Doping in perovskite nanocrystals, perovskite solar cells with organic carrier transport layers, and Selenium solar cells

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**Doping in Perovskite Nanocrystals, Perovskite Solar
Cells with Organic Carrier Transport Layers, and
Selenium Solar Cells**

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School of Electrical & Electronic Engineering

2020

**Doping in Perovskite Nanocrystals, Perovskite Solar
Cells with Organic Carrier Transport Layers, and
Selenium Solar Cells**

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

23-7-20

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Fan Weijun

Authorship Attribution Statement

This thesis contains material from 6 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as Wenbo Liu, Bingqing Yao, Xinxiong Li, Ahmed Ali Said, Jingxi Lv, Zhili Dong, Weijun Fan, Xiao Wei Sun, Qichun Zhang, “*Introducing Cations (Zn^{2+} , Sn^{2+} and Mg^{2+}) and Anions(Cl^-) to Tune Mn Photoluminescence Intensity of Doped Perovskite Nanocrystals($CsPbCl_3$)*” Chemistryselect, 2018, 3, 11986-11992.

The contributions of the co-authors are as follows:

- Prof. Qichun Zhang and Prof. Weijun Fan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Prof. Xiao Wei Sun.
- I performed all the laboratory work at the School of Materials Science and Engineering.
- All Photoluminescence spectra measurement and Absorption measurement, including sample preparation, was conducted by me in the School of Materials Science and Engineering for Analysis, Characterization, Testing and Simulation.
- Bingqing Yao, Xinxiong Li and Prof. Zhili Dong assisted in the collection of the transmission electron microscope data.
- Ahmed Ali Said and Jingxi Lv assisted in the collection of the X-ray diffraction spectroscopy data.

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- I performed all the laboratory work at the School of Materials Science and Engineering.
- All Atomic Force Microscope, Photoluminescence spectra measurement, J-V curve measurement, dark current measurement, EIS measurement and Absorption measurement, including sample preparation, were conducted by me in the School of Materials Science and Engineering.
- Dada B. Shaikh, Pedada Srinivasa Rao, Rajesh S. Bhosale prepared the organic carrier transport materials and related characterizations.
- Ahmed Ali Said assisted in the collection of the X-ray diffraction spectroscopy data.
- Adrian M. Mak conducted the density functional theory calculation.
- Mu Zhao, Prof. Weibo Gao assisted in the collection of Time-Resolved Photoluminescence data.
- Dr. Zongrui Wang assisted in the collection of the Organic Field Effect Transistors data.
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- Prof. Qichun Zhang provided the initial project direction and edited the manuscript drafts.
- Kexiang Zhao synthesized the materials and prepared the manuscript drafts.
- I performed the device fabrication, characterization part and finished the device part of the manuscript.
- Fei Yu, Guankui Long, Prof. Weibo Gao assisted in the analysis of the crystal structure of synthesized materials
- Ahmed Ali Said helped to measure the X-ray diffraction spectroscopy data.
- Zongrui Wang helped to measure the collection of the Organic Field-Effect Transistors data.

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- Zongrui Wang assisted in the collection of the X-ray diffraction spectroscopy data.
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Date

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Summary

Perovskite materials are materials with the perovskite structure ABX_3 ($X=Cl, Br, I$). Perovskite nanocrystals (PNCs) and perovskite bulk materials are studied in this thesis. The synthesis of PNCs under high temperature is studied firstly. A modified method that applies metal acetate and halogen acid as the separated B and X source was presented. Cations (Zn^{2+} , Sn^{2+} , and Mg^{2+}) and anions (Cl^-) were added into the precursor to study their influence on the Mn emission intensity of Mn-doped PNCs. The nucleation processes of doped PNCs were investigated at the same time. The Mn and Zn co-doped PNCs have been used as phosphors in the down-conversion light-emitting devices (LEDs).

Perovskite solar cells (PSCs) based on perovskite bulk materials have made remarkable progress in recent years. Nevertheless, the scientific significance of PSCs goes far beyond the simple pursuit of efficiency. PSCs can serve as a very good platform to try organic carrier transport materials and promote the development of organic semiconductors. Here, a series of small molecule organic materials with varied functional side chains have been applied as the electron transport layers (ETL) for perovskite materials. The morphology, internal aggregation of small molecule organic materials on the ITO/ poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS)/Perovskite layer substrate have been investigated, their influences on the device performance have been discussed.

Next, the interactions between the perovskite surface and organic transport layers are studied. A well-designed polymer has been applied as the hole transport layer (HTL) of PSCs. The side chains of this specific polymer could passivate the perovskite surface to improve the fill factor and stability of fabricated PSCs.

Since the lead (Pb)-containing PSCs is not friendly to the environment and the perovskite materials used in PSCs is not stable, it is necessary to explore the next generation of photovoltaic materials. Se absorber is nontoxic and stable under ambient conditions, which is a promising photovoltaic material. Se solar cells (SSCs)

based on the SnO_2 ETLs and polymeric HTLs has been fabricated. The aging dynamic of SSCs has been studied.

The study of doped PNCs helps to deepen the understanding of the nucleation process of PNCs. A variety of organic materials were used as the carrier transport layer of PSCs, which provides a reference for designing new functional molecules. The fabricated SSCs have excellent stability, which can be further modified and used in harsh environments.

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1) Introduction

1.1 Background and motivations

Perovskite materials have been the research hotspot in recent years due to the long diffusion length of carriers, high mobility of photogenerated carriers, easy tuning bandgap and optical absorption, high optical absorption coefficients, balanced carrier transfer. [1-4]. Perovskite materials are materials with a crystal structure like calcium titanium oxide (CaTiO_3), which is shown in Figure 1.1a. Figure 1.1b shows the structure of the most studied perovskite material MAPbI_3 (MA = methylammonium), which is widely used in high-efficiency PSCs. [5] The scanning electron microscope (SEM) image in Figure 1.1c exhibits the morphology of MAPbI_3 nanocrystals on the TiO_2 substrate. [6] According to the size of perovskite materials, perovskite materials are divided into nanocrystals and bulk materials. [1,7] To get a comprehensive understanding of perovskite materials, both the PNCs and bulk materials would be studied in this thesis.

Figure 1.1. (a) Example of an inorganic perovskite oxide, CaTiO_3 (orthorhombic, Pbnm). (b) Example of a typical perovskite material with an organic cation at the A-site, MAPbI_3 (orthorhombic, Pnma). [5] (c) Scanning Electron Microscope (SEM) image of MAPbI_3 nanocrystals on the TiO_2 substrate. The scale bar is 10 nm. [6]

The synthesis methods of PNCs could be divided into room temperature methods and high temperature methods. [7-10] A typical room temperature method is shown in Figure 1.2a. The perovskite precursors in good solvents (such as N, N-Dimethylformamide (DMF), Dimethyl sulfoxide(DMSO), or their mixtures) are dropped into the bad solvents(such as toluene).[7] With the assistance of surfactants such as oleylamine (OLA) and oleic acid (OA), the colloidal PNCs will form and evenly distribute in the solution. The disadvantage of this method is that the size of the PNC is not uniform due to the uneven nucleation. Another method is the high temperature method, in which the reaction temperature could be as high as 180°C.[8]

The high temperature methods are very suitable for the synthesis of all-inorganic PNCs because the organic cations such as MA^+ could not tolerate the high temperature. Even though the synthesis of PNCs has been well-studied, the related theories about the fast nucleation process still need to be enriched.[7] During the fast nucleation process, the ions dynamics in the solution is important. Directly monitoring the movement of the ions during the fast nucleation process is impractical. However, as shown in Fig. 1.2c, by changing the precursor composition and analyzing the resulting PNC, some information about the "black box" (rapid nucleation process) can be revealed. The compositional modification requires the separation of A, B, X sources, which motivates us to modify the synthesis route. The compositional modification in the B-site can also be used to study the Mn doping process. The PL spectra of Mn-doped PNCs are greatly influenced by the Mn doping process.[7] The adjustable Mn emission in Mn-doped PNCs makes the white emission of PNCs possible, which could be widely applied in the lighting and display.[7]

Figure 1.2. (a) Sketch of the room temperature method to synthesize PNCs.^[7] (b) Sketch of the high temperature method to synthesize PNCs.^[7] (c) The synthesis process of doped PNCs with the fast nucleation process as the "black box".

In 2005, Miyasaka's group started to work on the perovskite materials.^[1] Before 2005, studies of perovskite materials were focused on two-dimensional (2D) perovskite materials.^[11,12] In 2009, Miyasaka et al. reported the first PSCs with an efficiency of 3.9%.^[6] In the next three years, not too much attention has been paid to PSCs. In 2012, H. Snaith and N.G. Park reported the PSCs with an efficiency of more than 10%.^[13,14] After that, PSCs becomes the hottest topic in recent years, lots of works have been done in this area and the efficiency of PSCs has been boosted by more than 25%.^[15] The development of PSCs has been compared with other kinds of emerging solar cells in recent years in Figure 1.3.

Figure 1.3. Emerging PV including PSCs in recent years. [15]

The bulk perovskite films could be deposited by the spin-coating method and thermal evaporation method, which is shown in Figure 1.4.[11] The films deposited by thermal evaporation are reported to possess better film qualities. [11,16] But the problem of the thermal evaporation method is that it needs complicated thermal evaporation equipment. The spin-coating method is much easier, and many reported works are based on the spin-coating method.[11,17,18]

Figure 1.4. (a) Solvent engineering method to prepare perovskite film.[19] (b) Thermal evaporation method to prepare the perovskite film. [16]

The device structures of PSCs could be divided into the planar n-i-p

structure, planar p-i-n structure, mesoporous n-i-p structure, mesoporous p-i-n structure.^[1] The perovskite layers are treated as the intrinsic layer. “n” and “p” layers are the carrier transport layers. PSCs could serve as a very good platform to try all kinds of organic carrier transport materials and promote the development of organic semiconductors. Carrier transport materials used in the PSCs could also be used in other areas, such as organic thin-film transistors (OTFTs) and perovskite light-emitting devices. In this thesis, a series of carrier transport materials including organic small molecules and polymer have been adopted as carrier transport layers. The morphology of carrier transport layers and interactions between carrier transport layers and perovskite layers have been studied.

The relatively weak bonding among A, B, and X sites of perovskite materials makes the perovskite material naturally unstable. The lead-containing PSCs are not friendly to the environment. It is necessary to find a replacement for PSCs. Here, the Se absorber was chosen due to its advantage of nontoxicity and good stability. The crystal structure of Se is shown in Figure 1.5a and b. Se films and perovskite films share similar grains and grain boundaries (Figure 1.5c-f).

Figure 1.5. (a), (b) The crystal structure of t-Se with side view and top view.^[20] (c) The SEM image of the bulk perovskite surface.^[11] (d) The SEM image of Se surface.^[21] (e) The cross-sectional SEM image of PSCs.^[11] (f) The cross-sectional SEM image of SSCs.^[21]

1.2 Objectives

The objectives in this thesis could be divided into four parts and each part has a different target.

The first part is about doping in colloidal PNCs, which includes the following points:

- (1) Conducting a conscientious literature survey to introduce the structure of PNCs, typical synthetic methods, and B position doping of PNCs
- (2) Designing a suitable high temperature synthetic route.
- (3) Characterizing the as-synthesized PNCs through photoluminescence (PL) spectra, Absorption spectra, transmission electron microscopy (TEM) images, and related element mapping to discuss the properties of PNCs.
- (4) Fabricating the down-conversion LEDs based on the synthesized PNCs.

The second part is to study the PSCs with organic small molecules as the electron transport materials, which includes the following points:

- (1) Conducting a literature survey about the structure of perovskite bulk films, the formation of perovskite films, methods that could be used to improve the film qualities, and the introduction of carrier transport layers.
- (2) Adopting the new organic carrier transport materials as ETLs and character the PSCs with current density-voltage (J-V) curves, dark J-V curves, PL and absorption spectra, X-ray diffraction (XRD) patterns, atomic force microscopy (AFM) measurements, and electrochemical impedance spectroscopy (EIS) measurements.

- (3) Comparing the performance of PSCs with different organic carrier transport layers.

The third part explores the dope-free polymer carrier transport materials applications in the PSCs, which includes the following points:

- (1) Conducting a literature report about interface engineering in the PSCs and the introduction of dope-free polymer carrier transport layers applied in the conventional n-i-p PSCs.
- (2) Adopting the new organic carrier transport materials as hole transport layers (HTLs) and characterizing the PSCs with J-V curves, dark J-V curves, PL and absorption spectra, XRD patterns, AFM measurements, and EIS measurements.
- (3) Comparing the performance of PSCs with different polymer carrier transport layers.

The fourth part explores the possible replacement of lead-containing perovskite materials, which includes the following points:

- (1) Conducting a literature report about the comparison between SSCs and PSCs. The stability issues of SSCs should also be covered.
- (2) Measuring the J-V curves, dark J-V curves, XRD patterns, AFM images, and EIS measurements to get a basic understanding of SSCs.
- (3) Performing the stability test for SSCs with organic carrier transport materials and exploring the factors that affect the durability of SSCs.

The above are the major objectives of this work.

1.3 The major contributions of the Thesis

The major contribution of the thesis could be summarized into the following points:

- (1) The literature surveys cover all the aspects mentioned in 1.2.
- (2) PNCs and doped PNCs could be synthesized by a modified method, which could separate A, B, and X sources
- (3) Through a series of characterization including PL spectra, Absorption spectra, TEM images, and related element mapping, specific metal ions (Zn^{2+} , Mg^{2+} , Sn^{2+}) and halide ion Cl^- have been found to greatly influence the Mn doping processes of PNCs.
- (4) The down-conversion LEDs based on the doped PNCs have been fabricated.
- (5) PSCs with a series of new Naphthalene diimide (NDI) electron transport materials have been fabricated. Through a series of characterization including current density-voltage (J-V) curves, dark J-V curves, PL and absorption spectra, X-ray diffraction (XRD) patterns, atomic force microscopy (AFM) measurements, and electrochemical impedance spectroscopy (EIS) measurements, the aggregation of organic electron transport materials has been proven to greatly influence the fill factors.
- (6) PSCs with new organic electron transport materials have been fabricated. After similar characterizations mentioned in (5), the internal aggregation of organic materials is found to greatly influence the performance of PSCs.
- (7) PSCs with new polymer hole transport materials have been fabricated. Though similar characterizations are mentioned in (5), the interactions between perovskite and HTLs have been studied.
- (8) SSCs with organic transport materials have been fabricated. J-V curves, dark J-V curves, XRD patterns, AFM images, and EIS measurements have been done. The aging dynamic of SSCs has been analyzed.

1.4 Organization of the Thesis

The thesis consists of seven chapters. The first chapter introduces the background and motivation, objectives, and major contributions of this thesis. The second chapter is about PNCs, which includes the literature survey, the illustration of experiment and characterizations, results and discussion, and summarization. The following three chapters have a similar structure. The third chapter describes the PSCs with a series of organic small molecules as electron transport layers, the fourth chapter describes the PSCs with polymers as the hole transport layers, and the fifth chapter carefully discusses the SSCs and their aging dynamics. Chapter 6 makes the conclusion and recommendations, which summarize the works presented in this thesis. Besides, future research plans are discussed in this chapter. The last part is the reference, the author's publications, and bibliography.

2) The B-site doping in perovskite nanocrystals

In the literature survey, firstly, the synthesis methods of PNCs are introduced. The second section introduced the doping and ion substitution in PNCs. Then, the disadvantages of the ion exchanging reaction of PNCs have been discussed. Direct replacement of Pb with other metal elements during colloidal synthesis is proven to be easier. In the experimental and characterization section, the synthesis route of PNCs is described. Additionally, the introduction of characterization techniques is also provided. In the results and discussion section, the influences of cations (Zn^{2+} , Sn^{2+} , Mn^{2+}) and anions (Cl^-) on the Mn doping process were discussed. The Polymethyl methacrylate (PMMA) films with Mn and Zn co-doped PNCs as the phosphor are used to work as the down-conversion layer for LEDs.

2.1 Literature survey

The MAPbI_3 PNCs were first synthesized and used in photovoltaic applications (Figure 2.1a and b).^[22] Schmidt et al. first synthesized the MAPbBr_3 PNCs, which is shown in Figure 2.1c.^[23] The milestone work in the PNCs is all inorganic CsPbX_3 ($\text{X}=\text{Cl}$, Br , I) PNCs with visible fluorescence reported by Protesescu et al.^[8] Their method is very simple and high repeatable. The synthesized PNCs are very stable, and the PL wavelength could cover the whole visible wavelength.

Figure 2.1. (a) TEM image of MAPbI₃ deposited TiO₂, (b) TEM image of pure MAPbI₃.^[22] (c) HRTEM image of a single MAPbI₃ PNC and schematic representation of MAPbI₃ PNCs. The scale bar is 2 nm ^[23]

2.1.1 The synthesis of PNCs

Two commonly used methods to synthesize the PNCs are high-temperature hot injection methods and room-temperature ligand-assist reprecipitation, which could be abbreviated as high-temperature methods and room-temperature methods ^[24-26]. The classical high-temperature method raised by Protesescu et al.^[8] is described as follows; The lead halide is added into a solvent with a high boiling point. After drying under proper temperature, Oleic acid (OA) and Oleylamine (OLA) would be injected. The next step is increasing the temperature and injection of the prepared Cs-oleate solution. Fast nucleation processes would happen and the PNCs form. Fast cooling down after reaction could prevent the further growth of PNCs.^[27] Temperature is proven to be a crucial factor for controlling PNC size.^[8,24] As shown in Figure 2.2, under different temperature, the size and shape of synthesized all-inorganic CsPbBr₃ PNCs show distinguished differences.^[24]

Figure 2.2. Growth processes of CsPbBr₃ QDs with low-polarity solvents at different temperatures. ^[24]

The commonly used surfactants are OLA and OA. By modifying the concentration of surfactants, PNCs with double perovskite structure could be synthesized. ^[28] The kinds of surfactants and reaction temperature could greatly influence the anisotropic growth of PNCs. nanoplatelets,^[29] nanowires,^[30] and nanosheets ^[31] could be synthesized by changing the surfactant and reaction temperature (Figure2.3). High temperature methods could also be used to synthesize the CdTe, CdSe, CdS, HgS, PbSeInP, InAs, and CuInS₂ QDs.^[7] The disadvantages of high temperature methods include relatively complicated reaction processes and high requirements for the experimental conditions.

Figure 2.3. (a) TEM images of CsPbBr₃ nanocubes formed at 150 °C. (b) TEM images of CsPbBr₃ nanoplates formed at 130 °C. (c) TEM images of CsPbBr₃ nanoplates formed at 90 °C. [31] (d) TEM images of CsPbBr₃ nanowires. the scale bar is 100 nm. [32] 2D ultrathin CsPbBr₃ nanosheets: e) Low-magnification and f) high-magnification SEM images.[33]

The room temperature method was firstly reported in 2012.[32] The general process of the room temperature method is to drop the precursors in the “good” polar solvents (DMF and DMSO) into the “bad” solvents (such as toluene). In the “bad” solvent, the precursors would precipitate out from the solvent and form the mono monomer. With the assistance of surfactants OA and OLA, the monomers would grow up and form the PNCs. The precursors used here are usually halide salts. The room temperature methods have lower requirements for reaction conditions and equipment, which is suitable for large-scale industrial applications. OLA is used to control the size of PNCs and OA is supposed to suppress the aggregation of PNCs.[33] Other kinds of ligands such as 2-adamantylammonium bromide, (3-aminopropyl) triethoxysilane (APTES), polyhedral oligomeric silsesquioxane (POSS) PSS-[3-(2-aminoethyl)amino]-propylheptaisobutyl-substituted (NH₂-POSS), and octylammonium were also reported to control the size and aggregation of PNCs. [34-36] The room temperature methods could be used to synthesize MAPbI₃, FAPbX₃ (FA= Formamidinium), CsPbX₃, and mixed-A PNCs.[37-39] For the lead-free PNCs, Bi, Sb based PNCs could also be synthesized by room temperature methods.[40,41] The disadvantage of room temperature methods is the negative precursor-polar solvent interactions,[7,42] which means the left polar solvent in the poor solvent could cause the degrading and the formation of defects in PNCs. What's more, the MAPbI₃ PNCs synthesized under the room temperature method show the irregular spherical shape, which is shown in Figure 2.4. The size and shape of the MAPbI₃ PNCs are quite different from all-inorganic CsPbX₃ PNCs. Other

reported methods include the solvothermal synthesis method [43], ultrasonication-assisted synthesis method [44], and microwave irradiation strategy.[45]. But all these kinds of methods could be treated as modifications of high temperature methods and room temperature methods, which would not be discussed in detail.

Figure 2.4. TEM images of organometal Halide PNCs(MAPbI₃) synthesized by room temperature methods. [46-50]

In this work, the high temperature method is chosen to synthesize the PNCs. Because it is easier to control the size and shapes of resulted PNCs in the high temperature method. However, no matter in room temperature methods or high temperature methods, the B and X sources are usually lead halide salts. The ratio of B source and X source is fixed to 1:2. The stoichiometric ratio between B source and X source could not be modified. Many other B and X sources have been reported, such as NH₄X and PbI₂, Pb-acetate, and alkylamines, but the question of stoichiometric ratio has been neglected in these works. [29, 30] In this work, we proposed that the metal-acetate and halogen acid could be the B and X sources to achieve independent B and X source. The combination of metal-acetate and halogen acid has been reported, but this work is the

first time to apply this combination in the high-temperature method.^[29, 30] By keeping the vacuum in the reaction all the time, the water in the halogen acid could be removed under high temperature. The resulted PNCs show very good qualities and stability. Additionally, other metal-acetates could also be added into the precursor, which makes B position doping much easier.

2.1.2 Doping and ion substitution in colloidal PNCs

For A-site doping, the elements (i.e. Rubidium (Rb), FA, Titanium (Ti)) have been doped into the CsPbX_3 .^[51-53] For B-site doping, the elements Mn, Bismuth (Bi), Tin (Sn), Zn, Magnesium (Mg) have been reported to be doped into the CsPbCl_3 PNCs.^[54,55] Mn^{2+} has been firstly reported to dope into the CsPbCl_3 .^[56] A PL emission peak around 600nm is found in the PL spectra of Mn-doped PNCs. The stability of Mn-doped PNCs is improved.^[57] Other metal elements such as Germanium (Ge)^[58], Bi, and Antimony (Sb) have been used to replace the lead. PNCs with double elements such as Silver (Ag), Bi in the B positions are also recent hot topics.^[59] The influences of doping elements into perovskite materials have been summarized by other researchers and shown in Figure 2.5. Among these influences, tuning the emission wavelength is realized in the work. As mentioned in Chapter 1, another benefit of studying the doping process in PNCs is getting a better understanding of the fast nucleation process.

Figure 2.5. The elements that could be doped into perovskite materials and their influences.
[56]

Mn-doped CsPbCl₃ PNCs can be easily synthesized by high or room temperature methods. The thermal stability of Mn-doped CsPbCl₃ PNCs has been improved due to the higher formation energy.^[57] Due to the specific energy level structure of Mn-doped CsPbCl₃ PNCs, an emission peak at about 600nm from the Mn element appears in the PL spectra. Surprisingly, the emission peak of CsPbCl₃ at 400nm remained unchanged. The general PL peaks of CsPbX₃ PNCs range from 400nm (ultraviolet) to 685 nm(red), which covers the visible light spectrum.^[8] As shown in Figure 2.6, if the emission peak of pristine PNCs moves to 490nm, together with Mn emission at 600nm, white emission of Mn-doped PNCs is possible. It is easy to tune the emission intensity and wavelength of pristine PNCs. The bandgap of PNCs is decided by the Pb 6s,6p orbitals and outer p orbital of the halide (5p for I,4p for Br, and 3p for Cl).^[7] The ions in the A-site of PNCs could also affect the bandgap, the PL peaks would blue shift with ions in the A position of PNCs changing from FA to MA to Cs.^[60-64] By changing the composition of pristine PNCs, the PL peaks of pristine PNCs could be easily tuned. Tuning the Mn emission of Mn-doped PNCs is realized in this thesis.

Figure 2.6. 1931 CIE coordinates of Mn emission(orange) and assumed blue emission from PNCs(blue).

Even though directly changing the ratio of Mn to Pb in the precursor could tune the PL intensity, yet it would lead to the shift of Mn emission peak.^[64] Pradhan et al. reported that the Mn emission intensity of doped PNCs is increased by introducing the alkylamine hydrochloride besides the PbCl_2 and MnCl_2 .^[65] But the Cl^- ions in their work could not be controlled due to the existence of PbCl_2 . In another work, by partial post-synthetic cation exchange reaction, the Mn^{2+} emission intensity could be tuned by controlling the replacement of Mn^{2+} by Zn^{2+} with prolonged ion-exchange reaction time.^[66] The disadvantages of ions exchanging reactions would be discussed in the next chapter. Before our work, there are no reports about tuning the Mn emission intensity by directly introduce other cations during the formation of PNCs. Other cations such as Sn^{2+} , Cd^{2+} , Zn^{2+} , and Al^{3+} slightly affect the PL spectra. ^[67,68] Therefore, these ions could be used to tune the Mn emission intensity of Mn-doped PNCs.

Studying the doping process could help to understand the formation of PNCs. Exploring the ion dynamics during the synthesis process could offer a much clearer picture of the fast nucleation process.

2.1.3 Ion exchanging reaction of PNCs

Post synthetic ion-exchange reaction could be used to change the composition of PNCs. For the anion exchange reactions, each halide ions could be replaced by the other two kinds of ions (Figure 2.7).^[69-71] Different kinds of salts have different anion exchanging rates. For example, the anion exchanging speed of PbX_2 is much slower than that of ZnX_2 .^[72,73] And the anion exchanging reaction is very easy to be triggered and can be conducted in the solid-state and solid/gas interfaces.^[74,75] The anion exchanging reaction could also be suppressed by the PbSO_4 -oleate.^[76] The disadvantage of such easy exchanging reactions is that it makes the multi emission peaks unavailable by mixing PNCs since it would exchange with each other and form a single PL peak, which could be the impediments of the development of white emission of PNCs.^[69]

Figure 2.7. (a) SEM images of MAPbI_3 film. (b) SEM images of converted MAPbBr_3 films.

(c) SEM images of converted MAPbCl₃ films. (d) SEM images of MAPbBr₃ film. (e) SEM images of converted MAPbI₃. (f) SEM images of converted MAPbCl₃. (g) SEM images of MAPbCl₃. (h) SEM images of converted MAPbBr₃. (i) SEM images of converted MAPbI₃.
[70]

The elements such as Sn, Zn, Cd, and Mn could be doped into the B-site of PNCs by cation exchanging reaction (Figure 2.8a).^[67] Figure 2.8 c-e shows the morphology of these doped PNCs. Comparing with pristine PNCs(Figure 2.8b), the size and shape of doped PNCs by cation exchanging reactions are not uniform. Figure 2.8f shows the doping processes of the cation exchange reaction. The OLAM would take the X⁻ ions away and X vacancies would be left on the surface of PNCs, which is filled by OLAM-MX₂. The Pb²⁺ ions on the surface would then dissolve in the solvent in the format of OLAM-PbX₂. After that, the M²⁺ ions take the Pb vacancy.^[7,67] The complicated doping processes make it hard to increase the concentration of doping elements in the whole PNCs. Only the surface molecules would be exchanged, which would lead to uneven distribution of doping elements in the PNCs. The better method could be directly adding targeted metal ions into the precursors. Therefore, the cation exchanging reaction would not be an option for us to synthesize doped PNCs.

Figure 2.8. (a) Partial cation exchange reaction in CsPbBr₃ nanocrystals. (b-e) STEM images of doped nanocrystals. ^[67] (f) The process of cation exchanging reaction. ^[7]

Systematically studying the influence of cations (such as Zn²⁺, Sn²⁺, and Mg²⁺) and anions (such as Chlorine (Cl⁻)) on the Mn emission intensity is rarely reported when this work is done. Based on the changing variables and corresponding results, what happens in the “black box” (fast nucleation process) could be deduced.

2.2 Experiments and characterizations

2.2.1 PNCs synthesis

Chemicals used in experiments: $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ (Lead acetate, Hayashi, 99.99%), $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ (Manganese acetate, Sigma-Aldrich, 99.9%), SnAc_2 (Tin acetate, Sigma-Aldrich, 99.9%), $\text{MgAc}_2 \cdot 4\text{H}_2\text{O}$ (Magnesium acetate, Sigma-Aldrich, 99.9%), ZnAc_2 (Zinc acetate, Sigma-Aldrich, 99.9%), Cs_2CO_3 (Caesium Carbonate, Sigma-Aldrich, 99.9%), ODE (Octadecene, Sigma-Aldrich, 90%) and OA (Oleic acid, Sigma-Aldrich, 90%), OLAM (Oleyl amine, Sigma-Aldrich 80-90%), Hexane (Sigma-Aldrich), Toluene (Sigma-Aldrich), PMMA (Sigma-Aldrich) and HCl (hydrochloric acid, Emsure, 37 wt % in water).

Preparation of Cs-oleate: Cs_2CO_3 (0.407 g) was added into ODE (20mL), dried for 1h at 120 °C, and then OA (1.55 mL) was injected. After that, the reaction temperature was raised to 150 °C until all Cs_2CO_3 reacted with OA. After the reaction, the Cs-oleate was kept in the 3-neck flask and if needed, pre-heating at 100 degrees for 1h.

Synthesis of $\text{CsPb}_{1-x-y}\text{Mn}_x\text{M}_y\text{X}_3$ NCs (M=Zn, Sn): The synthesis route is shown in Figure 2.9. The details of A, B, and X sources are shown in Table 2.1. The first step would be preparing the precursor solution consisting of B^{2+} cations, which are ions 1 in Figure 2.9. For pure PNCs, 0.05 mmol $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ was dissolved into 2.5 ml ODE. The yellow solution in Figure 2.9 represents ODE. For Mn-doped PNCs, 0.05 mmol $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ and 10mg $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 2.5 ml ODE. For Mn-doped PNCs with Zn ions existing, 0.05 mmol $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$, 2.5 mg, 5mg or 10mg ZnAc_2 and 0 or 10mg $\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 2.5 ml ODE.

Figure 2.9. The schematic of the synthesis process. The ions 1 in the ODE solvent includes the metal ions and acetates. The ions 2 in the ODE solvent include metal ions, halide ions, and ligands.

Table 2.1. A, B, X sources, ligands, and solvent used to synthesize PNCs.

PNCs	A source	B source	X source	Ligands	Solvent
CsPbCl ₃	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O	50 µl HCl in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPbBr ₃	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O	50 µl HBr in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPbI ₃	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O	50 µl HI in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPb _{1-x} Mn _x Cl ₃	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O and 10mg MnAc ₂ ·4H ₂ O	50 µl HCl in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPb _{1-x} Mn _x ZnCl ₃	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O, 2.5 mg, 5mg or 10mg ZnAc ₂ and 0 or 10mg MnAc ₂ ·4H ₂ O	50 µl HCl in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPb _{1-x} Mn _x SnCl ₃	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O, 2.5 mg, 5mg or 10mg SnAc ₂ and 0 or 10mg MnAc ₂ ·4H ₂ O	50 µl HCl in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPb _{1-x} Mn _x Cl ₃ (Mg ²⁺)	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O, 5mg or 10mg MgAc ₂ ·4H ₂ O, 0 or 10mg MnAc ₂ ·4H ₂ O	50 µl HCl in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE
CsPb _{1-x} Mn _x Cl ₃ (Varied Cl ⁻)	0.2 mL Cs-oleate in ODE (0.125M)	0.05 mmol PbAc ₂ ·3H ₂ O and 10mg MnAc ₂ ·4H ₂ O	50 µl or 100 µl or 150 µl or 200 µl HCl in water	0.25 ml OA and 0.25 ml OLAM	2.5 ml ODE

For Mn-doped PNCs with Sn ions existing, 0.05 mmol $PbAc_2 \cdot 3H_2O$, 2.5 mg, 5mg or 10mg $SnAc_2$ and 0 or 10mg $MnAc_2 \cdot 4H_2O$ were dissolved into 2.5 ml ODE. For Mn-doped PNCs with Mg ions existing, 0.05 mmol $PbAc_2 \cdot 3H_2O$, 5mg or 10mg $MgAc_2 \cdot 4H_2O$, 0 or 10mg $MnAc_2 \cdot 4H_2O$ were dissolved into 2.5 ml ODE. Then the precursor was stirring for 15 min under room temperature under vacuum. The vacuum is achieved by connecting the reaction system to a mechanical pump. After that, the temperature was raised to 120 °C for 20 mins. Following that, 0.25 ml OA and 0.25 ml OLAM were injected. The second step would be the injection of X source, which is 50 μ l (or 100 μ l, 150 μ l, 200 μ l) HX (X=Cl, Br, I) 37wt% in water. The chemical reaction (taking $PbAc_2$ and HCl as an example) would be:

The water containing mixtures would be boiled. The water and acetic acid would change into moisture under such high temperature and move out immediately by the vacuum. Now the ions 2 shown in Figure 2.9 would be Pb^{2+} , other metal cations, halide ions and ligands. Then the temperature was raised to 190 °C. Finally, Cs-oleate solution (0.2 mL, 0.125 M in ODE, prepared as described above) was quickly injected and 5s later, the reaction was stopped by cooling ethanol bath.

Isolation and purification of NCs: The crude product was purified by centrifuging at 7000 rpm, the supernatant was discarded, and the precipitates were dispersed in hexane forming a long-term colloiddally stable solution. A second washing with hexane was achieved by centrifuging at 7000 rpm again.

Preparation of down-conversion LEDs: 7.5g PMMA was dissolved in 10 ml Toluene with rapid stirring (1500 rpm) for 10 hours under 60 degrees. Then different amounts of PMMA solution and PNCs solution were mixed and dropped on a smooth glass surface. The film would form after drying in the air for 24 hours. Finally, the films were fixed on the top of 370nm LED. The device structure is shown in Figure 2.10. The whole device could be lighted up by a Keithley-2400 current source.

Figure 2.10. The structure of the down-conversion LED.

2.2.2 Characterizations

2.2.2.1 Absorption spectra measurement

The absorption spectra could reveal information about the energy level structure of PNCs. The working principles of absorption spectra are provided in Figure 2.11. When the incident radiation containing photons with continuous wavelengths hits on a sample, the photons with the energy larger than the bandgap could be absorbed by the samples. The rest photons in the transmitted radiation would be collected by a detector. By comparing the number and kinds of rest photons with the photons in the incident radiation, the absorption spectra could be calculated and drawn. The absorption spectra of PNCs could be used to decide the excitation wavelength for the PL spectra measurement.

Figure 2.11. The working principles of absorption spectra. [77]

The equipment to measure the absorption spectra in this work is UV-Vis-NIR Lambda 950. The samples were measured in the formation of the solution. The solution was prepared by diluting the 100 μL PNCs solution in hexane (about 5mg/ml) into 3ml hexane. The holder used here is a quartz cuvette. Before measuring the samples, the absorption spectra of Hexane should be measured to remove the influence of solvent absorption. The scan range is from 250nm to 800nm. The scan step is 1nm. The absorption spectra of all inorganic PNCs have been reported in many works. The absorption spectra of synthesized PNCs could be used to check if the measured absorption spectra are matched with the reported works. The absorption spectra are also used to decide the excitation wavelength of PL spectra measurement.

2.2.2.2 PL spectra measurement

PL spectra are crucial for PNCs, especially in this work. The PL spectra have a direct relationship with the energy level structure. The energy level structure of PNCs is affected by metal ions in the B-site of PNCs. The changes in the composition of PNCs could reflect on the PL spectra. As shown in Figure 2.12, when the incident photons with the energy higher than the bandgap of the sample hit on the sample, the sample would be excited to the unstable excited energy state. Then, the excited molecules

of sample may go back to the ground state and release the energy in the form of photons. The wavelengths of these photons are depended on the energy level structure of samples.

Figure 2.12. The principle of the PL process.

The PNC samples used here are in the form of a solution or down-conversion layers. The solution was prepared by diluting the 100 μL PNCs solution in hexane (about 5mg/ml) into 3ml hexane. The holder used here is a quartz cuvette, which could remove the background noise. The PL measurement equipment used here is Cary Eclipse Spectrophotometer. The excitation wavelengths for perovskite materials are the strongest absorption peak of the absorption spectra, which is generally 365nm for PNCs. The scan range is usually from 375nm to 740nm, which would change slightly according to the properties of samples. The PL spectra measurements are the main techniques to learn about the optical properties of PNCs. By comparing the PL spectra of PNCs synthesized in this work with these reported works, we could judge if the targeted PNCs are achieved or not. PL spectra of PNCs could also be used to judge the aggregation of PNCs. If the emission peak shifts to a longer wavelength or the peak width at half height become broader, there would be the aggregation of the synthesized PNCs. Moreover, for Mn-doped PNCs, the emission peak around 600nm could be used to judge if Mn has been successfully doped into PNCs or not.

2.2.2.3 The XRD measurements

The XRD measurement is based on the constructive interference of electromagnetic radiation. The working principle has shown in Figure 2.13. When monochromatic X-rays hit on a sample, some of the monochromatic X-rays are directly reflected by the surface of the sample, but other parts of monochromatic X-rays may pass through the surface and be reflected by the second plane of the sample. These two parts of monochromatic X-rays would travel different distance if their path length difference is closer to half of wavelength λ , it is destructive interference and the intensity of monochromatic X-rays would be decreased and if their path length difference is closer to the whole wavelength λ , it is constructive interference, and the intensity would increase. In Figure 2.13, the lattice distance is d , the incident angle is θ . If the relationship $2d\sin\theta = \lambda$ is satisfied, the intensity of monochromatic X-rays reinforces. According to the incident angle θ and wavelength λ , the lattice distance could be deduced. By varying the incident angle θ and collecting the signals of reflected monochromatic X-rays, the XRD pattern could be drawn.

Figure 2.13. Working principle of XRD measurement.

The XRD samples were prepared by dropping 200 μL PNCs solution in

Hexane onto the silicon wafer. After drying for 36h under the ambient condition to remove the solvent, the samples would be ready to be tested. The XRD pattern of the silicon wafer should also be collected to serve as the reference. The test equipment is the D8 advanced diffractor. $\text{CuK}\alpha$ radiation = $1.5418\text{\AA}$. The scan range is from 10 to 60° . The XRD measurement could be used to further identify the crystal structure of synthesized PNCs. Here, we used the XRD measurement to study if the doping processes greatly influence the crystal structure of the synthesized PNCs.

2.2.2.4 The TEM measurement

Transmission electron microscopy (TEM) is a microscopy technique, in which a beam of electrons is transmitted through a specimen to form an image.^[110] An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen.^[110] The image is then magnified and focused onto an imaging device.^[110] The whole equipment of TEM is very complicated and expensive. The layout of optical components in a basic TEM is shown in Figure 2.14.

Figure 2.14. The layout of optical components in a basic TEM. [78]

The TEM measurements have very high requirements for the sample since the sample must be small and thin enough to pass through the electron beam. The TEM sample was prepared by dropping 10 μL of PNC solution onto the copper grid covered with carbon film and dried under the ambient condition for 5 minutes. The equipment to measure the TEM and EDX is JEOL JEM-2100F operated at 200 kV. The TEM measurement could be used to directly observe the morphology of synthesized PNCs and judge the qualities of synthesized PNCs. By compared the TEM images of PNCs with/without doping, the influence of doping on the crystal structure could also be speculated.

2.3 Results and Discussion

The application of acetate and halogen acid makes the separation of B and X possible. The modified synthesis route makes it much easier for B-site doping. Mn-doped PNCs have been synthesized and the PL intensity of Mn emission has been modified by ions engineering (cations: Zn^{2+} , Mg^{2+} , Sn^{2+} anions: Cl^-). Our work firstly reported that Zn and Mn ions could be co-doped into PNCs during the formation of PNCs. Through a series of experiments, we have made some deductions about the fast nucleation process. Besides, the as-prepared Mn and Zn co-doped PNCs have been used as a phosphor in down-conversion LEDs.

Figure 2.15. The Absorption spectra (a) and PL spectra (b) and of undoped CsPbX_3 ($X = \text{Cl, Br and I}$). The inserted figure in figure (b) is the undoped CsPbX_3 ($X = \text{Cl, Br, and I}$) solution with UV light.

Pure CsPbX_3 ($X = \text{Cl, Br, I}$) PNCs can be successfully synthesized by this modified method. The absorption spectra and PL spectra are shown in Figure 2.15a and b. The absorption edge and PL emission peaks are matched with the reported work.^[8] The synthesized PNCs were stored under ambient conditions for more than two weeks. The absorption spectra and PL spectra of the PNCs remain unchanged, which proves the synthesized PNCs are very stable. Mn-doped CsPbCl_3 were synthesized by this modified method. Their absorption spectra and PL spectra of the samples are shown in Figure 2.16a and b. An obvious emission peak at 600nm could be found in the PL spectra, which is the direct evidence that Mn^{2+} has been successfully doped into CsPbCl_3 PNCs.^[30]

Figure 2.16. The Absorption spectra (a) and PL spectra (b) of Mn-doped CsPbCl_3 . Inserted

figure in figure (b) is the Mn-doped CsPbCl₃ solution with or without UV light.

Figure 2.17. Absorption spectra of Mn-doped PNCs with adding different amounts of cations and anions.

The absorption spectra of Mn-doped PNCs with different amounts of cations (Zn^{2+} , Mg^{2+} , Sn^{2+}) and anions (Cl^-) are shown in Figure 2.17. The first exciton absorption peaks of different PNCs were located at around 365nm, which is matched with reported work. [80] The second exciton absorption peaks of most PNCs are located at 330nm, which keeps unchanged for most PNCs except Mn-doped PNCs with more HCl added. The B-site doping process has a slight influence on the absorption spectra of PNCs, but inducing more Cl^- may bring a strong influence on the absorption spectra. The possible reason for the influence of Cl^- would be discussed in the next part. Comparing with the absorption spectra of pristine CsPbCl₃ shown in Figure 2.15, the absorption spectra show slight differences, which could be due to the relatively low doping concentration of Mn^{2+} . [81]

Then, the effects of anions (Cl^-) and cations (Zn^{2+} , Sn^{2+} , and Mg^{2+}) on the Mn emission intensity are studied. In Figure 2.18a, with the amount of HCl increasing from 0.05 ml to 0.15 ml, the Mn emission intensity

increases from 0.5 to 1.4. Pradhan et al. reported that by changing the amount of alkylamine hydrochloride (RNH_3Cl), the intensity of Mn emission would be tuned, and the reason is that the function of RNH_3Cl is expected to provide more Cl^- , which is helpful to form more particles and provide more opportunities for Mn^{2+} to react with Pb^{2+} .^[65] But in their work, PbCl_2 and MnCl_2 were also used, which means multi Cl^- sources exist in the reaction system. Here, HCl , functioning as the sole Cl^- source, is used to tune the Mn emission intensity. In Figure 2.18a, with the amount of HCl increasing from 0.05 ml to 0.15 ml, a shoulder peak at about 430nm appears. The reason could be that too many Cl^- promote crystal growth. PNCs with larger sizes could also form during the very short reaction time, which may also lead to different absorption spectra shown in Figure 2.17. Independent X source could create the condition of a limited X source. Under this condition, doping in the B-site of PNCs has been studied.

Figure 2.18. (a) The PL spectra of Mn-doped PNCs with different amount of HCl adding. (b) The PL spectra of Mn-doped PNCs with different amounts of ZnAc_2 adding. (c) The PL

spectra of Mn-doped PNCs with different amounts of MgAc_2 adding. (d) The PL spectra of Mn-doped PNCs with different amounts of SnAc_2 adding.

Under limited Cl source, other cations besides Mn^{2+} have been added into the precursors. Their influences on the Mn emission in the PSCs have been studied. In Figure 2.18b, with the amount of ZnAc_2 precursor increasing from 0 mg to 10 mg, the emission intensity at 600nm (the Mn d-d emission) decreased greatly from 0.5 to 0.1. We proposed two hypotheses to explain this phenomenon. The first one is that Zn^{2+} could be doped into pure PNCs and Mn-doped PNCs. Therefore, if those three ions exist in the same solution, Zn^{2+} could compete with Mn^{2+} to dope into the lattice structure of PNCs and decrease the opportunities for Mn^{2+} to dope into the lattice structure of PNCs. The Mn emission intensity of PNCs would decrease. The EDX data in Figure 2.19(Mn and Zn codoped PNCs) and Figure 2.20(Zn-doped PNCs) could prove the existence of Mn and Zn elements in the PNCs and support this hypothesis. Then another similar ion Sn^{2+} has been used to test this hypothesis and a similar effect has shown in Figure 2.18d. But Sn ions may form other by-products in this reaction system.^[79] The Sn ions used here is Sn^{2+} , which would be easily oxidized to Sn^{4+} under ambient condition.^[79] As Sn^{4+} is mismatched with the valence of Pb^{2+} , the Sn^{4+} would distort the PNC structure. The synthesized PNCs are with non-uniform size and shoulder emission peak in PL spectra.

Figure 2.19. (a) The scan area of Mn and Zn co-doped PNCs for EDX spectroscopy (b-f) EDX map of Cs, Pb, Mn, Zn, and Cl element in the Mn^{2+} and Zn^{2+} co-doped PNCs.

Figure 2.20. (a-b) HRTEM images of Zn^{2+} doped PNCs under different resolution ratios; (c) The scan area of Zn^{2+} doped PNCs for EDX spectroscopy; (d-g) EDX map of Cs, Pb, Zn, and Cl element in the Zn^{2+} doped PNCs.

and Cl element in the Zn doped PNCs.

The second hypothesis is that instead of doping into the PNCs, the existence of these cations only disturbs the process of Mn^{2+} doping into PNCs. To confirm this hypothesis, Mg^{2+} , of which atom radius is too small to replace Mn^{2+} and Pb^{2+} , has been used. In Figure 2.18c, Mg^{2+} could also influence the PL spectra of Mn-doped PNCs, which proves the second hypothesis is credible. The reason may be due to Mg^{2+} ions forming bonds with the limited Cl^- ions. The decreasing amount of Cl^- ions further limits the Mn^{2+} doping process. However, when comparing Figure 2.18b with Figure 2.18c, with the amount of ZnAc_2 and MgAc_2 increasing from 5 mg to 10mg, Mn emission intensity decreases 60% and 15% respectively. The ability of Zn ions to tune the Mn emission is much stronger than that of Mg ions. Thus, it is supposed that both hypotheses are correct, but the first hypothesis predominated. The broader PL peak at a shorter wavelength in Figure 2.18 c is due to the formation of PNCs with a larger size. But the shoulder peaks in Figure 2.18c are not as strong as those in Figure 2.18a and Figure 2.18d. Additionally, no shoulder peaks have been found in PNCs with only Mg^{2+} ions adding (Figure 2.21a). The reason could be too many Mg^{2+} ions together with Mn^{2+} ions disturb the nucleation processes and the resulted PNCs are of low quality.

Figure 2.21. The PL spectrum (a) and Abs spectrum (b) of Zn-doped CsPbCl_3 PNCs, CsPbCl_3 PNCs with adding Mg ions, CsPbCl_3 PNCs with adding Sn ions. (c-e) HRTEM images of Mn^{2+} and Zn^{2+} co-doped PNCs under different resolution ratios after 122 days. (f) XRD pattern of Mn^{2+} and Zn^{2+} co-doped PNCs.

The PL spectra of Zn-doped CsPbCl_3 PNCs, CsPbCl_3 PNCs with adding Mg ions, and Sn-doped CsPbCl_3 PNCs are shown in Figure 2.21a and b. The broader PL spectra of Sn-doped PNCs has been explained above. After comparing the TEM images of Zn and Mn co-doped PNCs taken after exposing to air for 43 days and 122 days (Figure 2.22a-c and Figure 2.21c-e, respectively), it is found that Mn^{2+} - and Zn^{2+} co-doped PNCs could maintain the uniform size (10 nm X 10 nm), cubic shape and homogeneous distribution for more than 122 days. Mn and Zn co-doped PNCs are very stable. Figure 2.21f shows the XRD pattern of Mn^{2+} - and Zn^{2+} co-doped PNCs. The XRD patterns of synthesized PNCs have

strong intensity peaks at (100), (110), (210), (211), and (220) lattice planes. The XRD patterns of Mn and Zn co-doped PNCs are structurally identical to the undoped PNCs. The sharp peak at about 33 degrees in the Mn and Zn co-doped PNCs is from the silicon wafer.

Figure 2.22. a-c) HRTEM images of Mn^{2+} - and Zn^{2+} - co-doped PNCs under different resolution ratios after leaving in the air for 43 days.

HCl is first used as the Cl^- source for the high temperature method. Cl^- ions are used to tuning the Mn emission intensity. Then, under the condition of limited Cl^- ions, other cations(Zn^{2+} , Sn^{2+} , and Mg^{2+}) could affect the Mn emission intensity of Mn-doped PNCs negatively. Based on the above discussions, we could make two deductions for the fast nucleation processes. The first one would be halide ions have a very important influence on the fast nucleation process. The second one would be under a limited halide source, metal ions with similar atomic radius could compete for occupying the B position of PNCs. These two deductions reveal that during the fast nucleation process, the metal ions may have to form bonds with the halide ions before occupying the B position. The possible nucleation process has been described in Figure 2.23.

Figure 2.23. Possible fast nucleation process in doped PNCs.

Then, Mn and Zn co-doped PNCs are used as a phosphor in down-conversion LEDs. The structure of the down-conversion LED is shown in Figure 2.24a. The structure contains the holder, blue LED, and down-conversion layer. The down-conversion layer is fabricated by mixing the PNCs precursor and the PMMA precursor, dropping it on a clean glass, and drying the mixture under ambient air for 36 hours. The drying process would greatly affect the PL properties of PNCs. If both PMMA and PNCs precursors use the toluene as the solvent, a strong shoulder peak at 450 nm is observed in the PL spectra of the down-conversion layer (Figure 2.24b). The strong shoulder peak might be due to the severe aggregation of PNCs, which causes the formation of larger particles and a new red-shift emission peak. To eliminate such a shoulder peak, a different solvent (hexane) that PMMA was hardly dissolved was employed to disperse the PNCs. After dropping PNCs precursor with hexane as the solvent into PMMA precursor, PMMA would quickly precipitate out. The whole mixture becomes sticky and the movement of PNCs would be slow down, which helps to decrease the PNCs aggregation. Figure 2.24b and c show the PL spectra of the modified down conversion layer. The shoulder peak intensity is decreased greatly. In Figure 2.24c, as the amount of PNCs hexane solution increases from 0.2ml to 0.4ml, the Mn emission intensity changes from 0.5 to 1.2. The reason could be the weak aggregation of

PNCs. Increasing the concentration of PNCs would cause more aggregation and uneven distribution of PNCs. The PNCs concentration in specific areas would increase. If excitation photons hit on the sample, more excited electrons on the valence band would form in those specific areas, which leads to a higher density of excited electrons on the valence band. According to Klimov's theory, the Mn emission is determined by the interplays of rates of four competing processes, two of which are forward (k_{ET}) and back (k_{BET}) energy transfer between the PNC and the impurity.^[9] A higher density of excited electrons on the conduction band would lead to more forward (k_{ET}) and less back (k_{BET}) energy transfer between the PNC and the impurity. Then, there would be more excited electrons on the Mn 4T_1 energy level, which would result in stronger Mn emission. The slight redshift of the 400nm emission peak could also prove the existence of weak aggregation. Through meticulous modification of PNCs aggregation, the PL spectra of the down-conversion layer could also be tuned.

Figure 2.24. (a) Schematic illustration of a typical down-conversion LED. (b) The comparison between PL spectra of the film made by dropping perovskite toluene (PET shown

in Figure b) solution into the PMMA toluene (PMT shown in Figure b) solution and film made by dropping perovskite hexane(PEH shown in Figure b) solution into the PMMA toluene(PMT shown in Figure b) solution. (c) The PL spectra of films made from the solution by dropping different amounts of perovskite hexane solution into the PMMA toluene solution. (d) The comparison between PL spectra of the film made by dropping perovskite hexane solution into the PMMA toluene solution and perovskite hexane solution.

Figure 2.25 shows the optical properties of down-conversion LEDs under the current 8 mA (inserted pictures). The strong emission at 370nm is from the commercial blue LED. The emission intensity at about 400nm becomes very weak. The strong emission at ~ 600nm comes from the Mn emission. The CIE1931 color coordinate of this down-conversion LED is (0.5135, 0.3963), which is shown in Figure 2.25. As the visible wavelength ranges are from 380 to 700nm, only the Mn emission from the down-conversion LED could be detected by human eyes, implying that the fabrication of orange down-conversion LEDs is successful.

Figure 2.25. The CIE1931 color coordinate of fabricated orange down-conversion LED. The inserted figure above is the spectra of fabricated orange down-conversion LED under the current 8 mA. The inserted figure below is the picture of the down-conversion LED.

2.4 Conclusion

Based on a modified synthesis route, the A, B, and X sources are independent. Pristine PNCs and Mn-doped PNCs have been synthesized. Cl^- is proved to influence the Mn emission intensity of synthesized PNCs. By limiting the Cl source and inducing other cations such as Zn^{2+} , Sn^{2+} , Mg^{2+} , the Mn emission intensity of the synthesized PNCs could be tuned. The interactions between metal ions and halide ions are deduced to greatly influence the fast nucleation process. The down-conversion LED based on the synthesized Mn and Zn co-doped PNCs has been fabricated. By controlling the ratio of PNCs and PMMA, the Mn emission intensity of PNC-PMMA films in the down-conversion LEDs could also be tuned. The CIE1931 color coordinate of the final down-conversion LED is (0.5135, 0.3963). In this chapter, the synthesis of PNCs, doping process of PNCs, and down-conversion LEDs have been investigated. The understanding of the fast nucleation process of PNCs and the interaction between composition and PL spectra of PNCs have been enhanced.

3) Perovskite solar cells with organic small molecules as the electron transport materials

PSCs with organic small molecules as ETLs are studied in the chapter. In the literature survey, firstly, the properties of perovskite materials are introduced. Then, the formation of perovskite films is explained. thirdly, different kinds of organic carrier transport layers are introduced and discussed. In the experiment and characterization section, the fabrication of PSCs is carefully described and a series of characterization techniques are presented. In the result and discussion section, the abilities of carrier extract among these NDI derivatives are compared. The relationships between the morphology of these NDI derivatives and the device performance are discussed. After that, the dark current measurement and electrochemical Impedance Spectroscopy (EIS) measurement of corresponding PSCs are conducted and discussed. Moreover, the internal aggregation of ETLs is studied with another series of organic ETLs.

3.1 Literature survey

3.1.1 Properties of perovskite bulk materials.

The perovskite lattice structure is shown in Figure 3.1a and Figure 3.1b. The specific energy level structure of perovskite materials like MAPbI₃ is displayed in Figure 3.1 c and d.^[1,82] The valence band (VB) of MAPbI₃ is constructed by I 5p orbitals and Pb 6s² orbitals (lone pair), the conduction band (CB) is made up of a mixture of Pb 6p and other orbitals.^[4,82] The direct bandgap structure of MAPbI₃ leads to high optical absorption coefficients (105 cm⁻¹).^[83] The specific energy level structure avoids the

formation of deep traps in the middle of the bandgap and leads to trapping states around the CB and VB, which makes electrons or holes easily escape from the traps formed by vacant Pb and I ions.^[1]

Figure 3.1. (a) The lattice structure of perovskite materials. (b) Perovskite bulk materials. (c) Energy level structure of MAPbI₃. (d) Simulated electronic structure of MAPbI₃. ^[1,83]

MAPbI₃ is a kind of ambipolar semiconductor.^[84] Excitons generated by light irradiation would easily decompose to free carriers due to low exciton binding energy. The exciton binding energy is used to judge the facility of excitons changing back to electron and hole. The carrier could move as the free carriers inside the perovskite layer for a long time.^[85] PSCs show different work mechanisms with DSSCs and the semiconducting scaffolds are not necessary.^[1] PSCs also show disparities with the typical n-i-p or

p-i-n structure devices such as Si solar cells. One difference is that the Voc of PSCs is not decided by the quasi-Fermi level difference between ETLs and HTLs.^[1] The solid theories about the formation of Voc in PSCs have not been built.

Figure 3.2. Based on the refinement of HRPND data, (a), (b), (d), (e), and (g) show the structures of d6-MAPbI₃ at different temperatures. (c), (f), and (h) shows the position changing of PbI₆⁴⁻ octahedra due to temperature.

The lattice structures of MAPbI₃ under different temperatures are shown in Figure 3.2. There are three phases of MAPbI₃: orthorhombic (Figure 3.2c), tetragonal (Figure 3.2f), and cubic lattice (Figure 3.2h) structures.^[86] Measured by high-resolution powder neutron diffraction (HRPND), MAPbI₃ has a cubic lattice system at 327-352K. When the temperature goes below about 327 K, the crystal structure of MAPbI₃ could

be the tetragonal lattice system. The cubic-tetragonal transition is in the 165-327 K range.^[86] This transition is affected by anisotropy of the molecular disorder, inorganic octahedral deformation, and tilting, which changes from predominately two dimensions (tetragonal) to three dimensions (cubic).^[87] Thus, at room temperature (25°C), MAPbI₃ has a mixture of cubic and tetragonal lattice structure. Moreover, PbI₆⁴⁻ octahedra inside the cubic or other lattice systems are far from ideal. Pb-I-Pb bond angles between two PbI₆⁴⁻ octahedra of 165-172° exists in the relaxed cubic structure.^[87,88] But the local distortions do not affect the cubic structure and display a dynamic second-order Jahn-Teller instability.^[89] CH(NH₂)₂PbI₃(FAPbI₃) is a cubic lattice structure under room temperature and high temperature. Research about ions movements inside the structure showed that the ions are rotationally mobile at room temperature.^[90]

Figure 3.3. (ca) Relativistic splitting of the band edge states. (b) a multidomain ferroelectric thin film and possible carrier transport tunnels.^[87,94]

MAPbI₃ shows a longer exciton lifetime compared with other kinds of photovoltaic materials. The intrinsic dark carrier mobilities of 8-66 cm²V⁻¹S⁻¹ and long carrier diffusion length could help to extract photogenerated charges at the carrier transport layer/perovskite layer interface before recombination.^[91] The dominant carrier scattering mechanism has been

attributed to acoustic phonons.^[87,92,93] There is supposed to an internal mechanism that suppresses direct electron-hole interactions.^[87,92,93] The relativistic splitting of the conduction band in reciprocal space due to momentum selection rules would also contribute to non-Langevin recombination, which is shown in Figure 3.3a.^[93,94] Separating electrons and holes in real space by the local structure of molecular dipoles and octahedra distortions would also lead to non-Langevin recombination, which is shown in Figure 3.3b.^[93,94]

Due to the advantages of direct bandgap, high optical absorption coefficients, long carrier diffusion lengths, ambipolar carrier mobility, and high intrinsic dark carrier mobilities, MAPbI₃ absorber was also used in this work. MAPbI₃ has a mixture of cubic and tetragonal lattice structures at room temperature. To modify the structure of the perovskite films, FA⁺ ions have been induced to improve the performance of PSCs.

3.1.2 The morphology of perovskite films

Halide perovskites are ionic crystals which like silver halide ionic materials.^[4] The structure of inorganic-organic halide perovskite materials is supposed to be stabilized by the electrostatic interaction between the A-site cations and anionic B-X octahedra.^[11] The chemical bonds maybe the hydrogen bonding between MA/FA and halogen anions.^[95] The octahedral factor about B and X should be satisfied for values between 0.4-0.9.^[96] Figure 3.13a and b show the conditions to form the perovskite structure. Due to good stability and multi choices of organic cations, 2D perovskite materials have also been considered for solar cells. A van der Waals gap is formed between two adjacent lead halide sheets.^[11] The lead halide sheets with varied thickness layers are terminated by the large organic cations, which are called Ruddlesden-Popper or Dion-Jacobson

phases (Figure 3.13c and d).^[97] These large organic cations are the key factors that influence stability and bandgap.^[98]

Figure 3.4. (a)(b) t-μ structure map to show the conditions for forming the perovskite structure.^[96] (c) 2D perovskite materials with Ruddlesden-Popper crystal structure. (d) Schematic representation of a 2D perovskite crystal.^[98]

A good perovskite film should have large grain sizes and tailored grain boundaries.^[11] The grain size is very important for PSCs. The ideal grain size should be directly connected to two surfaces of perovskite films, which means one single grain could connect the HTL and ETLs at the same time. This is quite different from the LED application, in which the grain size should be as small as possible to confine excitons and enhance radiative recombination.^[99]

One disadvantage of grain boundaries is that it could benefit the detrimental transport of ions and environmental species, which would affect the stability of the whole devices (Figure 3.5a).^[100,101] Due to low Schottky defect formation energy, vacant lattice sites would be formed by the thermodynamic driving force, and ions current have been proven to

exist in the MAPbI_3 (Figure 3.5a).^[87,102] Compared with the electron transport process, the ions transport process is a relatively slow process, which is also treated as one of the important reasons for the hysteresis of the PSCs J-V curve.^[103,104] Each part of ABX_3 could lead to the vacant lattice sites and ions current, which is affected by material stoichiometry and material composition.^[87,105-107] Additionally, moisture would also infiltrate along the grain boundaries and cause the degradation of grains.^[101] The degrading process is shown in Figure 3.5b.

One method to deal with the grain boundaries is enlarging the single grain of perovskite films, which could decrease the grain boundary density. One way to increase the grain size is to add Cl^- (Figure 3.5d).^[109] The perovskite films with larger grains exhibit better stability than perovskite films with smaller grains.^[11,108] Another typical way to deal with the grain boundary is to add polymers such as poly (ethylene oxide) and poly (propylene oxide) to protect the grain boundaries.^[109,110]

For the grain orientations of perovskite films, the lattice facet with good conductivity should be perpendicular to the substrate.^[11] For example, MAPbI_3 tends to have better performance at (110) grain facets.^[111]

Figure 3.5. (a) Illustration of the ion migration pathways.^[100] (b) Degradation process of the perovskite film under moisture condition.^[101] (c) Perovskite film formation process from liquid to MAPbI_3 solid film with the assistance of MACl .^[109]

In our case, due to the limitation of lab conditions, the transfer of perovskite films and measurement of PSCs would be exposed to air. The grains and grain boundaries of perovskite films would be damaged by moisture and oxygen in the air, which would result in serious hysteresis of the PSCs J-V curve.^[103,104] To modify this situation, MAI is also added into the perovskite precursors to enlarge the grain size.^[109]

3.1.3 The formation of perovskite films by spin coating methods

Before talking about the formation of perovskite films, it is necessary to introduce the perovskite precursors first. The solvents of perovskite precursor include DMSO, DMF, N-Methyl-2-Pyrrolidone (NMP), γ -Butyrolactone (GBL), Acetonitrile (CAN). Generally, PbI_2 is dissolved in the solvent by the strong coordination bond formed between the O-donor ligands of the solvent and Pb atoms.^[113] But GBL is an exception since it could dissolve the PbI_2 under the existence of MAI.^[11] The choice of solvents could also greatly affect the perovskite films and mixed solvents such as DMSO/DMF, DMSO/GBL have been used. DMSO could also broaden the antisolvent dropping window. Moreover, the halide salts in the perovskite precursors are not dissolved in the solvent and exist as clusters and colloidal particles. (Figure 3.6 a and b)^[114]

Figure 3.6. Wet-TEM images for perovskite materials precursors (with different MAI: PbI₂ ratio) as clusters (a) and colloidal particles (b).^[114]

The spin coating method has been widely used to deposit the perovskite films. The strong centrifugal force of the spin coater would remove most perovskite precursors. The fast gas flow under high rotation speed would remove the solvent quickly. Then, the residual perovskite precursor would be under the state of supersaturation. The nucleation process would happen, and the perovskite film would form. There is a debate about whether intermediate solid phases are existing during the supersaturation process. Even the wet TEM images in Figure 3.6 could not strongly prove the existence of intermediates, since very few precursors are dropping on the holder for TEM measurement. The solvent would evaporate very fast, the nucleation process would happen when preparing the sample for wet TEM measurement.

Figure 3.7. Different crystallization processes.^[115] The crystallization process of perovskite film is ions-(monomer-by-monomer crystal growth)-(polycrystal).

The classical nucleation theories could be used to describe the formation of perovskite films under the assumption that there is no intermediate solid phase formed.^[11] After the gradual removal of the solvent, molecules

with a perovskite structure would appear in the saturated solution, which is called monomers.^[115] The monomers would cluster together into single-crystal nuclei. (Figure 3.7)^[115] Then, there would be heterogeneous (happened in the substrate/perovskite solution) and homogeneous nucleation (perovskite solution).^[11] The critical nucleus radius would be an important index to judge if a nucleus could continue to grow up (nuclei with radii larger than critical nucleus radius) or dissolve back to the solution (nuclei with radii smaller than critical nucleus radius).^[116] The heterogeneous nucleation dominates at low supersaturation due to the lower energy barrier.^[116] The homogeneous nucleation dominates at high supersaturation due to enough sites for nucleation.^[116] The nucleation rate is directly related to temperature and could influence the uniformities of perovskite film. Secondary heterogeneous nucleation on colloidal particles in the solution would be possible, which would be incorporated into the thin film.^[117] A high density of heterogeneous nuclei on the substrate is necessary to form a full-coverage thin film on the carrier transport substrates.^[118] During the process of removing all the solvent, the perovskite precursor on the spinning substrate is always above the solubility limitation, which would lead to the growth of stable nuclei. The growth of perovskite film is supposed to be an island growth mechanism (Volmer-Weber).^[119,120] The rate-limiting step could be the low possibility of attaching irregularly moving monomers to the crystalline nucleus by interface reaction.^[119] For single crystal growth, monomers are deposited on the crystal layer by layer, and crystal facet could be found when observed as a whole. If there are multiple “monomer” layers formed, the resulted crystal would be polycrystal with round grains.^[11,121]

When the solid intermediate-phase exists, it could be another story. The commonly encountered intermediates would be $\text{PbI}_2 \cdot \text{DMF}$, $\text{PbI}_2 \cdot \text{DMSO}$, $\text{MAI} \cdot \text{PbI}_2 \cdot \text{DMF}$ or $\text{MAI} \cdot \text{PbI}_2 \cdot \text{DMSO}$.^[11] The formation of $\text{MAPbI}_3 \cdot \text{DMSO}$

intermediate is reported to benefit the performance of PSCs by reducing the stains, pinholes, and voids and improving the mobility of grain boundaries.^[13] The structure of those intermediates is similar to the octahedral network of PbI_2 .^[11,19, 122,123] Thus, the resulted macrostructure is usually a 1D structure like a rod-or fiber-like structure, which exists as colloids in the precursors.^[13] $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ has been found in the solvent removed perovskite precursor in GBL: DMSO(7:3).^[124] The intermediates are supposed to be stabilized by the hydrogen bonds between DMSO and MA^+ .^[11] Thus, this intermediate is stable under room temperature. In the perovskite precursor based on DMSO/GBL solvent system, the GBL would evaporate and the antisolvent toluene would remove excess DMSO, which would result in the intermediate-phase formation.^[11] One possible reason why Cl^- ions could enlarge the grain size is explained that the DMSO and MAI interaction could lead to the larger intermediates colloidal grain size and finally result in larger grain size.^[125] In our work, the DMSO/GBL mixed solvent has been chosen due to the above reasons and MACl is added to increase the grain size.

3.1.4 The fabrication route of perovskite films by spin coating methods

Then we need to explore how to deposit the perovskite film. The spin coating method is favorable by researchers since it is very easy and simple. There are three stages in the spin-coating method, at the first stage, most precursor solution is removed by centrifugal force. At the second stage, the left precursor solution reaches a dynamic balance with the centrifugal force. The solvent would evaporate under fast airflow. The supersaturated MAI and PbI_2 would be precipitated and tend to crystallize. The detailed nucleation processes have been discussed above. The third stage is that after most solvents have been removed, MAI and PbI_2 would

continue to crystallize with the help of remained solvents. Most perovskite films are fabricated under an inert environment since the growth of perovskite film is very sensitive to oxygen and moisture.

When the ratio of MAI: PbI_2 in the precursor solution is stoichiometric 1:1, the resulted film was a very rough surface with pinholes and insufficient coverage on the substrate. The reason could be the slow evaporation rate of solvent, which could lead to a chaotic nucleation process.^[11] Also, the formation of intermediates such as rod/needle-like MAI- PbI_2 -DMF and rapid growth would also cause lots of voids in between (Figure 3.8).^[126] Therefore, it is necessary to remove the solvent quickly to accelerate the nucleation and decrease the amounts of the intermediates. Rapid nucleation matching well with the pace of solvent removal could lead to the uniform and condense perovskite film. Solvent engineering such as usage of antisolvents and exposing the film to vacuum immediately after the spin, replacing the solvents with other less polar solvents with the lower boiling point could improve the film qualities.^[127-129] Xiao et al. reported that methanol, ethanol, and ethylene glycol would bring the MAI away during the evaporation of solvents.^[130] Tetrahydrofuran, nitriles, diethyl ether, p-xylene, isopropanol, and chloroform are also not suitable as the anti-solvent.^[130] Xylene, toluene, ethyl acetate, and chlorobenzene would work well as the antisolvents.^[130]

Figure 3.8. (a-f) MAPbI₃ Perovskite films growth process from a droplet at 50 °C.^[126]

The antisolvents accelerate the supersaturation of the precursor solution by reducing the solubility of the mixed solvents.^[11] But the time to drop the antisolvent is very important since it should be the gelation point to let the antisolvent permeate through the channels in the gel.^[131] If it is too early, the antisolvent will damage the perovskite surface, such as the formation of small scratches or spirals. If it is too late, the solvent has already been removed and the antisolvent would be useless. ^[11,131] The gelation point varies from lab to lab and from solvent to solvent. But Kerner et al. found out that there was an abrupt transition of the film from transparent to hazy. The gelation point is generally 1-2s before the transition. ^[131] The temperature of antisolvent seems to greatly affect the perovskite film by improving the miscibility of antisolvent.^[132] Another method is the immersion of the samples in a bath of antisolvent after the spin-coating, which needs the cooperation of solvents and anti-solvents, such as NMP and diethyl ether.^[133] The advantages of this method are that there is no glue point and the surface damage caused by the solvent jet is avoided.^[11,133]

The next step is annealing, of which the purposes are removing the left solvent, helping to nucleation and growth of perovskite grains, and

coarsening the grains.^[11] 110 degrees is proper for MAPbI₃ film. Even though the high temperature could benefit grain growth, at the same time, the film would be thermally decomposed. Annealing is a simple process. But many factors could affect this process, such as the hot-plate materials, the substrate to deposit the perovskite film, and the distribution of temperature. The MAPbI₃ films would form periodic twin domains to compensate for the strain caused by phase-changing during the cooling down process.^[113]

Annealing under the solvent environment (Figure 3.9a) could also further improve the film qualities by softening the surface and allowing facile migration of grain boundaries.^[134] The solvent annealed perovskite surface (Figure 3.9c) shows a much larger grain size than the thermally annealed perovskite surface (Figure 3.9b). The commonly used solvent is DMF, GBL, and DMSO. DMSO tends to have better effects due to reducing the activation energy barrier of the perovskite phase transformation.^[135]

Additionally, annealing under the MAI atmosphere was also reported, because it could provide a saturated atmosphere of MAI to reduce the evaporation of MAI in the perovskite films.^[194] Even the MA gas is reported to improve the phase stability of liquid MAPbI₃·X(CH₃NH₂), which results in a pinhole-free, uniformed (110) orientation and smooth surface.^[136] Other organic gases such as NH₃, C₂H₅NH₂, C₄H₉NH₂, FA, and Pyridine are also used.^[11]

Figure 3.9. (a)solvent vapor annealing treatment process. ^[135] SEM images of the (b)thermally annealed and (c)solvent annealed perovskite films; the scale bar is 2 μm . ^[134]

Another method is to leave the samples in a vacuum environment to fast remove unwanted materials such as MAOI, which is hard to remove and would aggregate around the grain boundaries.^[137] Oven, NIR, microwave irradiation, halogen lamp, pulsed-laser irradiation, and xenon flashbulb have also been tried to anneal the perovskite film and the results seemed to be promising.^[11] The physical way to anneal the perovskite film could be the mechanical compression to remove the pinholes and smooth the surface.^[138]

In this work, the perovskite precursor is prepared by mixing the FAI, MAI,

PbI_2 , and PbCl_2 into GBL/DMSO solvent. To achieve a better morphology of perovskite film, the anti-solvent toluene has been adopted. The annealing method used here is solvent annealing, which is supposed to achieve a larger grain size. The solvent used for annealing is DMSO. The fabrication of perovskite films shown in Figure 3.9a is the same as ours.

3.1.5 Organic carrier transport layers for PSCs

When photons hit the PSCs the photo-induced carriers would generate and diffuse in the perovskite film. Then, these carriers may move to the perovskite layer/carrier transport layer interfaces and be extracted by carrier transport layers. Hence, hole and electron transport layers are needed in PSCs and discussed in this section.

3.1.5.1 Choosing suitable structures of PSCs for new carrier transport layers

Figure 3.10. Four most used device structures of PSCs. ^[139,140]

Figure 3.10 shows the four kinds of device structures. ^[139,140] When trying a new carrier transport material, the solubility of the carrier transport material should be considered firstly. For example, if the HTL is the organic material that could easily be dissolved in the DMF, GBL, or DMSO, it could not be used as the substrate to deposit the perovskite film.

Because solvents such as DMSO could damage the substrate by dissolving the organic material. In this case, it could only be adopted as the top transport layer and the structure to adapt this specific organic material should be an n-i-p structure.

The second consideration is the absorption spectra. If an ETL could absorb photons with wavelengths ranging from 300 to 800nm and work as the substrate, it could affect the light absorption of perovskite films. Thus, the device structure should choose the p-i-n structure to avoid the light absorption of carrier transport materials. Therefore, it needs to analyze the practical situations to choose the suitable structure for PSCs.

3.1.5.2 Organic materials as the carrier transport materials

Figure 3.11. The chemical structure of the NDI compound.

NDI(Figure 3.11) is an electron-deficient class of aromatic compounds with high melting points.^[141] NDI possesses high electron affinity and mobility, relatively low LUMO levels, tunable energy levels, and excellent thermal and oxidative stability.^[142,143] NDI derivatives have been widely applied in the area of fluorescence spectroscopy, molecular sensors, OFET, solar cells, and Metallo-supramolecular and supramolecular architectures.^[144-149] Hundreds of NDI based compounds with modification at the imide position and replacements at 2,3,6 and 7 have been synthesized.^[149] NDI molecules could also be applied to self-assemble supramolecular systems, which are made from building blocks

that are linked together by noncovalent interactions.^[141,150]

NDI derivatives could form different kinds of microstructures and 2D materials.^[149] The advantages of NDI derivatives include good solubility in organic solvents, good stability, and uniform film morphologies. NDI with N-substituted side-chains has been used as the ETLs in PSCs.^[151-153] Also, NDI based polymers have also been used in the PSCs with a D-A molecule structure.^[149] NDI-based polymers such as N2200, PNVt-8, PNDI2OD-TT, N-DMBI, PNDI-2T, PFN-2TNDI, P(NDI2DT-TTCN) have also been adopted as ETLs for PSCs.^[154]

The advantages of NDI derivatives as ETLs include enhanced thermal stability, high electron mobility, tunable energy levels, enhanced electron extraction, and hole blocking ability, modifying the cathode work function, reducing surface recombination, interfacial resistance, passivating the perovskite surface against ambient conditions, and enhanced electron transport ability.^[149,154] Most works about NDI-based PSCs focus on improving the efficiency of PSCs, passivating the perovskite surface, and enhancing carrier transport and extraction.^[154] These reported NDI-derivatives shows no distinguishing features of NDI compared with other kinds of small organic molecules. As mentioned above, self-assembly could be a good feature of NDI derivatives.^[149] The NDI derivatives may not be able to form some self-assemble morphology on the perovskite substrate. But NDI derivatives with different side chains could show different levels of molecule interactions. Adjusting the interactions of NDI derivative to form desirable morphology on the perovskite films could be an interesting point. As NDI derivatives are dissolved in the DMF or DMSO, NDI derivatives are usually deposited on the top of the perovskite layer. The device structure would be an inverted p-i-n structure. It is necessary to find suitable HTLs.

The most used hole transport material in the inverted p-i-n structure

are PEDOT: PSS. ^[155,156] The advantages of PEDOT: PSS are good film-forming ability, high transparency in visible light range (higher than 90% at 550 nm), high mechanical flexibility, high electrical conductivity (10^{-2} to 10^3 S/cm), and good stability in air.^[155] The PEDOT: PSS aqueous solution is commercially available. The PEDOT: PSS films could be deposited by spin coating, slot die coating, doctor blade coating, spray deposition, screen printing, inkjet printing.^[155] The work function of PEDOT: PSS film is (-5.0 eV) -(-5.2 eV), which well matches with the HOMO of perovskite materials (-5.4 eV) and benefits the hole transport.^[155] Due to high mechanical flexibility, PEDOT: PSS is used in flexible photoelectric devices. PEDOT: PSS could also work as a transparent electrode. The drawback of PEDOT: PSS is the relatively lower work function, which would negatively influence the Voc of the PSCs. Additionally, the electrical conductivity of PEDOT: PSS is changed with the thickness. The defects of PEDOT: PSS films would also greatly influence the carrier transport and cause the uneven distribution of charges inside the PEDOT: PSS. ^[155,157,158]

To modify the characteristics of PEDOT: PSS, the compounds such as sulfonic acid functionalized graphene oxide (SrGO), Vanadium Pentoxide (V_2O_5), chromium trioxide (CrO_3), tungsten oxide (WO_3), polyethyleneglycol-200 (PEG200), graphene oxide (GO) solution, CuSCN, water rinsing followed by H_2O_2 oxidation, ethylene glycol and methanol have been added into PEDOT: DOS.^[251] Another way to improve the carrier transport of PEDOT: PSS is doping, chemicals including ammonia, Cetyl trimethyl ammonium bromide (CTAB), ammonium metatungstate hydrate (AMH), TiO_2/MoO_3 core/shell nanoparticles(40 nm), nonionic surfactant Triton X-100 (TX) additive, alanine, polymer electrolyte sodium polystyrene sulfonate (PSS-Na), AuAg core-shell alloy nanocrystals (ANCs), polyethylene oxide (PEO), DMSO, carbon black, Zonxl, EMIC (1-

ethyl3-methylimidazolium chloride) ionic liquid, nontoxic mild organic salt sodium citrate, soluble sodium salt (NaCl), rubidium chloride (RbCl) and graphene oxide (rGO) were doped into PEDOT: PSS.^[155]

When judging a new organic ETL, it usually needs a reference ETL to make a comparison. This reference should be a very popular ETL. The performance of this reference should be stable and reported by many labs. The performance in different labs should be at the same level. The most used reference ETL for inverted PSCs is phenyl-C61-butyric acid methyl ester (PCBM). PCBM is firstly used in the organic solar cells as the acceptor. PCBM could fully dissolve in the commonly used solvents such as dichlorobenzene and form very smooth films on the perovskite surface. PCBM itself can passivate the trap states around the top surface and/or along the grain boundaries of perovskite films, which would reduce interface carrier recombination, extend carrier lifetime, and enhance electron mobility.^[158] The PSCs based on PCBM ETLs are usually highly repeatable and suitable for serving as the reference.

The disadvantages of PCBM are instability and high concentration sensitivity. PCBM-based devices would degrade very fast in an ambient atmosphere even in several hours. The spin coating process must be processed in an inert and dry glove box, or the performance of PCBM-based PSCs would be very poor. Additionally, the performance of PCBM is very sensitive to changes in thickness. The concentration of PCBM is usually 23 mg/mL, if the practical concentration is slightly higher or lower, this change would directly reflect on the performance. PCBM could not prevent the diffusion of moisture and oxygen. If putting PCBM-based PSCs in ambient conditions, the color of the devices would change from deep black into yellow, which is due to the evaporation of MAI and the formation of PbI_2 . Therefore, PCBM-based devices could be influenced by many factors. If the performance of different batches of PCBM-based

PSCs is at the same level, it indicates that the fabrication process is very mature and stable. In this way, the performance of devices based on other kinds of ETLs would be convincing. Since the fabrication of PCBM-based PSCs is very mature in our lab. The PCBM-based devices with 15% efficiency could be repeated in different batches and by different people. Therefore, PCBM-based PSCs were used as the reference in this work.

3.2. Experiments and characterizations

3.2.1 Device fabrication of PSCs

Figure 3.12. The fabrication process of PSCs. The detailed fabrication process of the perovskite layer is provided in Figure 3.9.

The perovskite precursor contains the DMSO, GBL, which would dissolve the NDI derivatives. Therefore, the device structure adopted here is an inverted p-i-n structure, of which the NDI derivative is on the top of the perovskite layer. PEDOT: PSS is used as the HTL. ITO glasses were cleaned firstly by the diluted Decon 90 detergent under ultrasonic

treatment for 20mins to remove the organic oil stains, metal salts such as (NaCl) from the operator's fingers, and dust particles. After that, the ITO glasses were washed by DI water under the ultrasonic for 20mins. Then, the glasses were immersed in acetone under the ultrasonic for 20mins to remove the water and organic wastes. Continually, the ITO glasses were washed with isopropyl alcohol to further remove organic contaminations. The final cleaning step would be washing in the ethanol under the ultrasonic for 20mins. Then, the ITO glasses were transferred to the oven and dried at 80 °C for 1 hour. To increase the hydrophilia of ITO glasses, the dried ITO glasses were plasma treated for 20 mins. The device fabrication process is shown in Figure 3.12. The HTL precursor is PEDOT: PSS aqueous solutions. The PEDOT: PSS, which would not be dissolved in the DMSO and GBL solution, was spun on the plasma-treated ITO glasses at 5000 rpm and then annealed at 135 degrees for 12 mins. Then, the samples were transferred to the glove box to deposit the perovskite film under an inert atmosphere. The reason is that the perovskite film could be easily destroyed by moisture and oxygen during the spin coating processes. The perovskite precursors exist in the form of sol-gel during the spin coating processes, the MAI would be easily decomposed by water and oxygen. The perovskite precursor includes MAI, FAI, PbI_2 , and PbCl_2 . The reason for adding FAI is to stabilize the octahedral of PbI_6^{4-} . PbCl_2 has been proved to improve the grain size and decrease the density of grain boundaries of the perovskite films, which would suppress the recombination rate at the grain boundaries. The solvent used here is GBL: DMSO (7:3). GBL could dissolve the PbI_2 under the existence of MAI. DMSO could form the intermediates with MAPbI_3 , which are proved to improve the grain size (mentioned in the literary survey). The spin coating speed was firstly 1000 rpm for the 20s to let the perovskite precursors homogeneously cover on the PEDOT: PSS coated substrate. Then the

speed increases to 4000rpm to achieve the desired thickness. The fast speed could also remove redundant precursors and solvents. With the evaporation of the solvent, the left precursor would become the supersaturated solution and the nucleation process would begin. At the beginning stage, the solution would form the sol-gel state and the MAPbI_3 and DMSO would form the intermediates. To achieve a fast nucleation process and keep the solution being supersaturated, the anti-solvent toluene was injected after spinning for 30 seconds. Then, the fast nucleation would happen, and the color of the film changes from transparency to yellow. But with the intermediates and residual solvents existing, the growth of nuclei is limited. After the spin-coating process, the samples were transferred to the 100-degree hot platform. The solvent annealing methods were adapted (Figure 3.9a). At this temperature, the intermediates would decompose, and the solvent would evaporate fast. the nuclei would fast grow and form the $\text{MAFAPbI}_{3-y}\text{Cl}_y$ films. The film would change from yellow or brown color to deep black color at a very fast speed. After about 20 mins, the smooth and uniform perovskite film would form under the DMSO atmosphere. But during the annealing process, the MAI would evaporate and leave PbI_2 on the surface, which could be detected by the XRD measurement. These vacancies would also lead to active Pb ions and I ions, which may react with the oxygen to form the I_2 and vacancies. These ions and vacancies would form the surface recombination centers. The NDI derivatives have been applied as the ETLs. The solvent of NDI derivatives is dichlorobenzene, which would not dissolve the perovskite layer. The NDI derivatives were dissolved in the dichlorobenzene with different concentrations. After spin-coating at 2000rpm for 1 minute, the samples were transferred to a hot platform and annealed at 90 degrees for 10 mins. The annealing process is to remove the residual solvents. For organic electron transport materials, it is very

hard to crystallize on the perovskite surface with solvent fast evaporating. The organic electron transport materials usually form amorphous films, which could not be detected by XRD measurement. After deposition of ETLs, the samples are transferred to thermal evaporation equipment to deposit the electrode. The transfer process of slices would expose to air. The electrode used in the conventional structure is often Au. But in the inverted structure, the electrode used is often Ag. The reason for using Ag is that Ag possesses good conductivity. But both Au and Ag would affect the stability of the whole PSCs due to the diffusion of metal molecules. The cathode used here is silver and the thickness is 100 nm.

3.2.2 Characterization

3.2.2.1 current density-voltage curve (J-V curve) measurement.

The measurement of the J-V curve was conducted by a solar cell measurement system, which includes a current-voltage source, a light source to simulate sunlight, and software to control the current-voltage source and collect the primitive data. Besides the photo-induced J-V curve, this system could also measure the dark J-V curve, voltage-light intensity curve, and current-time curve. Even though the structures of PSCs are usually p-i-n or n-i-p structure, the classical p-n junction theory could be used to explain the J-V curve of PSCs. The J-V formula of PSCs could be:^[159]

$$J = j_0 \left\{ \exp \left[\frac{q}{nKT} (V - R_T \cdot J) \right] - 1 \right\} - j_L + \frac{V - R_T \cdot J}{R_P} \text{-----}(1)$$

In this equation, j is the current density, j_0 is the dark saturation current density, j_L is the light-induced current, q is the unit charge, V is the voltage, n is the dark ideality factor, K is the Boltzmann constant, T is the

temperature, R_T is the transport resistance and R_p is the parallel resistance.^[159] When measuring the J-V curve with/without light, there would be only a curve. If we want to get more information about these two curves, we need to do some derivations of Formula (1).^[159]

$$G_P = \frac{1}{R_P} \text{-----} (2)$$

$$\frac{dj}{dV} = j_0 \frac{q-R_T \frac{dj}{dV}}{nKT} \exp \left[\frac{q(V-R_T \cdot J)}{nKT} \right] + G_P \text{-----} (3)$$

$$\frac{dV}{dj} = R_T + \frac{nKT}{q} (j + j_L - G_P V)^{-1} \text{-----} (4)$$

$$\ln(j + j_L - G_P V) = \ln j_0 + q(V - R_T \cdot J)/nKT \text{-----} (5)$$

$$\left(\frac{dj}{dV} \right)_{V \leq 0} = G_P \text{-----} (6)$$

To easily express the connections and Simplify the derivations, the parallel resistance R_p has been represented as electrical conductance G_p as shown in equation (2). Then, we could transfer the equation of (1) into (3), (4), (5). If the V is very small or in the reverse direction ($V \leq 0$), the first item in the equation (3) could be very small and negligible. Then, equation (3) could rewrite as equation (6). These parameters in equation 1-6 could reflect the electrical properties of PSCs, According to these parameters of a specific PSC and equation (1), the theoretical J-V curve of this PSC could be drawn.

Next, some important parameters, which are used to judge the performance of PNCs would be introduced. The short-circuit current J_{sc} is the photogenerated current density when the solar cell is short. The open-circuit voltage (V_{oc}) is the photogenerated voltage between the two electrodes of the solar cell when the circuit of the solar cell is open. Fill

factor is the ratio of the product of the voltage and current density in the max power to the product of the Voc and Jsc. ^[160] The power conversion efficiency (PCE) is the ratio of incident light power to output electrical power.

3.2.2.2 measurements of UV-Vis absorption spectra

The absorption spectra could decide the absorption edge of perovskite materials. The absorption spectra have a negative relationship with the absorption coefficient $\alpha(E)$, which is the intensity attenuation of the light passing through a material. The absorption coefficient did not change with the distance. The absorption coefficient depends on the material and wavelength of light.^[161] The equation to describe the light intensity inside the semiconductor could be:

$$I = I_0 \exp(-\alpha x) \text{-----}(7)$$

I_0 is the initial light intensity and x is the distance to the surface. And its connection with the bandgap (Tauc law) could be described as:^[161]

$$[E\alpha(E)]^{\frac{1}{2}} = B(E - E_g) \text{-----}(8)$$

B is a material-related constant. The number of $1/2$ for indirect bandgap materials. It is impractical to directly measure the absorption coefficient $\alpha(E)$. The method is utilizing the equation (8) and the relationship between energy E , wavelength λ :

$$E = hc/\lambda \text{-----}(9)$$

Absorption coefficient $\alpha(E)$ is in proportion to the practical value of

absorption intensity at each wavelength and could be used to replace the absorption coefficient $\alpha(E)$ in the equation (8). Then, equation (8) could be treated as a linear equation with E as the X and $(E\alpha(E))^{1/2}$ as the Y, the intercept on the x-axis would be the primitive value of bandgap (E_g).

The absorption spectra are affected by the morphology of samples. The thickness of films of organic materials are tens to hundreds of nanometers, under this scope, the distribution of molecules could have a direct influence on the energy level structure. If the organic molecules do not aggregate, the absorption spectra of the film would be like that of the solution with the sample evenly dispersed. But if the interactions among molecules are very strong, there would be an aggregation of molecules, which would influence electron cloud density distribution and energy level structures. The absorption spectra would become broader and the major absorption peaks would shift. Comparing the absorption spectra of organic films with that of solution could be used to judge the molecule interaction and aggregation.

The principles of absorption spectra measurement have been introduced in the last chapter. For PSCs, the samples are in the form of films. The structure of samples is usually Glass/ITO/PEDOT: PSS/perovskite layer/HTLs. For the thin film of organic HTLs, the structure is Glass/HTLs. All layers were deposited by spin-coating. The scan scope starts from 1100nm to 250nm. The step is 1nm. The measured results would be discussed in the result and discussion section.

3.2.2.3 Measurements of PL spectra

The first function of PL spectra is to check the optical properties of perovskite film. If the qualities of MAPbI₃ film are good, there would be strong fluorescence under external excitation. The second one is to judge the carrier extraction abilities of different ETLs. ETLs with effective

electron extraction ability could sufficiently extract the photo-generated carriers from the perovskite layer and suppress the radical recombination of these carriers in the perovskite layer. The result would be the decline of fluorescence intensity of the perovskite layer. By comparing PL spectra of perovskite films with different ETLs covered, one could rule out the sequences of carrier extraction ability of these ETLs. The third one is that PL spectra could be used to judge the aggregation of films of organic materials. If the organic materials aggregate seriously, the PL spectra of organic materials would be broadened. The fourth one is to evaluate the passivation effect of organic materials on the perovskite surface. The functional groups of organic materials such as Lewis bases may deactivate the exposed and uncoordinated Pb ions to suppress the surface traps, which could also influence the PL spectra. The decline of surface traps could lead to the decreased deep energy level traps and recombination, which would blue shift the PL emission peaks.

The working principles of PL spectra have been introduced in the last chapter. To measure the PL spectra of organic carrier transport materials or perovskite film, the organic films are deposited on the glass substrate. To measure the PL spectra of perovskite film with organic carrier transport layers covered, the incident light should come from the perovskite side. If the purpose is to find out if the carrier transport layer could passivate the perovskite surface, the incoming light should hit the carrier transport layer side first to make sure the excitation source falls on the perovskite film/ETL interface. The excitation wavelength should be decided by the absorption spectra. The wavelength, where the samples show the highest absorption should be used as the excitation wavelength.

3.2.2.4 Time-resolved photoluminescence (TRPL) spectra.

Figure 3.13. Schematic of the TRPL measurement. ^[162]

Figure 3.13 shows the schematic of the TRPL measurement. The waveform generator could control the laser diode to generate the pulse laser and serve as the clock for the single-photon counting detector. When a very short laser pulse hits on the samples, the samples would be excited. Then, the excited sample would lose their energy in radical and nonradical recombination. The number of generated photons could be an indicator to show how many excitons left in the samples, which are greatly affected by nonradical recombination processes such as the thermal recombination caused by interaction with the crystal lattice, recombination caused by deep energy level traps and defects, and the extraction of carriers by conjoint carrier transport layers. The photons would be detected and counted by the single-photon counting detector. The data about the number of photons detected over some time would be sent to the computer, which could draw the final TRPL spectra. TRPL spectra are used to investigate the non-recombination processes in the perovskite layers and the carrier extraction ability of carrier transport layers. The TRPL curve of perovskite films could be fitted into the primary exponential decay equation and secondary primary exponential decay equation:

$$y = A + B \exp(-t/\tau_1) \text{-----}(10)$$

$$y = A + B \exp\left(-\frac{t}{\tau_2}\right) + C \exp\left(-\frac{t}{\tau_3}\right) \text{-----}(11)$$

These two equations could be used for different photon decay processes. The most important parameters are τ_1 , τ_2 , and τ_3 , which represent the rate of photons decaying. Equation (10) indicates there is one major decaying process. Equation (11) is used to fit the system which has two decaying processes. The samples for TRPL measurement are in the format of thin films, which is similar to these for PL measurements. The excitation wavelength is also decided by the absorption spectra.

3.2.2.5 X-ray diffraction spectra

The working principles of XRD have been introduced in Chapter 2. The interplanar crystal spacing could only provide limited information. Matching the theoretical XRD patterns to the measured XRD patterns could be used to get the lattice plane information about samples. The XRD patterns of perovskite films have been reported by many works and could serve as references to explain the measured XRD patterns of the perovskite layer. The structure of perovskite samples is Glass/ITO/PEDOT: PSS/perovskite layer/ETLs. The scan angle is from 10 degrees to 60 degrees. XRD patterns could be used to judge the orientation and uniformness of perovskite films. If the organic materials could passivate the perovskite surface and promote more dissociative MAI react with unbinding PbI_2 on the surface, the intensity of PbI_2 in the XRD pattern of perovskite film would decrease. XRD spectra could also be used to judge the morphology of organic films.

3.2.2.6 AFM measurements

AFM measurements are used for mapping the surface of perovskite films and the organic carrier transport layer. AFM images could display the grain size of the perovskite layer and estimate if there are pinholes on the surface. The 3D AFM images would exhibit the stereo structure of the whole surface. The root mean square (RMS) roughness data could be calculated to quantitatively compare the roughness of different samples. The AFM images could be also used to judge the aggregation and morphology of organic materials. Additionally, by comparing the RMS roughness of perovskite film with/without organic materials covered, it is easy to tell if the organic materials could smooth the surface or not. What's more, AFM measurement could measure the film thickness. The detailed method is using sharp blades to scratch a line on the surface. The cross-section line of corresponding AFM images could be used to calculate the thickness. A more advanced application of AFM measurements could be measuring the surface current distribution at the same time. By comparing the current of different grains under light, the efficiency of each grain could be calculated and compared to study the photo-generated carrier movements, the locations of carrier extraction area, carrier recombination area, and recombination processes.

Figure 3.14. The working principles of AFM measurement.

The working principle of AFM measurement has been shown in Figure 3.14. The AFM system is based on the interaction between the surface atoms and a very sensitive tip on a cantilever. As the tip contacts the surface, the cantilever bends, and the bending is detected by a split photodetector. This bending is indicative of the tip-sample interaction force. This tip is used to image a sample by raster scanning across the surface line by line.^[162] The max and min area of AFM measurement could depend on the specific equipment used, usually from 30 μm X30 μm to 1 μm X1 μm . The roughness of the surface could not be so high, which may damage the tip. The tips are very sensitive and easy to break. There are usually two kinds of probes including hard and soft tips. The soft tips could be used to scan the smooth surface and more details could be revealed. The hard tips could be used to scan the relatively rough surface to get basic information about the sample surface. The roughness of fabricated perovskite films and films of organic materials is in the nano-level, which is very suitable for the AFM measurements. The smaller the scan area is, the more details the images could reveal. The resolution limit of AFM measurement is about 100nm and the grain size of perovskite film in this work is usually about 400nm. Therefore, the scan area used here is usually $1 \times 1 \mu\text{m}^2$.

3.2.2.7 EIS measurement

EIS measurement explores the circuit model of PSCs. EIS analysis could be used to build the circuit model of PSCs to explain some phenomena of PSCs. The basic electronic Components are resistance and capacitance. Referring to Gratzel et al.'s work, we construct the equivalent circuit of planar PSCs, which is shown in Figure 3.14.^[163]

Figure 3.15. The equivalent circuit of PSCs.

In Figure 3.15, R_{si} , R_{sh} , R_{sp} , R_{se} , and R_{sa} are the series resistance inside each layer. R_{ih} , R_{hp} , R_{pe} , and R_{ea} is the interface resistance. R_{csh} and R_{cse} is the surface recombination resistance. R_c is the recombination resistance inside the perovskite layer and R_l is the light-induced resistance. C_{ih} , C_{hp} , C_{pe} , and C_{ea} are the interface capacitors. As we could find out, the whole system is quite complicated, and many factors need to be considered. The equivalent circuit could be simplified to the circuit shown in Figure 3.16. In this simplified circuit, R_s is the series resistance of the whole circuit. R_{ct} could be the carrier transport resistance inside the PSCs. R_{rc} could be recombination resistance. And as the circuit is built under ideal conditions, the equivalent circuit should be modified according to the real situations.

Figure 3.16. The simplified equivalent circuit of PSCs.

In the EIS measurement system, the applied voltage is the small sinusoidal voltage. The equation of voltage is shown in equation (13).^[164]

$$V(t) = V_0 + v_{amp} \cdot \sin(\omega \cdot t) \text{-----(13)}$$

where V_0 is the offset voltage, V_{amp} is the voltage amplitude and ω is the angular frequency $2 \cdot \pi \cdot f$.^[159] The V_0 is usually from 0 to 1 V. V_{amp} is usually 0.05 V. The frequency is from 1000k-1Hz. The Nyquist plot curve could be achieved and be simulated by the software Zview to match the equivalent circuits.

3.3 Results and discussion

Scheme 3.1. The chemical structure of five NDI derivatives.

Firstly, we investigated the effects of different NDI derivatives as the ETLs on the PSCs. NDI derivatives NDIF1, NDIF2, DNDIF3, N11 and N12 were synthesized by our cooperators and shown in Scheme 3.1. When designing suitable ETLs for PSCs, the morphology of ETLs should be considered. Because a good morphology would help to facilitate carrier transport. Here, by elaborately designing the side chains, the molecular

interaction and aggregation of NDI derivatives could be modified. Through a series of characterizations, NDIF1 are proven to have the appropriate internal aggregation to smooth the contact with the cathode and low series resistance, the power conversion efficiency (PCE) is 15.6%. With the ability to prevent the Ag thermal diffusion towards the perovskite surface due to strong molecule interaction, NDIF2 under high concentration shows the highest fill factor (80%).

Figure 3.17. (a) The device structure of PSCs with different ETLs. (b) Energy level diagram of each material in the device structure. (c) Cross-sectional SEM image of PSCs.

To investigate the roles of NDIF11, NDIF12, DNDIF3, N11, and N12 as ETLs in PSCs, inverted planar PSCs with the same architecture of ITO/PEDOT: PSS/perovskite/ETLs/Ag were fabricated and shown in Figure 3.17a. The detailed fabrication process has been provided in section 3.2.1. The energy level diagram is shown in Figure 3.17b. The electrochemical properties (lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO)) of NDIF1, NDIF2, DNDIF3, N11 and N12 are studied by CV measurement. The whole calculation process was conducted by our cooperators. Based on the first reduction potential of these three NDI derivatives and reference ferrocene, LUMOs of NDIF1, NDIF2 and DNDIF3 are -3.8eV, -3.9eV, and -3.8eV, respectively, well-matched with the conducting band position of perovskite layer(-3.9 eV), which could facilitate the electron transport and extraction. The bandgap could be figured out from the UV-vis absorption

spectroscopy. Then HOMO could be calculated according to the LUMO and bandgap. The HOMO of NDIF1(-5.68eV) and NDIF2(-5.6 eV) are lower than that of perovskite(-5.4eV), which suggests that NDIF1 and NDIF2 could form effective hole blocking energy barrier to prevent the hole diffusion. However, the HOMO of DNDIF3 is -5.0eV, which means that no sufficient energy barriers are formed. N11 and N12 show much lower LUMO and deeper HOMO than these of perovskite layers, which show a very matched energy level structure with perovskite films. Figure 3.17c offers a cross-sectional scanning electron microscope (SEM) image of PSCs.

Figure 3.18. Steady-state PL spectra of pristine perovskite film, perovskite film/NDIF1, perovskite film/NDIF2, and perovskite film/DNDIF3 with excitation light from air side(a) and ITO side(b). Steady-state PL spectra of pristine perovskite film, perovskite film/N11, perovskite film/N12 with excitation light from air side(c).

The electron extraction phenomena are investigated by steady-state PL spectra (Figure 3.18). The steady-state PL spectra are collected from the samples of perovskite, perovskite/NDIF1, perovskite/NDIF2, perovskite/DNDIF3, perovskite/N11, and perovskite/N12 fabricated on glass/ITO/PEDOT: PSS substrates. The excitation wavelength is 532 nm. When incident light comes from the air side, the pristine perovskite film shows typical strong emission with a maximum at 780nm, while the emission peaks of perovskite/NDIF1, perovskite/NDIF2, and perovskite/DNDIF3 are located at 779nm, 776nm, and 775nm, respectively. The blue shift of emission peak is due to the slight

passivation of the perovskite surface by these NDI derivatives. ^[258] When incident light comes from the ITO side, all emission peaks of these three samples are the same (779nm). The PL intensity is quenched by coating NDIF1, NDIF2, and DNDIF3 onto the perovskite layers. These ETLs could enhance interface carrier extraction. From Figure 3.17c, the N11 and N12 show similar PL spectra with that of perovskite with HTL covered, which means N11 and N12 could not effectively extract the carriers from perovskite layers.

Table 3.1. The results of simulated TRPL curve.

Structure	T ₁ (ns)	A ₁	T ₂ (ns)	A ₂	T _{aver} (ns)
Perovskite	220.1	9590.00	N/A	N/A	N/A
ITO/PEDOT: Pss/Perovskite	4.11	1.11x10 ¹²	14.24	8.57 x10 ⁶	4.11
ITO/PEDOT: Pss/Perovskite/NDIF1(6 mg/ml)	3.68	1.89 x10 ¹³	17.56	3.50 x10 ⁶	3.68
ITO/PEDOT: Pss/Perovskite/NDIF1(10 mg/ml)	3.65	2.15 x10 ¹³	15.39	4.50 x10 ⁶	3.65
ITO/PEDOT: Pss/Perovskite/NDIF2(6 mg/ml)	4.30	6.93 x10 ¹¹	21.00	1.92 x10 ⁶	4.30
ITO/PEDOT: Pss/Perovskite/NDIF2(10 mg/ml)	4.37	7.60 x10 ¹⁰	22.85	2.40 x10 ⁵	4.37
ITO/PEDOT: Pss/Perovskite/DDIF3(4 mg/ml)	4.15	4.87 x10 ¹¹	17.58	1.59 x10 ⁶	4.15
ITO/PEDOT: Pss/Perovskite/DNDIF3(6 mg/ml)	3.72	6.30 x10 ¹²	15.00	4.75 x10 ⁶	3.72

Figure 3.19. TRPL curve of Glass/perovskite layer(a), Glass/ITO/PEDOT:PSS/perovskite layer(b), NDIF1 6mg/ml(c), 10mg/ml(d), NDIF2 6mg/ml(e), 10mg/ml(f), DNDIF3 6mg/ml(g), 10mg/ml(h) on the Glass/ITO/PEDOT:PSS/perovskite layer.

The TRPL curve of samples Glass/perovskite layer, Glass/ITO/PEDOT:PSS/ perovskite layer, and Glass/ITO/PEDOT: PSS/ perovskite layer/ ETLs are shown in Figure 3.19 and 3.20. The fitted data is summarized

in Table 3.1. The ETLs are measured under the concentration of 6 mg/ml or 10 mg/ml. In table 3.1 the existence of PEDOT: PSS strongly decreases the lifetime due to effective hole quenching. The ETLs with varied concentrations could hardly affect the TRPL performance. No electron energy barriers at the perovskite layer/ETL interface are formed.^[259] The reported TRPL data of Glass/ITO/PEDOT: PSS/ perovskite layer/PCBM is also similar to that of Glass/ITO/PEDOT: PSS/ perovskite layer/ ETLs(NDI derivatives), which also shows the strong hole extraction ability of PEDOT: PSS.^[165] As the PL spectra of N11 and N12 covered on the perovskite films show a slight difference with that of pristine perovskite films, the TRPL spectra of N11 and N12 are not studied here.

Figure 3.20. TRPL curve comparisons between without ETLs and with NDIF1(a), NDIF2(b), and DNDIF3(c) under different concentrations.

Figure 3.21 shows the UV–vis absorption spectra of the perovskite films covered by NDIF1, NDIF2, DNDIF3, N11, N12, and PCBM ETLs. Similar absorption edges and tendencies are observed for all the samples, which indicates that ETL layers have a slight influence on the perovskite bandgap. The absorption intensities of ETL-covered perovskite films are higher than that of pristine perovskite film. The enhanced absorption could contribute to the intrinsic absorption of ETLs.

Figure 3.21. UV-vis absorption spectra of NDIF1, NDIF2, and DNDIF3(a), N11, and N12(b) covered on perovskite film compared with the perovskite film and PCBM covered on the perovskite film.

Figure 3.22. AFM images(a-d) and corresponding 3D profiles(e-h) of pristine perovskite layer, perovskite layer covered with NDIF1, perovskite layer covered with NDIF2, and perovskite layer covered with DNDIF3, which were prepared on the ITO/PEDOT: PSS substrates.

AFM is conducted to study the morphologies of ETLs. To explore the morphology of ETLs under the real situation, the AFM samples were taken from the area ($1\mu\text{m}\times 1\mu\text{m}$ or $5\mu\text{m}\times 5\mu\text{m}$) near the Ag cathode. The concentration of NDI derivatives is 4 mg/ml (Figure 3.22a-h). Also, to study the influence of the concentration, 6 mg/ml and 10 mg/ml are used. The resulted films are shown in the Figure 3.23. Figure 3.22a shows the typical perovskite surface with large grain domains. In Figure 3.22b, many small

NDIF1 islands are found on the crystal domains (yellow area) and the grain boundary (violet area) of the perovskite layer, which means that NDIF1 aggregates slightly and mild interaction between molecules exists. With the concentration increased from 4mg/ml to 6 mg/ml (Figure 3.23a-c), the diameter of NDIF1 islands increases from about 0.2um to 0.4 um. The reason could be higher concentration promotes the growth of molecule aggregated area. When the concentration increases to 10 mg/ml, the aggregated areas continue growing and are integrated to form a relatively smooth surface. The boundary of NDIF1 islands becomes not obvious. For NDIF2, the wire-like configuration could be seen in Figure 3.22c. This result might be due to strong molecule interaction and serious aggregation, leading to the uneven accumulation to form wire-like morphology. After the concentration increases to 10 mg/ml, in Figure 3.23d-f, more wire-like configurations are formed in the same area and show no trend to merge to form a planar structure, which greatly increases the roughness. When it comes to DNDIF3, in Figure 3.22d, the lattice boundaries could be seen inside the red square grid, which means that DNDIF3 may not be able to cover the crevices between grains. This might be due to the weak interaction among DNDIF3 molecules, resulting in insufficient coverage of the perovskite active layer. Even with the concentration increase from 4 mg/ml to 10 mg/ml, as shown in Figure 3.23g-l, the weak interaction among molecules leads to no apparent changes in the morphology.

Figure 3.23. AFM images and corresponding 3D profiles(1 μ m $\times$ 1 μ m) of NDIF1 under the concentration of 4mg/ml(a,d), 6mg/ml(b,e) and 10mg/ml(c,f), NDIF2 under the concentration of 4mg/ml(h,k), 6mg/ml(i,l) and 10mg/ml(j,m) and DNDIF3 under the concentration of 4mg/ml (n,q), 6mg/ml(o,r) and 10mg/ml(p,s). All the NDI derivatives are based on ITO/PEDOT: PSS /perovskite layer substrate.

As N11 and N12 have different side chains and morphologies on the perovskite substrate, the AFM images of N11 and N12 on the perovskite substrates have been provided in Figure 3.24. From Figure 3.24c and d,

the morphology of N11 and N12 is similar to that of the perovskite layer shown in Figure 3.22a, which means that N11 and N12 could not effectively cover the perovskite surface. The grain boundaries of the perovskite layer are exposed and would contact the following metal electrode, which may bring damages to the perovskite surface.

Figure 3.24. AFM images of Perovskite layer(a), PCMB layer on the Perovskite layer(b), N-11 layer on the Perovskite layer(c), N-12 layer on the Perovskite layer(d).

Large crystal domains (about 400nm) are found from the as-prepared perovskite film, of which the root-mean-square (RMS) roughness is 16.476nm. When NDIF1 or DNDIF3 is deposited on the perovskite films, the RMS roughness reduces to 13.409nm and 13.449nm, respectively. A smoother surface means a more condensed contact with the metal electrode. However, when it comes to NDIF2, the RMS increases to 21.537nm. The rough surface is caused by the serious aggregation of NDIF2. When the concentration increases, the RMS roughness of NDIF1 decreases to 11.18nm, the RMS roughness of NDIF2 increases to 23.211

nm, and that of DNDIF3 keeps almost the same (15.096 nm). Mild aggregation of NDIF1 molecules could improve the quality of the film and decrease the RMS even under higher concentration, while serious aggregation would roughen the surface. The results of the AFM data exhibit the sequences of molecule interactions. Additionally, the relationship between aggregation of NDI derivatives and film roughness has also been built.

Inspired by Wu's method ^[166] to explain the morphology of the as-formed ETLs, the schematic depictions of the sandwich structure (perovskite film/ETLs/cathode) speculated from AFM images are shown in Figure 3.22i-l. The possible effects of silver electrodes are discussed here. NDIF1 shows mild molecular interaction and with the concentration increase, the island-like NDIF1 surface becomes more uniform and smoother. NDIF1 ETL could form a compact surface to prevent the thermal diffusion of Ag molecules. NDIF2 shows the strongest molecular interaction and the roughest surface morphology. As the concentration increases, the roughness becomes higher. The uneven NDIF2 ETL surface may cause silver atoms not to be sufficiently deposited on the ETL surface. Some vacuoles may form between ETLs and cathodes, which would increase the resistance of electron transport. But the strong interaction and aggregation could also prevent the diffusion of Ag molecules. DNDIF3 has a weak molecule interaction and may not be able to cover the grain boundary of the perovskite active layer. The silver atoms have great opportunities to pass through the ETL layers and directly contact with the perovskite layer, which may lead to diffused Ag molecules reacting with iodine of the perovskite layer and the formation of iodine vacancy.

Figure 3.25. XRD patterns of pristine perovskite film, perovskite film/NDIF1, perovskite film/NDIF2, and perovskite film/DNDIF3. (a) XRD patterns of pristine perovskite film, perovskite film/N11, perovskite film/N12(b)

Figure 3.25 compares the X-ray diffraction (XRD) plots of pristine perovskite film and perovskite films coated with each ETL. The strong and sharp diffraction peaks of (110), (112), (220), and (310) crystal planes in the XRD patterns confirm the excellent crystallinity of pristine perovskite films. The diffraction peaks at 12.22° can be assigned to the existence of PbI_2 . No indication of the crystallinity of the NDI derivatives has been found in the XRD data. The reason could be it is very hard to form the crystal under strong centrifugal force and fast solvent evaporation.

Figure 3.26. Transfer characteristics of organic thin-film effect transistors based on NDIF1(a), NDIF2(b).

Carrier transport properties inside NDIF1, NDIF2, and DNDIF3 layers were studied by OTFT devices. The transfer and output characteristics of the OFETs thin film based on NDIF1 and NDIF2 are depicted in Figure

3.26. NDIF3 cannot be used to fabricate OTFT. The reason is poor film qualities on SiO₂ substrate. The electron mobilities, on-off ratios, and threshold voltages of the thin-film OFETs for NDIF1 and NDIF2 are tabulated in Table 3.2. Both NDIF1 and NDIF2 exhibit N-type semiconductor characteristics. The organic field-effect electron (μ_e) mobilities of NDIF1 at room temperature is $5.91 \times 10^{-6} \text{ cm}^2/\text{Vs}$, which is slightly lower than that of NDIF2 ($1.53 \times 10^{-5} \text{ cm}^2/\text{Vs}$).

Table 3.2. OFET data of NDIF1 and NDIF2.

	Mobility (cm^2/Vs)	$I_{\text{on}}/I_{\text{off}}$	$V_t(\text{V})$
NDIF1	5.906×10^{-6}	$2.717 \times 10^{+1}$	$4.21 \times 10^{+1}$
NDIF2	1.531×10^{-5}	$1.626 \times 10^{+2}$	$2.68 \times 10^{+1}$

The J–V characteristic curves were measured under simulated solar irradiation (AM 1.5, 100 mW cm^{-2}) for the PSCs incorporated with NDIF11, NDIF12, DNDIF3, N11, and N12 as ETLs. The measurements have proceeded under the ambient condition (temperature: 25°C , humidity: 66%). The scan scope is 0–1.2V, the step is 50mv. The dependence of device performance on ETL thickness was explored by varying concentrations of NDIF11, NDIF12, DNDIF3, N11, and N12 in 1,2-dichlorobenzene spun onto active layers with the same rotate speed (2000 rpm). Table 3.3 compared the performance of PSCs based on NDI derivatives. In table 3.3, NDIF1-based PSCs show the highest efficiency of 15.6%. But for NDIF2, ‘wire-like’ morphologies and higher roughness make its contact with metal electrode insufficient. The series resistance of the whole device increases, which would negatively affect the photocurrent performance. But on the other hand, strong interaction among NDIF2 molecules make it hard for Ag molecules to diffuse through the ETL layer. The traps caused by the direct contact between Ag electrode and perovskite active layer would decrease. Fewer interface

traps lead to a high fill factor (80%). Due to weak interaction among molecules, DNDIF3 may not be able to cover the perovskite layer effectively, which makes diffusion of Ag molecules easier and increase the possibilities of formations of iodine vacancy and other traps. Additionally, from the LUMO and HOMO comparison between the perovskite layer and DNDIF3, the DNDIF3 layer could not form an effective hole blocking barrier at the ETL/perovskite interface. Then those drawbacks finally reflect on the fill factor performance of DNDIF3 based devices. Thus, the aggregation of ETLs could affect the performance of PSCs in two major ways: (1) affecting the roughness of ETL surface and series resistance; (2) the extent of preventing the diffusion of metal electrode and formation of traps caused by contact between electrode molecules and perovskite layer. The trend of main parameters changing with the concentration is shown in Figure 3.27a-d. The comparison of the J-V curve between NDIF1 and NDIF2 under luminescence is shown in Figure 3.26e-h. some points of CV are skipped to clearly show how the current density changed with voltage in the NDI-based PSCs. The J-V characteristics of DNDIF3-based PSCs are shown in Figure 3.27i. N11 and N12 show similar problems with DNIDF3, therefore, the efficiency is also quite low due to the diffusion of silver. In our case, due to the limitation of lab conditions, the fabricated perovskite films would be exposed to air, which results in serious hysteresis of the PSCs J-V curve. The stability of the fabricated inverted PSCs is not good. Since the glovebox and thermal evaporation are not directly connected, the perovskite layer would be exposed to air for more than one minute. Also, the devices are measured under ambient conditions in an organic synthesis lab. Therefore, many uncontrollable environmental factors affect the device performance, the stability is not studied here.

Dark saturation current J_0 could be decided by the slope extension line

near the open current voltage on the y-axis. From Figure 3.28a and b, the J_0 of PSCs with NDIF1 is lower than that of NDIF2 and far lower than that of NDIF1. Lower J_0 means suppressed surface recombination, which could further prove that NDIF1 films could better prevent the diffusion of Ag and form better morphology on the perovskite substrate.

Table 3.3. Summary of the photovoltaic properties

Materials	Concentration (mg/ml)	Jsc(mA/cm ²)	Voc(V)	FF(%)	PCE(%)	Highest PCE(%)
NDIF1	4	22.83±0.21	0.74±0.03	68±1.63	11.53±0.35	12.2
	6	21.39±1.44	0.96±0.02	62.21±3.89	12.66±0.18	13
	10	23.66±0.42	0.97±0.02	64.0±0.68	14.72±0.44	15.6
	14	22.88±0.79	0.82±0.06	58.1±2.58	10.19±0.33	11.5
NDIF2	4	17.52±0.47	0.76±0.01	67.12±2.50	9.04±0.45	10
	6	18.91±0.89	0.8±0.01	68.8±3.39	10.47±0.31	11.1
	10	18.25±0.82	0.8±0.01	72.4±3.41	10.64±0.15	10.9
	14	16.42±0.50	0.82±0.01	76.3±2.64	10.3±0.2	10.7
DNDIF3	4	23.10±0.64	0.75±0.02	58.7±2.83	10.22±0.39	10.7
	6	22.11±1.10	0.91±0.03	56.0±1.88	11.17±0.26	11.7
	10	23.08±0.40	0.81±0.03	40.5±1.85	7.62±0.58	8.6
	14	22.10± 0.45	0.8±0.09	27.0±3.25	4.73± 0.11	4.9
N11	8	0.75±0.02	16.22±0.92	58.1±4.2	7.08±0.22	7.4
	15	0.76±0.016	22.21±0.94	45.8±1.7	7.71±0.12	7.9
	20	0.79±0.08	23.21±0.6	45.54±0.84	8.4±0.12	8.7
	22	0.81±0.044	22.55±0.39	52.7±0.77	9.6±0.14	10.2
N12	5	0.79±0.01	22.26±1.28	44.4±2.13	7.8±0.19	8.1
	8	0.82±0.086	22.97±0.64	45.79±0.99	8.6±0.11	9.1
	10	0.83±0.029	22.90±0.91	36.1±0.59	6.86±0.58	8.0
	15	0.73±0.015	16.90±0.87	53.8±3.53	6.61±0.29	6.9
PCBM	20	22.29±0.19	0.97±0.01	68.5±1.35	14.83±0.11	15

Figure 3.27. The trend of short current(a), open-circuit voltage(b), fill factor(c) and PCE(d) changed with the concentration. The J-V curve(e-h) of NDIF1 and NDIF2. The J-V curve(i)

of DNDIF3. The J-V curve(j) of N11 and N12 based PSCs.

Figure 3.28. Dark J-V characteristics of NDIF1, NDIF2 and DNDIF3 based devices with the concentration 6mg/ml(a) and 10mg/ml(b).

To further confirm our conclusion about the relationship between aggregation of ETLs and performance of NDI derivatives-based PSCs, an analysis has been conducted by the EIS measurement, which could be used to analyze the series resistance and recombination processes at the interfaces. The concentration we choose here is 10 mg/ml for three ETLs. Under this concentration, NDIF1 film and NDIF2 show the biggest difference in film surface morphology, and NDIF3 is supposed to achieve enough thickness (50nm) to prevent the diffusion of Ag molecules. The scan scope is 1Hz to 1MHz and the initial voltage is 0.6V. The results are shown in Figure 3.29 and the simulated results are shown in Table 3.4. In Table 3.4, we could see that the sequence of series resistance(R_1) is NDIF2>NDIF1>DNDIF3. The electron mobility of NDIF2 is slightly larger than NDIF1(Table 3.2), but the series resistance of NDIF2 is larger than NDIF1. The reason could be that the rough surface of NDIF2 has insufficient contact with the metal evaporated electrodes, which resulted in higher resistance. In Figure 3.29, the EIS curve of DNDIF3 is quite different from that of NDIF1 and NDIF2. The Simulated curve could not match well with the practical EIS curve of DNDIF3 when using the same equivalent circuit as NDIF1 and NDIF2. The reason is supposed to be the

diffusion of Ag electrode across the DNDIF3 and contact with the perovskite layer, which would lead to lower series resistance and reaction happening between Ag and the iodine ions of the perovskite film. Ag molecules may react with the iodine ions, which would cause the formation and migration of vacancy I under bias, so a Warburg element should be added, and the fitting results are matched.

Figure 3.29. EIS characterization of PSCs based on a) NDIF1 and NDIF2 b) NDIF3 as ETL at forwarding bias V_{app} (0.6V) under dark condition. Inserted figure in the (a) Equivalent circuit used for modeling NDIF1 and NDIF2, where R_1 is the series resistance, R_2/C_1 the resistance/capacitance associated with the electrode, and R_3/C_{pe1} the resistance/capacitance related to the ETL/perovskite layer interface. Inserted figure in the (b) Equivalent circuit used for modeling DNDIF3.

Table 3.4 Simulated data of EIS of solar cells based on NDIF1, NDIF2, and DNDIF3.

ETL	$R_1(\Omega)$	$R_2(\Omega)$	$C_1(F)$	$R_3(R_4 \text{ for DNDIF3})$	$CPE1-T$	$CPE1-$	$W1-R$	$W1-$	$W1-$
				(Ω)		p		T	P
NDIF1	12.87	8930	4.21E-	148800	1.32E-6	0.706	N/A	N/A	N/A
			9						
NDIF2	26.14	1772	3.3E-9	59981	1.81E-6	0.847	N/A	N/A	N/A
DNDIF3	10.66	2600	2.15E-	31402	2.322E-	2.06	139880	0.28	0.52
			9		6				

In the next part, we would talk about the effects of the internal aggregation

of ETLs on the performance of PSCs. The compound 6-9 shown in Scheme 3.2 were synthesized by our cooperators.

Scheme 3.2. The chemical structure of a series of imide-fused diazatetracenes.

The crystal structures provided by our cooperators are shown in Figure 3.30. (the crystal structure of compound 5 is not available) For compound 6, one-dimensional stacking is observed with antiparallel co-facial p–p stacking distances of 3.43 and 3.44 Å. The dihedral angle between the thiophene moieties and azatetracene backbone are 61.738 and 65.418. Because of the less steric hindrance imposed by the thiophene sidechains, there is a decrease in p–p stacking distance compared to compound 7. In the crystal of compound 7, molecules form pairs through p–p stacking with a distance of 3.51 Å. The pairs are further held together by carbonyl–p interactions with a shorter distance. Compound 8 is more twisted in the solid-state and no p–p stacking is observed. The degree of planarity is quantified by the dihedral angle between the imide segment and the farthest benzene ring from the imide segment. Instead of p–p interaction, the carbonyl–p interaction and CH–p interaction dominates the crystal of

compound 8 with distances of 3.42 Å and 2.76 Å, respectively. To overcome the steric hindrance, compound 8 shows a slipped one-dimensional packing.

Figure 3.30. The crystal structures of a) compound 6, b) compound 7, and c) compound 8.

To explore the application of imide-fused diazatetracenes inorganic electronics, PSCs with compound 5–8 as ETLs were fabricated. The inverted planar PSCs architecture and the energy-level diagrams are shown in Figure 3.31a and b. The statistical photovoltaic performances are shown in Figure 3.31c-h. It is found that the open-circuit voltage (V_{oc}) and J_{sc} of the methyl-substituted compounds (compound 5 and 7) are higher than those of cyclohexyl-substituted compounds (compound 6 and 8). The possible reason could be the better contact between the methyl group and the perovskite surface, which further results in better electron extraction. However, better contact with the perovskite layer does

not mean better PCE performance. Even though the V_{oc} of compound 5-based PSCs is larger than that of compound 6-based PSCs, the PCE of compound 5 is lower than that of compound 6, which

Figure 3.31. a) Device architecture of PSC used in this work; b) Corresponding energy level diagrams; c) J–V curves of the PSCs with compound 5 and 6 as ETLs; d) J–V curves of the PSCs with compound 7 and 8 as ETLs. The comparison of Voc (a), Jsc (b), fill factors (c), and PCE (d) of PSCs with these four compounds.

is caused by a higher fill factor (FF) of 6-based PSCs (average FF= 66.4%). The reason could be the lower series resistance and better aggregation of compound 6 as ETL. While PSCs based on compound 5–7 show reasonable similarities in device performance, the average PCE for 8 is 5.15%, which is 3% lower than devices based on compound 5–7. This result might be unexpected at first glance since the electronic properties of compound 5–8 are quite similar. However, in the solid-state, compound 8 exhibits rather weak p–p interactions, which is supported by its crystal structure and the unquenched solid-state fluorescence compared with compound 7. Thus, we propose that the weak p–p interaction of compound 8 in the solid-state may result in less efficient electron transport in PSCs, which then leads to a lower PCE.

3.4 Conclusion

In this chapter, we have investigated a series of organic materials as ETLs for PSCs. We found that the specific side chains on NDI derivatives would greatly affect the accumulation of molecules and then lead to the formation of different morphology of ETLs. Strong aggregation caused by molecular interaction would increase the RMS, lead to insufficient contact with the metal cathode, and decrease the current density. Proper aggregation and molecular interaction could help to form a smoother ETL surface and achieve better photocurrent performance. Strong interaction among molecules could promote the formation of compact ETLs and prevent the thermal diffusion of cathode metal molecules, which could lead to improved fill factors of PSCs. Moreover, the aggregation inside the

ETL could also be found to influence the performance of PSCs. Our work suggests that it is crucial to pay more attention to the relationship among sided chains, molecular interaction, and morphology when the research community considers the strategy of designing efficient ETLs for PSCs.

4) Perovskite solar cells with polymer as hole transport layer

In the last chapter, the PSCs with small organic molecules have been discussed. The aggregation of small organic molecules greatly influences the performance of PSCs. But the interactions between the perovskite layer and carrier transport layer have not been covered, which is also very important. Therefore, in this chapter, the interactions between the perovskite layer and carrier transport layers are studied. Firstly, the carrier transport and recombination in the PSCs have been discussed. Then, the interactions between perovskite films with outside factors have been explained. Continually, the polymers with the amine-tethered diketopyrrolopyrrole (DPP) main chain have been simply introduced. In the experimental part, the device fabrication of PSCs has been presented. In the result and discussion part, the performance of PSCs with different polymers as HTLs has been discussed.

4.1 Literature survey

4.1.1 Carrier transport and recombination inside the PSCs

The target of interfacial engineering is to modify the carrier transport in the PSCs. Then, it is necessary to study the carrier transport and recombination inside the PSCs. Under illumination, there would be the generation of excitons in the PSCs. But as mentioned in the last chapter, the exciton binding energy of the perovskite layer is relatively small, which makes it easy for the excitons to degrade into free electrons and holes. One of the advantages of perovskite materials is the long diffusion length tunnels. These carriers could easily move to the interfaces between the perovskite layer and the carrier transport layer. The carrier movement

inside the PSCs has been shown in Figure 4.1.

Figure 4.1. Carrier movement and recombination inside the PSCs. ^[168]

At the perovskite layer/HTL interface, there are two kinds of ways leading to the decline of carriers. The first one, also the expecting one, is the holes passing through the interface to the HTLs. The contact between these two layers would affect this process. If the HTLs could not sufficiently cover the perovskite surface, the holes may aggregate in these un-contrast areas and recombine with the electrons. One solution is applying a single-walled carbon nanotubes interlayer at the perovskite/HTL interface, which could help to extract the carriers and suppress the back-recombination.^[169] Additionally, the energy barriers for holes would also impede the carrier transport from the perovskite layer to the HTLs((2) in Figure 4.1). Therefore, the energy levels of HTLs should match with perovskite layers. The second way is the perovskite surface recombination caused by lattice strains, defects, and traps ((3) in Figure 4.1). Two main recombination processes of perovskite materials are radiative recombination and nonradiative or Shockley-Read-Hall(SRH)

recombination(Figure 4.2a).^[11] The perovskite surface recombination would be the latter. These recombination centers in the middle of the bandgap could make electrons and holes recombine before being extracted from the perovskite layer and could negatively affect the Voc. Some works reported that the recombination at interfaces influences the diode ideality factor and is the major threat for the photovoltage loss. ^[170-172] The theoretical limitations of Voc could be affected by the quasi-Fermi level splitting in the PSCs, which is decided by the pinning of electron Fermi level close to the ETLs and pinning of hole Fermi level close to the HTLs(Figure 4.2b and c).^[173] The energy level misalignment between carrier transport layers and perovskite layers could be a very important issue and matching the energy levels between perovskite layers and carrier transport layers is supposed to improve the Voc, but the results were not positive and Fermi level pinning exists.^[174,175] Therefore, the energy level engineering may not be so powerful to modify the Voc performance, of which the reasons could be related to the surface states and specific situations of the interfaces.^[173] Therefore, the targets of interfacial engineering are assisting the carrier extraction and suppressing the surface recombination.

Figure 4.2. (a) Carrier recombination processes in PSCs. ^[170] (b) Energy diagram splitting at

the carrier transport layer/perovskite layer interfaces. ^[171] (c) The influence of energy level alignment on the influence of Voc. ^[172]

4.1.2 The interactions between perovskite surfaces with outside factors

4.1.2.1 Introduction of the perovskite surfaces

The surface of the perovskite film is supposed to contain four kinds of morphologies.^[176] The first kind of morphology is the halide X site and organic A site exposing to the outside environment. The second kind of morphology is the lead as the B site and halide X site exposing to the outside environment. The third kind of morphology is the B site, halide X site, and A site exposing to the outside environment. The fourth kind of morphology is like the third condition but in different planes. These four kinds of surface morphology may mix to form the perovskite surface.^[176] Some works reported that by applying the DFT calculation, MAI termination is more likely to grow in thermodynamic equilibrium. ^[177,178] Three different competing effects that influence the perovskite surface include the contraction of MAI under PbI_2 rich conditions, hydrogen bonds between MA and I, and directional alignment of the dipole of the MA groups. ^[179] Under practical conditions, these surface positions are impossible to be all filled and there are inevitably existing vacancies, other kinds of defects, and moving ions. The practical perovskite surface is shown in Figure 4.3. The perovskite films are not so stable and would slowly degrade. The loss of MA species and I content could fit first-order kinetics, which results in the formation of PbI_2 on the surface. ^[180] The degraded perovskite films would result in the yellow PbI_2 films and the formation of defects on the perovskite surfaces.

4.1.2.2 The interactions between perovskite films with outside factors

Three factors that affect the perovskite films are discussed here. The first one is the carrier transport layers, which passivate, sensitive or damage the perovskite surfaces. The second one is oxygen and moisture in the air. The third one is the diffusion ions from the electrode or carrier transport layers. [168]

Figure 4.3. The surface of perovskite films and possible ways to passivate the surface of perovskite ways. [183]

The organic carrier transport layers contain specific functional groups, which would interact with the vacancies, ions, and defects on the perovskite surfaces. The possible interactions between perovskite surface and carrier transport materials have been summarized in Figure 4.3. The functional groups include cations, anions, ammonium, Lewis acid, Lewis base, Fullerene. The mechanism of passivation is based on the Lewis acid-base reaction. [183] Figure 4.4 a-d shows how the functional groups passivate the traps (Figure 4.4 a-c) and vacancies (Figure 4.4d) on the perovskite surface. Figure 4.4g has listed a series of materials that could passivate the perovskite surface. A very thin interlayer such as iodopentafluorobenzene (Figure 4.4a and b), HAT-CN, thiophene (Figure 4.4d), and pyridine has been adopted to react with the corresponding part

and passivate the perovskite surfaces. [183-185] TRPL in Figure 4.4e could be used to judge the passivation effects. [185] The reason is that due to suppressed surface recombination, the carrier lifetime of perovskite films would become longer. [185] In Figure 4.4c, the anisole in the Spiro-MeOTAD molecule and other polytrialkylamine derivatives could interact with the protruding I and Pb^{2+} ions by the methoxy group. [179] Other organic materials shown in Figure 4.4.g such as Iodopentafluorobenzene, Thiophene, Pyridine, 4-Mercaptobenzoic acid, Benzylamine, Poly(4-vinylpyridine), 3-Hexylthiophene and Poly(3-hexylthiophene) (P3HT) have been reported to passivate the perovskite surfaces with their specific functional groups. [183]

Figure 4.4. (a) Schematic view of the halogen bond interaction between the iodopentafluorobenzene and perovskite material. (b) The interaction between iodopentafluorobenzene and perovskite surface.^[183] (c) The assistance of iodopentafluorobenzene to extract the holes.^[183] (d) Possible passivation mechanism of Lewis base.^[185] (e) TRPL comparison of perovskite films covered with different carrier transport layers.^[185] (f) Iodopentafluorobenzene, Thiophene, Pyridine, 4-Mercaptobenzoic acid, Benzylamine, Poly(4-vinylpyridine), 3-Hexylthiophene, and P3HT that have been found to passivate the perovskite surface.^[183] The green areas are the functional groups that could passivate the perovskite surface.

On the other hand, the interaction with inorganic materials like TiO_2 could not be neglectable. The metal oxides are usually deposited on the ITO or FTO covered glasses. These metal oxides should form compact films to prevent the diffusion of perovskite film. But the metal oxides could also lead to the degradation of the perovskite layer, which negatively affects the stability of perovskite layers. The solution to this issue could be resolved by inserting an interface layer such as PCBM.^[166,186,187] Another case could be the ZnO ETL. The perovskite layer on the ZnO substrate suffers from thermal instability and degradation, which are caused by the deprotonating of methylammonium cation.^[146] By doping with Al and the modification of the fabrication process, the stability performance could be improved.^[188,189] The popular TiO_2 substrate would lead to PbI_2 -rich perovskite films at a reactive oxide interface and one solution to this problem could be applying the SAM-modified TiO_2 for achieving a uniform stoichiometric MAPbI_3 phase.^[168] The perovskite surface could also be affected by the substrate by the formation of intermediates. For example, PbSO_4 could be formed on the PEDOT: PSS/perovskite interfaces.^[181] The interfaces could serve as a nucleation site for intrinsic and extrinsic defects.^[168] These defects and moving ions could greatly influence the stability of the whole device.

The second one is the interaction between the perovskite layer and moisture, oxygen in the environment. The degrading of perovskite grains

caused by moisture has been mentioned in the last chapter. The water could ingress into the perovskite layer and react with the perovskite grains, which would form the monohydrates or dihydrate phase of PbI_6^{4-} octahedra. ^[190,191] Water tends to form the hydrogen bond with the NH_3^+ group than with the CH_3^+ . Water could also form a bond with the Pb^{2+} . ^[192] The surface conditions could also affect the interaction between water and the perovskite surface. Interaction with water would lead to the degradation of the MAI-terminated surface. But when it comes to the PbI_2 -terminated surface, the perovskite surface could become more stable after aqueous treatment. The existence of oxygen could also degrade the perovskite films. ^[193] Under illumination, the oxygen at the I vacancies could grasp the electrons and be activated. The oxygen ions could react with the perovskite materials to form the PbI_2 , I_2 , H_2O , and CH_3NH_2 , which could easily decompose the perovskite films. ^[194]

To reduce the influence of moisture and oxygen in the environment, it is very important to decrease the surface I- vacancies. Additionally, the perovskite films with large grains would decrease the surface-to-volume ratio and the contact area with oxygen, which further improves the stability of perovskite films. Another kind of method could be passivating the perovskite surface by the organic carrier transport layers, especially for amine molecules with extended alkyl branches, such as tetraethylammonium (TEA) and longer-chained tetra-alkyl ammonium. ^[168, 195] The ammonium groups could substitute the methylammonium in the A position of the perovskite surface and passivate the perovskite films. ^[287]

The third one is interaction with the diffusion ions from the electrode or carrier transport layers. There are three kinds of transport channels of metal ions. The first one is directly migrations across the carrier transport layers. ^[196] Ag and Au have been found to diffuse through the carrier transport layer and contact with perovskite surface, which have been

confirmed by the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurements.^[197] An interface layer such as Aluminium oxide (Al_2O_3) or Molybdenum oxide (MoO_3) could help to prevent the diffusion of metal ions.^[197, 198] The second channel could be the pinholes of carrier transport layers. The third one could be the direct contact between the perovskite layers and electrodes in the carrier transport layer free devices.^[199] The contact between the perovskite layer and electrode could be treated as an idealized Schottky-contact.^[200] The diffused Au molecules would not react with ions on the perovskite surface. But Au could influence the energy level structure of perovskite films.^[201] Other metals like Al could reduce the Pb^{2+} to Pb^0 and oxidize themselves.^[202] There is also an opposite migration, in which the decomposed individual components in the perovskite layer travel through the carrier transport layers towards the outside. This opposite migration is more related to the stability issues, which are not covered here. But the left vacancies and defects could work as the surface recombination centers, which has mentioned above. ^[168]

Based on the above discussion, the ways to stabilize the perovskite surface and improve the device performance include passivation of the perovskite surface, protecting the perovskite layers from the invading of moisture and oxygen as well as preventing diffusion of metal ions from the electrodes. Carrier transport layers could be used to realize these functions. In this chapter, a newly designed polymer has been used as the dopant-free HTL and the interactions between this polymer and perovskite surface have been studied.

4.1.3 Polymers as the dopant-free HTLs for PSCs

Due to the advantages of polymeric chain entanglement, the suitable

energy level of their HOMO, and the tunable hydrophobicity, polymeric HTMs have attracted lots of attention. [203-205] For example, P3HT, with the advantage of good optoelectronic properties, has been demonstrated as a promising dope-free HTM. [206-208] Seo et al. reported the PSCs with P3HT as a hole-transport material on a double-layered halide architecture (DHA). [209] However, without this DHA layer, the devices with P3HT on the normal perovskite substrate show the problems of additional non-radiative recombination at the perovskite/P3HT interface and physically poor contact, which hamper the efficient hole transfer from the perovskite to P3HT. [209-211] Therefore, P3HT may not be the best choice of polymers to work as the HTL in a simple device structure.

Scheme 4.1. DPP polymers units with different aromatic substituents. [212-215]

Janssen et al. demonstrated double-junction organic solar cells based on a low bandgap polymer (pDPP5T, Scheme 3.1) containing DPP and thiophene units in the main chain [212,213]. After that, a series of DPP polymers shown in Scheme 3.1 have been used in the photovoltaic area. In 2013, Brabec et al. adopted pDPP5T-2 as the active layer in the organic multi-junction solar cells. [214] In 2017, the same research group reported that, with a tantalum-doped tungsten oxide (Ta-WO_x) interlayer between HTL and metal anode, polymers including P3HT, PTB7, pDPP5T-2, PffBT4T-2OD, PDBT-T1, and PDCBT have been adopted as HTLs in the

regular PSCs, which proves the potential of undoped polymers containing DPP as the HTMs.^[215] However, these reported polymer-based PSCs normally have a relatively complex device structure, where interlayers have been widely applied to modify the interfaces and carrier transport. Thus, to address this issue, by simply modifying the functional group of repeated units in polymers to engineer the interface at the perovskite layer/HTL, we found that it is possible to achieve good performance in a very simple device structure without those above-mentioned interface layers.

4.2 Experiments

The conventional planar n-i-p device structure would be used in this work. The ITO-coated glass substrates were cleaned successively with Decon 90 (detergent) diluted solution, deionized water, acetone, isopropanol, and ethanol in an ultrasonic bath for 20 min, respectively, and dried with nitrogen gas purge. The ETL adopted here is the commercially available SnO₂ films. An electron transport layer of SnO₂/H₂O (1:5, v/v) was spin-coated onto cleaned ITO transparent glass substrates at 6000 rpm for 60 s in ambient condition and annealed at 150 °C for 30 min. The perovskite films were deposited using a single-step deposition method from the precursor solution containing FAI (0.26 M), PbI₂ (1.26 M), MAI (1.08 M), and PbCl₂ (0.14 M) in DMSO/GBL (3:7, v:v). The precursor solution was spin-coated onto the SnO₂ substrate at 1200 and 4300 rpm for 18 and 60 s, respectively. During the second step, 600 µl of toluene was dropped on the spinning substrate 30 s before the end of the spin coating. After spin coating of the perovskite films, the slices were transferred to a hot plate and heated at 105 °C for 30 min. HTMs in 1,2-Dichlorobenzene (DCB) solution with different concentrations was spun at 2000 rpm for the 60s and immediately heat-treated at 100 °C for 10 min. The deposition of the

perovskite layer and HTLs was conducted under inert condition. Finally, about 100nm silver was deposited on the HTL by vacuum evaporation.

4.3 Results and discussions

Herein, we presented a new dopant-free polymer HTL P25NH (Figure 4.5b) which could greatly push the fill factor of perovskite solar cells (PSCs) towards the theoretical limit. Compared with the commonly used HTM Poly(3-hexylthiophene) (P3HT), P25NH is based on a DPP main building block. The ratio of each part in the P25NH was optimized to achieve proper molecule interactions. P25NH possesses proper chain interaction and aggregation. A condensed P25NH film could form under the concentration at as low as 1.6mg/ml. Unique lamellar morphology of P25NH films could form at 6mg/ml, which could help to prevent the diffusion of metal anode. Moreover, the mobility of P25NH without doping is three orders of magnitude higher than that of P3HT, which could guarantee effective carrier transport and reduce the series resistance. Furthermore, by utilizing the regioregularity tethering primary amine at polymer side chains, under-coordinated Pb atoms on the annealed Pb surface could be efficiently passivated. With those advantages, The PSCs with P25NH(1.6mg/ml) as HTM exhibited a decent power conversion efficiency of 18.1% with a high fill factor of 81.9% (at 6mg/ml, the fill factor is 83.2%).

Figure 4.5. (a) Energy level diagram of materials adopted in PSCs. (b) Molecular structures of P25NH. (c) Molecular structures of P3HT.

Table 4.1. A summary of synthesized dopant-free polymeric HTLs

Reference	Structure	Highest factor (%)	Fill
November 2018 [217]	ITO/NiO _x /perovskite/PN-F25%/Ag	71.8	
April 2019 ^[218]	FTO/TiO ₂ /PCBA/(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /P1/Au	76.7	
April 2019 ^[219]	ITO/C ₆₀ /perovskite /FBA3/MoO ₃ /Ag	79.9	
May 2019 ^[220]	FTO/SnO ₂ /Cs _{0.05} FA _{0.81} MA _{0.14} PbI _{2.55} Br _{0.45} /P2/ Au	72.7	
June 2019 ^[221]	FTO/c-TiO ₂ /m-TiO ₂ /Cs _{0.05} FA _{0.81} MA _{0.14} PbI _{2.55} Br _{0.45} /DTB (xDEG) /Au	75.08	
July 2019 ^[222]	FTO/TiO ₂ /PCBA/ Perovskite/PDTITT/Au	75	
August 2019 ^[223]	FTO/Compact-TiO ₂ / Mesoporous-TiO ₂ /Perovskite/PBT1-C /MoO ₃ /Ag	81.22	
August 2019 ^[224]	FTO/SnO ₂ /perovskite/2-MA/Au	79.8	
August 2019 ^[225]	FTO/SnO ₂ /perovskite/P3/Au	80	
September 2019 ^[226]	ITO/SnO ₂ (20nm)/PCBA-(FAPbI ₃) _x (MAPbBr ₃) _{1-x} (600 nm)/ P-Si /Au	77	
September 2019 ^[227]	ITO/SnO ₂ /perovskite/PBDTT/MoO ₃ /Ag	76.67	
October 2019 ^[228]	FTO/SnO ₂ /Perovskite /PBDT[2F] T/Ag	72.60	
This work	ITO/SnO ₂ /perovskite/P25NH/Ag	81.9(1.6mg/ml) /83.2(6mg/ml)	

The HOMO and LUMO energy levels of P25NH were estimated to be -5.18 and -3.50 eV, respectively (data provided by the cooperator). The energy level diagram is shown in Figure 4.5a. All the energy level data are obtained from the previously reported works except P25NH.^[216] As

shown in Figure 4.5a, the LUMO of P25NH (-3.5 eV) and P3HT (-2.7 eV) are higher than that of the perovskite active layer (-3.9 eV), which means that an electron energy barrier has been formed at the perovskite/HTL interface and blocks the electron diffusing into the HTL. Additionally, the HOMO of P25NH (-5.18 eV) and P3HT (-4.7 eV) are also higher than that of the perovskite absorber layer, which indicates that photo-induced holes could easily transport to P25NH and P3HT without energy barriers. Thus, energy level patterns of both P25NH and P3HT are well-matched with that of the perovskite layer, which proves that both materials are suitable HTMs for PSCs.

The device structure of n-i-p heterojunction PSCs in this research was glass/ITO/SnO₂/perovskite layer/HTLs/Ag. The device architecture was shown in Figure 4.7a and HTLs were P25NH or P3HT. The concentration of P25NH has been optimized to be 1.6 mg/ml, while that of P3HT for PSCs was 16 mg/ml. Because under the low concentration of 6 mg/ml, the devices based on P3HT showed no performance. At the concentration of 16 mg/ml, the devices showed the best performance. On the other hand, the PSCs based on P25NH with 1.6 mg/ml showed the best efficiency. The electron transport material applied here was the previously reported SnO₂ via a simple low-temperature sol-gel route. SnO₂ precursor was commercially available SnO₂ colloid. The perovskite active layer was based on the previously reported mixture of lead compounds (PbI₂ and PbCl₂) and two cation salts (namely, methylammonium iodide (MAI) and formamidinium iodide (FAI)) with the composition (MA_{0.8}FA_{0.2})Pb(I_{0.93}Cl_{0.07})₃. The perovskite films were prepared by the two-step dripping method with toluene as an antisolvent in a glovebox. Details of each layer fabrication process are provided in section 4.2. The current density–voltage (J–V) characteristic curves were measured under the simulated solar irradiation (AM 1.5, 100 mW cm⁻²) for the PSCs. The

measurements proceeded under ambient condition (temperature: 25 °C, humidity: 85%). The scan scope was 0 - 1.2 V, and the step was 50 mv.

Figure 4.6. (a) Schematic demonstration of the device configuration. (b) J-V curves, (c) Dark J-V curves, and (d) Steady-state output under continuous simulated AM1.5G 1-sun illumination. of PSCs based on P25NH and P3HT. (e) J_{sc} , (f) V_{oc} , (g) fill factor, and (h) PCE

comparison between PSCs based on P25NH and P3HT.

The best J–V curves of the P25NH- and P3HT-based PVSCs were shown in Figure 4.6b. The P25NH-based PSC exhibited a PCE of 18.1% with a Voc of 0.998 V, a short-circuit current density (Jsc) of 22.18 mA cm⁻² and a fill factor of 81.9%. In contrast, the P3HT-based devices only showed a PCE of 15.5% with a Voc of 1.027 V, Jsc of 20.85 mA cm⁻², and fill factor of 72.3%. The most distinguished difference between the P25NH- and P3HT-based PSCs was the fill factor. The fill factor of P3HT-based PSCs in this work was like that of Seo's research. The reason for the low fill factor of P3HT-based PSCs is the higher series resistance (Rs) of amorphous P3HT-based PSCs, which may block the interfacial charge transfer and transport through the P3HT layer.^[307] The impedance analysis of P25NH- and P3HT- based PSCs has been shown in Figure 4.7, and the fitting data has been summarized in Table 4.2. From Table 4.2, the series resistances of P25NH- and P3HT- based PSCs are 7.24 and 27.9 Ω, respectively, which tells us that P3HT-based PSCs have much larger series resistance than that of P25NH, confirming that one reason for higher fill factors of P25NH-based PSCs is due to the relatively lower series resistance. Another reason for the low fill factor mentioned by Brabec et al. is the formation of a non-ohmic contact that impedes the extraction or injection of holes at the perovskite/HTLs interface.^[216] From the dark j-v curves shown in Figure 4.6c, P3HT-based devices showed lower current density and suppressed the injection at the diode diffusion current region of high bias, proving that P25NH has better contact with the perovskite surface.^[216] A statistical analysis of the photovoltaic parameters of 15 corresponding device couples with P25NH and P3HT as HTLs were shown in Figure 4.6e-h. The hysteresis of PSCs with P25NH is also very poor. The possible reasons have been discussed in

chapter 3.

Figure 4.7. EIS characterization of PSCs based on P25NH and P3HT as HTLs at forwarding bias V_{app} (0.4V) under dark condition. Inserted Figure is the equivalent circuit used for modeling PSCs based on P25NH and P3HT, where R_1 is the series resistance, R_{c1}/C_1 the resistance/capacitance associated with the electrode, and R_{c2}/C_2 the resistance/capacitance related to the HTL/perovskite layer interface.

Table 4.2. Stimulated data of EIS of solar cells based on P25NH and P3HT.

	$R_s(\Omega)$	$R_{c1}(\Omega)$	$R_{c2}(\Omega)$	$C_1(nF)$	$C_2(nF)$
P25NH	7.24	5328	124300	7	5.12
P3HT	27.9	659	22970	2.6	5.4

Figure 4.8. AFM images of (a) perovskite surface on the SnO₂/ITO substrate, (b) P25NH (1.6 mg/ml), (c) P25NH (6 mg/ml), (d) P3HT (6 mg/ml), (e) P3HT (16 mg/ml) on the perovskite/SnO₂/ITO substrate. 3D AFM images of (f) perovskite surface on the SnO₂/ITO substrate, (g) P25NH (1.6 mg/ml), (h) P25NH (6 mg/ml), (i) P3HT(6mg/ml), (j) P3HT (16 mg/ml) on the perovskite/SnO₂/ITO substrate. (k) XRD pattern of perovskite layer, perovskite layer covered by P25NH and P3HT. (l) XRD patterns (12-15 degree) of perovskite layer, perovskite layer covered by P25NH and P3HT.

In the following part, we would discuss the reasons that lead to the disparities between P3HT and P25NH, such as the influence of concentration of HTLs on the device performance, better ability of P25NH to passivate the perovskite surface, and lower series resistance of P25NH. The reason that P3HT could not work well under low concentration might be the poor morphology of the HTL surface. AFM measurement was conducted to explore HTL aggregation on the perovskite substrate. The sample of AFM measurement was taken from the exposed HTL surface near the Ag anode. The film morphologies of P25NH and P3HT film with different concentrations were compared. To display the surfaces of all

samples, all AFM images were presented in two-dimensional (2D) and three-dimensional (3D) patterns, which could afford more details of their morphologies. Figure 4.8a and f exhibit 2D and 3D images of the representative perovskite surfaces with large grain domains. Figure 4.8b and g display the P25NH layer (1.6 mg/ml) deposited on the perovskite layer. One could find out that the P25NH layer from 1.6 mg/ml possesses a surface with homogenous distribution of small islands on the perovskite substrate, indicating that the P25NH polymer is evenly distributed on the perovskite surface with a slight aggregation. Figure 4.8c and h showed the P25NH surface (6mg/ml) with uniform lamellar morphology. The reason could be that the aggregated islands could continue growing under high concentration and then were integrated to form many relatively smooth and thin P25NH domains, which were further overlapped layer by layer to form the multilayer morphology.^[9] P25NH films under high concentration show smooth and lamellar morphology, which could lead to a high fill factor (83.2%). But the thicker transport layer caused by the high concentration of P25NH results in a lower J_{sc} and a lower PCE (17.3%), which were summarized in Figure 4.9 and Table 4.3. Figure 4.8d and i showed the P3HT layer of 6 mg/ml covered on the perovskite substrate. Figure 4.8d and i could be divided into two parts (above and below) for comparison. The bright yellow grains at the below part of Figure 4.8i are smoother than those at the above part with many island-like morphologies. The reason could be that under low concentration, weak interaction among P3HT molecules leads to poor aggregation, which makes P3HT more difficult to cover the uneven perovskite surface with rising and falling grains.^[1] Another evidence of insufficient coverage of P3HT could be offered in the below PL spectra comparison. P3HT with a low concentration could not sufficiently cover the perovskite surface. The exposed perovskite surface would directly contact the electrode. The Ag molecules

would destroy the perovskite film, which is the reason for no performance of P3HT(6mg/ml)-based devices. The P3HT film(16mg/ml) on the perovskite substrate is shown in Figure 4.8e and h, the aggregated P3HT small islands started to merge, but there are still obvious boundaries existing. From the comparison between the surfaces of P25NH and P3HT under low concentration, one could conclude that P25NH shows stronger chain interaction and higher aggregation than P3HT. The root-mean-square (RMS) roughness of the perovskite layer shown in Figure 4.8a is 19.510 nm while the RMS roughness of P25NH film on the perovskite substrate with the concentration (1.6 mg/ml) was 18.745 nm and that of P3HT (16 mg/ml) was 18.423 nm, which indicates that the roughness of P25NH and P3HT displays slight differences in contact with the anode.

Figure 4.9. J–V curves of PSCs based on P25NH HTL under the concentration of 6mg/ml.

Table 4.3. Performance of PSCs based on P25NH HTL under the concentration of 6mg/ml.

HTL		Jsc(mA/cm ²)	Voc(mV)	Fill factor (%)	PCE (%)
P25NH 6mg/ml	Aver.	20.33	1025.133	77.75	16.14
	Max.	19.81	1049	83.2	17.3

Figure 4.8k and l show the XRD plots of pristine perovskite film and perovskite films coated with each HTL. The strong and sharp diffraction peaks of (110), (112), (220), and (310) crystal planes in the XRD patterns confirm the excellent crystallinity of pristine perovskite films. Also, no distinguished peaks of either P3HT or P25NH films were found in the XRD pattern, implying the P3HT and P25NH layers are amorphous films on the perovskite substrate. The diffraction peaks at 12.22° can be assigned to the existence of PbI_2 .^[228] The main difference between these three samples is the intensity of PbI_2 . From Figure 4.8l, the intensity of PbI_2 was decreased when P25NH was covered on the perovskite surface. The reason could be as follows: during the annealing process of perovskites, halide and methylammonium ions could be lost from the crystal, resulting in under-coordinated Pb atoms and the formation of a net positive charge on the atom, which would then create favorable conditions for coordination or bond formation with electron-rich Lewis Base.^[218] You et al. proved that the perovskite surface with the existence of PbI_2 could be easily affected by the next deposited layer.^[228] Here, as both P3HT and P25NH contain the thiophene functional groups, we believed that the specific tethering primary amine functional groups of P25NH has a better ability to stabilize under-coordinated Pb atoms than thiophene functional groups.^[217] The 90°C -annealing process after spinning the P25NH layer may promote some of the methylammonium ions back to crystal ($\text{CH}_3\text{NH}_2 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{NH}_3^+$)^[87] by tethering primary amine functional groups and decrease the amount of PbI_2 , which could be confirmed from the PXRD performance. The better passivation effect of P25NH on the perovskite surface together with uniform film morphology could reflect on higher V_{oc} (1.05V) and high fill factor (83.2%) of P25NH (6 mg/ml)-based PSCs (Figure 4.9) and higher recombination resistance at the

P25NH/perovskite surface (Table 4.2).

Figure 4.10. (a) Transfer and (b) Transport curves of OFET based on P25NH.

Table 4.4. Characteristics of OFET based on P25NH.

Temperature (°C)		Mobility (cm ² /Vs)	I _{on} /I _{off}	V _t
RT	Aver.	1.93×10 ⁻²	10 ¹	12.4
	Max.	2.10×10 ⁻²	26.7	12.0
140	Aver.	2.57×10 ⁻²	10 ¹	19.8
	Max.	3.01×10 ⁻²	51.2	18.8
200	Aver.	1.74×10 ⁻²	10 ²	18.9
	Max.	1.82×10 ⁻²	2.19 X 10 ²	21.1
230	Aver.	3.88×10 ⁻²	10 ²	12.1
	Max.	4.21×10 ⁻²	2.45 X 10 ²	11.2

Carrier transport properties, which greatly influence the series resistance of the whole PSCs, were studied by OFET devices. The transfer and output characteristics of the P25NH-based OFETs were depicted in Figure 4.10. The electron mobilities, on-off ratios, and threshold voltages of P25NH-based OFETs were tabulated in Table 4.4. P25NH exhibited a P-type semiconductor characteristic. The hole (μ_h) mobility of P25NH at room temperature was $2.10 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is much higher than

that of the amorphous P3HT film ($10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).^[307] The distinguished disparities in mobility could be the main reason for the differences in series resistance.

Electron extraction phenomena were investigated by steady-state PL spectra and TRPL (Figure 4.11). The steady-state PL spectra with excitation wavelength at 532 nm were collected from the samples of perovskite, perovskite/P25NH, and perovskite/P3HT fabricated on glass/ITO/SnO₂ substrates. All three samples contain the SnO₂ layers, which could rule out the influence of absorption and carrier extraction of the SnO₂ layer. The incident light comes from the ITO side to make sure the excitation light source directly reaches the perovskite layer without passing through HTLs. The emission peaks of HTLs are all located at 779 nm, which is the distinguished typical wavelength of perovskite materials. The PL intensity is quenched by coating P25NH and P3HT onto the perovskite layers, confirming that these HTLs could enhance the rate of interface carrier extraction. P3HT displays better electron extraction ability at the perovskite layer/P3HT interface, which could be the reason why P3HT-based PSCs exhibits better Voc than that of P25NH(1.6mg/ml)-based PSCs. Better electron extraction ability means less aggregation of electrons in the perovskite layer, which would further decrease the carrier recombination in the perovskite layer and improve the performance of Voc. PL spectra of perovskite/P25NH under different concentrations display little distinctions, however, the PL intensity of perovskite/P3HT at high concentration (16 mg/ml) is only half of that of perovskite/P3HT at low concentration (6 mg/ml). The reason is that at low concentrations, P3HT could not sufficiently cover the perovskite surface and extract the carriers at the interface, which is matched well with the AFM studies.

Figure 4.11. (a) The absorption spectrum of perovskite on the ITO/SnO₂ substrate, P25NH, and P3HT on the perovskite/ITO/SnO₂ substrate. (b) Comparison of PL spectrum of P25NH with different concentration covered on perovskite/ITO/SnO₂ substrate. (c) Comparison of PL spectrum of P3HT with different concentration covered on perovskite/ITO/SnO₂ substrate. The inserted figure is the PL spectra from 750 nm to 825 nm. (d) TRPL of perovskite layer, P25NH, and P3HT covered on the perovskite layer.

Table 4.5. The results of simulated TRPL curve. The fitted equation is $y = y_0 + A_1 \cdot e^{-x/\tau_1} + A_2 \cdot e^{-x/\tau_2}$.

Sample	y_0	A_1	τ_1	A_2	τ_2
Perovskite	0.06 ± 0.01	135657.83 ± 49128.33	18.04 ± 0.49	2.29 ± 0.05	185.84 ± 3.42
Perovskite/P25NH	$0.02 \pm 4.52 \times 10^{-4}$	$3.31 \times 10^{13} \pm 6.64 \times 10^{12}$	7.58 ± 0.05	1525.62 ± 60.93	25.58 ± 0.09
Perovskite/P3HT	$0.01 \pm 3.81 \times 10^{-4}$	$9.43 \times 10^{16} \pm 1.45 \times 10^{16}$	6.08 ± 0.02	$1.48 \times 10^{11} \pm 5.75 \times 10^{10}$	8.98 ± 0.11

Figure 4.11d showed the TRPL spectra, which were simulated by a two-component exponential decay model. Fitted parameters were

summarized in Table 4.5. The time constant τ_1 can be assigned to the carrier extraction and nonradiative recombination, while the long-time constant τ_2 was attributed to the bimolecular recombination in bulk perovskite.^[218,219] The sequence of τ_1 lifetime was that pure perovskite film > perovskite film/P25NH > perovskite film/P3HT, showing the same tendency of the ability of carrier extraction appeared in the PL spectra. Thus, we propose that the shorter τ_1 lifetime of perovskite film/P25NH is due to charge extraction, not the increased nonradiative recombination.^[229] On the other hand, the longer decay time τ_2 of perovskite/P25NH might be caused by the reduced interface recombination, which is due to the efficient passivation of the perovskite surface.^[230] This is matched well with the XRD pattern and the reason could be the contribution from tethering primary amine functional groups.

Figure 4.12. (a) Stability test of PSCs based on P25NH(6mg/ml) and P3HT(10mg/ml). (b) (a) Stability test of PSCs based on P3HT (16mg/ml).

We monitored the long-term stability of unencapsulated devices by using different HTM stacks under varied concentrations. The measuring environment was under 85% relative humidity atmosphere at room temperature. After testing, the devices were kept in the N_2 atmosphere. The P25NH (6mg/ml) based PSCs showed a long-term photostability with the remained 70% of its original PCE after about 100 h. From the above AFM analysis, we could know that P25NH could form a uniform and

condense film on the perovskite substrate, which could be relatively efficient to prevent the diffusion of moisture and oxygen. On the other hand, PSCs based on P3HT at the same concentration of 6 mg/ml did not give any performance due to the insufficient coverage on the perovskite surface. Then, when the concentration increased to 10 mg/ml, as shown in Figure 4.12a, the efficiency quickly dropped to 30% of its original PCE after 48 hours. When the concentration continued increasing to 16 mg/ml, the stability has been greatly improved (Figure 4.12b). The reason that P3HT showed higher stability (even much better than that of those reported works) is due to its thicker thickness.

4.4 Conclusion

In this chapter, we presented a new polymer P25NH that could be adopted as HTL in PSCs. Compared with the traditional HTM P3HT, P25NH showed higher mobility, better aggregation and stability under low concentration, more economy, and better passivation effect of the perovskite surface. All these advantages lead to relatively high efficiency (18.1%) and high fill factor (83.2%) of P25NH-based PSCs. Under the low concentration, devices based on P25NH as HTLs displayed better stability than these devices with P3HT as HTLs. The higher efficiency and better stability suggest that P25NH is a promising alternative to dopant-free HTLs in regular PSCs. Our work proposed a specific route of designing efficient hole transport polymer materials for PSCs, which is employing suitable main building blocks to make sure the internal favorable chain interaction, effective carrier transport as well as modifying side chains to embellish the surface of the perovskite layer. The good performance of P25NH under low concentration means low cost in raw material consumption. Moreover, the simple device structure and mature fabrication process could ensure stable reproduction in factories. All these

results show that P25NH has great potential in large-scale industrial applications.

5) Study on stability of Selenium solar cell

No toxicity and long-term stability are indispensable conditions for the commercialization of photovoltaic devices. Compositionally instability of lead-containing PSCs pushes researchers to find the next-generation photovoltaic materials. In this chapter, the nontoxic and stable Se absorber has been explored. The easy fabrication process, nontoxicity, and high stability under a complicated environment are the main reasons that SSCs are chosen. Se absorber is the oldest photoconductive materials.^[231,232] But the studies of SSCs are much less compared with other kinds of photovoltaic devices such as PSCs, Silicon solar cells, DSSCs, organic solar cells, and CdTe solar cells.^[233-238] More attention should be paid to SSCs. In many works of SSCs, the stability performance of SSCs is only presented without further discussions. Therefore, in this chapter, the stability of SSCs is studied. Firstly, to get a better understanding of the Se absorber, Se absorber is compared with perovskite materials in many fields, including crystal structures, orientation and crystal phase, fabrication processes, morphology, and optical properties. Then, SSCs with metal oxide ETL and polymer HTL have been fabricated and their aging dynamics have been carefully studied.

5.1 literature survey

5.1.1 The comparisons between SSCs and PSCs.

Here, the oldest photovoltaic material Se material has been explored and discussed. Se-based solar cells (SSCs) have been reported for more than 100 years,^[231,232] the development of SSCs is very slow since the electrical properties of Se absorber could be hardly modified.^[239] But Se absorber is nontoxic and very stable, which makes it very competitive for next-generation photovoltaic materials. Structural and electrical properties of Se have been compared with well-known perovskite materials to understand the Se absorber.

Firstly, the crystal structure of Se has been compared with the perovskite materials. Perovskite materials could exist in the polycrystalline and monocrystalline form. But there are amorphous Se films. The Se with the amorphous phase could not be used in the solar cells since the periodic structure is necessary for efficient carrier transport. The photoactive Se crystal phase is the trigonal Se(t-Se), which has the polymeric long chain of Se along the z-axis in a hexahedral structure, the Se molecules are not connected in the x- and y-axis.^[239] The advantage of the t-Se crystal is polymeric long chains of Se make it relatively stable. The performance of PSCs is sensitive to the composition changes and condition changes, which decrease the repeatability. As Se film is the single element absorber, the repeatability of SSCs is relatively high.

Secondly, the fabrication processes are quite different. Perovskite films deposited by the spin-coating methods usually need the antisolvents to remove the residual solvents. No antisolvents are used in the Se films deposited by spin coating methods. Additionally, the perovskite precursors could be dissolved in most polar solvents, the spin coating

methods are widely used to deposit the perovskite films. But the Se could not be dissolved in most solvents and the choices of solvents for Se are quite limited.^[241] Therefore, the spin coating method is rarely used for SSCs. Moreover, the annealing processes of perovskite films have to be done in the gloveboxes, but the annealing processes of Se films could be conducted in ambient conditions because the Se films possess high resistance to moisture and oxygen.^[240] The thermal evaporated Se films show high repeatability. The untreated thermal evaporated Se films are usually amorphous. The post-annealing processes are necessary for Se films since the Se in the solid-state could hardly move and need external energy to crystallize.^[239] The transfer temperature for Se film is 100 °C. Under this temperature, the Se films would transfer from the amorphous red-brown state to the crystallized dark red state.^[239] The annealing treatments of the perovskite films are used to remove the left solvents. The thermal evaporation methods of perovskite films usually need two sources to provide the AX and BX₂ to form the ABX₃ films.

Figure 5.1. (a) AFM image of perovskite surface. (b) AFM image of Se surface.

Thirdly, the morphologies of Se films and perovskite films have been compared by AFM images. In Figure 5.1, both the photoactive Se films and perovskite films show typical polycrystalline surfaces. Hence, the theories that are built for explaining the functions of grains and grain boundaries in perovskite materials may also be used to explain the

phenomenon observed in the SSCs. For the perovskite films, the grain size could be as large as 1 μm , while that of Se films is relatively smaller. A larger grain size could lead to lower grain boundary density, which would decrease the carrier recombinations and enhance the Voc. The surface properties of perovskite films and Se films are different. As the perovskite films are the ABX_3 structures, there would be different vacancies and uncoordinated ions on the perovskite surface, which have been described in the last chapter. But in the Se film, there would be only the Se vacancies and uncoordinated Se ions. It is much simpler to study the passivation of Se films and interactions with the carrier transport layers.

Figure 5.2. Calculated XRD pattern of t-Se crystal.^[242]

The XRD pattern of Se films is presented in Figure 5.2. The (100) plane (22.72°) and (001) plane (28.86°) are the dominant planes. The (001) plane shows much higher conductivity since it is the direction of Se polymeric chains, and the carriers could easily move along this chain.^[239] But for the (100) plane, the Se molecules would hardly interact with each other in the same plane, which leads to lower conductivity in this direction. Even though the Se films show better conductivity in the (001) plane, the Se films dominated by (001) plane would form the columnar structure, which would result in large pinholes among the adjacent grains.^[239] The carrier transport materials would infiltrate through these pinholes and

greatly affect the performance of SSCs. On the other hand, the Se films with well-oriented (100) plane could form the uniformed, compact, and smooth surface, which shows better performance of SSCs. The crystal orientations of the perovskite layer are quite different from Se films.

The optimized thickness of perovskite films is usually several hundred nanometers. But there have been conflicts about the best thickness for the Se films. Different works show great disparities about the best thicknesses, many works reported that the best thickness would be in the micron level, but some works achieved good performance based on the Se films with several hundred nanometers. ^[239,240,243] Therefore, there is still no agreements about the best thickness of Se films in the SSCs. One possible reason that leads to such disparities may be that different substrates have been used to grow the Se films. ^[239,240,243]

Fourthly, the crystal phases and strain in two kinds of polycrystalline films could be quite different. Generally, there are several different crystal phases of perovskite film and they would transform to each other under certain conditions, which have been described in Chapter 3. But the crystal phases of Se films could only transform into other kinds of crystal phase under external force, like direct pressure on the crystal. ^[244] The tensile strains exist in perovskite films and Se films. In the perovskite films, the strain is not a big issue, since the strains could be resolved by involving different kinds of cations in the A site. But in the Se films, the fixed structure and composition of Se film make it hard to release the strain under external assistance. The natural releasing process of the strains could be the only way. ^[245] The strains could bring distortion to the crystals and cause the formation of deep-level traps and recombination centers. The strain releasing processes in the Se film could be very long since the Se molecules could hardly move in the solid-state.

Fifthly, the optical characters and absorptions features are compared.

The PL peak of perovskite films is located at about 780nm with the excitation light at 532nm. For the PL spectra of Se films, at present, the PL spectrum is not widely studied. The reason is that the PL intensity of Se films is very weak. For the perovskite layer, the absorption spectra are different if the composition of perovskite materials changes, but the absorption spectra of t-Se films show slight differences.

Sixthly, both the perovskite materials and t-Se crystals are direct bandgap semiconductors.^[239] The energy level diagrams of perovskite materials are directly decided by the B site and X site and affected by the A site. The LUMO, HOMO of typical perovskite materials like MAPbI₃ are -3.9eV and -5.4eV, respectively. And the energy level structures could also be affected by the B site or X site doping. The energy level structure of t-Se films is fixed, but could also be affected by the fabrication processes.^[240]

Seventhly, The ETLs of mesoporous n-i-p PSCs are usually TiO₂. TiO₂ has also been adopted in the SSCs in the 1980s. ^[246] In recent years, the organic carrier transport materials have also been adapted in the SSCs, such as PTAA and P3HT.^[241] But until now, the performance of SSCs with organic carrier transport materials is not good. The reasons could be that the Se film surface is not affiliated with organic materials and could not form beneficial interactions with organic transport materials.

By comparing with the perovskite materials, the properties of the Se absorber including crystal structures, fabrication process, morphology, optical properties, and device structure have been discussed.

5.1.2 The carrier transport layers used for SSCs

To build highly stable SSCs, suitable charge carrier transport materials with excellent charge carrier extraction and transport abilities are

necessary. TiO_2 as the ETL has been widely adopted in organic solar cells and perovskite solar cells due to its large bandgap, suitable energy levels for charge injection and extraction, and long lifetime of excited electrons [247, 248]. However, the internal weaknesses of TiO_2 are serious: low electron mobility (only about $3.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), instability in mesoporous TiO_2 -sensitized solar cells arising from light-induced desorption of surface-adsorbed oxygen, existing charge traps caused by bulk oxygen vacancies, titanium interstitials, and reduced crystal surfaces.[249-252] As a contrast, SnO_2 shows high mobility ($1.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), wide bandgap, good optical transparency, less UV light absorption, lower hygroscopicity, and good acidity resistance compared to the traditional TiO_2 . [253,254] Brabec et al. applied SnO_2 together with C_{60} -SAM and PCBM as the hole transport layer in PSCs and achieved an efficiency of more than 21%. [219] The unencapsulated device under continuous 1-sun illumination in a home-built chamber filled with N_2 could maintain almost 95% of its efficiency after 1000 hours. [219] However, even though SnO_2 shows better stability and similar carrier transport properties compared to TiO_2 , it was rarely used in SSCs. [240,246] Thus, in this work, SnO_2 is used as the ETL and substrate to deposit Se polycrystalline film.

Compared with small molecules, polymers have the advantages of π -electron delocalization along the conjugated chains, high regioregularity, and greater stability. [255,256] Polymers PTAA and P3HT are widely used as hole transport materials. [209,257,258] For example, by doping with a fluorine-containing hydrophobic Lewis acid dopant, PTAA-based PSCs showed long-term stability of up to 70 days under air exposure without encapsulation. [259] Seo et al. reported that P3HT-based PSCs with a modified perovskite layer exhibited substantial long-term stability, maintaining more than 95% of its initial PCE for 1,370 h. [209] The efficiency of PTAA- and P3HT-based CsPbI_2Br perovskite solar cells only

decreased slightly under continuous 1 sunlight soaking at 85 °C for 1000 h.^[260] Since both PTAA and P3HT show promising long-time stability and are not supposed to be the “short slab” of the whole devices, it is logical for us to employ them as HTL in SSCs.

5.1.3 The aging dynamics of SSCs

The main research directions for SSCs are seeking suitable substrates for depositing the Se films and modifying the crystallization process of Se films.^[239] However, little attention is paid to investigate the stability of SSCs. Besides, one crucial point neglected by researchers could be the potential of low-cost SSCs applied in a complicated and tough environment. We found that the efficiency of fabricated SSCs gradually increased in a certain period. The phenomenon is similar to the reported results and is due to strain releasing.^[243,245] But no works studied the whole aging dynamics of SSCs. In this work, the aging dynamics of SSCs have been discussed. The factors that relate to the stability of SSCs have been explored.

5.2 Experiments and characterizations

The ITO-coated glass substrates were cleaned successively with Decon 90(detergent) diluted solution, deionized water, acetone, isopropanol, and ethanol in an ultrasonic bath for 20 min, respectively, and dried with nitrogen gas purge. An electron transport layer of SnO₂ was spin-coated onto cleaned ITO transparent glass substrates at 6000 rpm for 60 s in ambient condition and annealed at 150 °C for 30 min. After that, 0.5nm Te layer and Se layer with different thickness were deposited on the PEDOT: PSS substrate and annealed at the glove box with a slow crystallization process (10 °C/min). PTAA or P3HT in DCB solution with different

concentrations was spun at 2000 rpm for 60 s and immediately heat-treated at 80 °C for 10 min. Finally, about 100nm silver was deposited on the HTL by high-temperature vacuum evaporation.

5.3 Results and Discussions.

In this research, SSCs with the configuration of ITO/SnO₂/Se/HTL/Ag have been designed and fabricated, where HTLs were P3HT or PTAA. It is worth pointing out that this type of SSCs with this specific simple structure has not been reported before. The device performances with P3HT and PTAA as HTLs have been compared, where P3HT-based SSCs showed open current-voltage (Voc) of 758.18 mV, short circuit current density (Jsc) of 8.43 mA/cm², fill factor of 57.50%, and power conversion efficiency (PCE) of 3.7%. To the best of our knowledge, this PCE is the highest efficiency among all SSCs with organic materials as HTLs (Table 5.1).

Table 5.1. Summary of SSCs with organic HTLs.

Publication date ref.	Structure of SSCs	PCE (%)	Stability Performance
2014 ^[261]	FTO/compact-TiO ₂ /mp-TiO ₂ /Se (thermal evaporation)/P3HT/PEDOT: PSS/Ag	2.63	N/A
2014 ^[261]	FTO/compact-TiO ₂ /mp-TiO ₂ /Se (thermal evaporation)/Spiro-OMeTAD/PEDOT: PSS/Ag	1.83	N/A
2016 ^[241]	FTO/bl-TiO ₂ , mp-TiO ₂ /Se (spin-coating)/PTAA/Au	3.55	Maintaining 90% of efficiency after 720 hours
2018 ^[262]	FTO/TiO ₂ /Se (spin-coating) //Spiro-OMeTAD/Au	1.23	Maintaining 90% of efficiency after 720 hours
2018 ^[262]	FTO/TiO ₂ /Se (spin-coating)/P3HT/Au	1.08	Maintaining 90% of efficiency after 1440 hours
2018 ^[262]	FTO/TiO ₂ /Se (spin-coating) //PTAA/Au	0.62	Maintaining 50% of efficiency after 720 hours
This work	ITO/SnO ₂ /Se (thermal evaporation)/P3HT/Ag	3.7	Maintaining 92% of efficiency after 1512 hours

The device architecture is shown in Figure 5.3a, where ETL SnO_2 was spun on the ITO-coated glass substrate. The SnO_2 precursor was prepared from commercially available SnO_2 aqueous colloids. A discontinuous thin Tellurium (Te) layer has been thermally deposited on the surface of SnO_2 before the Se layer, which could enhance the adhesion of the Se layer.^[246] Then, a 200nm-thick Se layer was deposited on the SnO_2/Te substrate to form an amorphous thin film. After the gradient annealing process reported by Kanatzidis et al., the Se film was transformed into a dark polycrystalline t-Se with a smooth surface.^[243] Then, HTL P3HT or PTAA would be spun on the Se active layer without any doping. The metal electrode used here was Ag due to its better conductivity.

Figure 5.3. (a) The device architecture of SSCs consisting of glass/ITO/ SnO_2 /Se/HTLs(polymers)/Ag. (b) Energy level diagram of SSCs. Chemical structures of (c) P3HT and (d) PTAA.

The energy level diagram of SSCs with the above-mentioned structure is shown in Figure 5.3b. The energy level data was obtained from the

previously reported works. [240,249] The conduction band (-3.8 eV) of the Se layer is much higher than that (-4.6 eV) of the SnO₂ layer, which means that photo-generated electrons would easily transfer to SnO₂ layers. The valence band of the SnO₂ layer (-8.0 eV) is much lower than that of the Se active layer (-5.64 eV), which would block the drifting of holes inside the absorber layer. The LUMOs of P3HT (-5.0 eV) and PTAA (-5.1 eV) are much higher than the valence band of the Se layer, which could benefit hole extraction from the Se layer. Thus, the energy levels of the charge carrier transport layer are well-matched with Se active layer, and no charge carrier energy barriers exist. Figure 5.4 shows the photogenerated carrier movement of P3HT-based SSCs(a) and PTAA-based SSCs(b). During the photogenerated hole transport process, the photogenerated holes could transport from the Se layer through the P3HT layer or PTAA layers to the Ag electrode without energy barriers. Therefore, the Ag anode could work as the electrode for P3HT-based SSCs and PTAA-based SSCs. Figure 5.3c and d show the chemical structures of P3HT and PTAA. The thickness of the Se layer was measured by the quartz crystal monitor of evaporation equipment. The current density–voltage (J–V) characteristic curves were measured under the simulated solar irradiation (AM 1.5, 100mw/cm²) for the Se-based solar cell. No light soaking was used. The devices were measured immediately when they were fixed on the holder. The measurements proceeded under ambient condition (temperature: 25 °C, humidity: 80%). The scan scope was 0–1.2V, and the step was 50mv.

Figure 5.4. Photogenerated carrier movement of P3HT-based SSCs(a) and PTAA-based SSCs(b).

Figure 5.5. (a) J-V curves of SSCs with different HTLs under simulated AM 1.5G irradiation (100 mW cm⁻²). (b) Dark J-V curves of SSCs with different HTLs. (c) Impedance spectroscopy characterization of SSCs with different HTLs. Insert figure is the equivalent circuit of SSC. R1 represents the series resistance of the whole device and R2 is the recombination resistance. CPE1 is a constant phase element. (d) Recombination resistance vs voltage curve of SSCs with different HTLs. The performance of 15 SSCs comparison in Jsc (e), Voc (f), Fill factor (g), and PCE (h).

The J-V characteristics of SSCs with P3HT and PTAA as HTLs are shown in Figure 5.5a and photovoltaic performances are summarized in Table 5.1. P3HT-based SSC exhibits the PCE of 3.70% with Voc of 758.18 mV, Jsc of 8.43 mA/cm², and fill factor of 57.50%, while the PCE of PTAA-based SSC is 1.90% with Voc of 474.00 mV, Jsc of 8.08 mA/cm², and fill factor of 50.10%. As shown in Table 5.2, the reported device with TiO₂ as ETLs have been listed and compared, even with the same HTLs such as the PTAA and P3HT. Under the same fabrication process (thermal evaporation) as this work, the efficiency (0.62%) of SSCs with the FTO/TiO₂/Se/PTAA/Ag structure is much lower than that of this work (1.90%) with the ITO/SnO₂/Se/PTAA/Ag structure. The PCE of SSCs with FTO/TiO₂/Se/P3HT/Ag structure is also lower than that of this work (3.70%) with the ITO/SnO₂/Se/P3HT/Ag structure. Therefore, through comparison with reported works, the advantages of SnO₂ have been fully proved and could serve as the reference for further research. The overall performance of P3HT-based SSC is much better than that of PTAA-based devices. The reasons could be the smooth P3HT film on the SnO₂/Se substrate, and good passivation of Se surface brought by thiophene units in P3HT.

Table 5.2. Device performance of SSCs (15 devices) with P3HT and PTAA as HTLs.

HTL in SSCs		Jsc(mA/cm ²)	Voc(mV)	Fill factor (%)	PCE (%)
P3HT	Aver.	8.54±0.26	753.13±17.07	55.56±1.33	3.58±0.09
	Champion	8.43	758.18	57.50	3.70
PTAA	Aver.	8.10±0.35	383.80±44.86	45.53±4.11	1.43±0.27
	Champion	8.08	474.00	50.10	1.90

The charge carrier extraction and transport properties of P3HT- and PTAA-based SSCs were investigated through dark current

measurements and EIS investigation. Figure 5.5b shows the comparison of dark current density-voltage curves between P3HT- and PTAA-based devices. Saturated dark current density J_0 can be determined by HTL in SSCs intercept at zero voltage of the linear regression from the semi-logarithmic J–V plot in the region close to the diode turn-on voltage.^[263] From Figure 5.5b, J_0 of the device with PTAA as HTL is estimated to be larger than those of the devices with P3HT as HTL. High J_0 indicates a high leakage current density and significant carrier recombination outside the depletion region, which would negatively affect the V_{oc} and fill factor.^[263]

Table 5.3. EIS fitted data.

	R1(Ω)	R2(Ω)	CPE1-t($\text{ohm}^{-1}\text{s}^n$)	CPE1-p
P3HT	28.64	2693	3.532×10^{-9}	0.969
P3HT(days)	31.7	1219	1.147×10^{-8}	0.889
PTAA	41.77	126	6.607×10^{-10}	1.099

The impedance behaviors in different HTLs-based SSCs are shown in Figure 5.5c and summarized in Table 5.3. The equivalent circuit is provided in Figure 5.5c. In Table 5.3, the series resistance R1 of the P3HT-based device (28.64 Ω) is smaller than that of the PTAA-based device (41.77 Ω), which could explain why the J_{sc} and fill factor of the P3HT-based device are larger. Figure 5.5d shows that the recombination resistance R2 of P3HT-based devices is an order of magnitude higher than that of PTAA-based devices under varied voltage. Higher recombination resistance means low recombination rate and the difference between these two kinds of devices is only HTLs, which indicates that the P3HT could efficiently passivate the surface of Se active layer and suppress the surface trap recombination.^[264] The reason could be that the sufficiently weak Lewis base thiophene unit of P3HT has the

ability of electronic passivation of under-coordinated Se atoms within the lattice. Similar to Pb atoms in the perovskite solar cells and according to Snaith's postulation, the loss of Se molecules during the high-temperature annealing process may cause unsaturated or under-coordinated metal ions to be frequently found on the surface and at the grain boundaries of crystals.^[185] This under-coordination of the Se atom could result in the formation of a net positive charge on the atom, which would then create favorable conditions for coordination, or bond formation with electron-rich molecules with a lone pair available such as the thiophene group. The electrostatic attraction between the positive charge on metal and the lone pair could facilitate the formation of a coordinate or dative covalent bond.^[185] Passivating these defect sites would lead to the suppressed surface recombination, which increases the value of recombination resistance R_2 and V_{oc} of P3HT-based devices.

Figure 5.5e-h compares the performance of fifteen P3HT- and PTAA-based SSCs. In Figure 5.5f and g, the V_{oc} and fill factor of P3HT-based SSCs are greatly larger than that of PTAA-based SSCs, which could attribute to the lower series resistance of P3HT-based SSCs and passivation of Se surface by P3HT as discussed above. Moreover, the values of V_{oc} and fill factor of P3HT-based SSCs varied slightly around the average values, however, those parameters of PTAA-based SSCs changed dramatically in Figure 5.5f and g, which could prove that P3HT-based SSCs show better repeatability. The reason is related to the morphology of ETLs.

The morphology of P3HT on the Se substrate has been explored by AFM measurements. Figure 5.6a and b show two-dimensional (2D) and three-dimensional (3D) polycrystalline Se surface on SnO_2 substrates. The grains of the polycrystalline Se are very smooth and clear to identify due to the distinguished grain boundaries. The Se grain size could be as

large as 600nm, which exhibits good qualities of Se films. SnO₂ is proven to be a suitable substrate to grow the Se films and could be used in other kinds of SSCs which needs deeper work function. Figure 5.6c and d show the 2D and 3D images of P3HT film on the Se substrate. In Figure 5.6c, P3HT could homogeneously cover the falling/rising Se grain without exposing the grain boundary of Se film, which implies P3HT could greatly prevent the direct contact between Ag and Se atoms. In Figure 5.6d, no grain boundary could be found. All the rising and falling areas are evenly covered with the amorphous P3HT molecules. There is no obvious aggregation, which indicates that P3HT could evenly distribute on the Se surface.

Figure 5.6. (a) 2D and (b) 3D AFM images of Se film on the Glass/ITO/SnO₂/Te substrate. (c) 2D and (d) 3D AFM images of P3HT film on the Glass/ITO/SnO₂/Te/Se substrate. The same scale has been used for all images and colors are used to show depth.

The root-mean-square (RMS) roughness of Se film is 29.629nm and the RMS roughness of P3HT film on the Se substrate is 22.969nm, which implies that P3HT could smooth the rough Se substrate and form a compact contact with the metal cathode. When it comes to the morphology of PTAA film, PTAA would aggregate seriously on the Se surface and form dark points (Figure 5.7). The high roughness and uneven surface make it impossible to conduct the AFM measurement. Therefore, only the enlarged microscope image was provided in Figure 5.7. The shining area at the bottom left corner is the Ag electrode. The above area is the PTAA film on the Se substrate, from which there are lots of visible dark points formed by the aggregation of PTAA on the Se substrate. Moreover, the rough PTAA surface makes it difficult to form sufficient contact with the metal anode, which could greatly impede the carrier transport process, leading to high series resistances of PTAA-based SSCs. Additionally, the serious aggregation of PTAA could inevitably cause insufficient coverage of Se film, which makes it easier for Ag atoms to diffuse through the relatively thinner part of PTAA films (such as grain boundaries) and reaching the Se surface.^[263] The evidence is the degrading of Voc with the diffusion of Ag, which is matched with our results.^[263] This would also be the reason for the high J_0 of PTAA-based SSCs. As a contrast, P3HT could evenly distribute on the Se surface and no grain boundaries have been exposed, where Ag atoms could hardly diffuse through the Se layer, leading to the improved stability of the whole device. Furthermore, the unpredictability of serious aggregation of PTAA film would also cause huge differences in each device and poor repeatability.

Figure 5.7. The rough surface of the PTAA layer on the Glass/ITO/SnO₂/Te/Se substrate.

The crystalline properties of the annealed Se layer with/without HTLs covered have been studied by XRD measurements. Figure 5.8 shows the XRD pattern of ITO/SnO₂/Te/Se, ITO/SnO₂/Te/Se/P3HT, ITO/SnO₂/Te/Se/PTAA. The desired phase with the efficient photovoltaic effect is the t-Se phase, which has main typical reflections at 23.5° (100), 29.7° (101), 41.36° (110), 45.40° (111), and 51.76° (201).^[240] In Figure 5.8, all three Se layers with/without HTLs covered show typical t-Se peaks. The strongest intensity peak locates at 23.5°, suggesting that these three kinds of Se layers are preferably oriented along the (100) plane. The (100) plane is parallel to the substrate. The favorable qualities of the crystalized Se layer guarantee the good performance and stability of SSCs. The weaker peak at 41.36° (110) of PTAA-covered Se film may be due to strongly aggregated and unevenly distributed rough PTAA layers.

Figure 5.8. XRD patterns of Se film with or without HTLs.

Long term stability test of P3HT- and PTAA-based SSCs without encapsulation has been conducted in a nitrogen atmosphere. The devices were kept under dark conditions during the storage. Unlike the previous stability tests, where only one device was tracked, a dozen of devices has been measured and recorded to rule out more occasional factors, seek the possible reasons that affect the stability, and prove a whole picture of SSCs' stability. The atmosphere of measurement was different from the storage environment and was in the ambient condition (temperature of 25 °C and humidity of 80%). The reason the nitrogen environment was required for the storage is that the device fabrication lab is next to and connecting to the organic chemical synthesis lab, which is full of organic solvent in the air. All kinds of solvents, together with moisture, would bring untraceable damage to our devices. Therefore, to maintain consistency of storage conditions and study the internal degrading processes, the inert environment was adopted as the storage environment. The whole measurement duration was about half an hour each time. The variation

percent of property parameters during the aging of SSCs is presented in Figure 5.9. The efficiency of those 12 devices maintains 92% after more than 1500 hours. Device dynamics during aging have been analyzed. In Figure 5.9d, one could find out that the PCE of SSCs gradually increased for more than 700 hours, and the reason could be the stress relief of the Se crystal lattice.^[245] Here, we proposed that the source of crystal stress inside Se film might be lattice mismatch. Se, existing as a polycrystalline layer in SSCs, may form the lattice mismatch with the crystalized metal oxide substrate. The lattice mismatch then causes the formation of internal stress and defects during the crystallization process of Se, which would result in poor performance of the as-fabricated devices. But after releasing the stress for a certain time, the cell characteristic would gradually increase, which has been reflected in the fill factor performance. In Figure 5.9c, the fill factor kept increasing until 816h (strain releasing). By comparing our result with other works which also showed increased efficiency after aging, lattice constants (a and b) are supposed to have a negative relationship with the stress releasing time of Se film (Table 5.4). In other words, the bigger the difference of lattice constant between Se film and substrate is, the longer time is needed to release the tensile stress. After 1000 hours, the PCE slightly decreased to 92% of the initial value. The reason may be related to the diffusion of Ag. In contrast, PTAA-based devices showed very poor stability (Figure 5.10). The reason could come from the poor qualities of PTAA films covered on the Se substrate, which makes it much easier for Ag atoms to diffuse towards the Se surface and destroy the Se surface.

Figure 5.9. Normalized J_{sc} (a), V_{oc} (b), Fill factor (c), and PCE (d) performance of SSCs under the aging process.

Table 5.4. Comparison of the lattice constant of ETLs used in other works and crystal stress releasing time. From this table, we could find out that, the larger the difference between lattice constant a and b of Se and ETLs, the longer it needs to release the stress. Here, we only compared the SSCs with the thermal evaporated Se active layer. The reason for SSC based on SnO₂ showing shorter releasing time is that there are other degrading factors such as diffusion of metal anode existing in the SSCs.

ETL/Se used in the SSCs	Lattice constant(Å)	Days of stress releasing(days)
ZnMgO	a=b=3.25-3.26 c=5.16-5.20 ^[265]	~150 ^[243]
CdSe	a=b=4.30 c=7.01 ^[265]	~40 ^[245]
SnO ₂	a=b=4.72 c=3.17 ^[265]	~35(this work)
Se	a=b=9.05, c=11.60 ^[265]

Figure 5.10. Stability performance of PTAA-based SSCs.

Figure 5.11a and b show the AFM images of P3HT covered on the Se layer after 1920 hours, which are similar to the initial AFM images (Figure 5.6c and d) measured immediately after the devices were fabricated. These results prove the superior qualities of the SnO₂/Se/P3HT configuration. One more interesting thing is that the RMS roughness of

P3HT film spun on the Se substrate after 1920 hours is 16.897 nm, smaller than that of the new-made P3HT layer. The reason is that after stress relief of Se crystal lattice, the Se surface is more uniform and smoother, which further improves the flatness of P3HT film. From Figure 5.11c, the recombination resistance of P3HT-based devices slightly decreased after 1800 hours. The reason could be that after the diffusion of Ag atoms towards the Se surface, Se-Ag alloy would form and under-coordinated Se ions are generated, which would increase the surface traps, non-radical recombination as well as decrease the Voc slightly.

Figure 5.11. (a) 2D and (b) 3D AFM images of P3HT film on the Glass/ITO/SnO₂/Te/Se

substrate after aging hours. (c) Comparison of recombination resistance vs voltage curve of SSCs before and after aging.

From the above discussions, we could divide the aging process into three stages. At the first stage (yellow part in Figure 5.9), with the tensile stress of Se film releasing, the efficiency slightly increased at the first 816h. At the second stage (purple part in Figure 5.8), although the stress was released, the PCE performance started to fluctuate due to the counteraction of degrading factors such as the diffusion of Ag atoms. The detailed process could be explained by device performance Gaussian distribution in Figure 5.9. Compared with the performance at 816h, the efficiency at 936h drops but the fill factor slightly raises, which means the speed of strain releasing rate could not counteract the degrading of Se films. The efficiency at 1036h greatly increased, the highest efficiency is similar to that at 720h and the median of the Gaussian distribution is slightly higher than that at 816h, which indicates, during these hundreds of hours, the strain releasing dominated and the efficiency recovered. At the third stage (green part in Figure 5.9), the PCE decreased to 92% of the initial value after another 500 hours since the stress relief process ended, and degrading factors became the domination. The J-V curves for the same device at different stages of the aging (stress release) process could be provided in Figure 5.12 in two different presentation styles. Even though the trend shown in the Figure 5.12 is not so clear as that in Figure 5.9, Voc in Figure 5.12 is showing some fluctuation at the beginning and ends in a decreasing trend, which is approximately matched with the Figure 5.9b. Thus, the factors that could affect the stability of SSCs with polymer HTLs are summarized below: (i) the intensity of tensile stress inside the polycrystalline Se film and its releasing rate; (ii) the interaction between HTL and Se layers; (iii) the morphology and stability of polymer-based HTL and the diffusion of the metal anode; (iv) high qualities of Se

polycrystalline layer. Degrading of electronic devices is inevitable, but in the future, finding a suitable inorganic ETL, which could control the stress releasing rate to counteract the natural degrading rate of the whole device, could make the SSCs possess very steady efficiency and ultra-long-term stability.

Figure 5.12. J-V curve of one SSC changing with time.

The reasons that P3HT-based devices showed better performance were analyzed through AFM images, XRD pattern, dark current-voltage curve, and EIS measurements. Furthermore, PTAA-based SSCs showed very poor stability due to serious aggregation and inferior film qualities of PTAA, while P3HT-based devices could maintain their performance for more than 1500h. Additionally, the aging process could be divided into three stages for detailed analysis. At the initial stage, with the releasing of the internal stress inside Se film, the fill factor was enhanced and the corresponding efficiency slightly increased. At the second stage, the tensile stress still kept releasing, while the V_{oc} started to decrease due to degrading factors such as the diffusion of metal atoms from the anode. In this situation, the efficiency started fluctuating. At the final stage, associating with the complete stress releasing, the degrading factors became dominant, leading to the decreased V_{oc} and PCE. These achievements in our work could greatly benefit the development of SSCs with organic carrier transport layers.

5.4 Conclusions

In this work, we adopted SnO_2 as the ETL and P3HT as the HTL to fabricate the well-performed SSCs with long-term stability (more than 1500h). The commercially available SnO_2 was proven to be a suitable substrate for growing Se polycrystalline film. Also, polymers P3HT and PTAA as HTLs have been compared. P3HT showed better aggregation and could sufficiently cover the Se falling and rising grains as well as grain boundaries, which leads to better efficiency and long-term stability. The proper stability of SSCs with organic HTLs in this work enables us to further study the strain releasing of Se active layer itself and its interaction process with external onefold degrading factors. The possible threat influencing the tensile strain inside the Se films has been discussed and the relationship between the morphology of HTL and stability of the whole device was explored. This work indicates that with careful optimization, low-cost SSCs with high stability can be fabricated for extensive industrial applications.

6) Conclusion and Recommendations

6.1 Conclusion

In our work, the influence of compositional modifications of PNCs on the PL performance has been carefully studied. Firstly, we proposed a modified method that could separate the A, B, and X sources to control the stoichiometric proportion. The Cs-oleate together with the $\text{Pb}(\text{OAc})_2$ and HCl sources have been adopted in this method. The synthesized PNCs show uniform cubic shape, good PL performance, and long-term stability. Other metal ions such as Mn, Zn, Mg, Sn have been added into the precursor. No obvious structural differences have been found in the TEM images of PNCs before/after doping. Their influence on the optical properties of PNCs has been studied. Secondly, the influences of other ions on the Mn doping process have been studied. The halide sources have a dramatic effect on the doping processes. If the halide sources are limited, other metal ions would compete to dope into the perovskite structure. We deduced that the bonding between metal ions and halide ions is very important for the nucleation of PNCs. Thirdly, the down-conversion LEDs have been fabricated, which could prove the stability of Mn and Zn co-doped PNCs.

Perovskite bulk materials show many different properties compared with the PNCs. The relatively smaller bandgap makes the bulk perovskite materials very suitable for solar cells. In this work, we explored the perovskite materials as the absorber for the solar cells. Firstly, the morphology of carrier transport layers was explored. We found that the morphology of carrier transport layers is greatly influenced by side chains and the concentration in the precursor solution. Modifying the side chains and the concentration of NDI derivatives could control the morphology of

the carrier transport layer. The morphologies of carrier transport layers are found to affect the carrier transport and the interaction with metal electrodes. Secondly, the internal accumulation of carrier transport materials is also found to influence the carrier transport in PSCs. Our work provided more insights into the morphologies of the carrier transport layer, which could serve as the reference for designing new carrier transport layers for PSCs.

The interactions between perovskite surface and carrier transport materials are another important issue. Here, we adopted a newly designed polymer with DPP main chain and the amino-terminal. The amino-terminal is supposed to interact with the perovskite surface. We found that the amino-terminal could passivate the perovskite surface effectively. The fill factors of PSCs were dramatically improved. Additionally, the morphology of the corresponding P25NH shows a very distinguished lamellar structure, which is proven to prevent the diffusion of metal electrodes and improve stability performance. Though exploring the interaction between the perovskite surface and P25NH, the understanding of the perovskite surface was enhanced. Besides, one possible reason that could greatly influence the fill factor was found.

The widely used and applied lead-containing perovskite materials are not environmentally friendly and stable. Therefore, Se materials, as the oldest photovoltaic materials, have been considered. The Se materials have been carefully compared with the perovskite materials. The aging dynamics of SSCs have been explained by theories built for PSCs. The thiophene functional group on the P3HT may serve as the Lewis base to passivate the Se surface. The fabricated SSCs shows good stability.

In summary, the newly designed PNCs synthesis method could offer more choices to modify the composition of PNCs. Adopting different organic carrier transport layers could help to understand the influence of

the interactions between carrier transport layers and perovskite films. Good stability and non-toxicity of SSCs make Se absorber very competitive for next-generation photovoltaic materials. In this thesis, the compositional modification of PNCs, interactions between the perovskite layer and carrier transport layers, stability of SSCs have been carefully studied, which could provide guidelines for further studying about the B site replacement of PNCs, designing suitable carrier transport materials for PSCs and next generation of solar cells based on Se absorber, respectively.

6.2 Recommendations for further research

6.2.1 Applications of PNCs

When applying in photodetectors, LEDs, and solar cells, the advantages of PNCs are not obvious. ^[7] Then, we need to explore the applications that could utilize the specific features of nanocrystals. One feature of PNCs could be small size and flexible shape.^[7] The PNCs could serve as the holders to carry the medicine. As the molecular weight is quite small, it would not be recognized by the immune system. But the PNCs that are applied in the medical areas must be lead-free. Also, modifying the shape of PNCs to convey the medicine could be another issue. Another application of PNCs could be nanorobots. The nanorobots consist of a control system and movement systems. The control system could be realized by the external electrical field or magnetic field. The dynamical system could be realized by the epitaxial growth of magnetic materials. Another application could be nanopatterns made by PNCs. PNCs have the shapes of nanocubes, nanowires, and nanoplates, which could be used as components for the nanopatterns such as nano-composite

scaffolds. But the existing problems could be how to control the movements of PNCs. Self-assembly or ion beam impact could be possible ways.

6.2.2 Improving understanding of PSCs.

Many strategies have been reported to modify the carrier transport and passivation of perovskite surface. But some of the strategies are conflicted with each other and more confusion has been raised in this process.^[7] Therefore, several aspects should be carefully discussed and supported by related evidence.

The first aspect could be carrier transport processes. The first remaining unanswered question could be if there are free carrier pairs or excitons generated after the light hitting on the PSCs. If it is the excitons generated by the light excitation, are the excitons existing for a long time and how are excitons transporting inside the real spaces of crystal structure? if the free carrier pairs exist, how are they moving inside the lattice structure and what is the driving force for the movement of free carriers? What is the influence of A site on the carrier transport processes? What is the driving force for free carriers moving inside the perovskite layer? What could prevent the transport of carriers or lead to the recombination of carriers? How could the carriers come across the interfaces between the perovskite layer and carrier transport layers? Are there other factors besides the energy level matching affecting the carriers coming across the interfaces between the perovskite layer and carrier transport layers? These questions remain unanswered.

The second aspect could be the interaction between carrier transport layers and perovskite layers. Even though there are lots of works about the passivation of perovskite surfaces by different carrier transport layers,

most of the works only discuss how the functional groups of organic carrier transport layers replace the A site or promote the pristine A site ions back to their positions. The hidden hypothesis is that the functional groups of organic transport layers are exposed to the defects of perovskite surfaces, which may not be true. Therefore, more efforts should be spent on studying the stacking of organic carrier transport materials on the perovskite materials substrate.

6.2.3 New directions for carrier transport layers in PSCs

P25NH-based PSCs with the highest PCE could not achieve the highest fill factor. Under thin thickness (1.6 mg/mL), the P25NH layer could show good conductivity, which would lead to better PCE. But the thin thickness of the P25NH layer cannot prevent the diffusion of the metal anode, which would lead to a lower fill factor. Therefore, new HTLs should be developed to resolve this question. As the conductivity of P25NH is its major drawback, a good way would be modifying the mobility of P25NH without affecting other important optical and electrical properties. We have presented our ideas to our cooperators. They have designed a series of compounds based on P25NH. The next step would be applying these new compounds into PSCs and characterizing them to find out if this idea is feasible or not.

One future function of the top carrier transport layer could be homogenous carrier transportability. Right now, the carrier transport layer could only show good carrier mobility perpendicular to the perovskite surface, but in the direction parallel to the perovskite surface, the mobility is usually very low. The advantages of improving the carrier transport in the parallel direction could be the removal of the top metal electrode, simplifying the electrode growing processes, and benefiting the

developments of the flexible device. For the flexible devices, if the top electrode is removed, a much larger curvature could be achieved by the PSCs.

6.2.4 Perovskite light-emitting devices based on bulk perovskite materials

The working principle of PSCs is converting luminous energy into electric energy. The devices with the reverse process are perovskite light-emitting devices (PeLEDs). The PeLEDs also achieved great progress in the past three years. The external quantum efficiency(EQE) of single-color PeLEDs has also pushed to more than 20%, which is similar to many other kinds of LEDs such as organic light-emitting devices and quantum dots light-emitting devices.^[266-272] In 2018, Kido et al. reported that the red quantum dot-based PeLEDs with the alkyl ammonium iodide salt exhibited an external quantum efficiency of 21.3% and high color purity.^[273] In the same year, Wei et al. reported that green PeLEDs that surpass the quantum efficiency milestone of 20% by managing the compositional distribution in the device.^[266] At present, only the EQE of blue PeLEDs has some space to improve.^[274-277] But with the great effects of researchers, the efficiency of blue PLEDs is supposed to achieve the same level shortly. The efficiency of PeLEDs is very important. But studying the device dynamics could also be very meaningful. Therefore, the fabrication of PeLEDs and characterization of the properties of PeLEDs could be the next step in the coming year.

6.2.5 Fabrication and crystallization of Se films

There are two ways to deposit Se films. The first one is spin coating and the second one is thermal evaporation.^[240,241] For the spin coating

methods, it is very hard to find a suitable solvent to dissolve the Se precursor.^[241] The problem with thermal evaporation methods could be complicated fabrication processes. Different annealing processes could produce different films. Moreover, the resulted SSCs show very low efficiency. Therefore, it is necessary to find new methods to deposit Se films.

It is very important to find the practical applications of SSCs. In Chapter 5, the long-term stability of SSCs has been carefully studied and the factors that affect the stability of SSCs have been discussed. One feature of SSCs is that the Se absorber could not be dissolved in many solvents including water, which makes us wonder if the whole device is hydrophobic, the corresponding SSCs would be very stable in the moisture environment and may even work underwater. In this way, SSCs may be applied in Marine transport. The first step would be finding the suitable carrier transport layers, which should possess effective carrier extraction and transport properties as well as have extremely-poor solubility in the polar solvents.^[279] Polymers could be a good choice since polymers adopted as the carrier transport layers in the PSCs achieved great success and many of them are not dissolved in an aqueous solution.^[280,281] Moreover, the side chains and main chains of polymers could be modified to tune the energy levels and improve the ability of carrier transport.^[282,283] Therefore, polymers could be suitable carrier transport layers for water-resistant SSCs. The next plan in the SSCs part would be finding suitable polymers to work as the carrier transport layers and fabricating SSCs with high water tolerance and good efficiency.

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Bibliography

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