35}

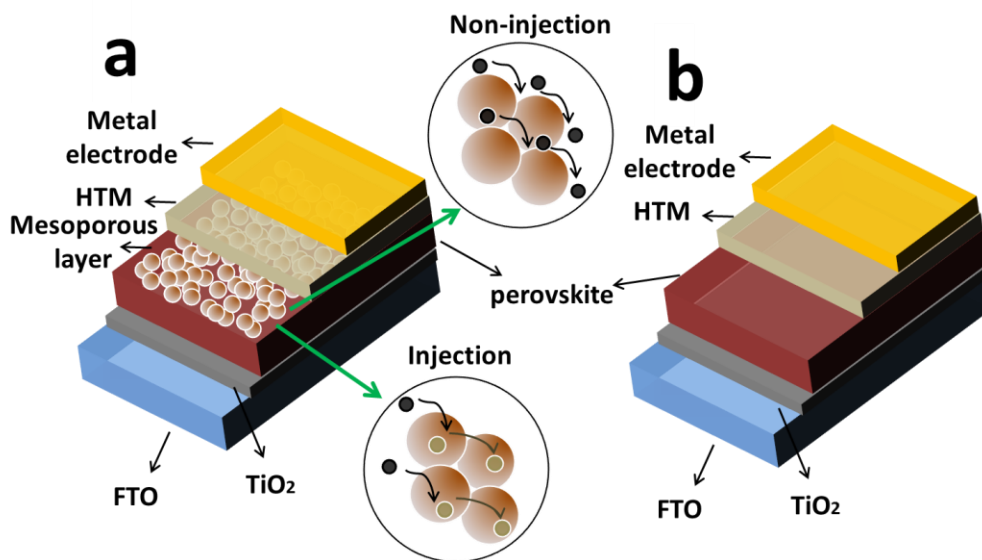


Figure 2.7 Devices structure for (a) mesoporous and (b) planar perovskite solar cell. In the inset the electron charge transport processes for injecting (e.g. TiO_2) and non-injecting (e.g. Al_2O_3) mesoporous materials are represented.

In the mesoporous TiO_2 configurations with extremely thin absorber, good carrier transport is not a basic requirement for perovskites as the performance is mainly determined by the interfacial properties. However, for thicker perovskite layers, as for meso- Al_2O_3 configuration and planar configuration, transport across the perovskite is important for device operation.³⁷ Using photoluminescence quenching experiments, electron-hole diffusion length (L_{eh}) can be extracted by modelling the photoluminescence decay curves according to a simple one-dimensional diffusion equation³². In $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), the L_{eh} obtained is about 100 nm.^{32,38} Whereas for the mixed-halide perovskite $\text{MAPbI}_{3-x}\text{Cl}_x$, the L_{eh} shows a high value exceeding 1 μm .³² The long diffusion length suggests that the generated charges can transport to charge collection layer without significant recombination loss, which makes possible the fabrication of devices with thicker active layers without compromising the collection efficiency of the generated charges. Electron beam-induced current (EBIC)

technique was further used to image cross-sections of flat cells based on MAPbI₃, which found that the diffusion length of electrons is shorter than that of holes ($L_{\text{eff}, e^-}/L_{\text{eff}, h^+} < 1$), with the latter being at least 1 μm .³⁹ This result explains why MAPbI₃ based solar cells require an electron transporting layer, but not necessarily a hole conductor.

2.4.4 Fabrication Techniques

The PSCs enjoy a versatility in fabrication techniques, which provides flexible choices of deposition methods on different substrates and for morphology control. So far, there have been four different film deposition methods reported: one-step precursor solution deposition^{19,21,35,40} (Figure 2.8a); two-step sequential deposition³⁰ (Figure 2.8b); dual-source vapor deposition²⁹ (Figure 2.8c) and vapor assisted solution process⁴¹ (Figure 2.8d).

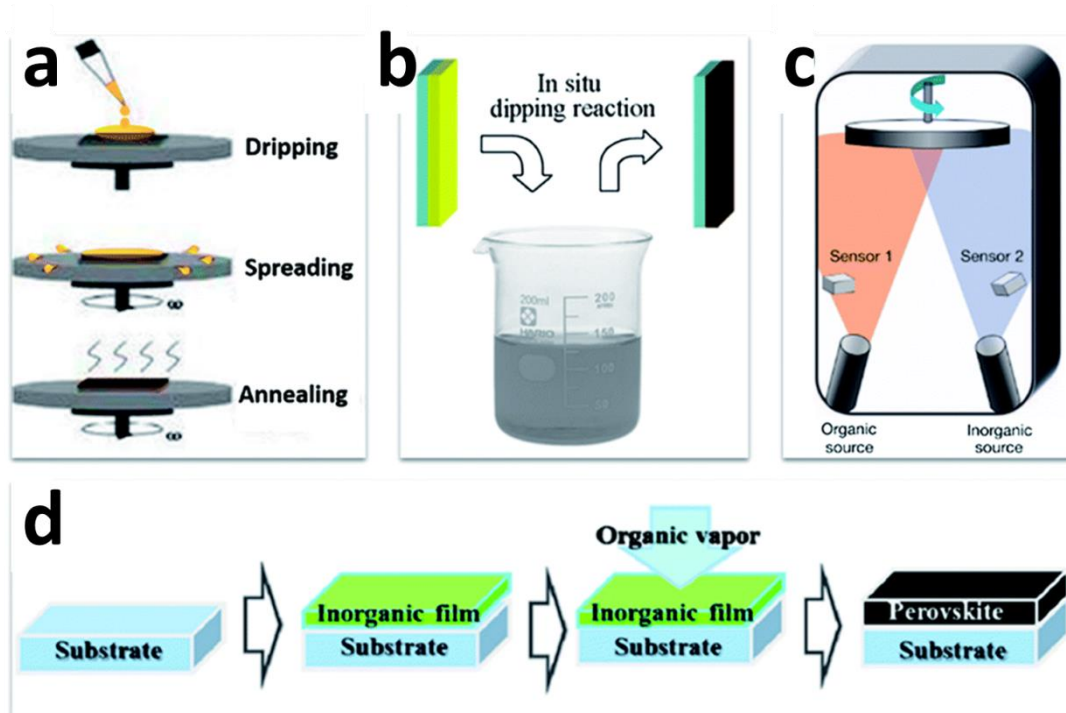


Figure 2.8 Four deposition methods for perovskite active layers. (a) One-step precursor deposition. (b) Two-step sequential deposition method. (c) Dual-source vapor deposition. (d) Vapor-assisted solution process. Figures were reprinted from ref.²³.

One-Step Precursor Deposition. Generally, the precursor solution of perovskite is prepared by mixing the powder of RAX (R: methyl, formamidine; X: I, Br) and PbX_2 (X: I, Br, Cl) at the 1 : 1 (stoichiometry) or 3 : 1 (non-stoichiometry) mole ratio in high boiling point aprotic polar solvents (DMF, DMAc, DMSO, NMP, GBL, *etc.*) at elevated temperature (e.g. 70 °C) for several hours to get a clear solution. This solution is then used for the *in situ* formation of organometal halide perovskite by spin-coating or drop-casting⁴² on a n-type contact layer, generally followed by an annealing process to complete the transformation from precursor to the perovskite crystalline film. After that a layer of HTM (e.g. spiro-OMeTAD) is deposited on top.

Sequential Deposition Method. In a typical procedure, the PbI_2 is first spin-coated from solution in DMF onto the mesoporous TiO_2 film and subsequently transformed into the perovskite by dipping into a solution of MAI in iso-propanol (IPA). The perovskite formation is instantaneous within the mesoporous host upon contacting the two components. After annealing, spiro-OMeTAD as a HTM was deposited by spin-coating on top. This method allows much better control over the perovskite morphology compared to the one-step deposition method by allowing better confinement of PbI_2 into the mesoporous nanostructure of TiO_2 .

Dual-Source Vapor Deposition. In this method, perovskite thin film is prepared under vacuum by vapor deposition. MAI and PbI_2 are deposited simultaneously with different deposition speed. It was demonstrated that vapor-deposited perovskite films were extremely uniform with crystalline platelets at the nanometer scale, which is the reason for the record efficiency of 15.4%.²⁹

Vapor-Assisted Solution Process. In this process, PbI_2 films were deposited on a compact TiO_2 layer, followed by annealing in MAI vapor at 150 °C in a N_2 atmosphere for 2 h to form the perovskite films. The perovskite film derived from this approach shows full surface coverage and uniform grain structure with grain size up to micrometers.⁴¹

2.4.5 Hole Transporting Materials (HTM) for Perovskite Solar Cells

There are some basic requirements that an ideal HTM should fulfil to work effectively in PSCs, such as a well-matched highest occupied molecular orbital (HOMO) energy level to the VB energy level of the perovskite, sufficient hole mobility, perfect thermal

and photochemical stability etc. A great number of HTMs have been studied and incorporated in PSCs, including organic and inorganic hole-conductors. Organic hole-conductors can be further divided into three categories: small molecule hole-conductors, conducting polymers and organometallic complexes.

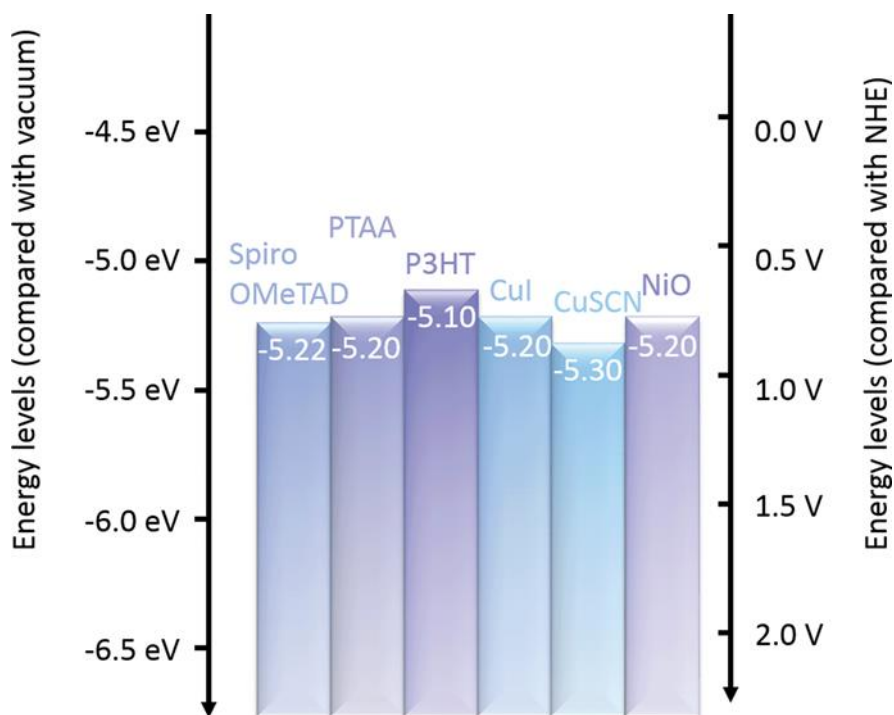


Figure 2.9 Schematic of literature values for energy level of different HTMs in solar cells. Figure was reprinted from ref.²³.

2.4.5.1 Spiro-OMeTAD

Spiro-OMeTAD as a small molecule hole-conductor has been the most prevalent used hole conducting material in PSCs. It was first developed by Bach *et al.* as HTM for dye-sensitized solar cells⁸, and was further employed in PSCs delivering improved PCEs and stability^{19,21}. Due to the relatively low hole mobility in its pristine form, additives such as lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) and

4-tert-butylpyridine (tBP) have been routinely incorporated into the spiro-OMeTAD solution to enhance the hole conductivity^{43,44}. However, the spiro-OMeTAD has a price at research scale that is more than 10 times that of gold and platinum⁴⁵, limiting the industrialization potential of PSCs based on this material. Furthermore, the hygroscopic nature of additives makes perovskite film sensitive to the moisture from environment⁴⁶. So far, the record PCE still comes from devices employing spiro-OMeTAD as HTM.

2.4.5.2 Conducting Polymers

Conducting polymers constitute a major class of organic HTMs in PSCs, such as poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(terephthalic anhydride) (PTAA)^{47–49} and poly(3,4-ethylenedioxythiophene) (PEDOT)⁴⁶, etc. Among them, P3HT as a polythiophene-based conducting polymer has been a model polymeric HTM being intensively studied, exhibiting agreeable results with the highest efficiency of over 10%.^{47,50–59} An interesting study that worth mentioning here is conducted by Johansson *et al.*, who carried out transient photovoltage decay measurements to compare the electron lifetimes of devices based on P3HT and spiro-OMeTAD. It is found that the recombination rate in device with P3HT is more than 10 times faster as compared to spiro-OMeTAD, presumably due to the closer contact between the flat molecular structure of P3HT and the perovskite surface, which results in the lower photovoltaic performance.⁵⁹ This result highlights the necessity of avoiding close contact between the HTM and the perovskite with proper molecular structure design.

Another important polythiophene derivative conductive polymer, PEDOT (Figure 2.10a), was invented by scientists at the Bayer AG research laboratories in 1980s.^{60–62}

This insoluble polymer exhibited an excellent conductivity up to $300\text{--}500\text{ S cm}^{-1}$.^{60–67} The electronic bandgap of neutral PEDOT, defined as the on-set of the $\pi\text{--}\pi^*$ absorption, is exhibited to be 1.6–1.7 eV, which makes the material deep blue in color.⁶⁶ Furthermore, its solubility issue can be solved by using a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDOT:PSS (Figure 2.10b).⁶⁵ Because of its high conductivity, high visible light transmissivity, and excellent stability, PEDOT is a promising material for antistatic, electronic, and optoelectronic applications.^{68–71} The application of PEDOT as counter electrode for DSSCs has been under intensive study realizing PCE over 8%.^{72–78} However, applying PEDOT in ‘regular’ structured PSCs is not a straightforward task, as the commonly used water solution dissolves perovskite immediately after deposition. Chapter 4 demonstrates a successful incorporation of a toluene base PEDOT ink in PSCs, achieving devices with high PCE up to 14.5%. The hysteresis and stability issues of as fabricated devices were studied extensively.

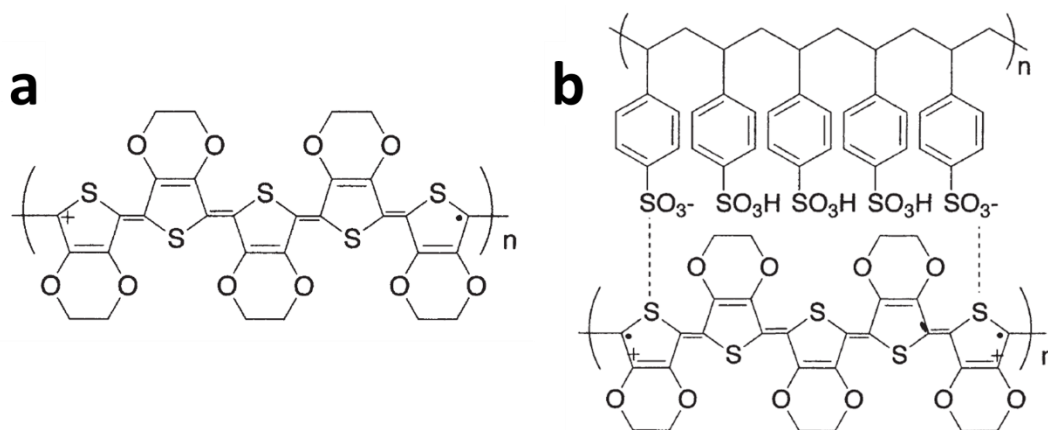


Figure 2.10 Chemical structures of (a) PEDOT and (b) PEDOT-PSS. Figures were reprinted from ref.⁷⁸.

2.4.5.3 Inorganic HTM

Inorganic p-type semiconductors appear to be another type of promising HTMs candidates for PSCs due to their high hole mobility, low production costs and good stability. Kamat *et al.* reported the first example using inorganic p-type hole-conductor copper iodide (CuI) in mesoscopic PSCs.⁴⁵ CuI-based devices exhibit average efficiencies of 3.7% with the highest value being 6% under 100 mW cm⁻² illumination (AM 1.5G). The V_{oc} (~0.50 V) is lower as compared to devices using spiro-OMeTAD (0.78 V), attributed to faster charge recombination rates in CuI-based devices as determined from the electrochemical impedance spectroscopy (EIS). EIS also shows that the electrical conductivity of CuI is two orders of magnitude higher than spiro-OMeTAD. Later, Spicca *et al.* incorporated CuI in planar structured PSCs, achieving a maximum conversion efficiency of 7.5% with an average efficiency of $5.8 \pm 0.8\%$.⁷⁹ They used PL quenching data to demonstrate that hole extraction at the perovskite/CuI interface is faster than at the perovskite/spiro-OMeTAD interface. And faster polarization relaxation was observed using EIS and open-circuit voltage decays (OCVDs) for the perovskite/CuI system compared with the perovskite/spiro-OMeTAD system. They believe these results demonstrate that a smaller local electric field generated in the perovskite/CuI system, leading to the diminished hysteresis in $J-V$ measurements.⁷⁹

Another copper-based inorganic p-type hole-conductor, copper thiocyanate (CuSCN), has also been actively studied in PSCs.⁸⁰⁻⁸⁷ CuSCN is a molecular, metal pseudohalide of singly-ionized copper, the properties of which have been studied since the first half of the twentieth century.⁸⁸ Nowadays, it is readily available from commercial sources while it is inexpensive and can be processed at low-temperatures using solution-based techniques.⁸⁹ Moreover, CuSCN demonstrates excellent thermal stability since decomposition of the material into copper sulphide can be only

observed at temperatures above 300 °C.⁹⁰ The large bandgap (>3.5 eV) of CuSCN greatly exceed photon energies corresponding to the visible spectral region, indicating a highly optically transparency of the material.⁹¹ Ito *et al.* first used doctor-blading technique to deposit CuSCN on top the mesoporous TiO₂/MAPbI₃, achieving device with an efficiency of only 4.85%, J_{sc} of 14.5 mA cm⁻², V_{oc} of 0.63 and FF of 0.53, respectively.⁸⁶ With further maximizing the light harvesting of MAPbI₃ layer with sequential deposition method, Ito and Nazeeruddin *et al.* achieved maximum efficiency of 12.4% based on HTM CuSCN with ~600 nm capping layer.⁸⁵ Recent progress comes from the incorporation of CuSCN HTM in inverted planar PSCs realizing PCE over 16%.^{82,83}

Although high performance from PSCs based on CuSCN has been achieved, few of the reports show an elaborate study on the stability of their devices. Specifically, the previously reported stability studies on CuSCN based PSCs were all conducted in ambient environment at room temperature, without any investigation on thermal stability. Furthermore, the stability test were either too short (<50 hours)^{83,86}, or failed to mention any detailed information about testing conditions⁸². Chapter 5 demonstrates a spray-coating method to deposit a fairly smooth layer of CuSCN on top of perovskite, realizing photovoltaic devices with PCE up to 13.3%. The thermal stability of the as fabricated devices was extensively studied, which revealed an accelerated perovskite degradation induced by CuSCN. The mechanism of the expedited degradation is presumed to be a reversible reaction between perovskite and CuSCN. It is further demonstrated that such degradation can be alleviated by simply sealing the device with a PMMA layer, realizing super stable devices that survive 85 °C thermal stressing over 1000 hours.

Chapter 6 demonstrates a successful combination of the two inorganic p-type

materials described above. By adding small amount of CuI in CuSCN (<5 wt. %), film with higher conductivity and better coverage can be obtained, leading to an increased PCE up to 14.4%. It is proved that both of the charge extraction effectiveness and transport are improved with this simple modification.

2.4.6 Stability of Perovskite Solar Cells

In order to get solar cells function under real-world atmospheric conditions, they must not physically degrade upon exposure to atmospheric stresses, such as oxygen, moisture and heat. Among them, moisture is the major factor that makes MAPbI₃ perovskite extremely unstable. In fact, the ionic solid readily decomposes to PbI₂ upon exposure to most polar solvents²⁰, limiting the choice of solvents used to deposit layers on top of the perovskite, such as the solution processed HTMs or electron acceptors⁹².

The work by several groups has elucidated the mechanism of MAPbI₃ perovskite degradation in the presence of water. Kamat *et al.* related the drop in photovoltaic performance of PSCs aged in humid conditions to severe changes in the perovskite absorption spectra at ground state and excited state, as well as changes in the microstructure and the XRD patterns.⁹³ Similar work by Kelly *et al.* reveals that the rate of degradation was strongly related to the humidity level as well as the property of material placed on top of the perovskite, where neat P3HT, with improved hydrophobicity, offered better protection comparing to spiro-OMeTAD and PTAA.⁹⁴ Both groups report that the degradation in ambient humidity levels (approximately 50% relative humidity at 20 °C) took place very slowly, whereas exposure to >80% relative

humidity resulted in extremely rapid (<3 days) degradation. Their XRD data show no evidence for the formation of PbI_2 , but the dihydrate phase $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$, which was first isolated and characterized by Knop *et al.*⁹⁵. More recently, Barnes *et al.* performed careful ellipsometry and XRD studies to conclusively show that exposure to moisture in fact results primarily in the formation of a monohydrate phase, which is in equilibrium with a small amount of the dihydrate phase, depending on the time and intensity of moisture exposure.⁹⁶ Their proposed hydration scheme is depicted graphically in Figure 2.11, while the reaction mechanism is given as

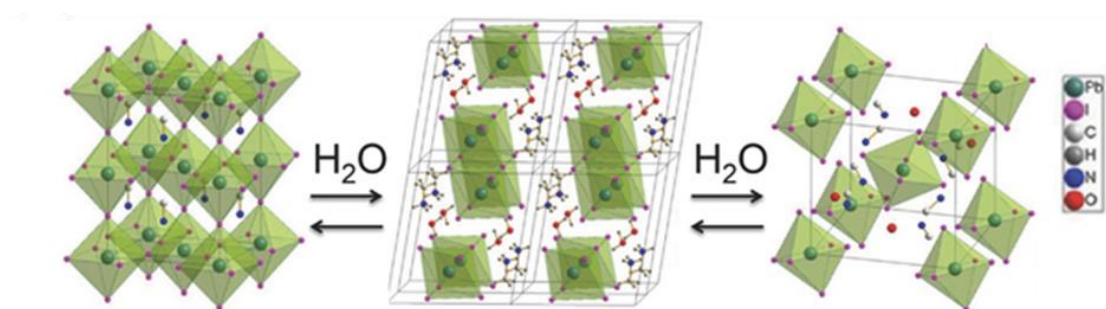
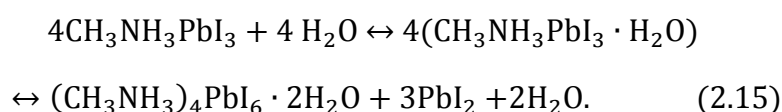


Figure 2.11 Depiction of the two hydrated structures of the MAPbI_3 perovskite proposed by Barnes *et al.*, where the MAPbI_3 can be hydrated first to the monohydrate structure and then to the dihydrate along with the formation of PbI_2 (Equation 2.15). Figure was reprinted from ref.⁹².

A crucial observation is that the hydration reaction was reversible when the films were subsequently exposed to dry air. However, as the hydration progresses and more of the dihydrate phase are produced, the associated formation and phase segregation of PbI_2 crystals may limit the reversibility of the hydration reaction in the long term.⁹²

Furthermore, as has been demonstrated by our group, the combination of moisture and heat results in an extremely rapid (<24 h) degradation.^{46,97} This degradation process results in the rapid formation of PbI₂ and a loss of the organic component from the crystal structure, as proved by the XRD patterns and absorption spectra of degraded films. However, such degradations can only be observed in the presence of moisture, and can be delayed by the use of protective barriers,⁹⁷ suggesting that it must be related to the previously observed hydration reactions. Therefore, the degradation of perovskite with CuSCN coverage under elevated temperature is governed by a completely different mechanism, which can take place even in an inert atmosphere without moisture. The details will be discussed in chapter 5.

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Chapter 3. Experimental Methods

3.1 Device Assembly

3.1.1 FTO Substrate Preparation

Fluorine-doped tin oxide (FTO) substrates ($15 \Omega\text{cm}^{-1}$, Pilkington) were etched with zinc powder and HCl (2M in de-ionized water). The patterned substrates were then consecutively cleaned with Hellmax cuvette detergent (2v% in de-ionized water), de-ionized water, acetone and ethanol, followed by drying with nitrogen air gun. Finally, the organic residues on substrates were removed with 10 min oxygen plasma treatment.

3.1.2 TiO₂ Compact Layer Deposition

TiO₂ compact layer was then deposited on substrates with the method as previously reported by Ball *et al*¹. Briefly, an acidic solution of titanium isopropoxide was prepared by mixing 350 μl titanium isopropoxide (98%, Sigma-Aldrich) and 35 μl 2M HCl in 5 ml anhydrous ethanol (99.5%, Sigma-Aldrich). Then the mixed solution was

spin-coated on cleaned substrates at 2000 rpm for 45 s, followed by 500 °C sintering for 30 min to form n-type electron selective TiO₂ compact layer.

3.1.3 Al₂O₃ Mesoporous Scaffold Deposition

An Al₂O₃ mesoporous layer was deposited by spin-coating (2000 rpm, 45 s) a colloidal dispersion of alumina (Al₂O₃) nanoparticles (Sigma-Aldrich) on the top of TiO₂ compact layer. The substrate was subsequently dried at 150 °C for 15 min to drive out the solvent. To control the thickness of deposited film, Al₂O₃ nanoparticles dispersion was further dispersed in isopropanol (IPA) with different volume ratio before spin-coating (Table 3.1).

Table 3.1 Correlation between the volume ratio (original Al₂O₃ colloidal dispersion: IPA) and the thickness of deposited mesoporous film.

Volume ratio	1:2	1:4	1:8	1:12
Thickness(nm)	~300	~150	~120	~80

3.1.4 CH₃NH₃PbI₃ Perovskite Layer Preparation

3.1.4.1 Synthesis of Precursor

The precursor was prepared by mixing methylammonium iodide (MAI, Dyesol) and lead chloride (PbCl₂, 98%, Sigma-Aldrich) with 3:1 molar ratio in dimethylformamide (DMF, 99.8%, Sigma-Aldrich) to reach a concentration of 35 wt%.² Typically, 1.06g MAI is first dissolved in 3 ml DMF, achieving a clear solution after shaking for 30s. Then the MAI solution was added with 0.61g PbCl₂, followed by stirring for 6 hours

to reach a light yellow clear precursor solution. All the above steps were operated in nitrogen (N_2) filled glovebox. For every 1 ml precursor solution, 3 μ l hypophosphorous acid (HPA) was added within 30 min before spin coating.³

3.1.4.2 Perovskite Deposition in Meso-structured Device

The whole perovskite film deposition and annealing process was operated in N_2 filled glovebox. All the perovskite solar cells fabricated in this thesis were meso-structured devices. Substrates with mesoporous Al_2O_3 scaffold were transferred into the glovebox and preheated at 70 °C with a hotplate. The $CH_3NH_3PbI_3$ precursor solution was then spin-coated on the substrates at 2000 rpm for 45 s. After spin-coating, the substrates were returned to the 70 °C hotplate until the films turn to a reddish colour. The perovskite film was then successively annealed at 100 °C for 90 min and 120 °C for 15 min on a hot plate.¹

3.1.4.3 Perovskite Deposition in Planar-structured Samples

Here, the perovskite films were deposited directly on cleaned FTO or glass substrates. The substrates were cleaned with O_2 plasma treatment for 5 min before being transferred to glovebox. After pre-heating the substrates at 70 °C, the precursor was spin-coated at 2000 rpm for 45 s, followed by heating substrates at 70 °C again until the film turns red. Perovskite films were then successively annealed at 90 °C for 150 min and 120 °C for 15 min.⁴

3.1.5 Hole Transporting Layer (HTL) Deposition

3.1.5.1 Spiro-OMeTAD Deposition

2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-Spirobifluorene (Spiro-OMeTAD, ordered from Lumtech) was dissolved in anhydrous chlorobenzene (CB) to reach a concentration of 8.5 w/v %. The solution was then added with 80mM tert-butylpyridine (*t*BP) and 25mM lithium bis(trifluoromethanesulphonyl)imide (Li-TFSI) within 1 hour before use. The HTL was deposited by spin-coating at 1500 rpm for 45 s in glovebox. Samples were then stored in desiccator for 12 hours to oxidize Spiro-OMeTAD before deposition of metal electrode.⁵

3.1.5.2 PEDOT Deposition

Toluene suspension of Poly(3,4-ethylenedioxythiophene) (PEDOT, Clevios NKB 717, Heraeus Precious Metals) was sonicated for 2 min and then filtered with a 0.45 μ m filter before use. When the perovskite has been sintered for 90 min, iodopentafluorobenzene (IPFB) was first spin-coated on perovskite surface at 2000 rpm for 45 s. Then the solvent was spin-coated on the substrate at 1500 rpm for 45 s, followed by 15 min sintering at 120 °C. Therefore, the perovskite layer for PEDOT devices had been sintered for 105 min in total, same as that of the Spiro-OMeTAD devices.⁶ All the processes were conducted in glovebox.

3.1.5.3 CuSCN Deposition

To prepare the solution, 240 mg of Copper(I) thiocyanate (99%, Sigma Aldrich) was dissolved in 30 ml of dipropyl sulfide (97%, Sigma Aldrich) to reach a concentration of 8mg/ml. A clear solution was obtained after stirring for 48 hours. Substrates were placed on 85 °C hotplate while spray-coating the solution at roughly 2ml/min (Figure 3.1).⁷

3.1.6 Metal electrode deposition

Metal electrode was deposited by thermal evaporation of silver for a 120nm film or gold for an 80nm film through a shadow mask. In this thesis, gold is preferred for device reproducibility and stability concern.

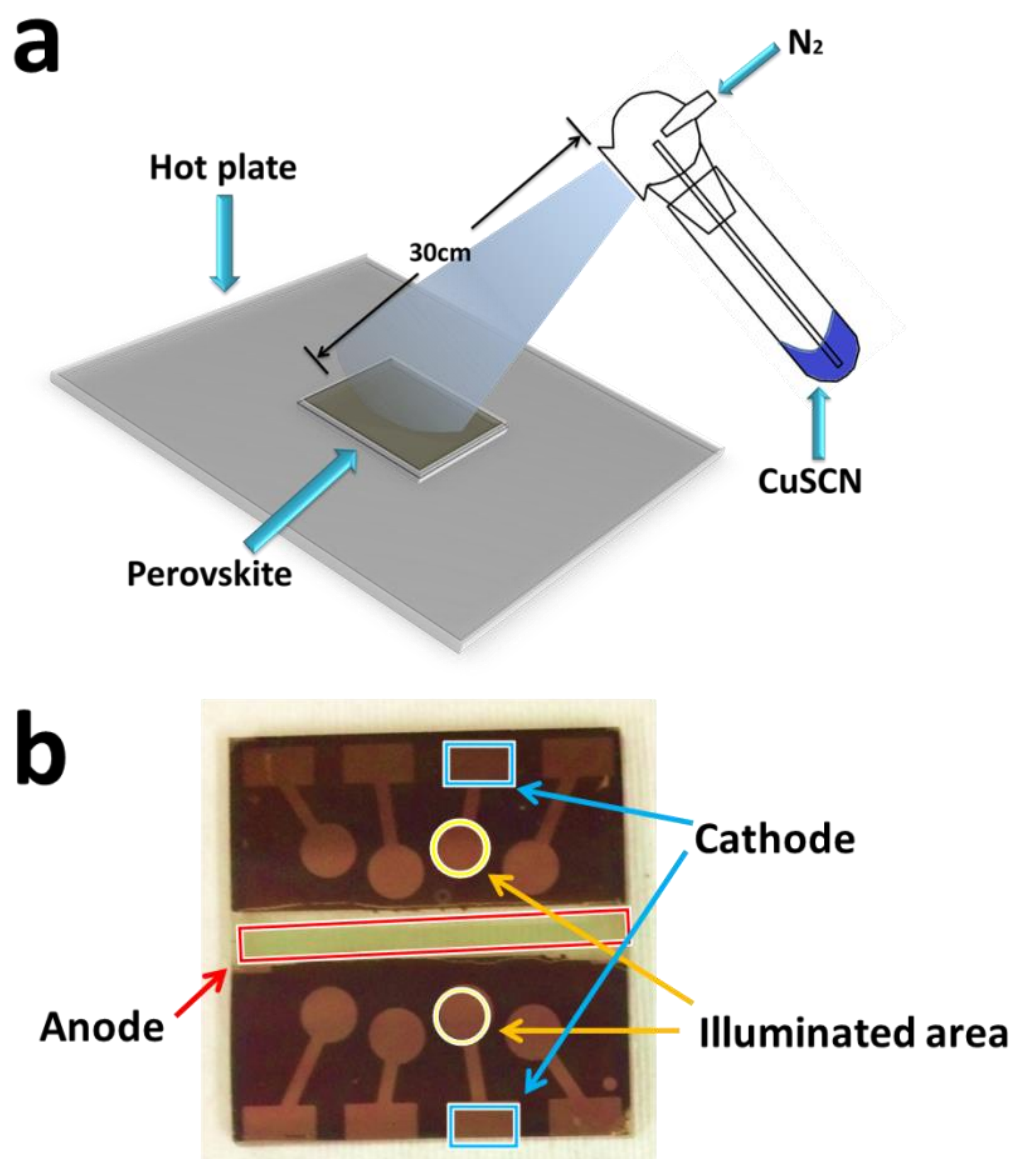


Figure 3.1 (a) Spray coating $CuSCN$ on perovskite surface. (b) Photo of fabricated solar cell. The illuminated area is 0.0625 cm^2 .

3.2 Characterization Techniques

3.2.1 Crystallographic Analysis by X-ray Diffraction (XRD)

XRD pattern was obtained with a Panalytical X'Pert Pro X-ray diffractometer, which employs a vertical goniometer with maximum usable range of $-40^{\circ} < 2\theta < 220^{\circ}$. The typical measuring parameters set are 0.0167° for step size and 80.010 s per step.

3.2.2 Microstructural Analysis by Scanning Electron Microscopy (SEM)

In order to increase the surface conductivity, samples were coated with 5 nm platinum (Pt) and stick with small piece of carbon tape at the edge (not covering the surface). SEM images were taken with Hitachi S-4300, which uses an electron beam accelerated at 0.5 kV to 30 kV enabling operation at a fixed filament current of 10 μ A. Acceleration voltage of 3 kV to 5 kV was preferred for images collection in this thesis.

3.2.3 UV-vis Absorption Measurement

Absorbance spectra were measured with a lambda 1050 UV/VIS/NIR Spectrometer (PerkinElmer). The samples were prepared by depositing films directly on glass substrates.

3.2.4 Photoluminescence (PL)

Photoluminescence (PL) measurement was taken using a time-correlated single photon counting (TCSPC) setup (FluoTime 300, PicoQuant GmbH). Samples were

photoexcited using a 510 nm laser head (LDH-P-C-510, PicoQuant GmbH) pulsed at 40 MHz, with a pulse duration of 117 ps and fluence of $\sim 0.1 \text{ nJ/cm}^2$.⁸

3.2.5 Electronic Impedance Spectroscopy (EIS)

Electrochemical impedance (EIS) measurements were performed under open-circuit conditions by illuminating the solar cells using a powerful LED array (maximum output power of 306 lumens at 700 mA driving current), emitting light at 627 nm. Light intensities were adjusted by controlling the diode's current by a LED driver; the LED was previously calibrated employing a Si reference photodiode. The illuminated area of the solar cells was set at 0.0625 cm^2 , using a mask. The spectra were recorded by varying the frequency range from 100 KHz to 40 mHz (amplitude of voltage perturbation: 15 mV RMS) using an electrochemical working station (Autolab PGSTAT302N, Ecochemie) and its built-in frequency response analyzer (FRA2). The recorded spectra were fitted using the NOVA software.⁶

3.2.6 Conductivity Measurements

Conductivity measurement was operated by four probe method with gold probe. In this configuration, two thin (200 μm) straight electrodes were spaced evenly between two larger (1 mm) straight electrodes at 6 mm apart, and with 1 cm channel width (perpendicular to electric field). The inner electrodes, with 2mm spacing, were placed only within the bottom 2mm of the channel. Potential was applied to the outer electrodes and the current measured. The potential drop across the inner electrodes was then measured and this was used to establish the contact resistance.⁹ Samples were deposited films on glass substrates, followed by evaporating Au electrode pattern through a shadow mask.

3.2.7 Solar Cell Performance Characterization

Current-voltage (JV) characteristics was measured under simulated AM 1.5 sunlight (ABET Technologies Sun 2000), calibrated to give 100 mW cm^{-2} using an NREL-calibrated KG5-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. The J–V curves were recorded with a Keithley 2400. The active area of the solar cells was defined with a metal aperture mask of about 0.0625 cm^2 . During the measurement, the voltage was swept with a 0.03 V interval and a 0.01 s delay at each voltage.

3.3 References

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Chapter 4. Employing PEDOT as the p-type Charge Collection Layer in Regular Perovskite Solar Cells

4.1 Contexts

Organic-inorganic halide perovskite solar cells have recently emerged as high performance photovoltaic devices with low cost, promising for affordable large-scale energy production, with laboratory cells already exceeding 22% power conversion efficiency (PCE). To date, a relatively expensive organic hole-conducting molecule with low conductivity, namely Spiro-OMeTAD (2,2',7,7'-tetrakis (N,N-di-p-methoxyphenyl-amine) 9,9'- Spirobifluorene), is employed widely to achieve highly efficient perovskite solar cells. However, this material suffers from high cost and hygroscopic feature, leading to worsened stability of perovskite devices. In this chapter, perovskite solar cells were fabricated by replacing Spiro-OMeTAD with much cheaper and highly conductive Poly(3,4-ethylenedioxythiophene) (PEDOT), casted from a toluene based ink, achieving PCE of up to 14.5%. However, the stabilized power output of the PEDOT based devices is only 6.6%, in comparison

to 9.4% for the Spiro-OMeTAD based cells. The accelerated recombination is deduced to be the cause for this lower stabilized power. The entirety of the materials employed in the perovskite solar cell are now available at commodity scale and extremely inexpensive.

4.2 Introduction

The application of photovoltaic (PV) devices is one of the most promising solutions for satisfying the global energy demand¹. Recently, organic-inorganic metal halide perovskite ($\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}^-, \text{Br}^-, \text{Cl}^-$)) have emerged as a promising photovoltaic material, with simple fabrication routes and high power conversion efficiency, with small area lab cells certified up to $\sim 22\%$ ². These perovskites were first employed in liquid dye solar cells employing iodide/triiodide redox couple, but this only delivered 3.5% efficient cells and degraded within a few minutes³. The first big breakthrough in device architecture was in-part a result of employing the organic hole-conductor 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenyl-amine) 9,9'- Spirobifluorene (Spiro-OMeTAD), delivering solar cell efficiencies of around 10%^{4,5}. However, the Spiro-OMeTAD has a price at research scale that is more than 10 times that of gold and platinum⁶. It is likely that this would come down considerably with increasing scale. However, the multistep synthesis and time consuming purification (sublimation) imply that it would be a significant component of the cost of the first commercial products for some time. There is therefore good motivation to develop perovskite cells based on already scaled “commodity” hole-conductors such as CuSCN ⁷, CuI ⁶, polyaniline or Poly(3,4-ethylenedioxythiophene) (PEDOT) amongst others. PEDOT specifically is an inexpensive conducting polymer with high conductivity and has long been applied in both organic photovoltaics and light emitting diodes as a charge collection or charge injection layer^{8–11}. However, PEDOT is typically heavily doped

by being stabilized with polystyrene sulfonate (PSS) and processed into an aqueous dispersion. Since the organic-inorganic metal halide perovskites are sensitive to moisture, this makes processing of PEDOT:PSS directly on top of the perovskite film challenging. Hence, although there are many reports of PEDOT:PSS employed in a device structure where the perovskite is processed on top of the cathode (and PEDOT:PSS layer on top of FTO or ITO transparent conductive glass)¹², there are no reports yet where PEDOT is processed on top of the perovskite in a “regular” device architecture. Here, a specifically formulated PEDOT ink (Clevios NKB 717, Heraeus Precious Metals), which is a dispersion of poly(3,4-ethylenedioxythiophene) and a sulfonated block-co-polymer dispersed in toluene, is employed as a hole transporting material (HTM). Power conversion efficiency of up to 14.5%, which is comparable to that of Spiro-OMeTAD based cells, is achieved employing this much lower cost hole-transporter. However, the steady-state stabilized power output is much lower for the PEDOT cells than for the Spiro-OMeTAD cells. The origin of this reduced stabilized power output is investigated by impedance spectroscopy. This work identifies future development directions for enhancing the perovskite solar cells employing PEDOT.

4.3 Method

4.3.1 Device Fabrication

The device fabrication process has been described in detail in section 3.1. All the solar cells in this chapter are meso-structured devices, with an optimized mesoporous Al₂O₃ scaffold thickness of ~ 250nm.

4.3.2 Measurement and Characterization

Characterization methods used in this chapter include: current-voltage characterization, photoluminescence (PL) measurement, UV-vis absorption measurement, conductivity measurement, and electrochemical impedance (EIS) measurement. The details of these characterization techniques have been described in section 3.2.

4.4 Thin Film Characterization

To determine the suitability of PEDOT as a HTM processed on top of the perovskite layer in hybrid perovskite solar cells, the optical and photo-physical properties of Spiro-OMeTAD and PEDOT films isolated and in contact with perovskite films were first investigated. The UV-vis absorption of the two hole-transporting materials is showed in Figure 4.1 a. The spectra match those previously reported for the two materials^{8,14}. Spiro-OMeTAD films exhibit a strong absorption in ultraviolet region (<400nm), along with weaker absorption bands at 500 and 670 nm associated with the oxidized Spiro-OMeTAD species. In contrast, the absorbance of PEDOT films is very low in the UV and visible region, while slightly higher than that of Spiro-OMeTAD film in the IR region. Since solid state devices with metal back electrodes benefit from a “second pass” of light reflected from the back electrode, it is apparent that PEDOT will cause less parasitic absorption losses during this second pass than would Spiro-OMeTAD, maximizing the obtainable photocurrent. For devices processed on metal foils, this may be even more important since in this case, the light is incident from the top and absorption losses in the visible region by HTM will be of critical importance.

To function effectively as a hole selective contact in photovoltaic devices, PEDOT must be capable of effectively extracting holes from the perovskite absorber layer. Stranks *et al.* have previously demonstrated that photoluminescence (PL) spectroscopy can be used to monitor charge extraction at the electron and hole selective contacts, where the rate and degree of PL quenching gives a good indication of the charge extraction efficiency¹⁵. Figure 4.1 b & c show the time-resolved and steady-state photoluminescence spectra of perovskite films coated with PMMA, PEDOT and Spiro-OMeTAD. Both the films coated with Spiro-OMeTAD and PEDOT show similar levels of PL quenching with similar decay rates. Therefore, it is reasonable to infer that the hole-transfer from the perovskite films to PEDOT is similarly good as to Spiro-OMeTAD.

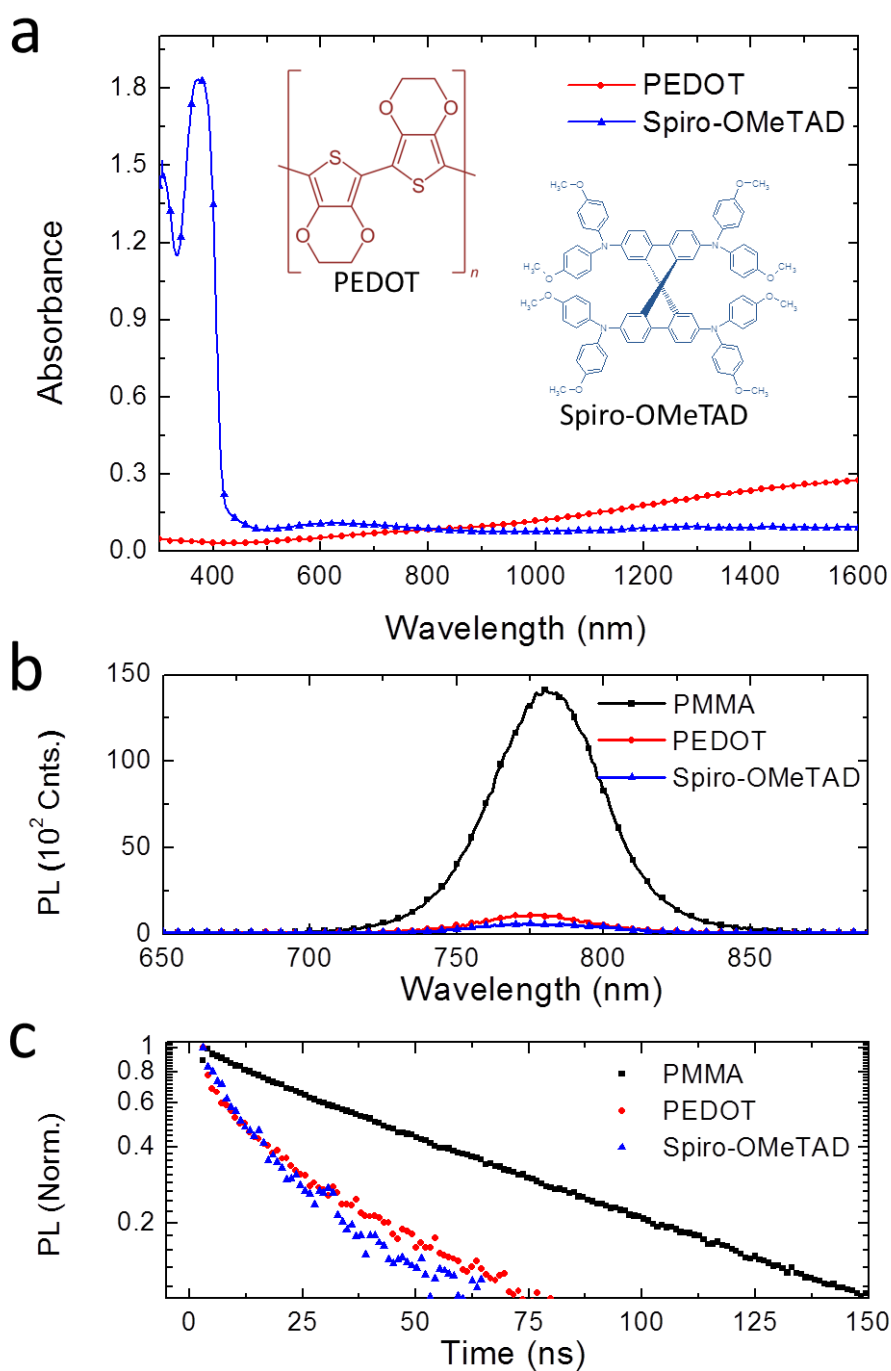


Figure 4.1 (a) Absorbance spectra of ~230 nm thick PEDOT films (red circles) and ~280 nm thick Spiro-OMeTAD films doped with Li-TFSI and (blue triangles) deposited on glass. (b) Steady-state PL spectra and (c) time-resolved PL decay excited at 507 nm of perovskite films coated with PMMA (black squares), PEDOT (red circles), and Spiro-OMeTAD (blue triangles), respectively.

Once extracted from the perovskite absorber layer, the holes must be effectively transported to the metal cathode to contribute to photocurrent in working solar cells. As a result, the conductivity of the HTM layer is directly related to the series resistance and can limit the fill factor of the devices, such that substantial conductivities are required for high performance devices^{14,16}. However, there is a limit to the required conductivity until there is no further benefit on reduced series resistance. On the other hand, if the conductivity is too high, there will be a lower shunt resistance in any instance where the HTM makes contact to the n-type collection layer through pinholes in the perovskite layer, and in addition, the recombination rate (or velocity) at the perovskite HTM interface is likely to increase with increasing p-dopant hole-density. A four-probe method is employed to measure the conductivity of the different HTM. The average conductivity of Spiro-OMeTAD film is $(2.7 \pm 0.5) \times 10^{-4}$ S/cm, whereas it is 3 orders of magnitude higher at $(2.7 \pm 0.3) \times 10^{-1}$ S/cm for PEDOT. This implies that the series resistance of the devices with PEDOT will be minimized. However, the high conductivity may induce some unfavorable recombination losses.

4.5 Solar Cell Performance Optimization

4.5.1 Device Structure

To fully assess the PEDOT material, perovskite solar cells were fabricated similar to the configuration as reported by Ball *et al.*¹⁷ Figure 4.2 a & b show schematics illustrating the basic device configuration and their respective energy levels. Figure 4.2 c & d show SEM cross-section images of the as fabricated solar cells with PEDOT and Spiro-OMeTAD as the HTMs. For the optimized devices in this study, the thickness of the mesoporous Al₂O₃ layer is ~250nm, with a perovskite capping layer

of $\sim 300\text{nm}$. The thickness of Spiro-OMeTAD is around 350nm , while the PEDOT hole-transporter layer is about 200nm . The difference in layer thickness is due to the processability (viscosity, solids content) of the solutions /dispersions.

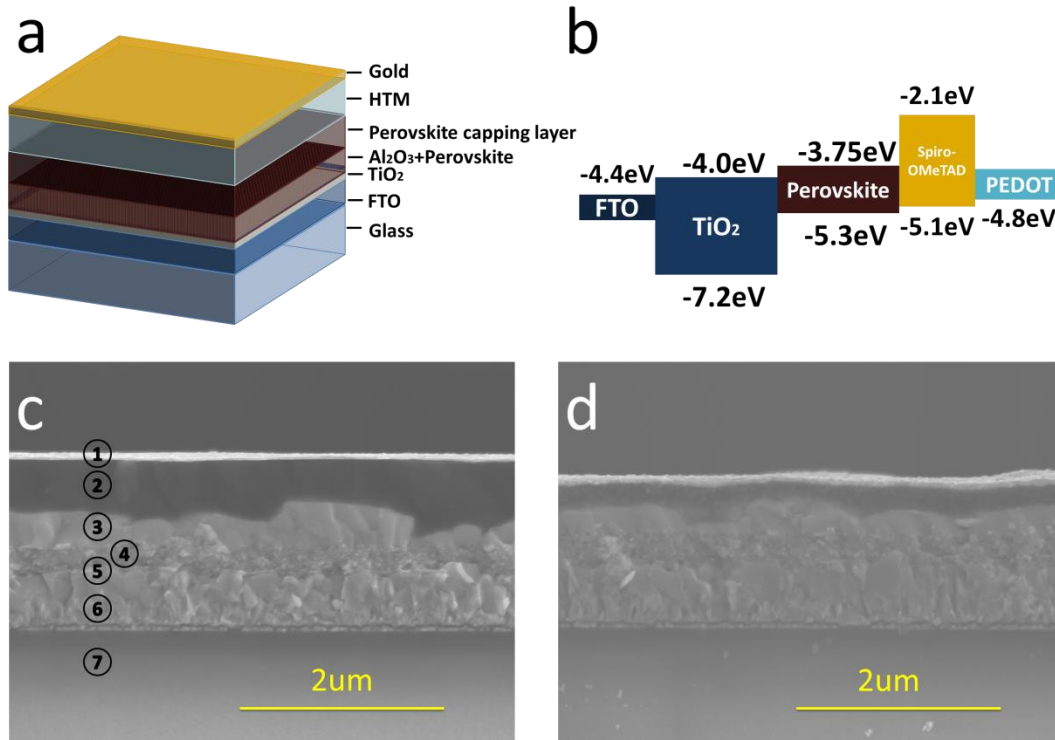


Figure 4.2 (a) Device schematic. (b) Approximate energy band diagram of the fabricated structure taken from references^{12,18}. (c)(d) Cross-sectional SEM images of photovoltaic device with (c) Spiro-OMeTAD and (d) PEDOT as the HTM. The structure from top to bottom are ① gold, ② HTM, ③ perovskite, ④ Al_2O_3 +perovskite, ⑤ TiO_2 compact layer, ⑥ FTO, and ⑦ glass.

4.5.2 Optimization of Solar Cell Performance

In order to optimize the solar cell performance, different interlayers were inserted between perovskite and PEDOT first, including Poly (3-hexylthiophene-2,5-diyl)

(P3HT) and Poly [2,6- (4,4-bis- (2-ethylhexyl) -4*H*-cyclopenta [2,1-*b*;3,4-*b'*]dithiophene) -*alt*-4,7 (2,1,3-benzothiadiazole)] (PCPDTBT). Theoretically, wide band gap polymers with lower conductivity than PEDOT should be capable of decreasing the recombination rate at the HTM side, which increase the charge collection effectiveness and open-circuit voltage.¹⁹ The parameters for the best cell of each configuration are showed in Table 4.1.

Table 4.1 Solar cell performance parameters of the best cell from different configuration.

Structures	J_{sc} (mA/cm ²)	PCE (%)	V_{oc} (V)	FF
PEDOT	20.3	11.4	0.86	0.65
5mg/ml PCPDTBT+PEDOT	19.5	10.1	0.85	0.61
15mg/ml PCPDTBT+PEDOT	19.6	10.9	0.91	0.61
5mg/ml P3HT+PEDOT	16.3	6.0	0.84	0.44
15mg/ml P3HT+PEDOT	20.7	10.6	0.89	0.58

Unfortunately, no clear trend can be observed from Table 4.1 about the influence of using P3HT and PCPDBT as interlayer between perovskite and PEDOT HTM. Thickness of P3HT and PCPDTBT layer was then checked by SEM (shown in Figure 4.3). However, the interlayer between perovskite and HTM cannot be detected clearly from the cross-sectional pictures. The thickness of the hole-transporting layer doesn't change observably with the insert of organic polymer. It might be possible that the

polymer doesn't stick well enough to the perovskite surface, and was subsequently washed out by toluene when spin-coating PEDOT. Or the concentration of the polymer solution might not be high enough to form a substantial layer.

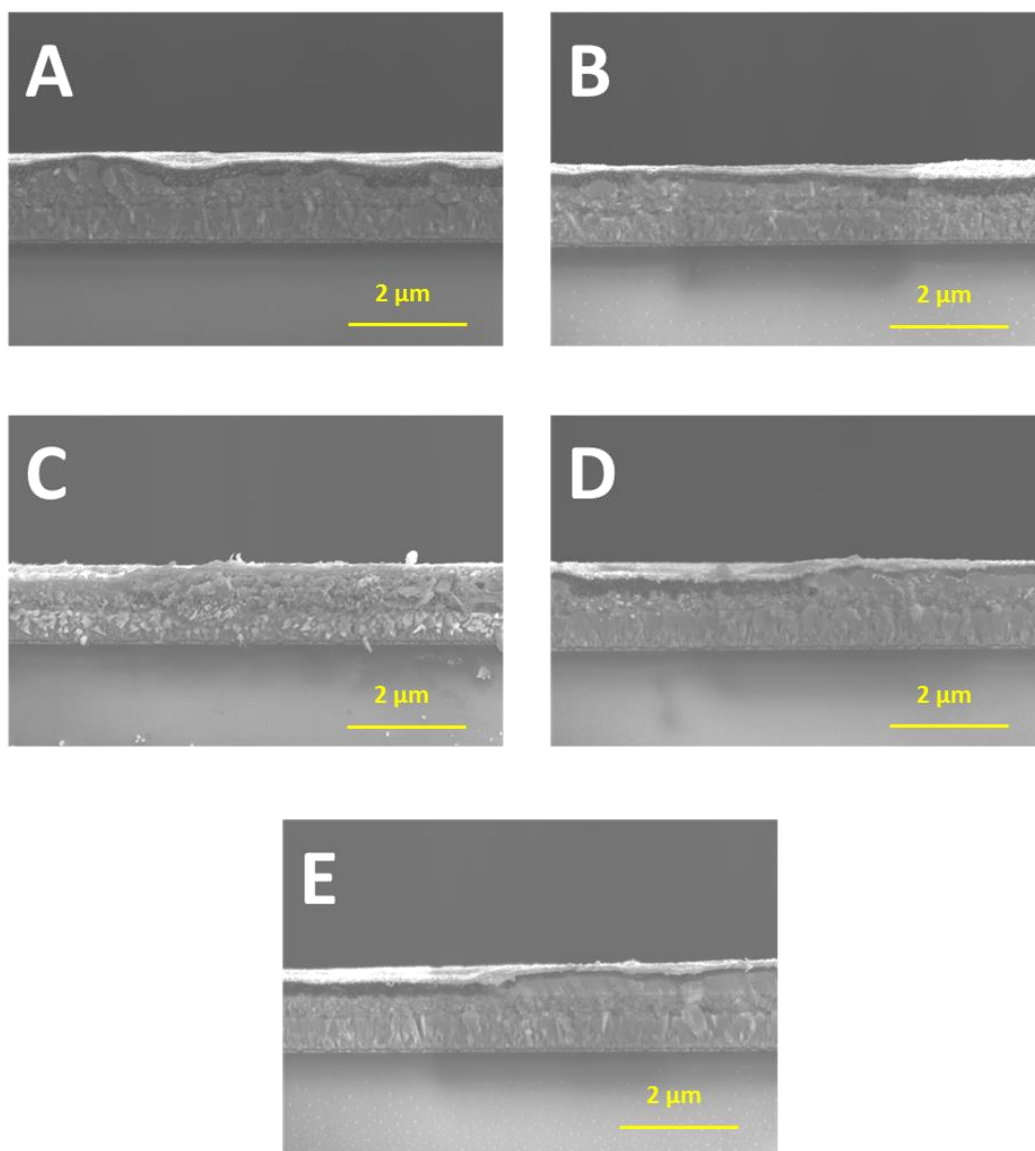


Figure 4.3 Cross-sectional SEM images of photovoltaic device Glass/FTO/C-TiO₂/Al₂O₃-MAPbI_{3-x}Cl_x/HTM/Ag with different HTMs. (a)PEDOT, (b)5mg/ml PCPDTBT/PEDOT, (c)15mg/ml PCPDTBT/PEDOT, (d)5mg/ml P3HT/PEDOT, and (E)15mg/ml P3HT/PEDOT.

Another optimization method is the surface treatment by iodopentafluorobenzene (IPFB) for perovskite, which has been developed by Abate *et al.* recently.²⁰ In this study, Abate *et al.* showed that perovskite surface without treatment has under-coordinated halide anions acting as hole-traps, which leads to a significant accumulation of charge at the perovskite/hole transporter heterojunction. This results in faster recombination and is likely to result in a disadvantageous charge density profile within the hole transporter and perovskite film, which should inhibit fast and efficient charge extraction under working conditions. The IPFB binds to and screens the electrostatic charge from the under-coordinated halide ions and decrease the recombination rate, thus leading to enhanced solar cell performance.²⁰

Here, IPFB treatment was applied for both devices based on PEDOT and Spiro-OMeTAD. The control group is composed of devices without this treatment. The solar cell performance parameters of the best devices from each group are listed in Table 4.2. Clearly all the parameters for both kinds of devices increase after applying this treatment, especially the J_{sc} and fill factor (FF), which leads to an overall increase of the solar cell power output.

Table 4.2 Solar cell performance parameters for the best cell of each configuration.

Structures	J_{sc} (mA/cm ²)	PCE (%)	V_{oc} (V)	FF
Spiro-OMeTAD	18.3	9.52	0.88	0.60
PEDOT	18.0	13.10	1.05	0.70
IPFB+ Spiro-OMeTAD	19.5	12.38	1.04	0.61
IPFB+PEDOT	20.2	14.55	1.06	0.68

Figure 4.4 a shows the recorded current density–voltage (J-V) characteristics of the as fabricated solar cells under AM 1.5G simulated sunlight (100 mW cm^{-2}) (Figure 4.4 a). The comparative J-V curves of the best devices highlight the relative photovoltaic performance of the solar cell containing PEDOT and Spiro-OMeTAD as hole transporting materials. Here we first compare the forward bias to short circuit (FB-SC) J-V curves of the two devices and show the device performance parameters in the inset. The small increase in the short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) is evident for the devices with PEDOT as compared with the Spiro-OMeTAD. The FF, however, shows even more significant improvements with the PEDOT, leading to improved derived power conversion efficiency for the devices incorporating PEDOT (14.5%) as compared to those using Spiro-OMeTAD (12.4%) as HTM. However, it is noted that within the experimental spread of average device performance, the solar cell operation is similar with PEDOT and Spiro-OMeTAD (Figure 4.4 c-f), indicating that PEDOT has the ability to perform at least as well as Spiro-OMeTAD as the p-type charge collection layer in a perovskite solar cell.

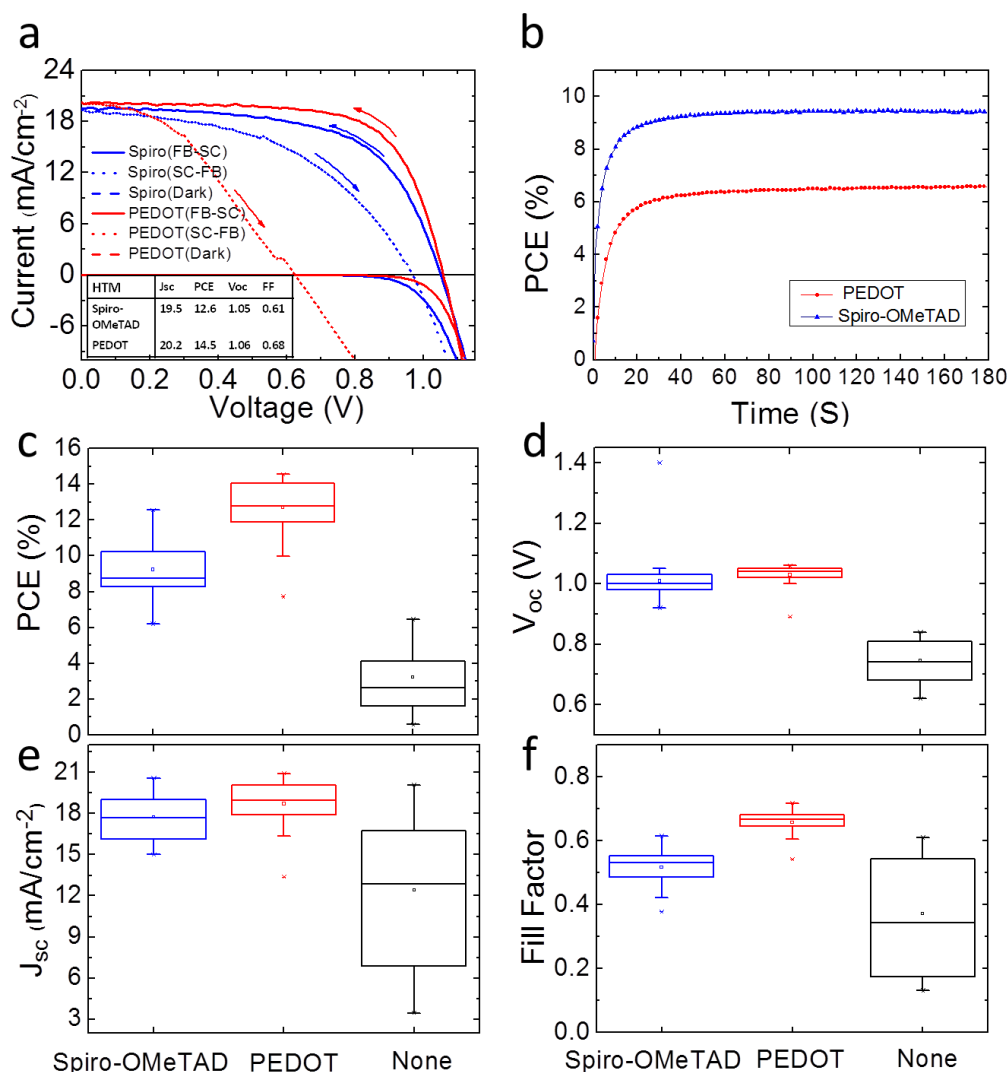


Figure 4.4 (a) Current voltage curves for best devices of PEDOT (red) and Spiro-OMeTAD (blue) configuration. Both forward-bias to short-circuit (FB-SC, solid line) and from short-circuit to forward-bias (SC-FB, dash line) J-V curves are showed. Inset shows the short-circuit current density (J_{sc} , mA cm⁻²), power-conversion efficiency (PCE, %), open-circuit voltage (V_{oc} , V) and FF for both device architectures determined from the FB-SC JV scans. (b) Power conversion efficiency as a function of time under illumination at a fixed voltage of the maximum power point on the JV curve (FB-SC) for best devices of PEDOT (red circles) and Spiro-OMeTAD (blue triangles). (c)(d)(e)(f) Comparison of PCE, V_{oc} , J_{sc} and fill factor of solar cells

with different configurations (Spiro-OMeTAD, PEDOT and no HTM just Au contact directly onto the perovskite). The data, obtained from FB-SC scan, are represented as a standard box plot where the box range is defined by ninety percent of all data points fall within the upper and lower whisker. Data points are averaged over 29, 45 and 24 devices for each configuration, respectively.

However, there is a non-negligible anomalous hysteresis between the forward bias to short circuit (FB-SC) and the short circuit to forward bias (SC-FB) J-V curves, which is especially pronounced in the solar cells incorporating PEDOT as the hole transporter. From the FB-SC J-V curve of PEDOT solar cell, a PCE of 14.5%, J_{sc} of 20.2mA cm^{-2} , V_{oc} of 1.06V and FF of 0.68 can be obtained. While from the SC-FB J-V curve, these numbers go down to 4.9%, 20.2mA cm^{-2} , 0.62V and 0.39. In the absence of a hole transporter at all, direct contact of the perovskite with a metal electrode can temporarily function as effective hole extraction contact. However, the hysteresis is much worse in the case of metal contact^{21,22}. To determine the true steady state stabilized power conversion efficiency of each cell, the PCE (%) over time at a fixed voltage close to maximum power point on the FB-SC JV curve is showed in Figure 4.4 b. After illuminating under 1 sun for 50 s, the PCE (%) of Spiro-OMeTAD devices reaches and remains at 9.4%, while the stabilized power output of PEDOT devices can only reach 6.6%. Our studies on anomalous hysteresis thus far indicate that the contact materials can strongly influence hysteresis, and that the forward biasing of the solar cell influences the nature of the contact, to give it a more selective charge collection. If for instance hysteresis pronounced due to an ineffective contact at the electron collection side, then there will be a large build up of electrons in the perovskite during operation, and less intuitively moreso under short-circuit conditions. If the electron transfer to the TiO_2 is slowed under

short-circuit conditions, electronic charge could still flow into the TiO_2 provided the electrons don't recombine with the holes either within the perovskite or at the perovskite hole-transporter heterojunction. Since the PEDOT is much more doped than the Spiro-OMeTAD, it is reasonable to expect a faster recombination at this heterojunction, which would lead to more losses, worse hysteresis and lower stabilised power output, as is observed. Therefore, a key target for future materials development is to reduce the doping level of the PEDOT. Although this observation appears to be at odds with many reports on “inverted” perovskite solar cells employing PEDOT:PSS and PC_{61}BM as the p- and n-type charge collection layers respectively, which exhibit low levels of hysteresis^{12,23}, however, PC_{61}BM is a very good electron collector when coupled to the $\text{CH}_3\text{NH}_3\text{PbX}_3$ which implies that the electrons will flow out of the perovskite more readily and be less prone to adverse recombination at the perovskite PEDOT interface. An alternative or addition factor may be that PEDOT:PSS is known to stratify upon spin-coating, whereby enrichment of PSS occurs at the surface²⁴. This PSS enrichment tunes the work-function, but may also act to reduce the recombination at this interface by assuming the role of an insulating buffer layer.

4.5.3. PEDOT Film with Decreased Conductivity

Following the previous discussion, a series of PEDOT samples with controlled conductivity are acquired from Clevios. The conductivities of these samples were determined on layers of about 100 nm in thickness (Table 4.3).

Table 4.3 Conductivity of PEDOT samples

PEDOT samples	SEJ 393	SEJ 393-1	SEJ 393-2	SEJ 393-3
Cond. (S/cm)	1.26E-02	5.02E-03	9.90E-04	2.83E-06

With these materials as HTM, perovskite solar cells were fabricated with the optimized solar cell structure as described before. The J-V curve and solar cell performance parameters are showed in Figure 4.5 and Table 4.4.

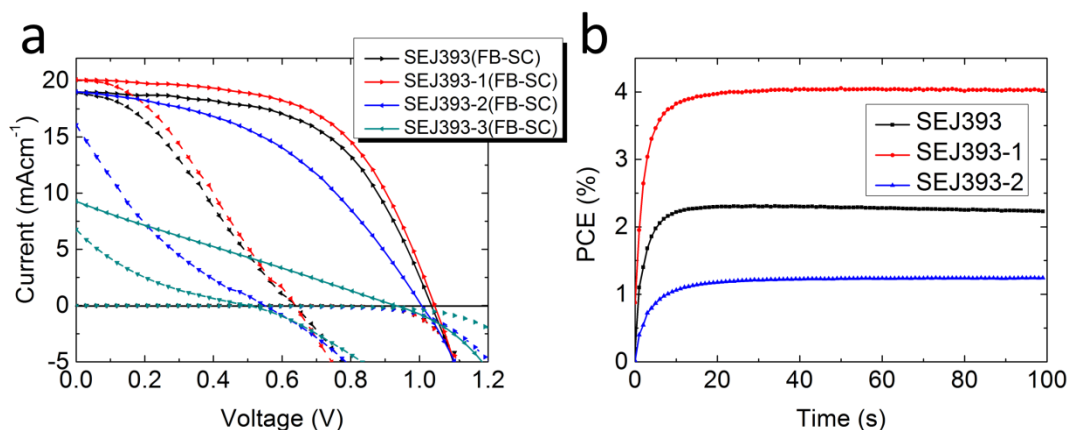


Figure 4.5 (a) Current voltage curves of the champion perovskite solar cell using different PEDOT sample as HTM. Solid line shows forward bias to short circuits (FB-SC) scan, dashed line shows the short circuits to forward bias (SC-FB) scan. (b) Stabilized power output of the champion perovskite solar cell using different PEDOT sample as HTM.

Table 4.4 Solar cell performance parameters from FB-SC scan.

	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF	PCE (%)
SEJ393	18.99	1.04	0.56	11.0
SEJ393-1	20.07	1.04	0.57	12.0
SEJ393-2	19.01	1.01	0.44	8.4
SEJ393-3	9.27	0.92	0.25	2.14

The J-V curve shows that the solar cell employed with SEJ393-1 gives the best

performance, with PCE of 12.0% from FB-SC scan, and 4.3% from SC-FB scan. The solar cell using SEJ393 provides slightly decreased PCE (11.0%/3.9%). SEJ393-2 shows PCE of 8.4%/1.5%, and SEJ393-3 gives PCE of 2.1%/0.5%. The stabilized power output of solar cell using SEJ393, SEJ393-1 and SEJ393-2 as HTM are also recorded. Figure 4.5 b shows that the solar cell employing SEJ393-1 gives the highest power output of 4.0%. While using SEJ393 and SEJ393-2, this number decreases to 2.2% and 1.2%, respectively.

These results prove that the problems of large hysteresis and the low stabilized power output cannot be solved by simply decreasing the conductivity of PEDOT film. Although there is a slight enhancement in the solar cell performance when the PEDOT film conductivity is decreased to 5.02×10^{-3} S/cm, the hysteresis and stabilized power output is basically of the same level as the results showed in 4.5.2. Further decrease of PEDOT conductivity results in even worse solar cell performance. Therefore, it is assemed that the best solution to decrease the hysteresis and increase the stabilized power output is replacing TiO_2 with a more effective electron collector, which can lead to faster charge separation and lower carrier recombination rate.

4.6 Charge Transport Analysis

To further understand the differences observed here between the devices employing the two hole transport materials, Spiro-OMeTAD and PEDOT, the recombination dynamics of the solar cells were examined under conditions where recombination is predominant (i.e. under open-circuit conditions). First, the V_{oc} at different values of light intensity (P_{in}) is determined and the V_{oc} against P_{in} is showed in Figure 4.6a. According to the standard diode model (assuming no shunt resistances)²⁵:

$$V_{oc} \propto \frac{2.303nkT}{q} \log_{10} P_{in}$$

where q is the electric charge, k is the Boltzmann's constant, T is the absolute temperature and n is the ideality diode factor. The derived ideality factors deviated from ideality ($n>1$) for both cells, however while in the case of Spiro, n is ~ 2 , consistent with literature²⁶, the ideality factor of PEDOT containing cell was higher than 5 which is physically unrealistic in a standard diode. It is speculated that these unusual high values are caused by severe non-linear recombination at the interface between PEDOT and the perovskite²⁷.

To further justify our findings, the electronic impedance spectroscopy (EIS) under illumination is conducted. The spectra exhibit two or three semicircles, in line with previous reports²⁸, and therefore the simple model is applied as discussed in the referenced manuscripts here. A full understanding of the origin of the measured capacitances is highly complicated^{29,30} and is out of the scope of this work, therefore we have drawn our attention to the recombination resistance which is the most reliable information derived by EIS fitting³¹. Thus after fitting, the values for the charge recombination resistance (R_{rec}) and plot R_{rec} against V_{oc} (Figure 4.6 b) are determined according to³²:

$$R_{rec} = R_0 \exp \left[\frac{-\beta q V_{oc}}{kT} \right]$$

where R_0 is the pre-exponential factor and β is the recombination order³³. R_{rec} values for Spiro-OMeTAD based cells are in very close agreement with results recently reported by Suarez et al. who studied cells of identical structure³¹. Additionally, β

values is found to be as high as 0.53 for the Spiro-OMeTAD based cells, in relative agreement with others⁶ in contrast with PEDOT-based cells where the values determined as low as 0.18. Assuming that the deviation from linearity mostly originates from non-linear recombination, β should represent the inverse of n^{34} ; in fact this holds almost entirely true, further justifying our conclusions drawn from V_{oc} vs. P_{in} plots (Figure 4.6 a). The clear difference in recombination dynamics between these two cells is consistent with most of the recombination in PEDOT cells arise from the interface between the perovskite and PEDOT, and likely to be due to a trap mediated process. Our findings are also consistent with the previous work by Guillen *et al.* who's results indicate that most of the recombination in the current generation of perovskite solar cells occurs at the heterojunction (TiO_2 /perovskite or hole transport material/perovskite) and that this type of recombination is likely to take place through surface states³⁵.

These results are also consistent with the observation of the importance of the selective contacts in perovskite solar cells in minimizing the level of hysteresis^{22,31,32}.

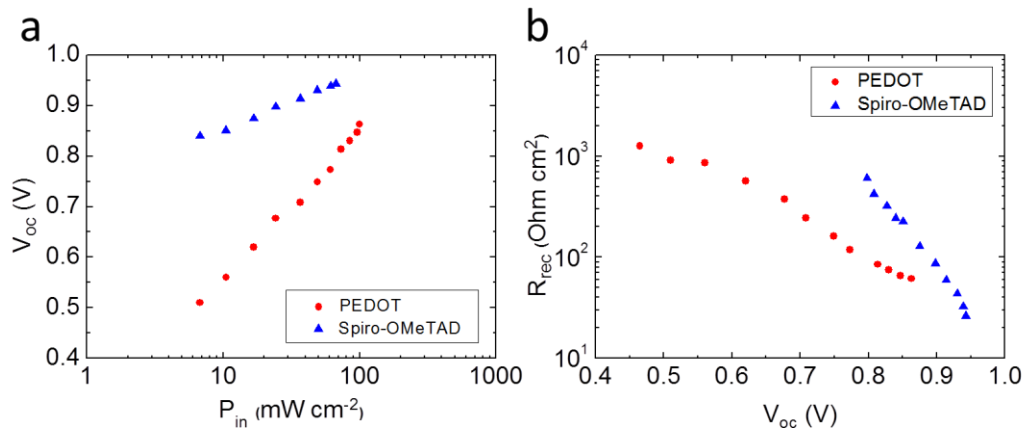


Figure 4.6 (a) Photovoltage, plotted against the incident light power density and (b) recombination resistance plotted against the V_{oc} for mesostructured solar cells

employing Spiro-OMeTAD and PEDOT hole transporting materials. The plots were derived by impedance spectroscopy measurements at open-circuit under illumination.

4.7 Perovskite Film Stability Analysis

Perovskite films are known to be very sensitive to the moisture and temperature, therefore, apart from its main function as a hole collection, the top hole transporting layer may play a crucial role in terms of acting as final defense against moisture ingress, and have a strong impact on the thermal resilience of the solar cell, and hence greatly influencing its long-term stability³⁶. Different hole-transporting materials can protect or damage the perovskite film. Since the PEDOT solution does contain a small amount of water, and PEDOT doped with polystyrene sulfonate (PSS) is known to be hygroscopic due to PSS, it worth investigating its impact on the perovskite layer here. Spiro-OMeTAD with and without additives (Li-TFSI and *t*BP) and PEDOT are spin-coated on top of perovskite films, and subjected them to thermal stressing (85 °C) up to 72 hrs in ambient conditions (air with RH ~ 60%). The photographs are recorded at regular interval (i.e. 0, 6, 20, 36, 48, and 72 hours). All samples appear to be stable up to 6 hrs of heating in air as they all retain their dark black color. The bare uncoated perovskite film (Figure 4.7 a, row 1) started to degrade within 20 h noticeable since the film started to turn yellow, indicating the conversion of perovskite to PbI_2 ³⁶. Perovskite films covered with neat Spiro-OMeTAD (row 4) are the most stable among these samples, as they mostly retain their color even after 72 h of heating. Spiro-OMeTAD with additives (Li-TFSI and *t*BP), however show early degradation after 20 hrs of ageing, likely to be due to the hygroscopic nature of the Li-TFSI salt drawing moisture in from the atmosphere. Perovskite film covered with PEDOT on top (row 2) started to change its color after 32 hrs, which is more stable than the films coated with Spiro-OMeTAD with additives containing film but

less than those coated with neat Spiro-OMeTAD. The UV-vis absorption spectra of the respective films at the similar time intervals are showed in Figure 4.8. The photographs match well with change in absorption spectra where the degradation of perovskite indicated by the loss of perovskite absorption features predominantly at ~750nm.

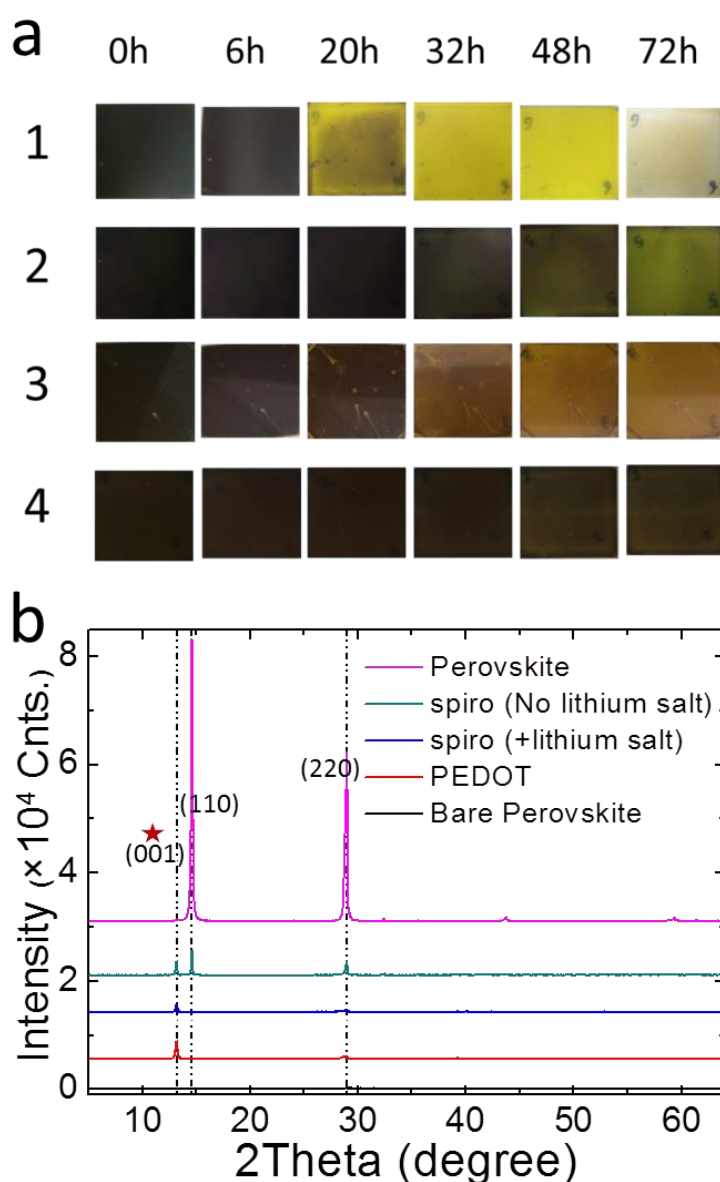


Figure 4.7 (a) Color change of MAPbI₃ perovskite film covered with (1) no cover (bare perovskite), (2) PEDOT, (3) Spiro-OMeTAD HTM (with Li-TFSI and *t*BP), and (4) neat Spiro-OMeTAD. The size of the samples are approximately 2cm $\times$ 2cm. (b) X-ray diffraction patterns of different samples after 72h stressing, comparing to a freshly made perovskite sample without aging. The (110) and (220) peaks are from perovskite structure, while the (001) peak (red star) indicates the existence of PbI₂.

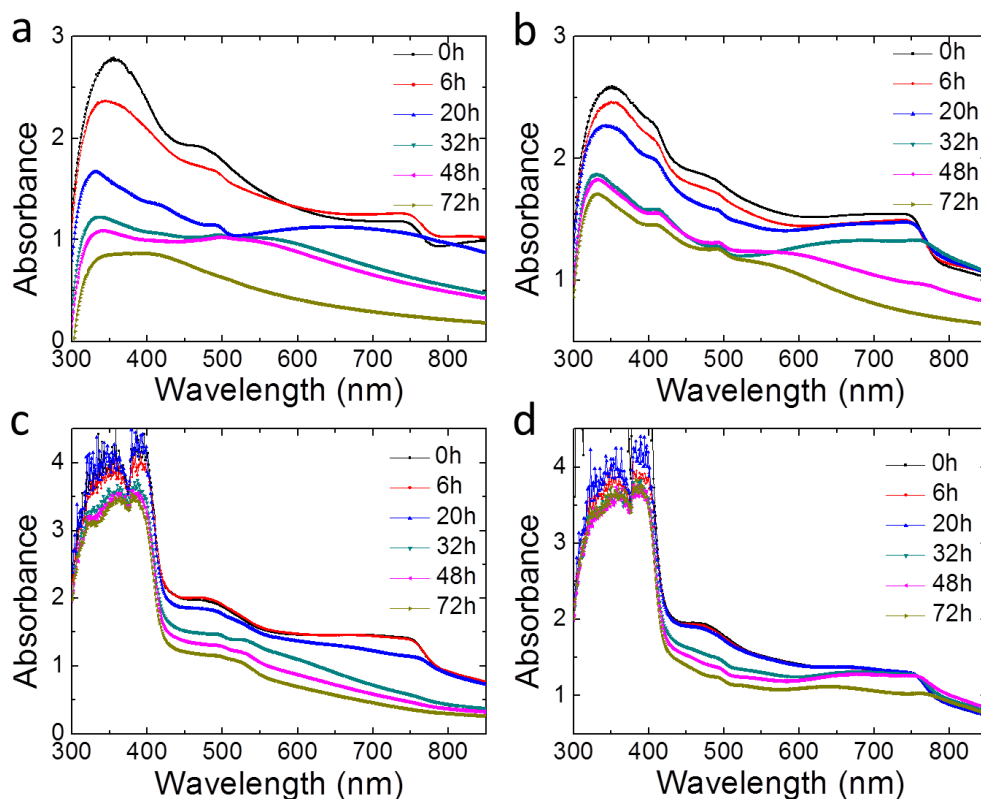


Figure 4.8 (a)-(d) UV-vis absorbance spectra of perovskite film covered with (a) no cover (bare perovskite), (b) PEDOT, (c) Spiro-OMeTAD HTM (with lithium-TFSI and tBP, “lithium salt”), and (d) neat Spiro-OMeTAD (without lithium salt).

After annealing for 72 hrs at 85 C in air, these perovskite films coated with Spiro-OMeTAD with and without additives and PEDOT visibly degraded to different extents. To identify the crystal structure after 72 h of annealing in air, X-ray diffraction (XRD) spectroscopy was performed on the films, as showed in Figure 4.7 b. The XRD pattern of freshly made perovskite films show two main diffraction peaks at 14.63° and 28.98° , indicating the (110) and (220) planes for a tetragonal perovskite structure⁴. After 72 hrs of ageing in air PEDOT and Spiro-OMeTAD doped with Li-TFSI coated perovskite films show no (110) peak at 14.63° , and instead here is a strong (001) peak at 13.20° , which can be assigned to PbI_2 ³⁷ as an end-product of the perovskite degradation. However, neat Spiro-OMeTAD still shows the peaks

pertaining to the perovskite (14.63 ° and 28.98 °) along with the PbI₂ peak at 13.20 °³⁷. The co-existence of peaks pertaining to both perovskite and PbI₂ suggests that the degradation was not complete over 72 hrs of ageing when the perovskite film is coated with the neat Spiro-OMeTAD, but notably the films are still partly degraded.

Based on these observations it can be inferred that these PEDOT films are slightly better than the most efficient Spiro-OMeTAD composition containing Li-TFSI and *t*BP at inhibiting thermal degradation of the perovskite films in the presence of moisture. However they do not protect the perovskite to the same extent as a film of neat Spiro-OMeTAD, and by a far lesser extent than carbon nanotubes encapsulated in a poly(methyl methacrylate) (PMMA) matrix, which have been previously demonstrated³⁶. This will be a critical aspect for perovskite solar cells if low levels of encapsulation are required, for instance for flexible applications, or if the moisture sensitivity of the perovskite film cannot be enhanced. However, how important this is for glass based applications where very effective hermetic sealing is possible, is yet to be determined.

4.8 Summary and Outlook

In summary, this work have demonstrated that PEDOT can be employed as the hole transport layer to fabricate efficient organic-inorganic metal halide perovskite solar cells in the regular configuration where the hole transporter is processed on top of the perovskite film. Devices containing PEDOT perform as well as the commonly used Spiro-OMeTAD on measured current voltage curves, but the stabilized power output is lower for the PEDOT cells. Here, the cause for increased hysteresis and reduced stabilized power output was accessed. However, the proposal that tuning of the doping and conductivity in the PEDOT layer may help improving the stabilized power

output cannot be proved by following experiment. Therefore, employing a more effective n-type layer might be the only way to alleviate the hysteresis problem. It is also identified that both Li-TFSI doped Spiro-OMeTAD and the PEDOT films, do not effectively protect the perovskite layer from degradation due to moisture ingress during thermal stressing in ambient conditions, identifying an area for future development. Despite the current shortcomings, this work identifies the potential for a PEDOT based organic hole conductor to deliver an extremely inexpensive solution for p-type charge collection from a perovskite solar cell.

4.9 References

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Chapter 5. Employing CuSCN as an Efficient and Affordable Hole Transporting Material, towards Thermally Stable Perovskite Solar Cells

5.1 Contexts

The previous chapter discussed the use of PEDOT as a replacement of Spiro-OMeTAD for perovskite photovoltaic devices. However, such as fabricated devices still suffer from limited stabilized power output and imperfect stability. In order to compete with traditional crystalline solar cells, it is still necessary to search for novel hole transporting materials to achieve devices with decent efficiency and stability. In this chapter, a 13.3% efficiency perovskite solar cell is achieved with spray coated CuSCN as HTM in regular, n-i-p solar cell structure. The relatively smooth spray coated CuSCN film can provide very reproducible solar cell performances. The stability of cells employing CuSCN is then compared with those devices employing the archetypical organic HTM, under elevated temperatures in ambient atmosphere. Unfortunately, the devices employing as spray coated CuSCN

appear to intrinsically facilitate the degradation of perovskite films. However, by including a thin mesoporous alumina (Al_2O_3) “buffer layer” directly on top of the perovskite, followed by CuSCN and an additional coating of insulating poly(methyl methacrylate) (PMMA) on top of the CuSCN, this degradation can be inhibited, and that leads to perovskite solar cells which survive for more than 1000 hrs at 85 °C in air.

5.2 Introduction

Organic-inorganic halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have attracted strong attention from photovoltaic research community since 2012, with power conversion efficiency (PCE) of perovskite solar cells (PSCs) rising up to 20.1%^{1–6}. The low cost of organometal halide perovskite precursors and their simple solution processability make them very promising to be developed as a next generation photovoltaic technology. However, the chemical instability of this material, especially in high humidity environment, is the main obstacle for its photovoltaic application in industry^{7,8}. To become an ultimate competitor to Si-based solar cell technology perovskite structure must be altered to make them inherently stable towards environmental conditions. The other approach to this problem is the efficient encapsulation of the perovskite solar cell to inhibit any ingress of humidity to the perovskite layer in the device. And in this approach hole transporting materials (HTM) can play an additional role in enhancing the stability of PSCs, serving as moisture blocking layers, apart from their main responsibility as a hole selective layer, which is critical for achieving high performance perovskite solar cell⁹.

The organic hole-conductor 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenyl-amine) 9,9'-Spirobifluorene (Spiro-OMeTAD) is one of the most efficient and prevalently used HTM in PSCs, with PCE crossing 20 %^{1,2,4,5}. However, the Spiro-OMeTAD has a

price, at research scale, that is more than 10 times that of gold and platinum.¹⁰ In addition, doping the Spiro-OMeTAD with lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) makes it highly hygroscopic, which in essence is required to enhance the hole conductivity of the Spiro-OMeTAD, causing acceleration of the perovskite layer degradation.^{8,9,11} Although, Spiro-OMeTAD can be pre-oxidized to avoid addition of the Li-TFSI dopant but this then further increases its cost, making it commercially not viable for large scale application.¹² In attempts to find a suitable alternative of the Spiro-OMeTAD, researchers have deployed several HTM's such as P3HT, PEDOT, carbon nanotubes, CuI and CuSCN, etc.^{10,13–22} Among them copper(I) thiocyanate (CuSCN), a solution processable inorganic p-type semiconductor with high mobility and low cost (0.5GBP/g), has shown promising results in PSCs application.^{23–29} High PCEs has been claimed such as 12.4% in 'regular' structure with TiO₂ as electron-transporting layer (ETL)²⁴ and 16% in 'inverted' with PCBM as ETL²⁶ However, despite one of the primary motivations for employing CuSCN being a promise for high stability, none of the reports so far have examined the long term stability in any rigorous level of detail: Ito *et al.* demonstrated that cells employing CuSCN, in combination with Sb₂S₃ as a TiO₂ surface passivation layer, could retain around 67 % of their initial power conversion efficiency after exposure to simulated sun light for half a day. Zhao *et al.* observed that when they stored their p-i-n perovskite solar cells in a nitrogen filled glovebox for a two-week period, the performance of the cells employing CuSCN dropped to 40% of the initial performance. Although this was better than the cells employing PEDOT:PSS, which dropped to 20% of their initial performance, it is not very encouraging. Woong Jung *et al.* also showed enhanced ambient stability of their p-i-n perovskite solar cells employing CuSCN, as compared to similar cells employing PEDOT:PSS, where the cells employing CuSCN retained more than 80% of their initial performance after 300 hours aging in ambient conditions (in air at room temperature). In addition, there is

also a difficulty in obtaining smooth CuSCN layer via solution processing, where doctor-blading is not a perfect technique to fulfil this need.

Here, perovskite solar cell is fabricated using CuSCN as a HTM and compared their performance as well as long-term device stability to devices employing the conventional organic hole-transporter Spiro-OMeTAD. A relatively smooth film of CuSCN is deposited by spray coating a solution in dipropyl sulfide solvent and achieved a solar cell PCE (%) of 13.3% in a “regular” n-i-p structure and with a stabilized power output (SPO) of 10.9%. Surprisingly, solar cells solely employing CuSCN as the hole-transport layer are not stable when aged at 85 °C in ambient conditions. The presence of CuSCN layer with multiple pin-holes appears to catalyze a degradation, rendering the device completely non-functional in 15 days. To overcome this issue, a multi-component hole-transport layer is applied, composing of mesoporous Al₂O₃ infiltrated with CuSCN and subsequently coated in a thin layer of Poly(methyl methacrylate) (PMMA). The mesoporous Al₂O₃ facilitates smooth continuous coating of the CuSCN and the PMMA fills any residual pinholes and/or unfilled regions of mesoporous Al₂O₃. The resultant devices then exhibit vastly improved ambient stability at 85 °C with the scanned efficiency retaining 77% of its initial power output after 1080 hrs.

5.3 Method

5.3.1 CuSCN Deposition

Two deposition methods are adopted in this chapter. The spin-coated CuSCN film was prepared by spin-coating a 10 mg/ml CuSCN solution for 8 times in glovebox. Films were dried on an 85 °C hotplate for 1 min between each time spin-coating. The

spray-coated CuSCN films were prepared with method as previously described in detail in section 3.1.5.3.

5.3.2 Device Fabrication

The device fabrication process has been described in detail in section 3.1. All the solar cells in this chapter are meso-structured devices, with an optimized mesoporous Al_2O_3 scaffold thickness of $\sim 250\text{nm}$.

PMMA layer was deposited by spin coating a 50mg/ml solution in chlorobenzene. Then chlorobenzene solvent was used to remove the PMMA that block the electrode contact area.

5.3.3 Measurement and Characterization

Characterization methods used in this chapter include: current-voltage characterization, photoluminescence (PL) measurement, UV-vis absorption measurement, and conductivity measurement. The details of these characterization techniques have been described in section 3.2.

5.4 Thin Film Characterization

Figure 5.1 a shows UV-vis absorption of the as deposited CuSCN film on glass substrate along with the conventional Spiro-OMeTAD. The thickness of CuSCN and Spiro-OMeTAD is maintained to approximately 300 nm. It has been reported widely that doping of Spiro-OMeTAD is important to achieve a higher conductivity,

increasing from 3×10^{-8} S/cm to 3×10^{-5} S/cm after doping with lithium salts and allowing exposure to air¹¹. However, this doping does result in absorbance in the visible region of the spectrum which could contribute to parasitic absorption in the solar cells. Comparing with doped Spiro-OMeTAD film with same thickness, the spray coated CuSCN film shows slightly stronger absorption in region from 420nm to 800nm. However, Spiro-OMeTAD shows very strong absorption at near UV region, while the CuSCN with wide bandgap is much more ‘transparent’ at the region from 320nm to 420nm. For the inverted, p-i-n, configuration³¹ or for cells illuminated from the p-type side³², the low absorption at the near UV region will allow more incident energy to reach perovskite active layer, giving an advantage over Spiro-OMeTAD.^{26,27} An effective p-type hole transporting layer should be capable of selectively extract holes from the perovskite absorber layer whilst “reflecting” electrons. This process is critical in preventing electron-hole pair recombination and increasing PCE of the solar cell. One means to assess the effectiveness of the hole extraction is to monitor the photoluminescence (PL), where the rate of PL quenching is a good indication of charge extraction³³. Figure 5.1 b & c show the time-resolved and steady-state PL data of perovskite film covered by Spiro-OMeTAD or CuSCN, comparing with the bare perovskite film. Here the PL quenching is as fast for the films coated with CuSCN as those coated with Spiro-OMeTAD, indicating just as effective hole-extraction. Beyond extracting the holes, the holes need to be effectively transported to the metal electrode. Hence, in order to assess this capability the conductivity of the HTMs was measured with four-point-probe method. The average conductivity is $(9.11 \pm 0.11) \times 10^{-5}$ S/cm for CuSCN and $(4.50 \pm 0.24) \times 10^{-5}$ S/cm for Spiro-OMeTAD. These results suggest that CuSCN can be applied as HTM with similar effectiveness as Spiro-OMeTAD.

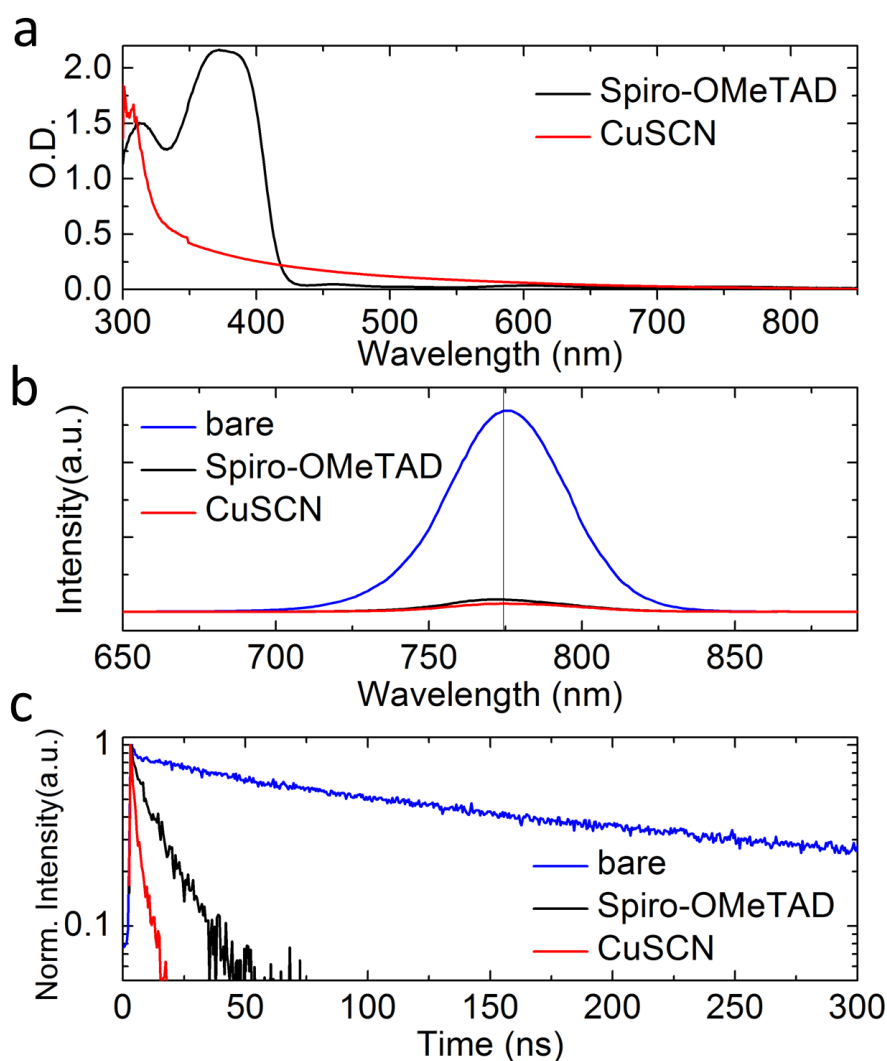


Figure 5.1 (a) Absorbance spectra of ~300 nm thick CuSCN films (red) and ~400 nm thick Spiro-OMeTAD films doped with Li-TFSI and *t*BP (black) deposited on glass. (b) Steady-state PL spectra and (c) time-resolved PL decay excited at 510 nm of bare perovskite film (blue) and perovskite films coated with Spiro-OMeTAD (black), and CuSCN (red), respectively.

5.5 Solar Cell Fabrication and Optimization

Perovskite solar cells were fabricated with regular device architecture, an illustration

of which is showed in Figure 5.2 a. Here, a 50 nm compact TiO_2 is used as an electron extraction layer and a 250 nm Al_2O_3 non-conductive mesoporous film is applied to prevent shunting between TiO_2 and HTM. Figure 5.2 b shows the respective energy level of each film.

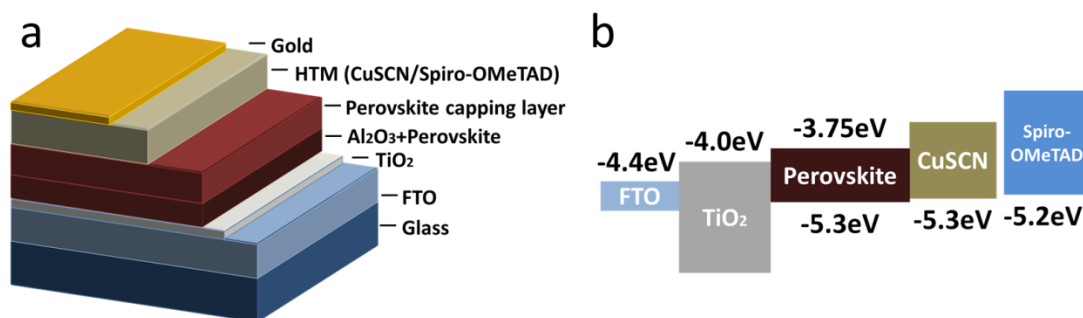


Figure 5.2 (a) Device schematic. (b) Approximate energy band diagram of the fabricated structure taken from reference.³⁴

5.5.1 Spin coated CuSCN

Two different deposition methods applied are spin coating and spray coating. Here we first discuss the results from spin coating CuSCN. Due to the low solubility of CuSCN in propyl sulfide, 10mg/ml solution was spin coated for 8 times after the perovskite layer was fully annealed. However as can be seen from Figure 5.3 c that instead of forming a compacted film, pillared structure of CuSCN can be obtained by multiple spin coating method, the structure of which is very similar to electrodeposited CuSCN crystals³⁵. Since the perovskite surface is not fully covered by HTM, there will be huge recombination at the interface between perovskite and gold electrode. Therefore 20mg/ml PMMA solution was further spin-coated on CuSCN to form an approximately 50nm PMMA film on top of pillared CuSCN before depositing metal electrode. The solar cell performance data of different structure are

showed in Table 5.1, where it shows that improved solar cell performance can be obtained with further PMMA coverage. The J-V curve and SPO curve are showed in Figure 5.3 a & b.

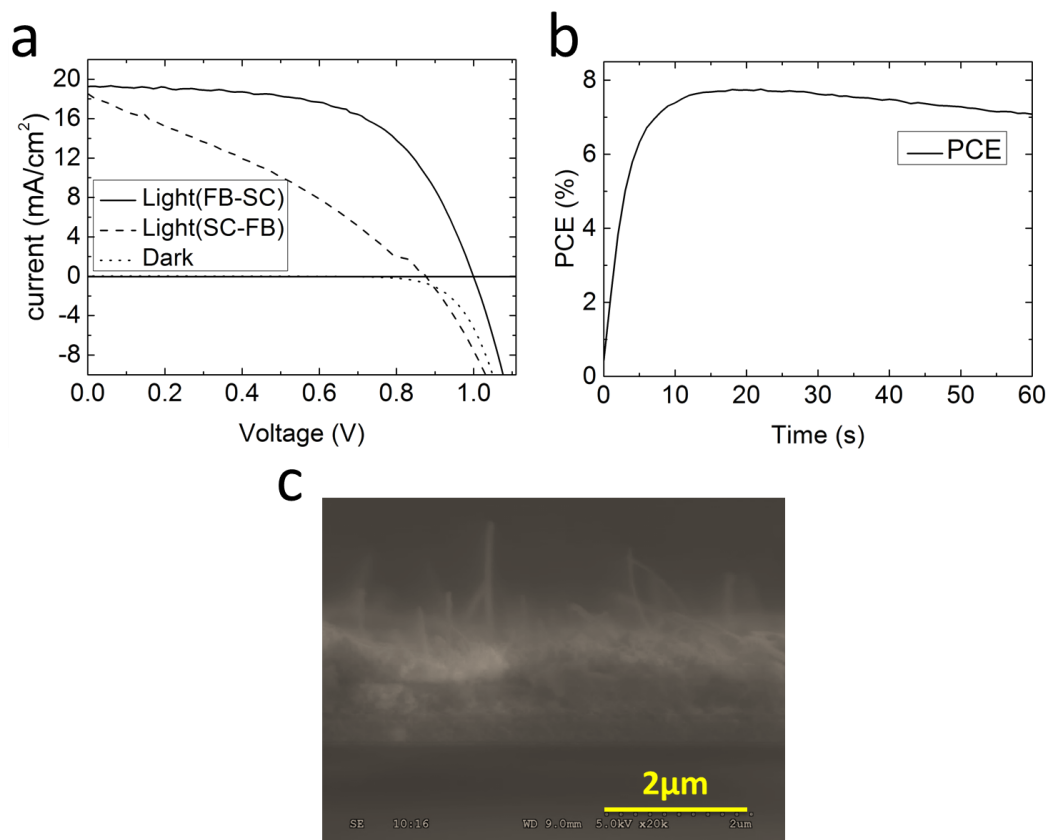


Figure 5.3 (a) Current voltage curves for best devices with spin coated CuSCN and 20mg/ml PMMA. Both forward-bias to short-circuit (FB-SC, solid line) and from short-circuit to forward-bias (SC-FB, dash line) J-V curves are showed. (b) Power conversion efficiency as a function of time under illumination at a fixed voltage of the maximum power point on the JV curve (FB-SC). (c) Cross sectional SEM image of pillar structure CuSCN spin coated on perovskite surface.

Table 5.1 Solar cell performance parameters of the best cells with different HTM configuration. The CuSCN was deposited by spin-coating for these cells.

Structure	J_{sc} (mA/cm ²)	PCE (%)	V_{oc} (V)	FF
CuSCN	17.14	10.4	0.93	0.65
CuSCN+PMMA	19.26	11.5	1.00	0.59
Spiro-OMeTAD	21.63	14.8	1.04	0.65

5.5.2 Spray coated CuSCN

Although the spin coating method provides working devices with PCE above 11%, it was further discovered that the result was very difficult to reproduce, since the crystallization process is very sensitive to atmosphere while spin coating. Therefore, the spray coating method was applied to produce a thick and compact CuSCN film with nice coverage resulting in much better device reproducibility. Figure 5.4 a shows the thickness of the spray coated film is about 300nm. And Figure 5.4 b shows that film is formed of CuSCN crystals about 200nm.

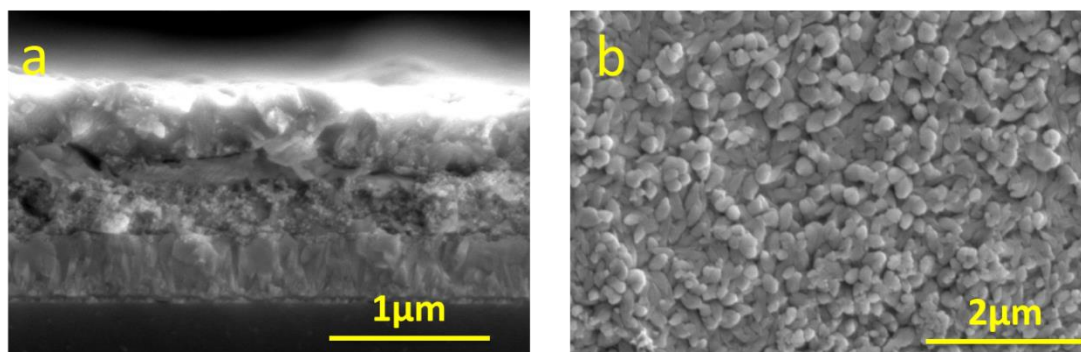


Figure 5.4 (a) Cross-sectional and (b) top view SEM images of spray-coated CuSCN

Figure 5.5 shows the current density-voltage (J-V) characteristics of the best performing solar cells with spray-coated CuSCN and Spiro-OMeTAD as HTM under AM 1.5G simulated sunlight (100 mWmA^{-2}). Both devices show reasonably similar short-circuit current density i.e. 21.07 mAcm^{-2} for CuSCN and 21.64 mAcm^{-2} for Spiro-OMeTAD. However, loss in the open-circuit voltage of devices with CuSCN is apparent, as CuSCN based device shows V_{oc} of 0.98V whereas devices with Spiro-OMeTAD show 1.07V. The overall PCEs obtained from the forward bias to short circuit (FB- SC) J-V curves are 13.3% and 14.3%, respectively. To the best of our knowledge, this is so far the highest efficiency obtained in ‘regular’ structure PSCs using CuSCN as p-type hole transporting layer and TiO_2 n-type electron transporting layer. Both CuSCN and Spiro-OMeTAD based devices show similar level of hysteresis between the forward and reverse scan JV curves. To determine the actual steady state stabilized power conversion efficiency of each type of devices, the SPO measurement was performed by measuring the PCE (%) over time at a fixed voltage close to maximum power point on the FB–SC JV curve (Figure 5.5 b). After illuminating under 1 sun for 90s, the PCE (%) of CuSCN device is stabled at 10.9%, and the stabilized power output of Spiro-OMeTAD settles at 12.2%. These results show that CuSCN can be applied in efficient perovskite solar cells with similar performance as using Spiro-OMeTAD. Figure 5.5 c & d show the statistics of PCEs from 22 pixels of 3 representative devices for each configuration. The results show solar cells with CuSCN as HTM are very reproducible with average PCE around 12.4%.

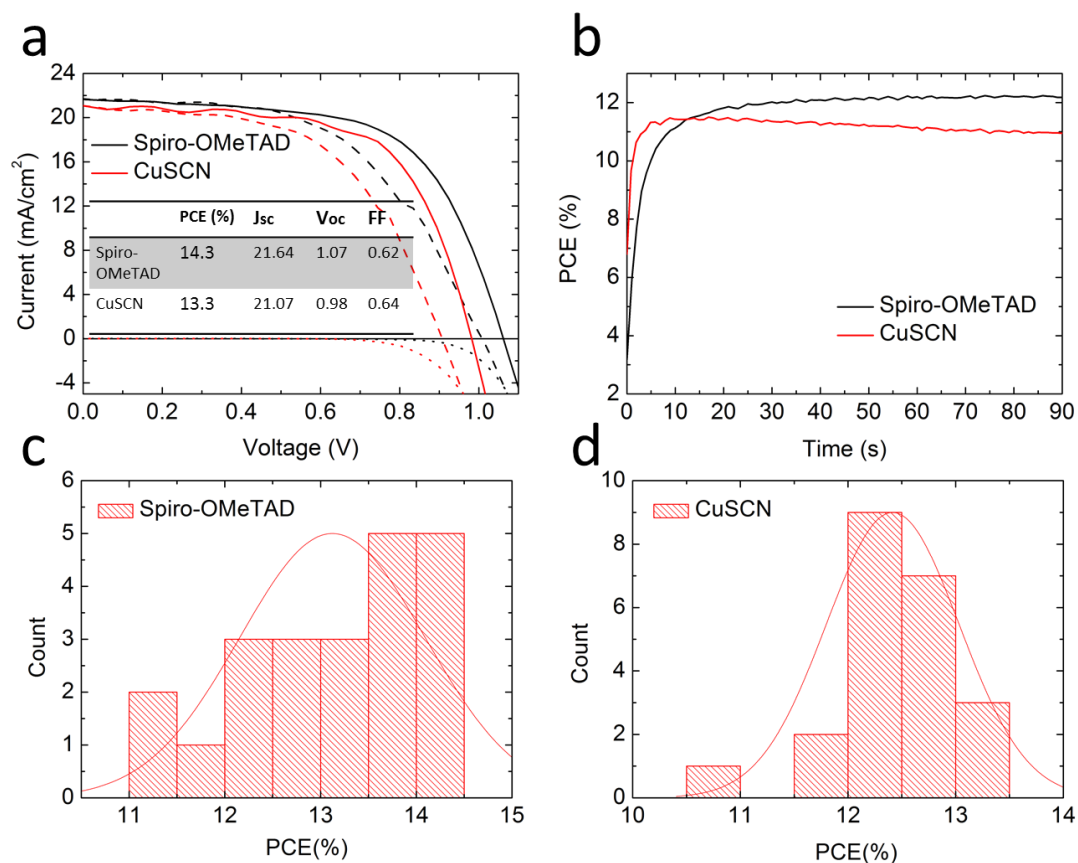


Figure 5.5 (a) Current voltage curves for best devices of CuSCN (red) and Spiro-OMeTAD (black) configuration. Both forward-bias to short-circuit (FB-SC, solid line) and from short-circuit to forward-bias (SC-FB, dash line) J-V curves are showed. (b) Power conversion efficiency as a function of time under illumination at a fixed voltage of the maximum power point on the JV curve (FB-SC) for best devices of CuSCN (red) and Spiro-OMeTAD (black). (c)(d) Statistics of the PCE of the optimized solar cells with Spiro-OMeTAD and CuSCN as HTM. For each configuration, data from 22 devices were counted.

5.5.3 Post thermal treatment of CuSCN devices

As the boiling point of the solvent employed for spray-coating (dipropyl sulfide) is 142 - 143 °C, it is reasonable to speculate that there might be residual solvent left in

CuSCN film after spray-coating at 85 °C. Therefore, a post thermal treatment at 100 °C was performed to remove the residue solvent for better solar cell performance and stability. However, as shown in Table 5.2, instead of bringing any benefit to photovoltaic device, this post thermal treatment induces a rapid degradation of the fabricated solar cell. After heating the device for more than 30 min at 100 °C, all the solar cell performance parameters start decreasing rapidly, with PCE changes from 13.3% to 3.4% after two hours heating. And this degradation speed is much faster than the degradation of pure perovskite film stressed at same temperature, suggesting the coverage of as fabricated CuSCN somehow make the perovskite solar cell thermally unstable. This phenomenon will be our next thing to investigate.

Table 5.2 Solar cell performance parameters of the best cell with different post heating time.

Heating Time	J_{sc} (mA/cm ²)	PCE (%)	V_{oc} (V)	FF
0 min	21.1	13.3	0.98	0.64
10 min	21.1	13.2	0.92	0.67
30 min	18.4	10.6	0.89	0.64
1 h	14.5	6.5	0.80	0.55
2 h	12.4	3.4	0.69	0.41

5.6 Long-term Stability of Perovskite Solar Cell based on CuSCN

The HTM not only function to extract the charges selectively at the perovskite/HTM interface, but must also in the first instance not induce an instability in the perovskite

film, and ideally be beneficial to the stability of the perovskite solar cell by acting as the final barrier to the ingress of atmospheric humidity, that would otherwise degrade the perovskite material. This context scrutinized perovskite films and devices coated with CuSCN in comparison to work with organic p-type material, Spiro-OMeTAD.

To investigate the effectiveness of the CuSCN as a barrier in ambient condition, perovskite films coated with and without CuSCN were aged at elevated temperature (85 °C), and the results were compared with the Spiro-OMeTAD coated perovskite films. It should be noted that CuSCN was spray-deposited in ambient condition from a dipropyl sulfide solution with relative humidity around 50%.

Figure 5.6 shows photographs of the perovskite films after the ageing for several days, for samples without any coating (bare, sample 1), covered with Spiro-OMeTAD (sample 2), with CuSCN (sample 3) and with CuSCN/PMMA (sample 4). Here the bare perovskite film doesn't show an obvious change after 24 hours heating, but completely turns white after four days. However, when the perovskite film is covered with the Spiro-OMeTAD (doped with LiTFSI and *t*BP), the film only turns to a light brown colour after the same time indicating some level of protection offered by the doped spiro-OMeTAD film. Unexpectedly, and disappointingly, the perovskite film covered with CuSCN (sample 3) starts showing yellow dots just after 24 hours of ageing and turns completely yellow after 4 days. It appears that the CuSCN coating offers no substantial resistance to degradation, and is possibly even introducing a new degradation pathway, otherwise absent in the bare film. This measurement was repeated many times and observed the same acceleration in the degradation of the perovskite films when coated with CuSCN.

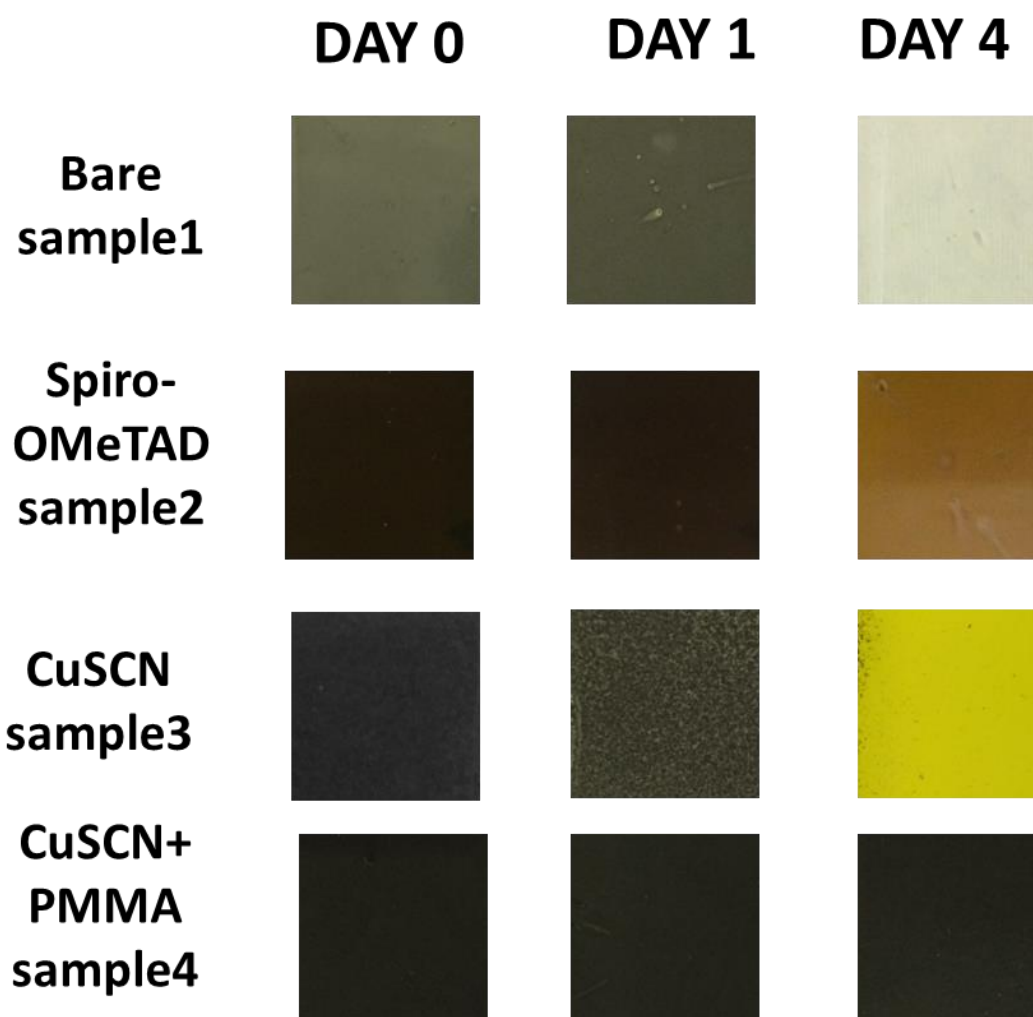


Figure 5.6 Photos of perovskite samples with different coating degrade in ambient environment with thermal treatment at 85 °C.

To differentiate if this is a moisture induced effect, or due to a chemical reaction between the CuSCN and the perovskite, similar aging experiments were performed in a nitrogen filled glove box ($<10\text{ppm O}_2$, $<1\text{ppm H}_2\text{O}$). In Figure 5.7, bare perovskite films were compared to those coated with CuSCN and coated with CuSCN/PMMA, heated at 85 °C on a hotplate for a number of days. In this experiment there is negligible discolouration for the control films. However, for film coated with CuSCN, there is a rapid discoloration and yellowing over the 1 to 4 day timescale. This confirms that even in the absence of moisture and oxygen, the presence of the CuSCN

induces or catalyzes a degradation in the perovskite film.

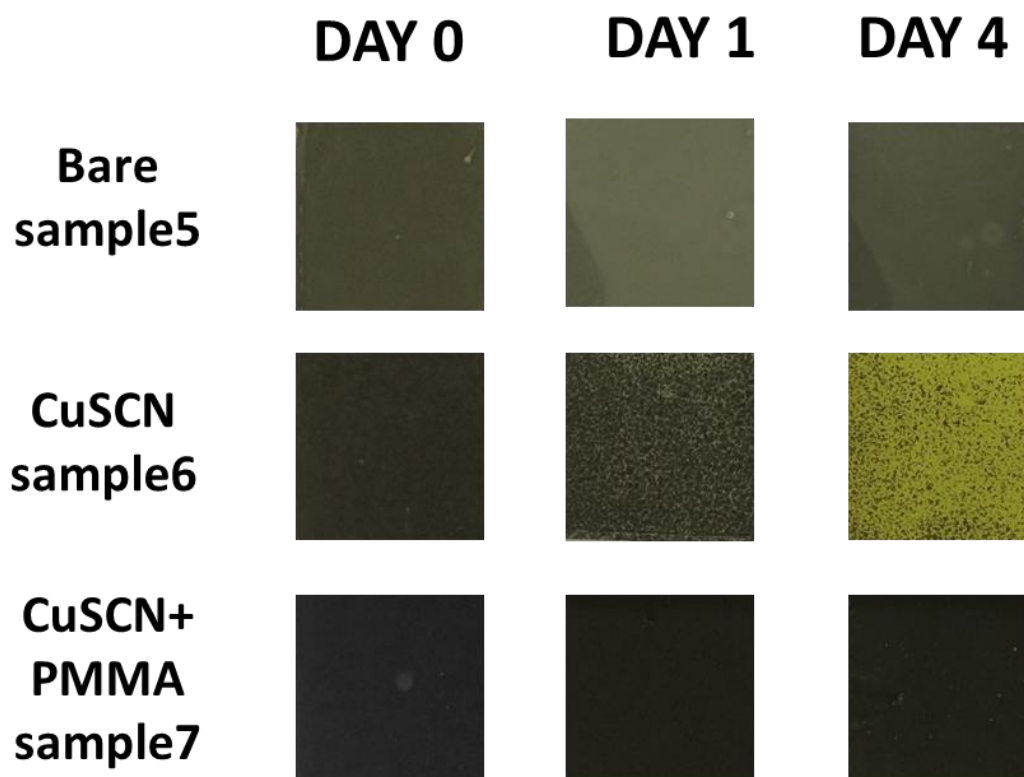


Figure 5.7 Photos of perovskite samples with different coating degrade in inert environment (N_2 filled glovebox) with thermal treatment at 85 °C.

Some additional experiments were conducted to determine the mechanism of this accelerated degradation. (i) In order to test the influence of the solvent, a bare perovskite sample was sprayed with pure dipropyl sulfide with the same spray coating technique as spraying CuSCN, and then thermally stressed in glovebox at 85 °C. Same as sample 5, this sample showed no change of colour during 4 days of aging. (ii) The second experiment is to remove the residue dipropyl sulfide after depositing CuSCN. This was realized by spin coating chlorobenzene on the prepared perovskite/CuSCN sample for several times. This sample shows the same rapid degradation trend as sample 6. The above two experiments approved that the rapid

degradation of perovskite is not related to dipropyl sulfide, and therefore it must be induced by CuSCN. (iii) Another experiment is to replace PMMA with other sealing materials such as polycarbonate and polystyrene, which give same protection effect as PMMA (sample 4 & 7). This proves the PMMA only plays the role as a blocking layer in this experiment.

To unravel the root of this change of colour, X-ray diffraction measurement was performed on the samples before and after the thermal aging in air, which is showed in Figure 5.8. For the bare perovskite samples (sample 1) (Figure 5.8 a), there is an increase in the intensity of PbI_2 (001) peak at 12.7° and at the same time decrease of perovskite (110) and (220) peak (14.2° and 28.5° , respectively). Here we zoom in to show the clear trend of the increase of PbI_2 (001) peak, which is a clearer degradation indication. After 4 days, there is no trace of the perovskite peaks left, with only PbI_2 peaks remaining. This is consistent with the colour change as is showed in Figure 5.6. This indicates that the observed degradation in the perovskite film is mainly induced and accelerated by the humidity and heat, which results in the irreversible rapid formation of PbI_2 and a loss of the organic component from the crystal structure.^{8,13,14} As previously showed by Habisreutinger *et al.*¹³, the rate of such a degradation is slowed down considerably when the film is coated with PMMA (Figure 5.8 c), since no increase can be observed in the peaks pertaining to PbI_2 , even after 4 days of ageing in a similar conditions. Looking at the X-ray diffraction of the CuSCN coated perovskite film (Figure 5.8 b), as with the bare film, there is a degradation of the perovskite crystals into the PbI_2 . Interestingly, in addition, new small peaks at 26° and 42° can be detected, which can be assigned to (111) and (220) peaks of CuI ³⁶. Notably, there remains a significant amount of CuSCN crystals even after the ageing for 4 days, since the main CuSCN (003) peak at 16.2° ³⁷ remains unchanged after the ageing.

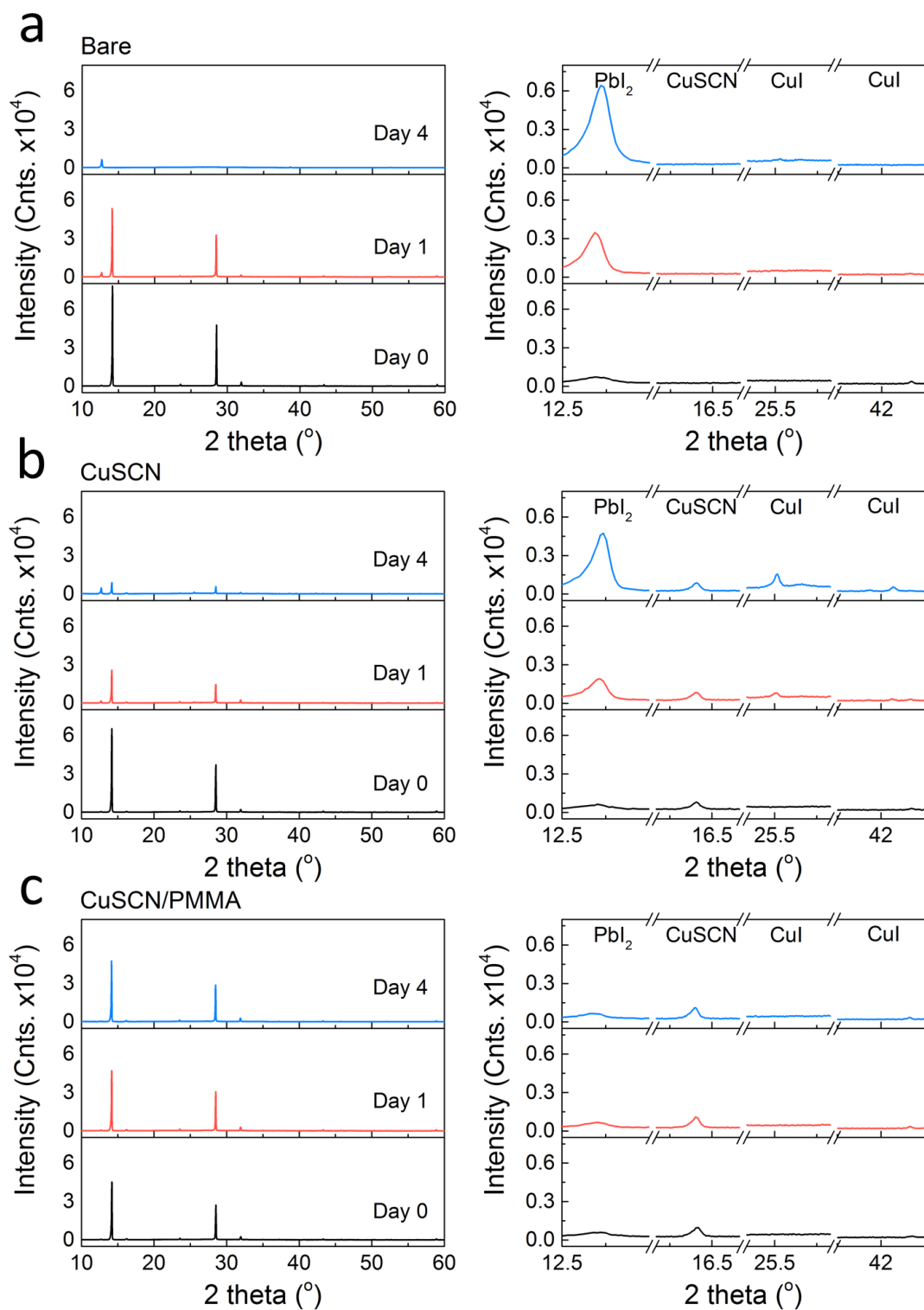


Figure 5.8 X-ray diffraction patterns of bare perovskite sample, CuSCN coated perovskite sample and perovskite sample coated with CuSCN plus PMMA (sample 1, 3 & 4) degrades in ambient condition (humidity ~50%).

Figure 5.9 shows the XRD patterns of samples (sample 5, 6 & 7) aged in inert atmosphere (N_2 filled glovebox). Here we can see bare perovskite sample (sample 5) doesn't show much degradation during 4 days aging experiment, with no decrease in the perovskite (110) and (220) peak (14.2° and 28.5° , respectively) (Figure 5.9 a). But when the sample is coated with CuSCN (Figure 5.9 b), rapid degradation occurs with same trend as sample aged in ambient environment (Figure 5.8 b). The (111) and (220) peaks of CuI can also be detected in this sample, which does not appear in the other two samples.

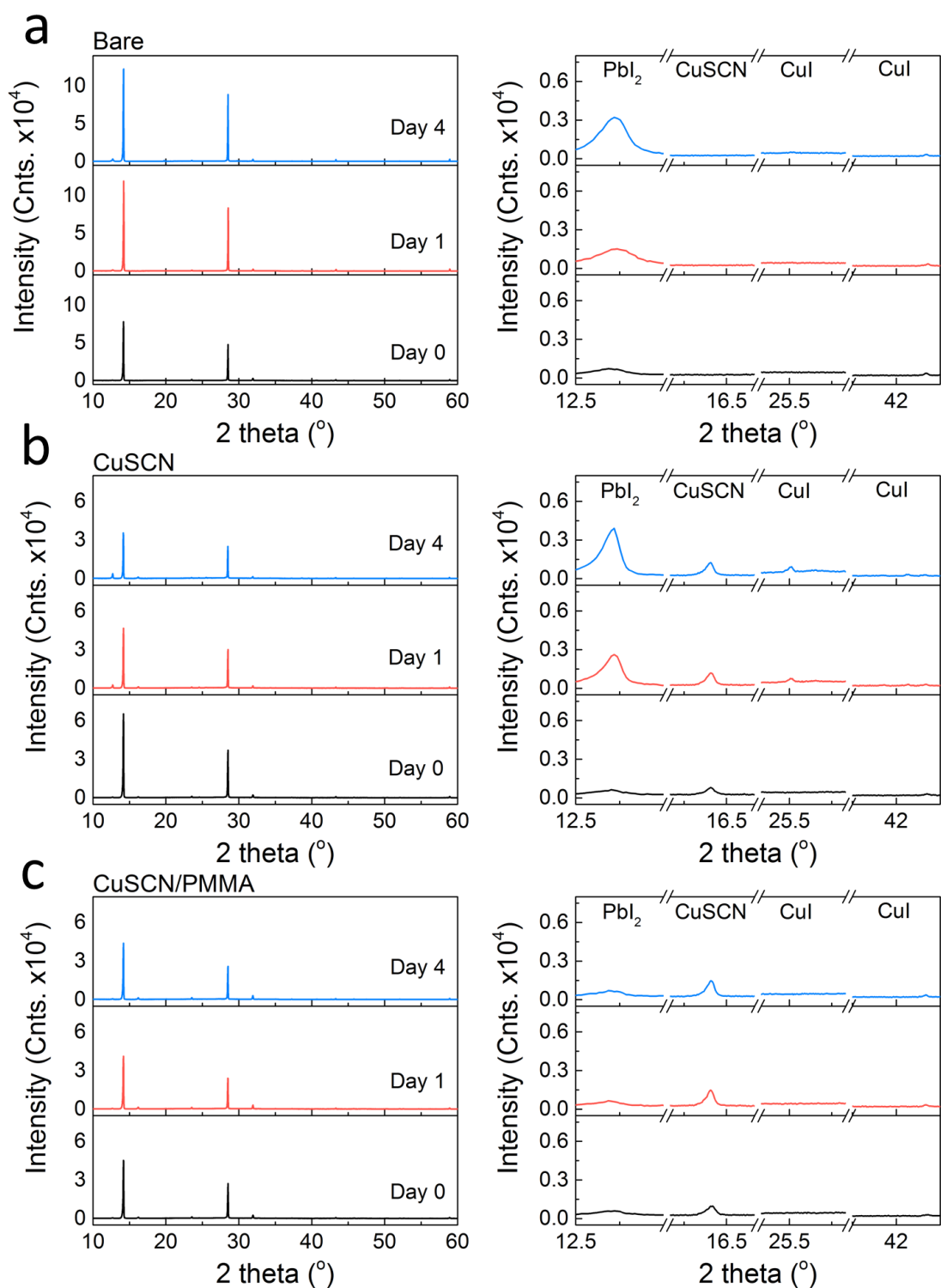
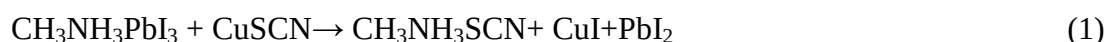


Figure 5.9 X-ray diffraction patterns of perovskite samples with different coating (sample 5, 6 & 7) degrade in inert atmosphere (Oxygen and water < 0.01ppm). (a) bare perovskite in glovebox, (b) perovskite/CuSCN in glovebox, (c) perovskite/CuSCN/PMMA in glovebox.

Therefore, the small signature of CuI, suggests that the degradation of the perovskite is induced by a reaction whereby CuI is formed, alongside a degradation and loss of the MA⁺ from the perovskite films. Here a postulated reaction is showed in scheme 1, whereby MAI and CuSCN react to form MASCN and CuI,



The above discussion has shown strong evidence that CuSCN does induce degradation in the perovskite film. However, for degradation to proceed, the volatile bi-products (which is postulated to be MA-SCN, m. p. 73-74°C³⁸) must be able to diffuse out and leave the film. Otherwise, a substantial vapor pressure will build up within the cell, until equilibrium between decomposition and reformation occurs, at which point the degradation would cease. Hence, it is reasonable to assume that this degradation should be able to be retarded if the films can be suitably sealed. Indeed, as can be observed in Figure 5.6 (sample 4) and Figure 5.8 c, when the CuSCN coated perovskite films were coated with PMMA, there is no observable degradation over the aging period. Therefore I proceeded to construct complete devices, where following gold electrode deposition, the devices were further coated with a layer of PMMA as a rudimentary encapsulation, serving a dual function of keeping the material in the devices, in addition to keeping the atmosphere out. Figure 5.10 shows cross sectional SEM images of the devices. From the top view image (Figure 5.4 b), we can see a highly mesoporous film with several pinholes throughout the film, consisting crystals of diameters around 200nm. These pinholes may not be easily detectable in cross-sectional SEM (Figure 5.10 a), but after coating PMMA it can be clearly seen that they are filled up with the non-conducting polymer (Figure 5.10 b). Without

coating, the pin holes may allow atmospheric humidity to ingress through the CuSCN film, in addition to allowing degradation bi-products out of the film. These pinholes are harmful not only for the stability of perovskite but also for the fabrication of high performance solar cell, as the top electrodes can protrude through the CuSCN making a direct contact with the perovskite film, which is harmful for overall device performance¹⁴. To further improve the homogeneity of the CuSCN film, an additional mesoporous Al₂O₃ “buffer layer” is inserted on top of the perovskite film prior to coating with CuSCN (Figure 5.10 c). This will in one instance reduce the contact area of the CuSCN with the perovskite which may slow the degradation process at this interface, and in addition it will help reduce pinhole formation, as has been widely observed when this sort of scaffold is employed in the perovskite active layer.^{39–41}

Perovskite solar cells were fabricated with CuSCN/Au, CuSCN/Au/PMMA, Al₂O₃/CuSCN/Au and Al₂O₃/CuSCN/Au/PMMA configurations respectively. Devices with Spiro-OMeTAD as HTM are also fabricated as reference. It is worth mentioning that it is not possible to coat the Spiro-OMeTAD containing cells with PMMA since the solvent used for the PMMA dissolves the Spiro-OMeTAD and the thermally evaporated Au electrode failed to offer suitable resistance. Detailed description of the device fabrication method is in experimental section. Briefly, CuSCN/Au/PMMA based solar cells were fabricated by simply coating PMMA on the top of the completed solar cells (i.e. with top electrode), which has no influence in the solar cell performance. And to deposit Al₂O₃/CuSCN film, a thin Al₂O₃ mesostructured buffer layer was first coated on the top of the perovskite film and then CuSCN was deposited upon it. With this structure, similar PCE from FB-SC scan (13.2%) can be obtained, but with lower stabilized power output (8.0%) and larger hysteresis (Figure 5.11). Devices with the combination of these two methods were also fabricated, with PMMA

further coated on top of CuSCN (Figure 5.10 d). All the devices show initial scanned PCEs between 12-14%

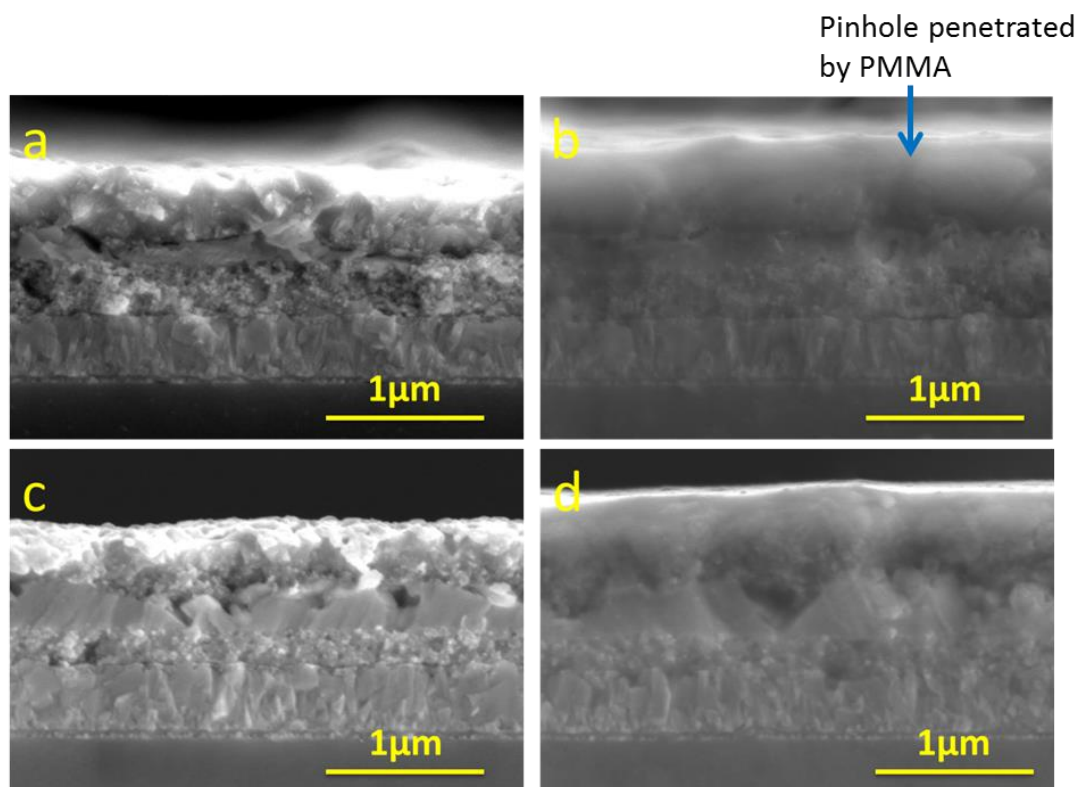


Figure 5.10 Cross sectional SEM images of as fabricated perovskite solar cell. The structure of hole transporting layer is (a) CuSCN, (b) CuSCN/PMMA, (c) Al₂O₃/CuSCN and (d) Al₂O₃/CuSCN/PMMA, respectively.

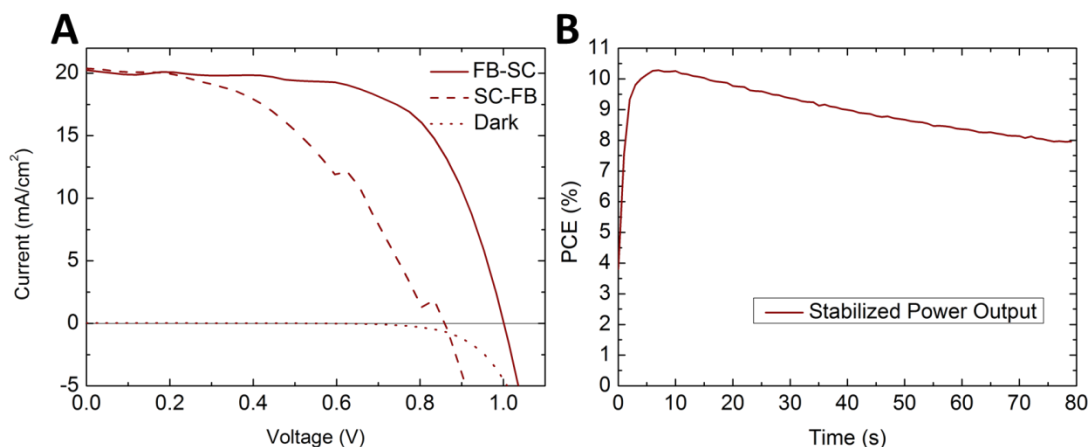


Figure 5.11 (a) Current voltage curves and (b) stabilized power output (SPO) of perovskite solar cells with Al₂O₃/CuSCN hole transporting layer configuration.

One of the key drivers to employing CuSCN is that it should be more thermally stable as a material than most organic hole-conductors. However, the degradation mechanism discovered here appears to put the prospects of this material in jeopardy. In order to assess if the cells could still prove to be stable with CuSCN, the as fabricated cells were subsequently thermally stressed by placing them in an oven at 85 °C in ambient condition, and then recorded the change of solar cell performance (PCE) from FB-SC scan and stabilized power output for 45 days. From Figure 5.12 a, we can see devices with only CuSCN as HTM (red circle) degrade rapidly, as compared to devices with Spiro-OMeTAD as the HTM (black square), with the cells retaining 9% and 28% of initial PCE after 45 days, respectively. This is consistent with the degradation in the films presented above. Applying an Al₂O₃ mesostructured layer (green triangle) slightly increases the device stability, while the coating of PMMA (blue triangle) significantly enhances the solar cells stability. With the combination of these two methods of introducing an Al₂O₃ buffer layer and coating the complete cell with PMMA (pink triangle), the devices become remarkably stable, retaining 77% of initial PCE after 45 days thermal stressing at 85 °C.

As has been repeatedly observed in the past, some perovskite solar cell device architectures exhibit hysteresis in the current voltage curves.^{42,43} This appears to result from a combination of defect sites responsible for trap assisted recombination, and mobile ionic species. The mobile ions can temporarily compensate for the presence of charge recombination centers, and enable high efficiency to be measured via JV scans, even when the steady state stabilized power output (SPO) is low.⁴⁴ We would therefore expect that as degradation proceeds, it may not be as visible in the JV curves as it is in the measurement of the stabilized power output. Figure 5.12 b shows the SPO for the same cells and do indeed observe that the SPO drops more rapidly than the JV determined efficiency. This indicates that there are defect sites generated during the thermal aging, even in the most stable structures presented here. Despite that however, the most stable cell architecture incorporating $\text{Al}_2\text{O}_3/\text{CuSCN}/\text{Au}/\text{PMMA}$, still retains 39% of its initial SPO after 45 days aging at 85 °C in ambient conditions. Since this study has been undertaken with MAPbI_3 , which is known to be thermally unstable at 85 °C, and it has been identified that CuSCN degrades the perovskite even in an inert atmosphere, this achievement with an extremely rudimentary form of encapsulation (single coat of ~100nm thick PMMA film) is surprising. It also offers great encouragement to achieving many 1000's of hrs thermal stability with thermally stable perovskites integrated with non-degradation-inducing hole-transporters with proper encapsulation.

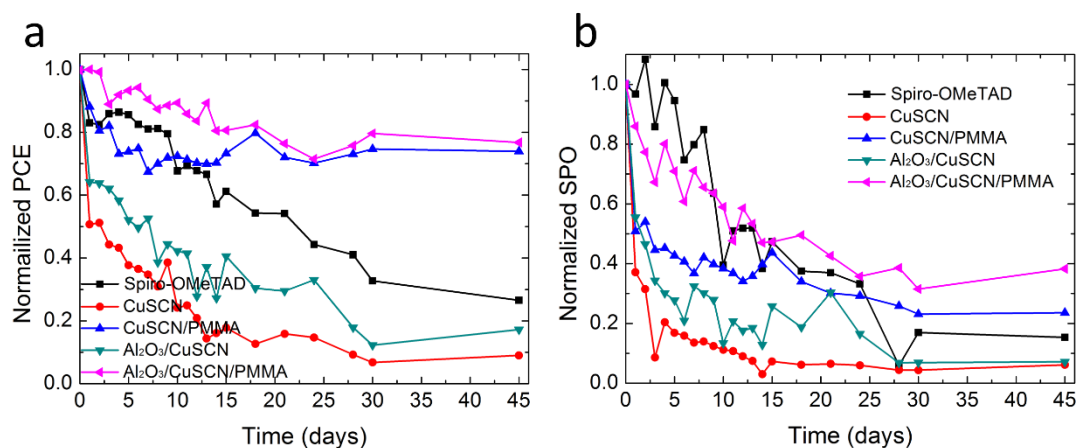


Figure 5.12 Stability of perovskite solar cells with different HTM structure stressed at 85 °C in ambient condition. Data showed here are from (a) normalized PCE from FB-SC scan and (b) normalized SPO, respectively.

5.7 Summary and Outlook

This chapter shows that spray-coated CuSCN can be employed as the hole-transporter in efficient perovskite solar cells with controllable and uniform hole transporter thickness and good device reproducibility. The champion solar cell exhibits a power conversion efficiency of 13.3% at FB-SC JV scan and stabilized power output at 10.9%. However, a critical instability introduced by the CuSCN is discovered, where it accelerates thermal degradation of CH₃NH₃PbI₃, even in an inert atmosphere. Despite the presence of the “degrading interface” and the known thermal instability of CH₃NH₃PbI₃, with a simple encapsulation via coating the cells with PMMA, 45 days thermal stressing in ambient conditions with the cells retaining 77% of their measured efficiency and 39% of their SPO is demonstrated. Firstly, this indicates that encapsulation is required to keep the potential perovskite film degradation products *in* the solar cell, in addition to keep the atmosphere *out*. Furthermore, it highlights that if CuSCN is to be employed as a hole-transporter in perovskite solar cells, the interface

between the perovskite and the CuSCN requires modifying in such a manner as to eliminate, or greatly retard, this process. With the multitude of different p and n-type materials available for integration into perovskite solar cells, this work further reinforces the notion that assessment of the chemical and structural stability of the heterojunction under a multitude of stressing conditions is a key requirement to find suitable semiconductors for perovskite solar cells.

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Chapter 6. Morphology and Electronic Property Engineering of CuSCN Hole Transporting Layer with CuI Doping

6.1 Contexts

In the previous chapter, copper (I) thiocyanate (CuSCN) has been demonstrated as a suitable inorganic hole transporting material (HTM) for perovskite solar cells, leading to photovoltaic devices with decreased cost and increased stability. However, the performance of CuSCN based solar cells is still lower than that of Spiro-OMeTAD based devices, probably due to the multi-pinhole morphology and the limited charge transport effectiveness of the spray-coated CuSCN film. This chapter demonstrates a simple route to improve the effectiveness of CuSCN HTM, that is doping the precursor with copper iodide (CuI). After doping, the CuSCN HTM shows improved charge extraction and transport effectiveness, leading to a significant increase of solar cell performance. An elaborate study is conducted to investigate the mechanism of this doping effect.

6.2 Introduction

Low-cost and simple processable organic-inorganic metal halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ has emerged as one of the most promising material to be developed as next generation photovoltaic technology since 2012, with power conversion efficiency (PCE) of certified lab cells rising up to 22.1%.^{1–6} To date, there are two main obstacles preventing the application of this magic material in industry: (1) Its instability in ambient environment conditions; (2) Relatively high cost induced by using traditional hole transporting material (HTM), that is 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenyl-amine) 9,9'- Spirobifluorene (Spiro-OMeTAD).^{7–10} There are therefore huge efforts contributed to searching alternative HTMs for perovskite solar cells (PSCs), aiming for decreased cost and increased stability.^{9,11–20} In terms of stability concern, low cost and solution processable inorganic semiconductors such as copper(I) iodide (CuI) and copper (I) thiocyanate (CuSCN) has a great advantage among those organic candidates such as poly (3-hexylthiophene-2,5-diyl) (P3HT) and poly (3,4-ethylenedioxythiophene) (PEDOT), etc. Specifically, the use of CuSCN has shown encouraging results in PSCs application, with highest PCE of 13.3% reached in 'regular' structured with TiO_2 as electron-transporting layer (ETL), and 16.6% in 'inverted' with PCBM as ETL.^{21–27} Besides that, it has also been shown in the previous chapter that by simply 'encapsulate' PSCs with a thin layer of Poly(methyl methacrylate) (PMMA), super stable devices can be achieved, which survive over 1000 hrs under 85 °C thermal stressing in ambient condition. On the other hand, CuI as another solution processable inorganic p-type semiconductor with higher solubility and higher hole mobility (CuI: $0.5\text{--}2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ vs. CuSCN: $0.01\text{--}0.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$)^{28,29} has also been reported to be applied in PSCs, with highest PCE of 7.5% with no hysteresis has been achieved.^{9,30} It is also widely reported that CuI can be applied as a p-type dopant to improve the effectiveness of hole injection layer in

organic light-emitting diodes and dye-sensitized solar cells.^{31,32} In this chapter, a simple route is demonstrated to improve electronic property of spray coated CuSCN film by adding small amount of CuI solution in the CuSCN precursor. Surprisingly, it is also found this doping technique can affect the morphology of as fabricated CuSCN film, leading to better electronic connection between CuSCN crystals. The influences of CuI and the added solvent (acetonitrile, ACN) on the film characteristics are studied and discussed separately. The doping improves the charge collection and transport of the as fabricated film, which is certified with photoluminescence (PL) and conductivity measurement. Then ‘regular’ n-i-p structured perovskite solar cells were fabricated with modified CuSCN HTM, achieving a PCE of 14.4% and a stabilized power output (SPO) of 12.3%, comparing to 11.5% (PCE) and 9.9% (SPO) for PSC with non-doped CuSCN as HTM. Solar cell stability test shows a tiny improvement in modified devices, proving that there is no sacrifice in stability for achieving higher performance.

6.3 Method

6.3.1 CuI Doping and CuSCN Deposition

Copper (I) thiocyanate (99%, Sigma Aldrich) was dissolved in dipropyl sulfide (97%, Sigma Aldrich) to reach a concentration of 8mg/ml. A clear CuSCN solution can be obtained after stirring for 48 hours. Copper (I) iodide (95%, Sigma Aldrich) was dissolved in acetonitrile (99.8%, Sigma Aldrich) to reach a concentration of 20mg/ml. A clear CuI solution can be obtained after shaking for 2 min. The two solutions were then mixed to obtain a homogenous solution with certain doping concentration. For example, 0.024 ml CuI solution was added in 5.94 ml CuSCN to reach a 1% doping level. The spray-coating method is the same as previously described in detail in

section 3.1.5.3.

6.3.2 Device Fabrication

The device fabrication process has been described in detail in section 3.1 and section 5.3.2. All the solar cells in this chapter are meso-structured devices, with an optimized mesoporous Al_2O_3 scaffold thickness of $\sim 250\text{nm}$.

6.3.3 Measurement and Characterization

Characterization methods used in this chapter include: current-voltage characterization, photoluminescence (PL) measurement, UV-vis absorption measurement, and conductivity measurement. The details of these characterization techniques have been described in section 3.2.

6.4 Thin Film Characterization

The impact of CuI doping on the morphology of CuSCN film was first checked with scanning electron microscopy (SEM). Figure 6.1 shows the top view images of CuSCN films with different CuI doping levels. Here the percentage of CuI weight to the total weight of CuSCN plus CuI in the mixed precursor solution was calculated as doping concentration. The details of doping protocol are described in method section. Figure 6.1 a shows that neat CuSCN film is consisted of CuSCN crystals of $\sim 200\text{nm}$, where the boundaries of crystals are very clear to recognize. When the doping level was increased to 1%, 2% and 5%, the crystal boundaries become blurred, suggesting better connection between crystals. As the doping level further increased to 10% and

20%, the round grain morphology of CuSCN vanishes completely and surface morphology of perovskite surface can be clarified from the top view image, which indicates that the spray coated film cannot crystallize properly on the perovskite surface to form a hole transporting layer (HTL).

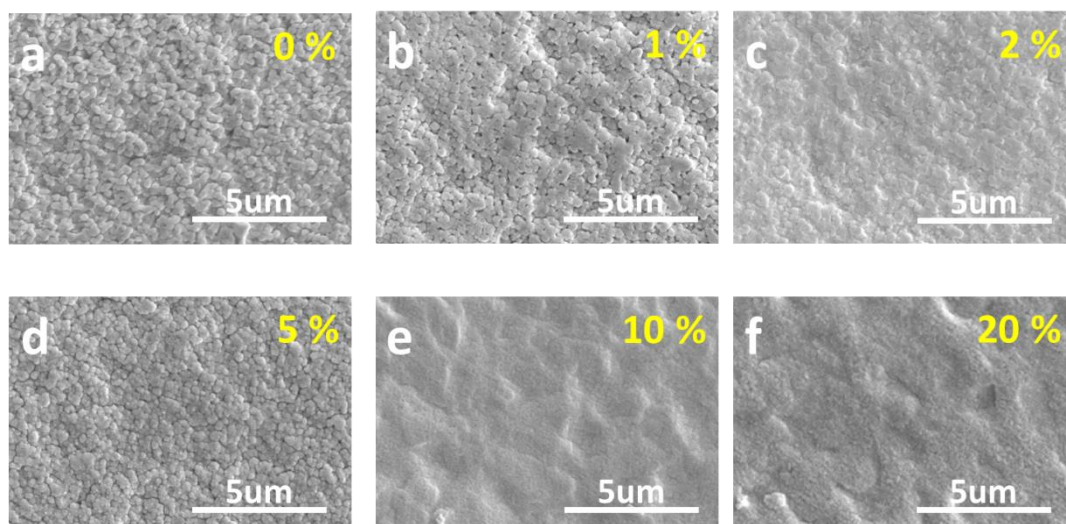


Figure 6.1 Top view scanning electron microscopy (SEM) images of CuSCN with different CuI doping levels. Here the percentage is calculated as the weight of CuI to the total weight of CuSCN plus CuI in precursor.

Noting that CuI is dissolved in acetonitrile (ACN), which has a boiling point (b.p. 82 °C) much lower than the solvent used to dissolve CuSCN (dipropyl sulfide, b.p. 142 °C), it is reasonable to assume that the morphology change might be related to the added solvent. In order to check the influence of pure solvent, CuSCN films with only different amount of ACN added in precursor are also deposited, and the morphology of these films is checked with SEM. The amount of ACN added here was controlled to be equivalent to the amount of solvent added when doping CuI, and the percentage of CuI doping is used to indicate the amount of ACN added. As can be seen from the SEM images (Figure 6.2), with the amount of ACN added increases, the size of

CuSCN crystal decreases. This should be due to the addition of low b.p. solvent facilitates the evaporation of solvent and crystallization speed of CuSCN during spray-coating process. However, no trend of crystal boundary blurring from these samples can be observed, confirming that CuI plays an important role in altering the film morphology.

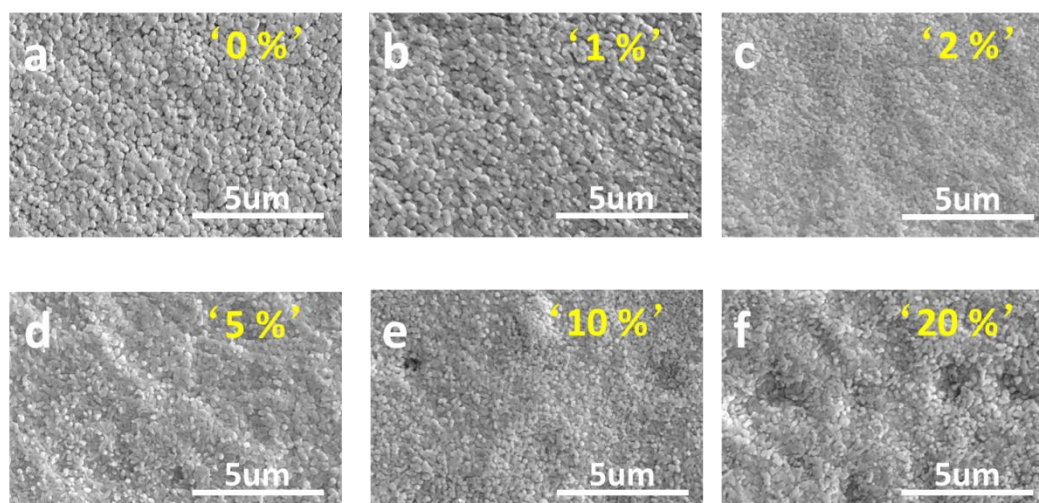


Figure 6.2 Top view SEM images of CuSCN with different amount of ACN added in precursor. Here the percentage indicates the equivalent amount of solvent added when doping CuI.

In order to identify the change of crystal structure on unit cell dimension, the X-ray diffraction (XRD) patterns of the doped and non-doped CuSCN films spray-coated on perovskite films were recorded. As can be seen from Figure 6.3, the intensity of CuSCN (003) peak (16.2°)³⁴ doesn't change obviously when the doping level is below 2%. But with further increase of CuI doping level, this peak intensity decrease notably. Therefore, it can be concluded that the low level CuI doping ($\leq 2\%$) does not change the CuSCN crystal structure of the spray coated film, while further increase of

the CuI doping level result in decrease of CuSCN crystallinity. In addition, there is no detectable peak of CuI (111) peak at 25.6° ²⁸ even when the doping level is up to 20%, which means no detectable CuI crystal forms in this process.

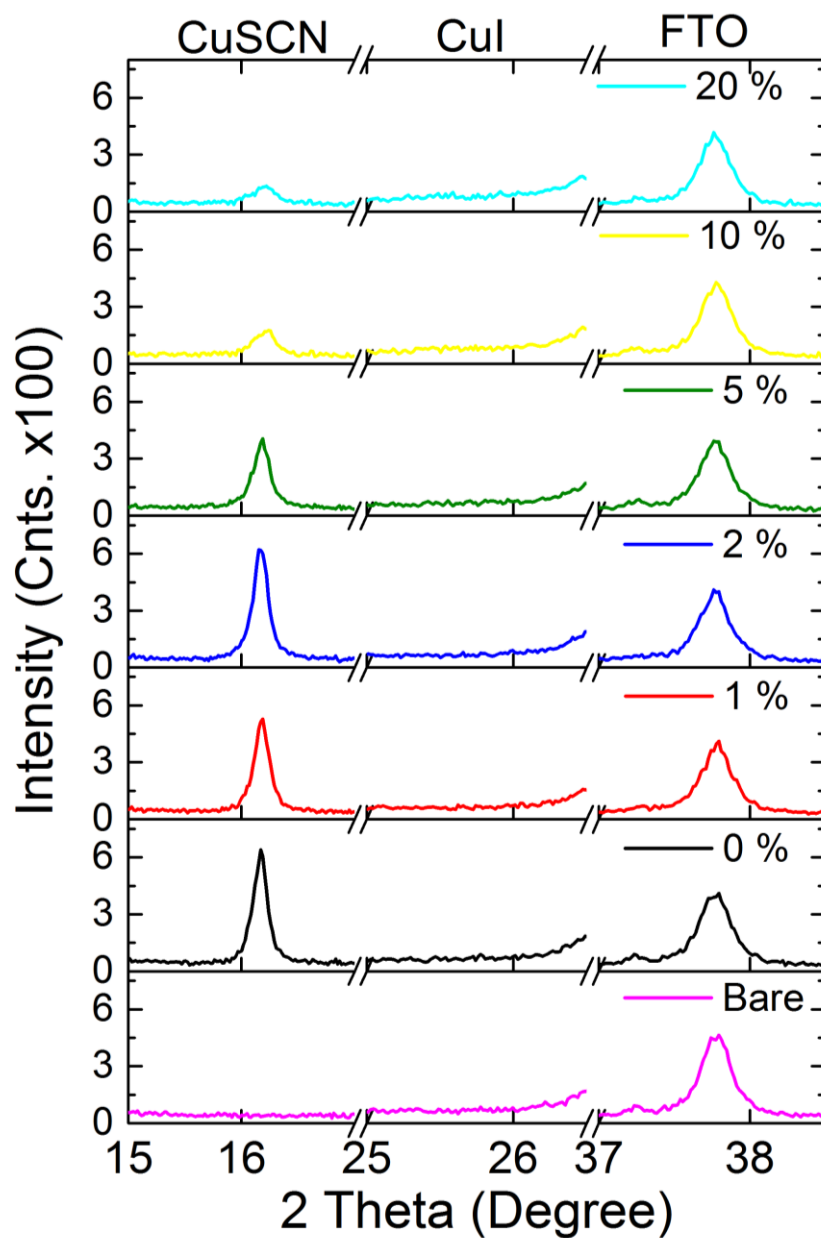


Figure 6.3 X-ray diffraction (XRD) pattern of CuSCN films with different CuI doping levels. All the films are deposited on top of perovskite films.

The XRD patterns for samples with only ACN added is recorded in figure 6.4, which shows no trend of change in CuSCN peak intensity. This further confirms that the reduced crystallinity of CuSCN observed here is caused by the adding of CuI.

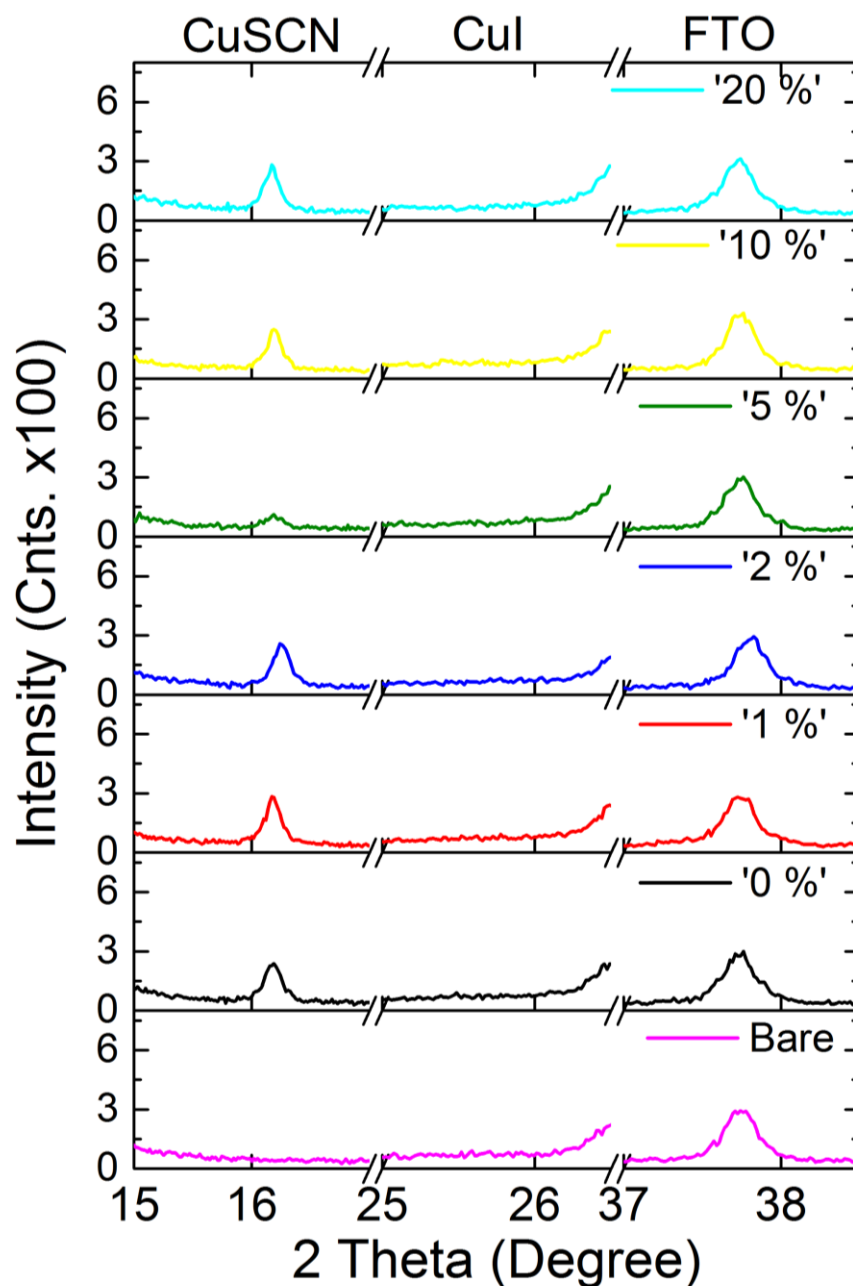


Figure 6.4 X-ray diffraction (XRD) pattern of CuSCN films with different amount of ACN added in precursor.

An effective p-type HTL should be capable of selectively extract holes from the perovskite absorber layer, and the rate of photoluminescence (PL) quenching is a good indication for accessing the effectiveness of the hole extraction.³⁵ Therefore, the steady-state and time-resolved PL measurements were performed for perovskite films covered by CuSCN films with different CuI doping levels (0%, 1%, 2% and 5%), comparing with bare perovskite sample without a quenching layer (Figure 6.5 a & b). Figure 6.5 a shows that after doping with 1% (red) or 2% (blue) CuI the quenching rate increases as the steady-state PL peak intensity decreases, indicating more holes are extracted to HTL before recombination happens. But when the doping level increase to 5% (green), the peak intensity increases again, suggesting a decrease of quenching effectiveness at high level doping. This result is consistent with the trend from SEM and XRD data, where high level doping ($\geq 5\%$) deteriorates CuSCN crystal structure. However, the trend of higher quenching rate at 1% (red) or 2% (blue) doping is not notable from the time-resolved measurement (Figure 6.5 b), suggesting the doping doesn't lead to an enhancement in the charge extraction speed. Nevertheless, it can still be seen at 5% doping (blue), the quenching effectiveness decreases as PL lifetime slightly increases. Therefore, it can be concluded that low level doping of CuI slightly improves the charge extraction effectiveness of CuSCN HTM, while further increasing the doping concentration will lead to the opposite result.

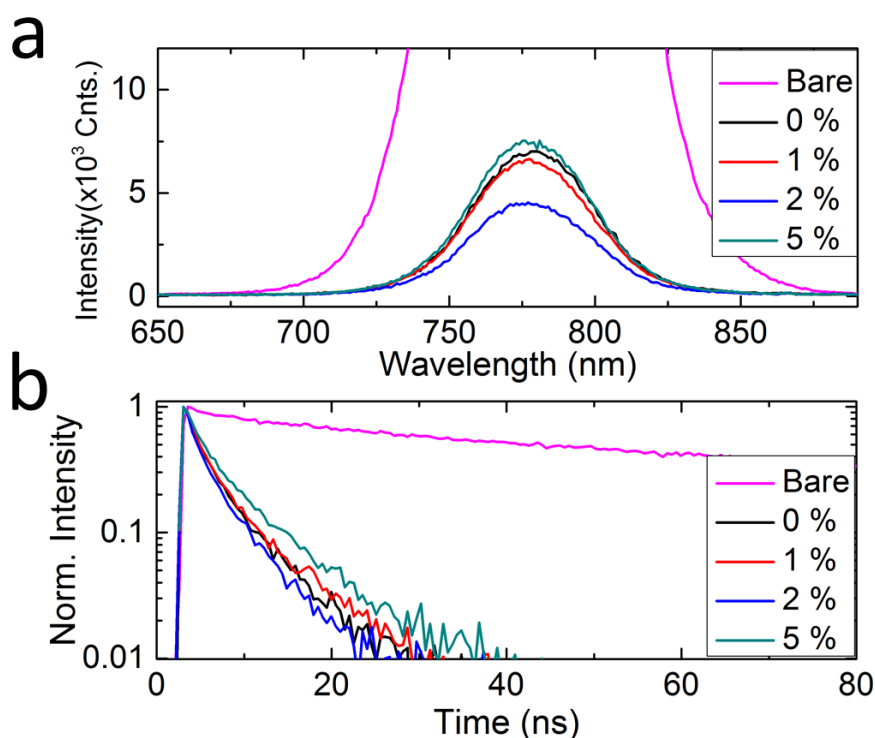


Figure 6.5 (a) Steady-state PL spectra and (b) time-resolved PL decay excited at 510nm of bare perovskite film (pink) and perovskite films coated with neat CuSCN (black), and CuSCN doped with 1% (red), 2% (blue) and 5% (green) CuI, respectively.

Beyond being extracted to HTM, the holes need to be effectively transported to the metal electrode. Hence, the conductivity of the CuSCN film with 0%, 1% and 2% of CuI doping was measured with four-point probe method, where the conductivity increases from $(2.4 \pm 1.6) \times 10^{-6}$ S/cm to $(6.4 \pm 0.9) \times 10^{-5}$ S/cm and $(1.6 \pm 0.8) \times 10^{-4}$ S/cm after doping. In addition, the conductivity of CuSCN samples with only ACN added in precursor was also measured, where no notable increase in conductivity can be observed ($(2.5 \pm 0.9) \times 10^{-7}$ S/cm for ‘1%’ and $(3.8 \pm 1.4) \times 10^{-6}$ S/cm for ‘2%’). This indicates that CuI doping can successfully increase the effectiveness of charge transport in HTL. Combining our observation from SEM and XRD, it can be concluded that the formation of CuSCN film can be

modified by doping CuI at controlled concentration, which leads to a better coverage and connection between the CuSCN crystals, and further improve the charge extraction and transport of the as fabricated HTL.

6.5 Solar Cell Performance and Stability Test

Perovskite solar cells were subsequently fabricated with regular device architecture, an illustration of which is showed in Figure 6.6 a. Here, a 50nm compact TiO₂ is used as an electron extraction layer and a 250nm Al₂O₃ non-conductive mesoporous film to prevent shunting between TiO₂ and HTM. Figure 6.6 b shows the respective energy level of each component.

The current-density voltage (J-V) characteristics of the solar cells with doped and non-doped CuSCN as HTM are measured under AM 1.5G simulated sunlight (100 mWmA⁻²). Table 1 shows the best performing devices with different HTL. Here the photovoltaic device based on non-doped CuSCN shows a short-circuit current (J_{sc}) density of 18.8 mA/cm⁻². After doping the CuSCN with 1% or 2% CuI, this number has increased to 21.24 and 20.79 mA/cm⁻², respectively. There is also an obvious increase in the open-circuit voltage (V_{oc}) and fill factor (FF), suggesting less recombination at perovskite/HTL interface. This improvement can be attributed to CuI doping, which significantly enhanced the effectiveness of both hole extraction from perovskite and hole transport in HTL, as has been previously suggested. As a result, there is an obvious enhancement in the photo conversion efficiency (PCE), which increases from 11.5% to 14.4% (1wt%) and 14.3% (2wt%), respectively. Figure 6.6 c shows the J-V curve of these three devices. However, the solar cell performance gets worse with further increase of the doping level. This might due to the change of crystallinity and worse film coverage as previously showed in SEM images (Figure 6.1) and XRD analysis (Figure 6.2). To determine the actual steady

state stabilized power conversion efficiency of each type of devices, the stabilized power output (SPO) measurement was performed by measuring the PCE (%) over time at a fixed voltage close to maximum power point on the FB–SC J-V curve (Figure 6.6 d). After illuminating under 1 sun for 50s, the PCE (%) of neat CuSCN device is stabled at 9.9%, and the SPO of 1% and 2% CuI doped CuSCN device settles at 12.3% and 11.7%, respectively.

Table 1. Solar cell performance parameters of perovskite solar cells applied with CuSCN HTM with different CuI doping levels.

CuI (%)	J_{sc} (mA/cm ²)	PCE (%)	V_{oc} (V)	FF
0	18.80	11.5	0.95	0.64
1	21.24	14.4	0.98	0.69
2	20.79	14.3	1.01	0.67
5	18.49	8.7	0.98	0.48
10	14.58	6.8	0.92	0.50
20	16.31	5.9	0.86	0.41

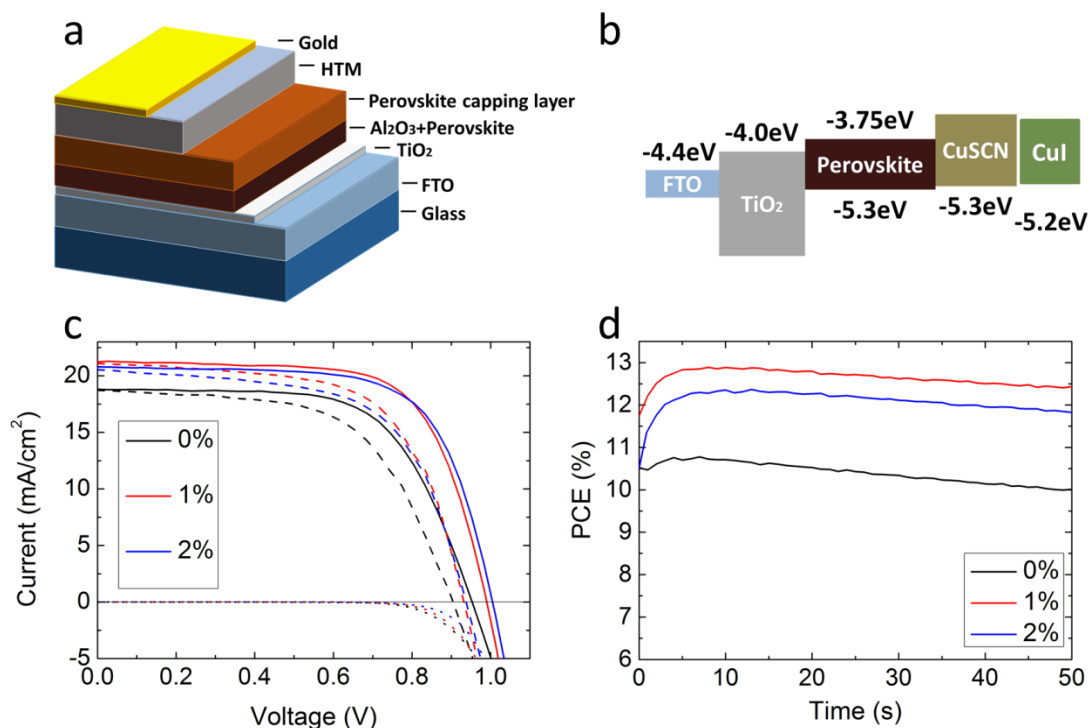


Figure 6.6 (a) Device schematic. (b) Approximate energy band diagram of the fabricated structure taken from reference.³⁶ (c) Current voltage curves for best devices with neat CuSCN (black), CuSCN doped with 1% (red) and 2% (blue) CuI as HTM, respectively. Both forward-bias to short-circuit (FB-SC, solid line) and from short-circuit to forward-bias (SC-FB, dash line) J-V curves are showed. (d) Power conversion efficiency as a function of time under illumination at a fixed voltage of the maximum power point on the J-V curve (FB-SC) for best devices with neat CuSCN (black), CuSCN doped with 1% (red) and 2% (blue) CuI as HTM, respectively. The reference cell with neat CuSCN as HTM has not reached the best performance as reported in the previous chapter.

To investigate the influence of ACN on solar cell performance, devices with only ACN added in CuSCN precursor are also fabricated, and the results of which are showed in Table 2. There is a clear trend that adding ACN also leads to an increase of

photo-current of as fabricated solar cells (16.54 to 19.92 mA/cm²), with best PCE of 13.9% can be obtained. Combining with the film morphology change showed in Figure 6.2, it can be assumed that the decrease of CuSCN crystal size leads to better coverage, which further results in improved hole collection effectiveness. However, the SPO of these devices remain very low comparing to CuI doped devices (<7%), suggesting a huge recombination at perovskite/HTL interface. Therefore, this result suggests that the increase of conductivity with CuI doping is necessary for minimizing the recombination at interface, which is crucial for achieving ideal PCE and SPO for devices.

Table 2. Solar cell performance parameters of perovskite solar cells applied with CuSCN HTM with different amount of ACN added in precursor.

ACN (%)	J_{sc} (mA/cm ²)	PCE (%)	V_{oc} (V)	FF	SPO
0	16.54	11.0	0.95	0.70	6.7
1	17.49	12.2	0.98	0.71	6.8
2	18.61	13.3	0.98	0.73	6.2
5	19.77	13.8	0.98	0.71	6.7
10	18.78	13.3	0.98	0.72	5.3
20	19.92	13.9	0.98	0.71	6.8

Besides selectively extracting holes from perovskite to increase the solar cell efficiency, an ideal HTM should also act as a moisture and oxygen blocking layer to improve the stability of the devices. However, the CuSCN, as demonstrated in the previous chapter, can accelerate the degradation of CH₃NH₃PbI₃ under elevated

temperature (85 °C). Therefore, perovskite solar cells with 0% or 1% CuI doped CuSCN as HTM, either covered or uncovered with PMMA were fabricated for stability test. The as fabricated cells were thermally stressed by placing in an oven at 85°C in ambient condition, and then recorded the change of solar cell performance (PCE) from FB-SC scan and stabilized power output (SPO) for 25 days. Without PMMA protection, as showed in Figure 6.7 a & b, both devices with doped or non-doped HTM degrade rapidly with a similar trend. With PMMA coverage, the PCEs of both devices show similar degradation in the first 17 days. While after 20 days, 1% CuI doped sample shows slightly better stability, retaining 69% initial PCE after 25 days stressing, comparing with 50% for the non-doped sample. As can be seen in Figure 6.7 b, the SPO degradation also shows a similar trend, where doped sample retains slightly higher SPO of 41% after 25 days, comparing to 25% for non-doped sample. This analyse suggests that CuI doping can effectively enhance the device performance without sacrificing its stability, and even give it a tiny improvement instead.

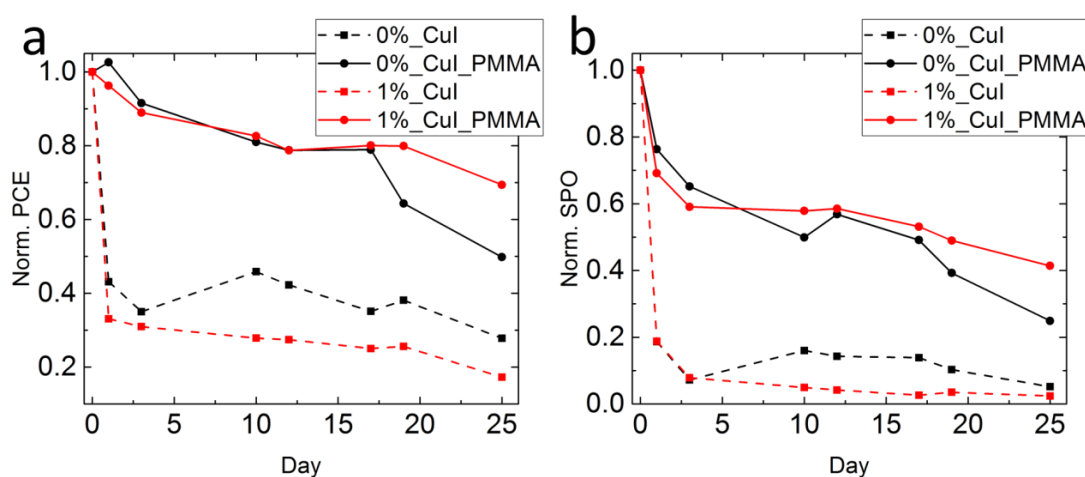


Figure 6.7 Stability of perovskite solar cells with different HTM structure stressed at 85°C in ambient condition. Data showed here are from (a) normalized PCE from FB-SC scan and (b) normalized SPO, respectively.

6.6 Summary and Outlook

In summary, a simple route is demonstrated for modifying the morphology and electronic property of spray coated CuSCN HTL for PSCs. By low level doping CuSCN with CuI, the film coverage and electronic connection between CuSCN crystals are increased with altered film morphology, leading to an improvement of the effectiveness of hole extraction and transport of as fabricated HTL. Perovskite solar cells with this modified HTL show improved PCE up to 14.4% and SPO of 12.3%, which is so far the highest efficiency for ‘regular’ structured PSCs with inorganic HTL and normal TiO₂ as ETL. Solar cell stability test shows that instead of bringing any negative effect, this doping treatment even provides a slight improvement on the stability for modified PSCs.

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Chapter 7. Conclusions and Outlook

7.1 Research Overview

This thesis has focused on novel hole-transporting materials (HTMs) for perovskite solar cells (PSCs), aiming at achieving devices with increased photo conversion efficiencies (PCEs) and enhanced stability. In particular, the thesis includes extensive studies of two kinds of HTMs, PEDOT and CuSCN, which have been previously reported to be stable and highly conductive p-type semiconductors widely used in other applications, but the utilization of which in PSCs has not been fully developed. Therefore, device optimization was conducted with modifications of HTM deposition techniques and perovskite surface treatment, accompanied with charge extraction and transport analysis, as well as a device stability study.

The adoption of a conductive polymer, Poly(3,4-ethylenedioxythiophene) (PEDOT), on regular structured PSCs was demonstrated in Chapter 4. As a material with high conductivity, high visible light transmissivity, and excellent stability, PEDOT is promising for antistatic, electronic, and optoelectronic applications.¹⁻⁴ Although the application of PEDOT as a counter electrode for dye-sensitized solar cells has been

under intensive study with PCE over 8% realized⁵⁻¹¹, employing PEDOT in ‘regular’ structured PSCs can be problematic as the commonly used water solution dissolves perovskite immediately after deposition. Therefore, in this chapter, a specifically formulated PEDOT ink, which is a dispersion of PEDOT and a sulfonated block-co-polymer dispersed in toluene, is employed as a HTM. The optimized deposition protocol is first treating the perovskite surface with iodopentafluorobenzene (IPFB), which binds to and screens the electrostatic charge from the under-coordinated halide ions, decreasing the recombination rate.¹² Consequently, the sonicated and filtered PEDOT solution was spin-coated on top, followed by sintering at 120 °C for 15 min, as described in detail in Chapter 2. The as fabricated devices showed a champion PCE of 14.5% from forward bias to the short circuit (FB-SC) *J-V* curve, which is comparable of that of Spiro-OMeTAD based devices. However, the PEDOT based devices suffered from a huge hysteresis (PCE=4.9% from short circuit to forward bias (SC-FB) *J-V* curve) and a low stabilized power output (SPO) (6.6%). This phenomenon was further analyzed with electronic impedance spectroscopy (EIS), which suggests a higher recombination rate at the perovskite/HTM interface for PEDOT based devices compared to that of Spiro-OMeTAD based devices. The following experiments suggests that this problem cannot be solved by simply reducing the conductivity of PEDOT film, and therefore a more effective n-type electron extraction layer, such as fullerene, is speculated to be helpful to balance the charge extraction of each side and improve the device performance. A stability test was subsequently conducted on perovskite samples covered with different HTMs. The analysis with X-ray diffraction (XRD) spectroscopy and UV-vis absorption suggests that PEDOT provides a better protection of perovskite film than doped Spiro-OMeTAD, but not so good as neat Spiro-OMeTAD (without doping).

Chapter 5 demonstrates an extensive study on copper (I) thiocyanate (CuSCN) based perovskite photovoltaic devices. CuSCN is a wide bandgap, highly transparent p-type inorganic semiconductor¹³, which is solution-processable at low temperatures and readily available from commercial sources at low cost¹⁴. In addition, CuSCN also exhibits excellent thermal stability with no observable decomposition below 300 °C.¹⁵ In this chapter, two deposition methods for CuSCN were tested separately. The spin-coated CuSCN showed pillared structured crystals formed on the perovskite surface. After further covering the perovskite surface with a thin film of PMMA to reduce recombination, devices with PCEs up to 11.5 % could be achieved. However, this crystal formation is difficult to reproduce, probably due to the unstable atmosphere of the glovebox used. On the other hand, efficient and reproducible CuSCN devices could be fabricated with the spray-coating method, achieving a PCE of 13.3% and a SPO of 10.9%, comparable to that of 14.3% and 12.2% from Spiro-OMeTAD based PSCs. Subsequently, a thermal stability study was conducted in both ambient (oxygen and humidity) and inert (N₂ filled glove box) conditions at 85 °C, from which an interfacial degradation mechanism at the heterojunction between the perovskite absorber and the CuSCN was discovered, rendering the device completely non-functional in 15 days. This degradation occurs even in a dry nitrogen atmosphere, identifying the presence of a critical instability. Fortunately, this issue can be significantly alleviated with the additional coating of the completed cells with a thin film of PMMA, functioning as a rudimentary ‘on-cell’ encapsulation, delivering efficient perovskite solar cells which survive for more than 1000 hours at 85 °C in the air with only 25% degradation in performance. Beyond identifying a critical area to address in order to enable CuSCN to be useful for long term operation in perovskite solar cells, these findings indicate that the role of the ‘encapsulant’ is to both keep the environment out, and keep degradation products within the cell.

The operation effectiveness of CuSCN was then further improved by copper iodide (CuI) doping, as demonstrated in Chapter 6. CuI is another inorganic p-type semiconductor with higher solubility and higher hole mobility compared to CuSCN^{16,17}. It has also been previously reported to be used as HTM in PSCs with a highest PCE of 7.5 % achieved.^{18,19} This chapter shows that the film morphology of spray-coated CuSCN film can be changed by adding a small amount of CuI solution (in acetonitrile, ACN) into the precursor, leading to better coverage and connection between crystals. The charge extraction and transport effectiveness was increased, which further resulted in improved photovoltaic performance with a champion PCE of 14.4 % and SPO of 12.3 % achieved, comparing to 11.5 % (PCE) and 9.9 % (SPO) for PSC based on non-doped CuSCN from the same batch. On the other hand, the influence of adding solely ACN solution in the precursor was also investigated; it was found to result in the decrease of the CuSCN crystal size and an improvement in PCE of up to 13.9%. However, the conductivity of fabricated CuSCN film remained unchanged and the SPO was low compared to CuI-doped devices (<7%). Therefore, CuI plays a crucial role in improving the operation effectiveness of the CuSCN hole conducting layer. A stability test was also conducted for devices in ambient condition at elevated temperature (85 °C), which suggests that there is no significant influence on the stability issue with this doping technique.

In summary, this thesis has presented several meaningful studies on novel, low-cost and highly stable HTM for efficient PCEs. Future work can be focused on applying the developed techniques on novel perovskite materials with higher efficiency and thermal stability, such as mixed-cation lead mixed-halide perovskite²⁰. These novel HTMs as well as their deposition methods can also be used in future tandem device fabrication, acting as either HTMs or interlayers.

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20. McMeekin, D. P. *et al.* A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* **351**, 151–5 (2016).

List of Publications

1. **Liu, J.**; Pathak, S. K.; Stergiopoulos, T.; Leijtens, T.; Wojciechowski, K.; Schumann, S.; Kausch-Busies, N.; Snaith, H. J. Employing PEDOT as the P-Type Charge Collection Layer in Regular Organic-Inorganic Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2015**, 6 (9), pp 1666-1673.
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4. **Liu, J.**; Pathak, S. K.; Leijtens, T.; Stergiopoulos, T.; Wojciechowski, K.; Schumann, S.; Kausch-Busies, N.; Snaith, H. J. Novel Low Cost Hole Transporting Materials for Efficient Organic-Inorganic Perovskite Solar Cells. In 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC); IEEE, 2015; pp 1–4.