Organic-inorganic lead-halide perovskite for stable optoelectronics

Guo, Xintong

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**ORGANIC-INORGANIC LEAD-HALIDE
PEROVSKITE FOR STABLE OPTOELECTRONICS**

GUO XINTONG

**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

2019

ORGANIC-INORGANIC LEAD-HALIDE PEROVSKITE FOR STABLE OPTOELECTRONICS

GUO XINTONG

Interdisciplinary Graduate School
Energy Research Institute @ NTU (ERI@N)

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

2019

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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This thesis contains material from 1 paper published in the following peer-reviewed journal in which I am listed as an author.

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The contributions of the co-authors are as follows:

- Dr. Koh T. M. provided the initial project direction, discussed on the results and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Koh T. M., Febriansyah B., and A/Prof Mathews N..
- I designed the study and performed all the laboratory work at the Energy Research Institute @ NTU and School of Materials Science. I also analyzed the data.
- I performed all the materials synthesis, and collected contact angle images, X-ray diffraction patterns and visible light spectra, scanning electron microscopy images, atomic force microscopy images, incident photon-to-current efficiency measurement and conducted data evaluation.
- Febriansyah B. conducted FTIR measurement.
- Dr. Bhaumik, S. guided me the synthesis of Cs-oleate.
- Dr. Han G. and Dr. Li J. assisted in device fabrication and testing.
- Jamaludin, N. F. assisted in steady state photoluminescence and conducted TRPL measurement.
- Ghosh, B. assisted in results discussion.

- Prof. Chen X. and Prof. Mhaisalkar, S. provided the facility and financial support to the project, and assisted in results discussion.

25 Jul. 19

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Date

郭欣彤

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Guo Xintong

Abstract

Despite their emergence as promising materials for low-cost and high performance optoelectronics, hybrid organic-inorganic lead-halide perovskites' instability towards moisture and heat stress remains a serious obstacle that needs to be tackled for commercialization. In this project, two methods to improve the intrinsic stability of perovskite materials are demonstrated. The performance and stability of the optoelectronic devices are also investigated.

The first method is surface passivation by cesium oleate to modify the perovskite/hole transporting material (HTM) interface. The organic species in the passivator are anchored on the perovskite surface while the Cs cations passivate the perovskite's surface and grain boundaries. As a result, enhanced hydrophobic character of perovskite film is realized upon passivation, evidenced by high water contact angle of 107.4 degree and improved stability at ambient condition (relative humidity of ~70%, room temperature). Concomitantly, the proposed passivation strategy leads to increase amount of cesium concentration within the films, resulting in beneficial enhanced thermal stability of the film at 85°C. Improved open-circuit voltage (V_{oc}) and unsacrificed short-circuit current density (J_{sc}) were obtained from the treated devices, leading to power conversion efficiencies of over 18%. When stored in a humid environment (relative humidity of ~55%), devices with cesium oleate passivation maintain 88% of its initial PCEs after 720 hours, degrading two times slower than those of the control. This method demonstrates a strategy of coating 3D perovskites with unique combination of inorganic cation and long chain organics to provide hydrophobicity and moisture stability to the solar absorber layer, while maintaining good device performances.

The other method is to substitute 3D perovskite with 2D/3D mix-dimensional perovskite, $PEA_2MA_{n-1}Pb_nI_{3n+1}$ ($n=1, 2, 3, 5$, where n refers to the nominal

composition of the perovskite starting precursor solution). The bulky organic cations provide a natural moisture barrier, which prevents the degradation of 3D perovskite layers. The mix-dimensional perovskite-based photodetectors show much improved moisture stability compared to 3D perovskite (i.e. MAPbI₃) based device, upon exposure to ambient environment. The resulted devices also exhibit inspiring performance of high on/off ratio more than four orders of magnitude under 1 V bias and 100 mw cm⁻² irradiance. This attributes to their suppressed dark current and selectively enhanced photocurrent through the combination of 2D/3D layers. Therefore, mix-dimensional perovskite is a promising material to substitute 3D perovskite in photodetector due to their outstanding performance and enhanced atmospheric stability.

This project also offers an idea by designing a self-protect energy harvesting system to improve the extrinsic stability of perovskites and to prolong the lifetime of their optoelectronic devices. The bio-inspired integrated system shows capability of being responsive to the environment, such as sunlight or weather. During nights or cloudy days, when humidity levels are generally much higher than sunny days, the system will close to protect the perovskite solar cells through the movement of soft actuator. This self-protect energy harvesting system can be realized through a series of devices integration and circuit design, and it shows potential to further improve the extrinsic stability of perovskite based optoelectronic devices.

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Abbreviations

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflectance
CBM	Conduction Band Minimum
CE	Current Efficiency
DC	Direct Current
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EDX	Energy Dispersive X-ray Spectroscopy
EQE	External Quantum Efficiency
ETL	Electron-Transporting Layer
eV	Electron volt
FA	Formamidineum
FF	Fill Factor
FTIR	Fourier Transform Infrared Spectroscopy
FTO	Fluorine-doped Tin Oxide
FWHM	Full Width at Half Maximum
GBL	γ -Butyrolactone
LDR	Linear Dynamic Range
ITO	Indium-doped Tin Oxide
IPCE	Incident Photon-to-Current Conversion Efficiency
J_{sc}	Short-Circuit Current Density
MA	Methylammonium
NMP	<i>N</i> -Methyl-2-Pyrrolidone
PCE	Power Conversion Efficiency

PEA	Phenethylamine
PEI	Polyethylenimine
PL	Photoluminescence
PSC	Perovskite Solar Cell
PTAA	Poly(triarylamine)
PV	Photovoltaics
PVDF	Polyvinylidene Fluoride
RH	Relative Humidity
SEM	Scanning Electron Microscopy
UV	Ultraviolet
Vis	Visible
V_{oc}	Open-Circuit Voltage
XRD	X-ray Diffraction

Chapter 1 Introduction

In this Chapter, the motivation for this thesis are discussed, followed by the hypothesis. The scope of the project and the objectives are described. Finally, the thesis overview and the originality of the research are presented in detail.

1.1 Motivation and Hypothesis

Organic-inorganic halide perovskites have emerged in various applications, such as solar cells, photodetectors, or light emitting diodes, from the confluence of many promising properties, including high optical absorption coefficient in the visible range¹⁻³, tunable direct band gap^{4,5}, and long minority carrier diffusion lengths⁶⁻⁸. Due to their solution-processability and earth-abundant starting materials, perovskites are considered low-cost material for optoelectronic applications⁹⁻¹³. However, perovskite-based optoelectronics are also very unstable, especially over the long-term stability under ambient conditions¹⁴⁻¹⁶. This has been ascribed to partly the hydrophilicity of small organic cation as well as low formation energy of the three dimensional (3D) perovskites^{12,17}. Thus, promoting the intrinsic stability of perovskites remained a key research focus.

Surface passivation of the perovskite layer is one of the primary solutions to address the material's intrinsic moisture instability¹⁸⁻²⁰. However, such approach often involves the use of organics with ammonium functionality, such as butyl ammonium (BA^+)^{18,21}, phenyl ethyl ammonium (PEA^+)^{19,22}, 5-ammonium valeric acid (AVA)²³, and cyclohexyl methyl ammonium (CMA^+)²⁴. Although they were suggested to be capable of passivating the small cation vacancy within the 3D perovskite surface or grain boundaries, their presence also tends to destroy the crystal structure of 3D perovskite due to the templating effect of the ammonium group^{25,26}. As a consequence, the power conversion efficiency of the overall PSCs often gets compromised. In addition to ammonium-based organic cation, the accompanying anion has often been halides (bromide and iodide) that are light sensitive and prone towards oxidation¹⁸⁻²⁴. It has been reported that moisture induced degradation of perovskite can be catalysed by other factors such as light and oxygen due to degradation of different component of the materials, such as the halides^{27,28}.

Similar to perovskite photovoltaics, other the perovskite applications, such as photodetectors, are facing the same stability problem that hinders their practical application^{29–33}. Two-dimensional (2D) perovskite is an alternative in photodetector applications due to its outstanding moisture stability^{34,35}. In 2D perovskites, the A-site cations are substituted with bulky organic ammonium cations, and subsequently the network of [BX₆] are expanded and separated, resulting in a layered structure. The alternating layers of inorganic framework and bulky organic cations act as wells and barriers respectively for the charge transport. The organic layers will also provide moisture insulation that protect the crystal structure, therefore, becoming a stable alternative material for optoelectronic applications^{26,36,37}. However, it still remains challenge for 2D perovskite to selectively suppress dark current and enhance photocurrent along charge transport direction in photodetector application.

In this project, the instability problem of perovskite material in optoelectronic applications, especially photovoltaics and photodetection are addressed. Two methods of improving the intrinsic stability of perovskite are demonstrated.

First, surface passivation method is employed in PSCs to improve the moisture tolerance of the absorber layer, without sacrificing their power conversion efficiency. The aim is to incorporate thin passivation layers that does not affect the perovskite's three-dimensional structure and does not contain any halide as the anion. To achieve this, cesium oleate (Cs-oleate) is selected, comprising a long hydrocarbon organic endowed with carboxyl functionality (COO⁻) and small inorganic cation (Cs⁺) as our passivating agent. The advantage of using the passivator is two-fold. First, the Cs ion can diffuse into perovskite lattice and passivate the cuboctahedral vacancies of the host 3D perovskites due to its size and mobility³⁸. The presence of excess Cs⁺ upon passivation is expected to improve the thermal stability of the material^{39–41}. Secondly, the presence of carboxyl head in the oleate anion opens-up the possibility of being anchored onto

perovskite surface through chemical bonding with undercoordinated Pb^{2+} moiety. This allows the hydrophobic hydrocarbon chain to be arranged upwardly to protect perovskite film from moisture, slowing down the degradation of the material under ambient condition. At the same time, the bonding with Pb^{2+} serves as passivation towards iodide vacancy, thus reducing the possible trap states within the material's surface and grain boundaries.

The other method is by mixing layered structured perovskite with three-dimensional (3D) perovskite, the dimensionality can be tuned, named mix-dimensional perovskites^{25,35}. Here, the mix-dimensional perovskites with a formula of $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=1, 2, 3, 5$, where n refers to the nominal composition of the perovskite starting precursor solution), is employed as an alternative to 3D perovskite. As reported in the literature, the mix-dimensional perovskite shows significantly improved moisture stability than 3D perovskite³⁴, where the organic layers effectively inhibit the moisture from degrading the perovskite film. In addition, it is proposed that the reason for low stability of 3D perovskites to be the low formation energy while the high formation energy of 2D perovskites accounts for their high stability^{12,17}. By incorporated PEA^+ into 3D perovskite, forming mix-dimensional perovskite, the formation energy of the perovskite will be increased, and thus mix-dimensional perovskite-based devices can achieve higher stability. Due to the bulky organic layers between inorganic building blocks, the conductivity of the film will be reduced, thus, the dark current will be significantly suppressed compared with 3D perovskite of MAPbI_3 . On the other hand, the mixture of 3D and 2D perovskite layers can also provide elevated photocurrent compared with pure 2D perovskite due to its improved conductivity by 3D layers. Therefore, the mix-dimensional perovskite-based photodetector can realize suppressed dark current and selectively enhanced photocurrent, results in an improved photodetection performance and high on/off ratio.

1.2 Objectives and Scope

The objectives and scope of this project are outlined below.

- To examine the surface property change of perovskite upon cesium oleate surface passivation. The device performance and stability of triple cation perovskite solar cells with and without Cs-oleate treatment is also investigated.
- To study the film quality difference of mix-dimensional perovskite films, $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=1, 2, 3, 5$), through hot casting and normal spin coating methods. The performance of flexible photodetector based on mix-dimensional perovskite is also examined. The stability of film and device stability of the mix-dimensional perovskite of optimum PEA/MA ratio is compared with three-dimensional perovskite.

1.3 Dissertation Overview

This thesis is organized as described below:

Chapter 1 discusses the motivation and hypothesis for this thesis. The scope of the project and the objectives are described. Finally, the thesis overview and the originality of the research are presented in detail.

Chapter 2 gives a comprehensive literature review on the related research and knowledge on the perovskite materials and devices, with a focus on the compositional and structural possibilities, the physical and chemical properties correlated with the materials compositions. Then, the stability of perovskite material is address including the mechanism of degradation and current methods

to improve the stability. Finally, detailed case study will be given to understand the state-of-the-art research progress made in perovskite optoelectronic devices.

Chapter 3 describes the fabrication and characterization methods of organic-inorganic lead-halide perovskite optoelectronics in detail. The basic principles of various characterization techniques are also summarized.

Chapter 4 demonstrates a feasible way to improve the stability of perovskite photovoltaics through interfacial modification. The moisture and thermal stability are improved through the use of cesium oleate, which modifies the perovskite/hole transporting material (HTM) interface. The bonding between cesium oleate and perovskite film is investigated and the resulted devices are characterized. The results are discussed in detail in this chapter.

Chapter 5 demonstrated another method of improving the intrinsic stability of three-dimensional perovskite by introducing bulky organic layers in the crystal structure. This chapter is devoted to improve the stability of perovskite optoelectronic devices using mix-dimensional perovskite. The hot casting method is used to fabricate mix-dimensional perovskite films, and the film quality is subsequently compared with the one by normal spin coating method. The hot casted mix-dimensional perovskite film shows better moisture stability, and the device exhibits longer lifetime compared with 3D perovskite based device. The mix-dimensional perovskite is also employed as the active material in flexible photodetector, and thus the device performance is discussed in detail.

Chapter 6 presents the scientific insights gained during this project to enhance the stability of three-dimensional perovskite and its optoelectronic devices. Suggestions for future work related to integrated system to protect perovskite devices in practical application is proposed.

1.4 Findings and Outcomes/Originality

The research led to several scientific outcomes by:

1. A unique passivation agent, cesium oleate, is found that improves the both moisture and thermal stability of 3D perovskite. The bonding between oleate and perovskite is investigated. With the organic chain of oleate facing outward, the contact angle of perovskite film increases from 76.7 degree to 107.4 degree, indicating that the modification of thin film surface changed from hydrophilic to hydrophobic nature.
2. First demonstration of cesium doping by surface passivation method. Due to the small size of Cs ion, it does not destroy the 3D structure of perovskite films, which may decrease the performance of the device. The resulted Cs-rich films also exhibit improved thermal stability.
3. Mix-dimensional perovskite, $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=1, 2, 3, 5$), was applied in flexible photodetector. The perovskite films are prepared through hot casting method and the film quality is compared with normal spin coated films. The performance of the devices with different PEA/MA ratio is investigated. The optimum ratio is found to be 2:2, and $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ based device shows good photodetector performance (on/off ratio more than four orders of magnitude), and improved stability compared to three-dimensional perovskite (i.e. MAPbI_3) device.

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Chapter 2 Literature Review

This chapter gives a comprehensive literature review on the related research and knowledge on the perovskite materials and devices, with a focus on the compositional and structural possibilities, the physical and chemical properties correlated with the materials compositions. Then, the stability of perovskite material is address including the mechanism of degradation and current methods to improve the stability. Finally, detailed case study will be given to understand the state-of-the-art research progress made in perovskite optoelectronic devices.

2.1 Lead-Halide Perovskite Materials

2.1.1 Crystal Structure of Perovskites

Perovskite refers to a family of materials with a general formula of ABX_3 , wherein A and B are cations and X is an anion^{1,2}. It contains BX_6 connected octahedra and A cations in the center of octahedra as intercalations (Figure 2.1). Perovskite originally represents the crystal structure of calcium titanate ($CaTiO_3$), which was discovered in 1839³, and it has been one of the most intensively studied crystal structures in material science. The crystal structures of perovskite can be cubic, orthorhombic or tetragonal⁴⁻⁷, and it can undergo phase transition through rotation and tilting of the BX_6 octahedra in the lattice. This class of materials exhibits many interesting properties, such as ferroelectric, dielectric, and piezoelectric properties^{8,9}. Manganese-based perovskite materials commonly possess the property of colossal magnetoresistance, which shows dramatically change of electrical resistance upon a magnetic field applied^{10,11}. Perovskite oxides are also used as catalyst for toxic carbon monoxide (CO) oxidation^{12,13}, NO_x reduction^{14,15} or oxygen electrocatalysis^{16,17} for fuel generation. Due to the various properties of perovskite oxides, it is widely adopted in many applications, and has drawn a lot of attention in research^{18,19}.

Figure 2.1 Crystal structure of organic-metal halide perovskites. A, B and X represent organic cations, metal cations and halide anions respectively.

Organic-metal lead halide perovskites are a kind of emerging perovskite materials, in which the A-sites are occupied by organic ammonium cations, while B-site is occupied by Pb^{2+} cation^{20,21}, as shown in Figure 2.1. Well-studied examples are methylammonium cation (MA^+), formamidinium cation (FA^+) and cesium cation (Cs^+). The bandgap of pb-iodide perovskites are around 1.55 and 1.48 eV, which fall into the ideal range of bandgap for attainable highest efficiency of single-junction solar cells²². Mix cation is also widely studied in the past few years^{23,24}. Double cation and triple cation systems also show promising optoelectrical properties and stability^{25,26}.

The perovskite systems mentioned above belong to three-dimensional perovskite (3D), which are the ones when organic cations of relatively small size fill the intercalation of corner-shared BX_6 octahedra. The maximum size of the A-site cation to form 3D structure can be calculated based on Goldschmidt tolerance factor (t), which is defined according to equation 2.1, where R_A , R_X , and R_B are the ionic radius of A-, B-, and X-site ions. For 3D perovskites, the value of t should be in the range of 0.8 - 0.9²⁷. If the sizes of organic cations are too big,

they cannot fit into the intercalation of inorganic framework any longer and thus, BX_6 octahedral networks become non-continues, naming two-dimensional (2D) perovskites. Commonly A-site cations in 2D perovskites are butyammonium cation (BA^+), and phenylethylammonium (PEA^+)²⁸⁻³¹.

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (\text{Equation 2.1})$$

When mixing bulky organic cations into 3D perovskites, mix-dimensional perovskites structures are formed, following a general formula of $(\text{RNH}_3)_2(\text{A})_{n-1}\text{B}_n\text{X}_{3n+1}$, where n is the number of inorganic layers and RNH_3 represents bulky organic molecules. Other than 3D and 2D perovskite, one-dimensional (1D) and zero-dimensional (0D) perovskite has also been discovered depending on the organic cation incorporated³², as shown in Figure 2.2. The band gaps of perovskite materials show a gradual increment as the dimensionality reduces, which is reflected in the color change from black to white.

Figure 2.2 Schematic demonstration of 3D, 2D, 1D and 0D perovskite crystal structure. Red and green spheres represent metal centers and halide atoms respectively, while other spheres represent the components of organic cations³².

Lastly, the X sites are halide anions, such as iodide anion (I^-), bromide anion (Br^-) and chloride anion (Cl^-). The optical properties of perovskite are also influenced by the halide anions. By controlling the halide composition in $CH_3NH_3PbX_nY_{3-n}$, where X and Y are I, Br or Cl, the emission of perovskite can be tuned from 390 nm to 790 nm³³ (Figure 2.3). Perovskite quantum dots based on colloidal $CsPbX_3$ are extensively studied in previous years, which shows a spectral range of 410-700 nm by tuning the halide composition³⁴. In addition, the bandgap is also found to be influenced by the variation of halide. From the excitonic peak position change in the absorption spectrum, one can indicate an increase or decrease of the bandgap.

Figure 2.3 The emission wavelength of $CH_3NH_3PbX_nY_{3-n}$ ³³.

2.1.2 Optoelectrical Properties of Perovskites

Organic-inorganic lead-halide perovskite materials have direct bandgap and it is continuously tunable from about 1.5 eV to 3.2 eV, through compositional engineering^{25,35}. The theoretical maximum efficiency of a single-junction solar

cell under 1 sun light shows a relation with E_g of the semiconductor, which is known as the Shockley-Queisser (SQ) limit^{2,36,37} (Figure 2.4). For perovskite semiconductors, the ideal E_g to obtain the highest power conversion efficiency (PCE) is around 1.3 eV³⁸. For the E_g that is too large, there will be a large portion of non-absorbed photons in the solar spectrum. Oppositely, a smaller E_g will result in inefficient absorption of solar light, where the energy of photons that excited electrons across the bandgap are more than necessary. The theoretical efficiency for MAPbI₃ based perovskite solar cell is around 31%, which is close to the SQ limit of 33%³⁹.

Figure 2.4 The SQ limit for theoretical efficiency of single-junction solar cells as a function of semiconductor bandgap⁴⁰.

Other than tunable bandgap, perovskites also show convincing properties for light absorber, including excellent optical absorption coefficient and long carrier diffusion length⁴¹, and low exciton binding energy for 3D perovskite. The absorption coefficient (α) is determined by the length that the photons of certain wavelength can penetrate before being absorbed, and the average length that the

photons penetrate is the inverse of the absorption coefficient, α^{-1} . Beneficial from the direct bandgap and p - p coupling⁴², the high absorption coefficient of perovskite materials allows the photovoltaics to fully utilize the light from UV to whole visible range, making this class of materials suitable for photovoltaic application. The absorption coefficient of MAPbI₃ is estimated to be $1.5 \times 10^4 \text{ cm}^{-1}$ at 550 nm and $0.5 \times 10^4 \text{ cm}^{-1}$ at 700 nm, corresponding to penetration lengths of 0.66 μm and 2 μm respectively⁴³. The charge carrier diffusion length is reported to be as high as 1 micrometer for mix halide perovskite (MAPbI_{3-x}Cl_x), while the one for MAPbI₃ is about 100 nm⁴⁴. The long carrier diffusion length is due to the long recombination lifetime which allows a larger absorber film thickness.

The exciton binding energy (E_b) describes the association energy of electron-hole pair induced by photon⁴⁵. The exciton binding energy was given by

$$E_b = \frac{\mu e^4}{2\hbar\epsilon_\infty^2} \quad (\text{Equation 2.2})$$

(μ : the reduced effective mass; ϵ_∞ : the dielectric constant at high frequency)

The value is associated with the reduced effective mass of exciton. The exciton binding energy (E_b) also shows an increasing trend according to reducing dimensionality. For example, the E_b of MAPbI₃ (3D) is 30-45 meV, while the E_b of PEA₂PbI₄ (2D) is 330-388 meV. And for (NH₂C(I)=NH₂)₃PbI₅ (1D) and MA₄PbI₆·2H₂O (0D), the E_b are 410 meV and 545 meV respectively⁴⁶. For 3D perovskite, the small value of E_b indicates the weakly bound excitons induced upon illumination. Charge accumulation phenomenon is also observed in perovskite by impedance measurement⁴⁷, which together lead to the high open-circuit voltage of perovskite solar cells⁴³.

2.1.3 Stability of Perovskites

Despite the amazing performance achieved by perovskite solar cells, the main issue that hinders the commercial applications of PSCs are the poor stability^{48,49}. Without ensuring good stability and long lifetime of devices, the

commercialization of PSCs will be severely hindered. Therefore, studies investigating the causes of 3D PSCs instability is becoming a critical research topic.

There are several factors that can cause PSCs degradation, including oxygen and moisture, UV light and temperature⁵⁰. Firstly, thermally induced phase transition of MAPbI₃ from tetragonal to cubic phase is reported to take place around 57 °C and the associated volume change may cause long term instability⁵¹. UV light in conjunction with the TiO₂ layer can degrade perovskite materials. Effective strategies has been carried out to eliminate this problem by passivating the TiO₂ surface with a thin layer of Al₂O₃^{52,53}. Among all the degrading factors, moisture is more threatening for perovskite materials, because it initiates the degradation by forming moisture complexation in very short time, which therefore, undergoes decomposition under oxygen and light⁵⁴. Thus, perovskite degradation processes are mainly due to moisture attack and it leads to fast degradation in a few days. Perovskites are highly sensitive to moisture, therefore during the assembly and testing process of PSCs, the devices can be attacked by moisture and it leads to decomposition. The mechanism of moisture assist degradation process was investigated by in situ techniques. J. Yang *et al* found an intermediate phase of hydrated compound, MA₄PbI₆·2H₂O formed during the degradation⁵⁵. Then, a chemical reaction routes for the formation of MA₄PbI₆·2H₂O is also established by utilizing single crystal X-ray diffraction and powder XRD, as shown in equation 2.3, 2.4 and 2.5⁵⁶. Increasing amount of water will shift the balance towards formation of MAPbI₃·H₂O in Equation 2.3. Then the chemical reaction will proceed to equation 2.4 and cause decomposition. Final degradation forms yellow PbI₂, while MAI is in solution and will be then evaporated or flow out, according to equation 2.5.

Due to the high sensitivity of PSCs to moisture, fabrication processes have to be carried out under inert gas condition. This increases difficulties in handling and processing devices and restricts scale-up applications^{57,58}. However, when the devices are tested in ambient condition, severe degradation of 3D perovskites can also be observed in a very short time. Significant color change from dark perovskite phase to yellow lead iodide phase can be observed during degradation⁵⁹. It will therefore reduce the PSCs performance, especially the power conversion efficiency and limit the outdoor application.

Light and oxygen can accelerate the degradation of perovskites. The moisture complexation can decompose, forming CH_3NH_2 (aq.) and HI (aq.) in equation 2.6⁵². In the presence of oxygen and light, HI can be oxidized forming I_2 , according to equation 2.7 and 2.8⁵⁴. Thus, it shifts the chemical reaction in equation 2.6 forward and accelerate the degradation.

2.2 Perovskite Optoelectronic Devices

2.2.1 Perovskite based Solar Cells

Organic-inorganic halide perovskites based solar cells have drawn significant attention due to their excellent optical properties and solution-processability. A typical p-i-n structure is commonly adopted, where the perovskite layer, acting as the intrinsic layer, is sandwiched between an electron transporting layer (n type) and a hole transporting layer (p type).

MAPbI_3 is a conventional light absorber that has optimum bandgap around 1.55 to 1.58 eV. However MAPbI_3 has a phase change at around 55°C , which is right

in the range of practical application. Therefore, tuning bandgap of this material without sacrificing the absorption property becomes more critical⁶⁰. Theoretically, the approachable are simply either varying components of A-site or modifying metal halogen bond, B-X. Formamidinium lead iodide (FAPbI₃) has narrower (1.49 eV) bandgap than MAPbI₃ with improved thermal stability up to 150 °C. However, it shows poor moisture stability and easy to form non-perovskite yellow phase⁶¹. A double cation perovskite as light harvesting material were studied to establish efficient and stable perovskite phase based on (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}, as shown in Figure 2.5a²⁵. Efficiency was pushed up by 2% compared to MAPbI₃. However, mix FA/MA perovskites are not thermally stable due to its intrinsic crystal structure of MAPbI₃ and thus it is highly sensitive to processing condition.

Figure 2.5 a) Power conversion efficiency of mixed FA/MA perovskite solar cell²⁵. b) Device performance of highest-efficiency triple cation perovskite solar cells²⁶.

Triple cations perovskites aroused huge attention by their excellent power conversion efficiency as well as stable perovskite phase²⁶. Comparing to the double cations (FA/MA perovskites), this work incorporated another inorganic A-site cation, Cs⁺ into the system. The Cs ions act as nucleation seed and

facilitate the crystal growth. It reduced the formation of impurity phases of FAPbI_3 and helped generate stable and uniform perovskite crystals. Only 5% molar ratio of Cs addition significantly boosted the power conversion efficiency to 21.1%, as shown in Figure 2.5b. It also solved the instability of mixed FA/MA perovskites and maintained high efficiency under working conditions after 250 hours.

Mix-dimensional perovskites have also been employed in photovoltaic since 2014. $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ as the active material, it has achieved a power conversion efficiency of 4.73%⁶². The devices achieved striking stability for 46 days exposing under 52% RH, because the organic layers separating inorganic frameworks act as moisture insulating layer. This work provides a facile approach to improving stability of PSCs and aroused more interests in mix-dimensional perovskites. Although the organic layers insulate moisture from degrading perovskites, it also hinders the charge transport by interrupting the continuity of BX_6 inorganic sheets where the electron and hole transfer along inorganic framework. L. Quan *et al* proposed the reason for low stability of 3D perovskites to be the low formation energy while the high formation energy of 2D perovskites accounts for their high stability⁶³. They incorporated PEA^+ about 3% moles of MA^+ , which increased the formation energy and thus higher stability. This device shows 15.3% PCE and remains at high level up to 60 days, as shown in Figure 2.6. However, further enhance the stability by increasing amount of PEA^+ will lead to decrease in power conversion efficiency. Therefore, there is always a trade-off between better performance and better stability.

Figure 2.6 Crystal structure and PCE change of solar cells based on $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ with varying n values⁶³.

The crystal orientations of layered perovskite are favorable to be parallel to substrate, which will hinder the charge transport between top and bottom electrode⁶⁴. Therefore, it is essential to look for the solutions to enhance charge transport and thus the overall performance. This problem can be addressed by a nanostructuring approach based on $(\text{IC}_2\text{H}_4\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ⁶⁵. The perovskite crystals grew perpendicular to substrate using sequential deposition technique, as shown in Figure 2.7a, by dipping 2D perovskite film in MAI solution for cation exchange. The champion cell achieved up to 9% efficiency and stable for 5 days at 40% RH. Improved charge transport is demonstrated by hot casting method in 2D perovskite⁶⁶. By preheating solution and substrate at high temperature before deposition, the favorable orientations of layered perovskite crystals are perpendicular to substrate, as shown in Figure 2.7b, while at room temperature, the orientations are more random. Thus, they achieved the highest efficiency of 2D perovskite so far, of 12.52% based on inverted structure, as shown in Figure 2.7c. The stability of encapsulated cells was significantly improved comparing to encapsulated 3D PSCs.

Figure 2.7 a) SEM top-view image of nanostructures of 2D perovskite⁶⁵. b) Crystal orientations of hot-cast 2D perovskite film. c) Device structure and current-voltage curve based on hot-cast 2D perovskite material⁶⁶.

By tuning the dimensionality of perovskite, the bandgap, band energy levels and charge transportation can be adjusted. Another approach to decrease the dimensionality of perovskite by adding polymeric ammonium cations, polyethylenimine (PEI)⁶⁷. The PEI molecule formed 2D perovskite structure with PbI_2 in 3D MAPbI_3 matrix, adding tunability and reducing the dimensionality of the system. Using two-step deposition method, PEI with different ratios was firstly added to PbI_2 to form 2D perovskite films, followed by deposition of MAI. on top of $(\text{PbI}_2)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ film to grow perovskite structure. Based on inverted solar cell architecture, 2% and 4% PEI added gave the maximum power conversion efficiencies of 15% and 12%, while the control cell without polymer showed 14.6% efficiency, as shown in Figure 2.8b⁶⁷. With increasing amount of PEI, the V_{oc} was found to improve, however J_{sc} reduced due to hindered charge transport in low dimensional structure. A 4% PEI addition further lead to polymer accumulation and had negative impact on the performance. Nevertheless, the stability was significantly improved over 400 hours at 50% RH, shown in Figure 2.8c⁶⁷.

Figure 2.8 a) XRD patterns of $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$, $x = 0\%$, 2% , 4% . b) PCE distribution of devices with different content of PEI. c) PCE evolution over time for devices with different ratio of PEI⁶⁷.

To further improve the performance and stability of perovskite solar cells, surface passivation method has been widely employed to passivate the surface defects in perovskite photovoltaics^{68–70}. The passivators commonly contain organo-ammonium and halides, such as methylammonium bromide (MABr) and butyl ammonium iodide (BAI)^{30,71}. Recently, J. You *et al* have achieved a 23.32% certificated efficiency through PEAI passivation on $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ mix perovskite film⁷². They found PEAI to be an effective additive to reduce the non-radiative recombination by preventing the formation of PEA_2PbI_4 (2D perovskite). This work provides a perspective that the formation of 2D perovskite by surface passivation could sacrifice the performance of solar cell devices.

Figure 2.9 a) Device architecture of planar structure b) Proposed mechanism of PEAI passivation⁷²

2.2.2 Perovskite based Photodetector

Due to the excellent optoelectronic properties of organic-metal perovskite materials, researches on other optoelectronic applications are done concurrently, such as photodetectors, light emitting diodes, field effect transistors and lasing^{73–77}. Perovskite shows promising potential in photodetection due to its excellent properties such as tunable bandgap, large carrier diffusion length, and solution-processability^{1,78,79}.

The performance of photodetectors can be characterized based on the following parameters: responsivity (R), specific detectivity (D^*), response time, external quantum efficiency (EQE), and linear dynamic range (LDR)⁸⁰. These parameters are defined as below:

Responsivity (R) characterizes the photocurrent generated per the irradiance power from a unit area of device, and it is defined in equation 2.9, where I_{ph} is the photocurrent and P is the irradiance power.

$$R = \frac{I_{ph}}{P} \quad (\text{Equation 2.9})$$

Specific detectivity (D^*) describes the ability of the device to detect weak light, and it is expressed in equation 2.10, where A is the detection area of the device, Δf is the electrical bandwidth, and i_n is the noise current.

$$D^* = \frac{R \cdot (A \Delta f)^{1/2}}{i_n} \quad (\text{Equation 2.10})$$

Response time describes how fast or slow the photodetector response to the light pulse by evaluating the rise time (t_r) and fall time (t_f) of the current, which define as the time taken from 10% to 90% of the maximum current and 90% to 10% respectively.

External quantum efficiency (EQE) is defined as the ratio of total number of electron-hole pairs generated to the number of incident photons. EQE is expressed in equation 2.11, where J_{ph} is the current density, P is the incident power, h and c are Planck's constant and light speed.

$$EQE(\lambda) = \frac{J_{ph}hc}{Pq\lambda} \quad (\text{Equation 2.11})$$

Linear dynamic range (LDR) refers to the linearly response range of photocurrent to the incident power. LDR is defined as follows:

$$LDR = 20\log \frac{I_{ph}}{P} \quad (\text{Equation 2.12})$$

Perovskite in photodetector application can be generally classified into two categories: broadband photodetectors and narrowband photodetectors^{81,82}. Broadband photodetectors response to wide range of wavelength from UV light to infrared region, which can be applied in visible light communication.

Figure 2.10 a) Schematic structure of perovskite photodetectors. b) Photocurrent and dark current curves of photodetectors with/without hole blocking layers. PD1: without blocking layer; PD2: with BCP layer; PD3: with PFN layer⁸³.

Organic-metal halide perovskite photodetector was firstly demonstrated for broadband detection based on MAPbI₃ by Y. Xie *et al* in 2014⁷⁴. This work achieved mechanical flexibility of photodetectors and showed the ease of assembly of photodetectors with simply perovskite and ITO layers, without any hole/electron transporting layers. However, the performance as a photodetector is not ideal, reflected on the low on/off ratio of less than 20 at a high bias of 8 V.

Then Y. Yang's group adopted inverted perovskite solar cell structure for highly sensitive photodetector based on $\text{MAPbI}_{3-x}\text{Cl}_x$, as illustrated in Figure 2.10a⁸³. Their strategy was to apply a hole blocking layer between electron transporting layer and metal electrode to reduce charge recombination. Through the interface engineering, the dark current was significantly suppressed and thus devices showed good on/off ratio at low voltage bias, as shown in Figure 2.10b.

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Chapter 3 Experimental Methodology

In this chapter, the fabrication and characterization methods of organic lead-halide perovskite optoelectronics are described in detail. The basic principles of various characterization techniques are also summarized.

3.1 Chemicals and Materials

Methyammonium bromide (MABr), formamidinium iodide (FAI), cesium iodide (CsI), methylammonium iodide (MAI), and phenylethylammonium iodide (PEAI) were purchased from Sigma Aldrich. Lead bromide (PbBr_2) and lead iodide (PbI_2) were from purchased from TCI Chemicals. Solvents including *N,N*-dimethylsulfoxide (DMSO) (99.8%), *N,N*-dimethylformamide (DMF) (99.8%), chlorobenzene and toluene (99%) were anhydrous, and purchased from Sigma Aldrich. Hole transporting materials used in this project include Spiro-OMeTAD, from Sigma-Aldrich and poly(triarylamine) (PTAA), from Solaris Canada. All the chemicals mentioned above were stored in glovebox, which was maintained in argon (Ar) atmosphere with $\text{H}_2\text{O} < 0.1$ ppm and $\text{O}_2 < 0.1$ ppm. As for electron transporting materials, TiO_2 nanoparticles paste (30NRD) were purchased from Greatcell solar, Australia. All other relevant chemicals were purchased from Sigma-Aldrich and without further purification unless specially mentioned. The glovebox was maintained under argon

3.2 Spin-Coating Methods

Spin-coating, known as a low-cost solution process method, is very popular in perovskite fabrication. During the spin coating process, evaporation of solvent and convective self-assembly occurs. Due to the ionic interactions between halogen ions and metal ions, a well-crystallized perovskite film formed immediately^{1,2}. Solvents for perovskite precursors are generally γ -butyrolactone (GBL), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylformamide (DMSO). The high performance of perovskite-based devices are necessary to possess large crystals and compact perovskite film^{3,4}. However, the simple spin-coated perovskite film shows rod-like crystals and poor surface coverage⁵. Since the quality of perovskite films are highly sensitive to coating process, the experimental conditions require precise control, such as the timing, temperature

and gas environment⁶⁻⁸. To improve the film quality, various coating techniques are employed to obtain large-grain perovskite film with less pin-holes, such as anti-solvent method⁹, hot-casting^{10,11}, two-step method^{12,13}, and so on. Anti-solvent method is widely adopted in fabricating 3D perovskite film, where the anti-solvent is dripped onto the spinning film, followed by heat treatment. This process has to be carried out in inert environment (nitrogen or argon glovebox), and the resulted films have good uniformity and reproducibility. For 2D perovskite film, hot casting method is used to achieve a fast crystallization during the spin-coating process and thus, a uniform film can be obtained¹¹.

3.2.1 Solvent Engineering

Due to the poor quality film resulted from simple spin-coating method, solvent engineering method is developed to significantly improve the crystal size and surface coverage of solution-processed perovskite films^{2,2}. Solvent engineering, also called anti-solvent method, is simply dripping an anti-solvent onto the spinning substrate with perovskite precursor. The procedure for solvent engineering method is shown in Figure 3.1. There are several requirements for choice of anti-solvents¹⁴. The anti-solvents need to be miscible with perovskite solvent and the solubility of perovskite components in anti-solvents should be low. The boiling point of anti-solvent are generally lower, compared with perovskite solvents. Once the anti-solvent is dripped on the spinning film, it will remove the residue solvent and facilitate fast crystallization of perovskite by frozen all constituents into a uniform film. Followed by heat treatment at 100 °C for certain time interval, the film is fully converted into perovskite film with excellent uniformity and crystallinity. Mixed solvent can be employed in anti-solvent method¹⁵, to slow down the evaporation during spinning, since the anti-solvent is to be applied before crystal formation starts.

Figure 3.1 Procedures for solvent-engineering method².

In figure 3.2, a plausible mechanism for the phase changes during anti-solvent spin-coating process is proposed, where the perovskite precursor contains MAI, PbI_2 and DMSO, and toluene is used as anti-solvent. At the initial stage of spinning process, layered PbI_2 is formed, where Pb ions is surrounded by iodide ions hexagonally. Due to the weak van der Waals force between PbI_2 layers, there is enough interlayer space for intercalation of guest molecules¹⁶. Once the anti-solvent (toluene), is dripped, all the constituents are frozen immediately by removal of residue solvent. Meanwhile, an intermediate phase of MAI- PbI_2 -DMSO complex forms, which is considered as key material for the resulted flat perovskite film. It has been reported that lead halide can coordinate with DMSO, forming $\text{PbI}_2\text{-(DMSO)}_2$ complex¹⁷. However here, they propose the complex formed is MAI- PbI_2 -DMSO instead of $\text{PbI}_2\text{-(DMSO)}_2$. Finally, the film is fully converted to MAPbI_3 through heat treatment at 100°C , resulted in a very compact and uniform film.

Figure 3.2 Proposed perovskite film formation process²

As shown in Figure 3.3a & b, the roughness of final perovskite film is slightly increased to 8.3 nm, compared with the 6.0 nm of intermediate phase. Figure 3.3c shows that the resulted film is compact and uniform, with a grain size range of 100-500 nm.

Figure 3.3 AFM topography images of a) intermediate phase and b) final perovskite film; c) SEM image of perovskite film².

3.2.2 Hot Casting

Hot casting is another method to improve the film quality and surface coverage. The hot-casting process of perovskite thin film is schematically shown in Figure 3.4a¹⁰. This method involves preheating of perovskite precursor at 70°C and substrates maintained up to 180°C. The precursor is casted on the substrate and subsequently spin coat to obtain a perovskite film. The resulted film is uniform and pin-hole free.

Figure 3.4 a) The procedure of hot-casting method; b) optical images of grain size by varying the substrate temperature; c) grain size difference by varying the precursor solvent; d) the function of average grain size with processing temperature by conventional post-annealing method and hot-casting method¹⁰.

By varying the substrate temperature and solvent of precursor, the grain size and film morphology is studied, as shown in Figure 3.4b-d. As the substrate temperature increases from room temperature to 190°C, the grain size increases dramatically. It also shows an improvement in grain size when using solvent of higher boiling point as processing solvent, such as DMF or *N*-methyl-2-pyrrolidone (NMP). There is a significant improvement of grain size using hot casting method, up to millimeter size, compared with micrometer size obtained through conventional post-annealing method. The key to get larger grain size in hot casting method is the presence of excess solvent when the substrate is heated. When the substrate temperature is above the crystallization temperature,

perovskite phase starts to form and the excess solvent prolonged the crystal growth, leading to larger grains.

Hot-casting method is also utilized in fabrication of 2D perovskite¹¹. The quality of hot-casted films is superior to that of conventional spin-coated films, not only in the pin-hole density, but also the crystallinity and orientation. The stark difference is confirmed by in-depth crystallography map from grazing incidence wide-angle X-ray scattering (GIWAXS). (Figure 3.5a & b)

Figure 3.5 GIWAXS images for (a) conventional spin-coated film and (b) hot-casted film based on $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ perovskite; c) the orientation of hot-casted 2D perovskite film¹¹.

The GIWAXS maps show that the conventional spin-coated film is polycrystalline and containing considerable randomness in the crystal domains. In contrast, the hot-casted film is nearly single crystalline with well-controlled orientation along the out-of-plane direction. The superior orientation of crystals allows efficient charge transport in the device and achieved the highest efficiency of 12.5% by 2D perovskite photovoltaics¹¹.

3.3 Device Fabrication

3.3.1 Solar Cell Fabrication

Pre-etched FTO substrates (NSG TEC™ 15), with the size of 2.1 cm x 1.7 cm, were ultrasonic cleaned in detergent, deionized (DI) water and ethanol consequently for 30 min each. After dried with nitrogen gas, the substrates surfaces were treated in UV ozone for 15 min before spin coating.

The precursor for TiO₂ compact layer was prepared by mixing tetrabutyltitanate, anhydrous ethanol, diethanolamine and DI water (weight ratio 227:890:28:70). The mixture was stirred for 24 hours, followed by standing for 24 hours. Then the compact TiO₂ layer was prepared by spin coating the precursor on FTO substrates at 5000 rpm and heat treatment at 500 °C for 2 hours. After cooling to room temperature, the substrates were treated in 20 mM TiCl₄ solution for 30 min in oven at 70 °C, followed by the annealing at 500 °C for 30 min. TiO₂ paste (30NRD) was diluted in ethanol (1:7 w/w) and kept stirring for 3 hours. Then the solution was spin-coated onto the blocking layer to form a mesoporous TiO₂ layer. TiCl₄ treatment was done to the substrates using 20 mM TiCl₄ solution at 70 °C for 30 min. Followed by annealing at 500 °C for 30 min before spin coating perovskite films.

Perovskite solution (1.35 M) was prepared by dissolving CsI, MABr, FAI, PbBr₂ and PbI₂ crystals (0.05:0.17:0.83:0.17:0.83) in DMSO/DMF mix solvent (volume ratio 1:4). Perovskite solution was dropped onto prepared substrates and spin coated at 6000 rpm for 30 sec. During spin coating, anti-solvent of chlorobenzene was dipped onto spinning sample after 12 sec to form smooth films. After that, the films were annealed at 100 °C for 60 min. The samples were cooled down to room temperature and a 70 mg/ml Spiro-OMeTAD (in chlorobenzene) solution was spin coated on perovskite film at 5000 rpm for 30 sec. Au electrodes (~100 nm) were thermal evaporated on samples with the size of 0.2 cm x 0.2 cm using a shadow mask.

3.3.2 Photodetector Fabrication

ITO glass was chemical etched by reaction of zinc powder with HCl (2 M) for

desired pattern and then was cut into 2.5 x 2.5 cm² pieces. The substrates were ultrasonic cleaned in detergent, DI water and ethanol consequently for 30 min each. After dried with nitrogen gas, the substrates surfaces were treated in UV ozone plasma for 15 min before spin coating.

Zn₂SnO₄ nanoparticle solution was deposited on prepared ITO substrate by spin coating at 3000 rpm for 30 sec, followed by annealing at 200 °C for 30 min. After cooling to room temperature, perovskite solution (1.2 M) was spin coated on substrate at 3000 rpm for 30 sec, followed by annealing at 120 °C for 20 min. Solution of PTAA was spin coated on cool perovskite film at 2000 rpm for 60 sec. Au electrodes (~100 nm) were thermal evaporated on samples with the size of 0.2 cm x 0.2 cm.

3.4 Film Characterization

3.4.1 X-ray Diffraction

X-ray diffraction (XRD) analysis was carried out to track phase changes during stability test. Thin film XRD patterns were collected with a Bruker D8 Advance diffractometer (Bragg Brentano geometry) equipped with a Cu K α X-ray tube ($\lambda = 1.5418\text{\AA}$), operated at 40 kV and 40 mA.

XRD is a widely used technique in research and industry for materials characterization, to obtain information about lattice parameters and the microstructure. The working principle of XRD is that the regularly arranged atoms in the crystal lattice are able to scatter X-rays of certain wavelength. The wavelength the scattered X-ray has a relation with the inter-atomic distance in crystals, called Bragg's Law (Equation 3.1)¹⁸. λ represents the wavelength of incident X-rays. By measuring the angle between transmitted and diffracted beam (2θ), the spacing of atomic planes (d) in the crystal can be determined.

$$2d \sin \theta = n\lambda \quad (\text{Equation 3.1})$$

Figure 3.6 Demonstration of Bragg's Law of x-ray diffraction.

XRD is only applicable in crystalline samples, powders or thin films, where the atoms are periodically arranged. The collected diffraction peaks position corresponds to lattice spacing or unit cell dimensions in the crystal. The diffraction peak width is related to microstructure information. Full width at half maximum (FWHM) can be used to estimate the crystal size (L), expressed in Scherrer Equation (Equation 3.2), where K refers to a dimensionless shape factor.

$$\text{FWHM}(2\theta) = \frac{K\lambda}{L \cos \theta} \quad (\text{Equation 3.2})$$

For nanocrystallites, the FWHM will be larger and the diffraction peak may be broadened. As for amorphous samples, no clear peak can be observed due to lack of long-range order¹⁹.

3.4.2 Scanning Electron Microscopy (SEM)

Surface morphology and cross-section images of the perovskite thin films and solar cell devices were recorded using a JEOL JSM-7600F field emission scanning electron microscope (FESEM), with an accelerating voltage of 5kV.

In the FESEM, the electron beam emitted by a field emission source are accelerated under high voltages and used to scan the sample in a zig-zag pattern. The electron beam interacts with sample surface and it produces signals, which provide information of topography of samples²⁰. In Figure 3.7, it shows the working principle of SEM and its components. The interactions of electrons and

the sample surface can be elastic or inelastic scattering, resulting in a variety of signals.

Figure 3.7 Schematic diagram of SEM parts.

Secondary electrons (SE) are inelastic scattered electron beam collected by SE detector. SE is used to generate images of topography with a resolution of less than 10 nm, and it is the most commonly used information of SEM. Back scattered electrons (BSE) are elastic scattered electrons, which is another very useful signal to determine compositional information. The yield of BSE depends on the atomic mass of nucleus in sample that scatter the electrons. Higher atomic number of an element will result in higher intensity of BSE signals. Therefore, the contrast of the image shows the compositional difference of the elements in sample.

The sample for SEM is required to be conductive, otherwise there will be a charging problem of accumulation of electrons. Therefore, normally deposition of a conductive layer on top of perovskite samples are necessary to improve the conductivity. A typical method is to sputter a thin layer of gold or platinum, while a conductive tape is used to electrically ground the sample.

3.4.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) measurements were conducted using Asylum Research Cypher S and used to measure the morphology and surface roughness of perovskite films. All measurements were performed in the standard tapping mode with OTESPA-R3 tips from Bruker.

AFM, a type of scanning probe microscope, is used to obtain topographical information of samples²¹. Generally, AFM contains a force probe, called cantilever, equipped with a sharp tip, which could oscillate at a certain frequency. The signals are generated through recording the phase and amplitude of the oscillation²². When the tip is brought into contact with sample surface, there is an interaction force between the spring-like cantilever and sample surface. As shown in Figure 3.8, a laser and a split photodiode are used to detect the deflection and motion of cantilever²³.

Tapping mode is commonly used in characterization of perovskite films in ambient condition. The interaction of cantilever and perovskite film surface is commonly repulsive force when the tip gets very close to the surface, which causes the change in amplitude of the oscillation. Thereby, this amplitude will provide a feedback and adjust the height of cantilever above the sample surface to maintain a set oscillation amplitude. In the AC mode, there is little contact between the tip and sample surface, therefore the damage to sample is minimized.

Figure 3.8 Schematic diagram of AFM parts and working principle.

There are a few advantages of AFM compared with SEM in perovskite characterization. AFM has no requirement in conductivity of the sample, little damage of sample surface, whilst a nanometer scale resolution can be achieved in ambient condition. In contrast, SEM is a destructive technique and it requires vacuum condition²⁴. However, the surface roughness of AMF sample has to be less than a few micrometers, and the scanning area is restricted to micrometer scale²⁵.

3.4.4 Steady State Absorption Spectroscopy

Light interacts with the sample and causes electronic transitions from conduction band to valence band. Therefore, the absorption of light is able to reflect the electronic band structure of a material²⁶. Ultraviolet–visible spectroscopy (UV-Vis) and Fourier-transform infrared spectroscopy (FTIR) are two types of steady state absorption spectroscopy that measures light absorption at ultraviolet-visible range and near infra-red range respectively.

UV-vis absorption was recorded using a SHIMADZU UV-3600 spectrophotometer, with an integrating sphere (ISR-3100) in the wavelength range 300-800nm. UV-vis spectroscopy was used to measure the absorption edge of perovskite films, which can be used to predict the optical band gap. For mix-dimensional perovskite, the exciton peak positions were also detected and used to analyze the multi phases of perovskite film.

IR spectra of the samples were measured in transmission mode using a VERTEX 80 V FTIR Spectrophotometer with an ATR (attenuated total reflectance) accessory and a scanning resolution of 4 cm⁻¹s⁻¹. The measurement was carried out under vacuum to minimize the effect of atmospheric particles of the surroundings.

In steady state absorption spectroscopy, monochromatic light beam (I_{in}) is continuously applied to the sample and the light passed through the sample (I_{out})

is measure. The transmittance (T) and absorption (A) are expressed in Equation 3.3 and 3.4²⁷.

$$T = \frac{I_{in}}{I_{out}} \quad (\text{Equation 3.3})$$

$$A = \log \frac{I_{in}}{I_{out}} \quad (\text{Equation 3.4})$$

$$A = -\log \frac{I_{out}}{I_{in}} = \epsilon cl \quad (\text{Equation 3.5})$$

The attenuation of light passing through a material is described by Beer-Lambert law in Equation 3.5. As shown in Figure 3.9, ϵ is the absorptivity or extinction coefficient of the material, c is the concentration of sample and l is the path length. There are some limitations of Beer-Lambert law, one being it is only valid for sample has low concentration ($<10^{-2}$ mol/L), where independent of the concentration. For sample of higher concentration, ϵ is affected by the concentration due to electrostatic interactions between molecules. In addition, the Beer-Lambert Law will be inaccurate when there is light scattering by particles in the sample or luminescence of the sample.

Figure 3.9 Schematic demonstration of light absorption of a sample.

FTIR spectrometer utilize the light source in near infrared range, which can cause the bond motions in the molecule, such as stretching, compressing, and bending. Each bonding motion corresponds to a certain wavenumber in the spectrum, being the fingerprint of the molecule. Therefore, FTIR can be used to determine the compositional and bonding information of an unknown material.

Unlike UV-vis spectroscopy, FTIR spectrometer collects data over all wavelength simultaneously. The raw data collected by FTIR spectrometer is called interferogram, and it is further converted into a spectrum through a Fourier Transform algorithm. This mechanism attributes to the high resolution of the equipment. Another advantage of FTIR spectrometer is that, since it does not require slits, higher throughput can be realized compared with a dispersive equipment.

3.4.5 Steady-State Photoluminescence (PL)

SSPL was recorded using Horiba Fluoromax-3 spectrometer, with 0.5 nm wavelength resolution, respectively

Steady-state PL spectroscopy is a simple and nondestructive equipment to probe the basic electronic properties. In PL, the sample is excited by a light of sufficient energy, and the spontaneous emission of light due to radiative relaxation is captured by a detector. The resulted spectrum describes the intensity of emission as a function of wavelength. In Figure 3.10, it shows a typical PL set-up. PL spectroscopy can also capture the intensity of emission light at certain wavelength by varying the excitation light wavelength, call photoluminescence excitation (PLE).

Figure 3.10 Schematic illustration of typical setup of PL spectroscopy.

The PL emission spectrum can be used to measure transition energies, and thus to determine electronic energy levels²⁸. It also provides information on evaluating surfaces/interfaces, and impurity levels. The PL intensity provides information on radiative and nonradiative rates in relative, as well as the quality of interfaces of samples. However, a major drawback of PL is that it can only analyze samples that emits light. In addition, it is also difficult to determine the absolute density of impurity states.

3.5 Device Characterization

Photovoltaic characteristics of the solar cell devices were measured in the reverse scanning direction (from V_{oc} to J_{sc}), with a sweep rate of 10 mV s^{-1} , under AM1.5G (100 mW cm^{-2}) spectral irradiation from a solar simulator (Newport 91190A) incorporating a 450 W xenon lamp (model 81172, Oriel) calibrated with a Si reference cell (Oriel PN91150). Devices were characterized through a 0.09 cm^2 black mask. Incident photon-to-current efficiency (IPCE) was measured using a photovoltaic quantum efficiency (QE) instrument, PVE300 (Bentham), with a dual xenon/quartz halogen light source, measured in DC mode, and no bias light was used in the wavelength range 300 – 800 nm. A Coherent OPerA

Solo optical parametric amplifier pumped with a Coherent LibraTM regenerative amplifier (50 fs, 1 kHz, 800 nm) was used to generate a 600 nm excitation beam.

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Chapter 4 Surface Passivation for Stable Perovskite Photovoltaics*

This chapter demonstrates a feasible way to improve the stability of perovskite photovoltaics through interfacial modification. The moisture and thermal stability are improved through the use of cesium oleate to modify the perovskite/hole transporting material (HTM) interface. The bonding between cesium oleate and perovskite film is investigated and the resulted devices are characterized. The results are discussed in detail in this chapter.

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4.1 Introduction

Over the last few years, perovskite solar cells (PSCs) have undergone a significant surge in efficiency, soaring from 3.8% in 2009 to over 24.2% in 2018¹⁻³. Organic-inorganic lead-halide PSCs emerge from the confluence of many promising properties, including tunable direct band gap⁴⁻⁶, high optical absorption coefficient in visible range^{7,8} and long carrier diffusion lengths⁹⁻¹¹. Owing to Earth-abundant starting materials and solution-processability, PSCs are considered low-cost solar technology^{12,13}. However, PSCs that have been developed are also notoriously unstable, especially over the long-term stability under ambient, atmospheric conditions¹⁴⁻¹⁶. This has been ascribed to partly the hydrophilicity of small organic cation as well as low formation energy of the three-dimensional (3D) perovskites^{17,18}. Thus, promoting the ambient stability of perovskites has become a key research focus.

Introducing relatively bulkier and more hydrophobic organic species on top of the perovskite layer is one of the primary solutions to address the material's intrinsic moisture instability¹⁹⁻²¹. However, such approach often involves the use of organics with ammonium functionality where common examples include butyl ammonium (BA^+)^{19,22}, phenyl ethyl ammonium (PEA^+)^{20,23}, 5-ammonium valeric acid (AVA^+)²⁴, and cyclohexyl methyl ammonium (CMA^+)²⁵. Although they were suggested to be capable of passivating the small cation vacancy within the 3D perovskite surface or grain boundaries, their presence also tends to induce reconstruction of perovskites due to the templating effect of the ammonium group^{26,27}. As a consequence, since charge conduction in the reconstructed perovskites is poorer, the power conversion efficiency of the overall PSCs often gets compromised.

Figure 4.1 a.) Molecular structure of cesium oleate used to passivate perovskite film in this study. Blue, red, and brown spheres represent cesium, oxygen, and carbon atoms, respectively. b) Schematic showing how the organic long chain orientates outwardly to protect the perovskite layer. Pink spheres represent FA, MA or Cs cations; cyan and yellow ones represent Pb and halide atoms (I or Br) respectively.

In addition to ammonium-based organic cation, the accompanying anion has often been halides (bromide and iodide) that are light sensitive and prone towards oxidation^{19–25}. It has been reported that moisture induced degradation of perovskite can be catalyzed by other factors such as light and oxygen due to degradation of different component of the materials, such as the halides^{28,29}.

Motivated to improve the moisture tolerance of the PSCs, without sacrificing their power conversion efficiency, the aim is to incorporate thin passivation layers that does not affect the perovskite's three-dimensional structure and does not contain any halide as the anion. To achieve this, cesium oleate (Cs-oleate) is selected, which comprising a long hydrocarbon organic endowed with carboxyl functionality (COO^-) and small inorganic cation (Cs^+) as the passivating agent (Figure 4.1a). The advantage of using the passivator is two-fold. First, by using

Cs⁺ as cation, low dimensional perovskite formation can be avoided. Instead, the Cs ion can diffuse into perovskite lattice and passivate the cuboctahedral vacancies of the host 3D perovskites due to its size and mobility³⁰. The presence of extra Cs⁺ upon passivation is expected to improve the thermal stability of the material^{31–33}. Secondly, the presence of carboxyl head in the oleate anion opens-up the possibility of it being anchored onto perovskite surface through chemical bonding with undercoordinated Pb²⁺ moiety. This allows the hydro-phobic hydrocarbon chain to be arranged upwardly to protect perovskite film from moisture, slowing down the degradation of the material under ambient condition (Figure 4.1b). At the same time, the bonding with Pb²⁺ serves as passivation towards iodide vacancy, thus reducing the possible trap states within the material's surface and grain boundaries.

4.2 Materials Synthesis

The perovskite films are based on the mixed-cation mixed-halide Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃ composition unless otherwise stated and were prepared as previously reported³⁴. Meanwhile, the passivating agent Cs-oleate was synthesized based on a published procedure³⁵ with little modification and used freshly upon preparation. Toluene was employed as the solvent in this project instead of the more common 1-octadecene because the former has a much lower boiling point and thus would only require moderate temperature to remove solvent residue. Cesium-oleate was prepared by mixing cesium carbonate (Cs₂CO₃), oleic acid (molar ratio 1:3) and anhydrous toluene in a round bottom flask. The mixture were stirred and heated in 100 °C-oil bath under inert gas environment, until the Cs₂CO₃ was fully dissolved. Then, the round bottom flask was transferred in glovebox. Measure the volume of the solution to calculate the concentration of Cs-oleate in toluene. The Cs-oleate salt would precipitate at room temperature. Heat the mixture at 80 °C, and add in anhydrous isopropanol (IPA) of 1:1 volume ratio with as-prepared solution. Thus, the Cs-oleate stock

solution was prepared in toluene and IPA mix solvent, which is clear with light-yellow in color. For the passivation solutions, Cs-oleate stock solution was diluted into 5 mM, 10 mM, 20 mM, and 40 mM with anhydrous toluene in glovebox. The as prepared Cs-oleate solutions were then spin coated on top of triple-cation perovskite, followed by an annealing process to form a hydrophobic layer on top of perovskite film. During the annealing process, color change of the films could be observed from blue to dark brown which becomes more obvious with higher concentration of the passivator, as shown in Figure 4.2. The color was observed due to the reflection of light. In the initial stage when color changed from blue to brown, it could probably due to the evaporation of toluene solvent. Then, the dark brown color gradually disappeared and the film was becoming smoother. This would probably be because the oleate chains changed their orientations and became more organized. So that the film looked smoother.

Figure 4.2 Photographs of a perovskite film treated with Cs-oleate (40 mM in this case). Color change was observed during the annealing process applied upon spin coating, implying the reaction happening between Cs-oleate and perovskite films.

To confirm the presence of Cs-oleate and its interaction with perovskite surface, the Fourier-transform infrared spectroscopy (FTIR) spectrum of passivated perovskite film was compared to that of bare perovskite film (Figure 4.3a). New peaks in the range of 2750 and 3100 cm^{-1} are ascribed to the C-H stretching bands in the organic oleate, and thus, it confirms the successful deposition of Cs-oleate on perovskite film after the spin coating process. The bonding between Cs-oleate and perovskite is assessed by measuring the FTIR peaks of Cs-oleate and PbI_2 .

Cs-oleate was deposited on top of PbI_2 film, and the FTIR spectrum is compared with the one of pristine Cs-oleate. The results shows that the $\text{C}=\text{O}$ bond stretching in oleate is shifted from 1553 cm^{-1} to 1533 cm^{-1} (Figure 4.3b), indicating that the chemical environment of the atoms has changed.

Figure 4.3 a) Infra-red (IR) spectra of the Cs-oleate-passivated and pristine perovskite films with blue shaded region indicates the C-H stretching of Cs-oleate passivator b) IR spectra of PbI_2 , Cs-oleate and Cs-oleate-treated PbI_2 . There is a shift in 1553 cm^{-1} peak to around 1533 cm^{-1} which is believed due to binding of the carboxylate group with the under-coordinated Pb in PbI_2 . The coordination causes the $\text{C}=\text{O}$ binding to weaken, which leads to stretching shift to lower wavenumber as schematically shown in Figure c) Green shaded region shows new peaks in Cs-oleate-treated PbI_2 that appear at 1323 and 1441 cm^{-1} .

In particular, the shift to smaller wavenumber is consistent with bond formation between the oleate and Pb^{2+} atom where the bond resonance within carboxyl functionality becomes restricted, leading to stronger bond stretching (Figure 4.3c). Moreover, new peaks appear at 1323 cm^{-1} and 1441 cm^{-1} , which probably

belong to Pb-oleate. It is believed that similar bonding between Pb and oleate has also occurred during the passivation of perovskite films. Such bonding can then help anchor the organic oleate onto the perovskite surface with preferred orientation where the organic tails is facing outward, forming a hydrophobic net. Such hydrophobic layer believed to be responsible for protecting the perovskite film from moisture attachment as has been seen from previously mentioned investigations.

4.3 Film Characterization

With Cs-oleate passivation, surface property of perovskite films was observed to change significantly. In order to monitor the water repellancy, water contact angle measurement was conducted (Figures 4.4a and b). For the bare perovskite film, the contact angle is 76.7 degree while the contact angle of Cs-oleate passivated perovskite film was found to be significantly higher (107.4 degree), indicating a much higher hydrophobicity profile that could potentially slow down the degradation of perovskite by repelling moisture from attacking the perovskite surface.

Figure 4.4 a) and b) Contact-angle measurement with water droplets for the pristine and Cs-oleate-passivated perovskite films, respectively.

The contact angle of water droplet on perovskite films changes over time due to the spread of water and degradation of perovskite, and it is monitored in Table

4.1.

Table 4.1 Contact angle measurement over time.

Time (min)	0	1	2	3	4
Control	77.1	59.6	57.8	56.0	54.2
Passivated	107.1	85.3	81.7	79.7	78.2

From the optical absorption spectra (Figure 4.5a and b), as the concentration of passivation increases, the absorption edges of perovskite films are found to be gradually blue-shifted. This suggests that the relative amount of Cs cations in the bulk perovskite films has increased after passivation using Cs-oleate. Due to its relatively smaller size, Cs^+ has no difficulties to diffuse into the perovskite lattice and this Cs-rich perovskite has larger bandgap compared with control triple cation perovskite, revealing the blue-shift in absorption edge.

Figure 4.5 a) Ultra-violet (UV)-visible light absorption spectra, and b) shows the zoom in of a) at the absorption edge.

The photoluminescence (PL) and time-resolved PL of perovskite films with and without Cs-oleate passivation were also examined and the spectra are depicted in Figures 4.6a and b. In agreement with their UV-vis absorption features, upon Cs-oleate passivation, the perovskite films emit PL peaks at lower wavelength compared with the pristine films. Additionally, the highest intensity PL of

passivated film exhibit longer lifetimes (all of the PL curves were fitted with a double-exponential decay function, to deconvolute the fast and slower decay kinetics) which could suggest that the non-radiative recombination paths on the perovskite surface are suppressed (Table 4.2). In particular, with 20 mM concentration of Cs-oleate the photo-generated charge carriers decay slowed down from ~ 130.7 ns to ~ 239.2 ns.

Figure 4.6 a) Photoluminescence (PL) spectra, b) Time-resolved PL spectra of pristine and Cs-oleate treated perovskite films

Table 4.2 Summary of photoluminescence lifetime of pristine and Cs-Oleate-treated 3D perovskites.

	τ_{ave} (ns)
Control	130.7
5mM Cs-Oleate	156.6
10mM Cs-Oleate	139.3
20mM Cs-Oleate	239.2
40mM Cs-Oleate	172.0

4.3.1 Stability

Optical absorption of both pristine and passivated perovskite films before and after moisture exposure was recorded to monitor the stability of perovskite films

(Figure 4.7a). The films were exposed to ambient condition with relative humidity of $\sim 70\%$ at room temperature for 7 days. It is clearly seen that over that period of time, the pristine perovskite film degrades much faster, evidenced by the diminishing visible light absorption of the 3D perovskite and concomitant increase of PbI_2 absorbance band at ~ 500 nm. Physically, while the bare perovskite film started to turn yellow, the passivated film did not show significant sign of degradation (Figure 4.7a, insets).

Figure 4.7 a) UV-visible light (UV-vis) absorption spectra of passivated and pristine films before and after exposure to ambient condition with relative humidity of $\sim 70\%$ at room temperature for 7 days. Green shaded region indicates the absorption of PbI_2 as a byproduct of perovskite degradation. Insets show photographs of aged perovskite films, demonstrating the enhanced moisture stability in the passivated perovskites. b) Associated glancing-angle X-ray diffraction (GAXRD) patterns of perovskite films before and after moisture exposure at the same condition as that of a). Consistently, severe degradation is observed in the pristine perovskite film. Asterisks and crosses denote the major reflections from hydrated perovskite and PbI_2 , respectively.

Glancing-angle X-ray diffraction (GAXRD) patterns of perovskite films before and after moisture exposure affirm the results of UV-vis absorbance data where PbI_2 peak at 12.6° increases more significantly in the pristine film than in the passivated one (Figure 4.7b) during the testing period. In addition, the peak at

10.6°, believed to derive from perovskite hydrate intermediate, also shows much higher intensity in the control than the passivated film¹⁴. These results attest to the passivating effect of the Cs-oleate on enhancing the moisture stability of the perovskite at ambient condition.

Figure 4.8a shows the GAXRD profiles of perovskite films with different passivation concentration of Cs-oleate (0 mM, 5 mM, 10 mM, 20 mM and 40 mM). It is worth mentioning that no traces of low dimensional perovskite peaks were detected under XRD even with 40 mM concentration of Cs-oleate, affirming the notion that the oleate chain just passivates the surface and grain boundaries of 3D perovskite film, instead of diffusing and forming any low dimensional perovskite species. This demonstrates an advantage of utilizing oleate chain to passivate perovskite film as it keeps the perovskite 3D structure intact.

Treating perovskite films with the passivator will concomitantly increase the cesium content in the materials. Figure 4.8b shows the GAXRD patterns of thermal testing of films treated with different concentration of Cs-oleate. It is found that concentration of Cs-oleate as small as 10 mM is able to improve the thermal stability of perovskite film. Heating the treated film at 85°C for 4 hours under inert argon atmosphere in the absence of light, 3D perovskite was found to be intact, as evidenced by the GAXRD patterns of the aged samples. On the other hand, PbI₂ peak at 12.6° can clearly be seen in the control films under the same condition and period of testing. It has been reported that inorganic cesium cation plays a very crucial role in improving stability of perovskite towards thermal stress^{36–38}. Thus, the method demonstrates a unique strategy of not only enhancing moisture resistance of 3D perovskite, but also thermal stability through cesium-doping.

Figure 4.8 Glancing-angle X-ray diffraction (GAXRD) patterns of pristine and Cs-oleate treated perovskite films before (a) and after (b) exposure to thermal stress at 85 °C for 4 hours under inert atmosphere environment. Asterix denote peak of PbI₂ produced upon degradation of the perovskite.

4.3.2 Morphology

Experiment has carried-on to probe the effect of different concentration of Cs-oleate towards perovskite films morphological, structural and optoelectronic properties. The surface morphology of pristine and passivated perovskite films is examined by Scanning Electron Microscopy (SEM; Figure 4.9) and Atomic Force Microscopy (AFM; Figure 4.10). As shown in Figure 4.9, the films treated with Cs-oleate feature compact uniform perovskite crystallites with grain sizes in the range of 200-400 nm, comparable if not better than the untreated film. This suggests that upon spin coating Cs-oleate solution, the 3D perovskite did not undergo reconstruction as no 2D perovskite was forming during annealing. The organic species instead only passivates the 3D perovskite's surface and grain boundaries rather than diffusing into its layer, as supported by the cross-sectional SEM images depicted in Figure 4.12 Cs-oleate treatment was also found to not significantly modify surface roughness of the 3D perovskite (Figure 4.10). Concentrations of Cs-oleate of up to 10 mM still afford films with similar surface roughness to that of standard (25.3 nm of roughness in comparison to 20.5 nm),

although a rougher film would be obtained at 40 mM concentration (30.3 nm), suggesting a thicker layer of passivator could have formed at higher concentration. Table 4.3 summarizes the change of roughness of perovskite films as the function of Cs-oleate concentration.

Figure 4.9 Top morphological view of field electric scanning electron microscope (FE-SEM) images of 3D perovskites without and with Cs-oleate treatment.

Figure 4.10 Topological views of perovskite films control (a and b), treated with 5 mM Cs-oleate (c and d), 10 mM Cs-oleate (e and f), 20 mM Cs-oleate (g and h), as well as 40 mM Cs-oleate (i and j), as collected from atomic force microscope (AFM).

Table 4.3 Summary of surface roughness of perovskite films with and without Cs-oleate treatment.

Sample	Area of (5×5) μm^2	Area of (10×10) μm^2
Control	17.669 nm	20.531 nm
5 mM	21.162 nm	23.427 nm
10 mM	23.631 nm	25.273 nm
20 mM	30.157 nm	30.951 nm
40 mM	27.000 nm	30.372 nm

4.4 Device Characterization

Figure 4.11 Perovskite solar cell architecture.

To assess whether the Cs-oleate-passivated perovskite films can enhance the solar cell performance, devices are fabricated based on an n type–intrinsic–p type (n–i–p) mesoporous heterojunction architecture (Figure 4.11). Patterned FTO/glass as conducting substrate, TiO_2 compact layer and mesoporous TiO_2 are used as electron-transporting materials, while Spiro-OMeTAD is utilized as hole-transporting material. The Cs-oleate passivation layer is used to modify the interface between perovskite film and hole-transporting layer.

Figure 4.12 shows the cross-sectional scanning electron microscopy (SEM) images of the solar cell devices prepared with standard triple-cation and Cs-oleate-treated perovskite films. The relative thickness of the perovskite layer for

both devices was found to be similar at approximately 500 nm. As can be seen, treatment with Cs-oleate with concentration as high as 40mM does not cause restructuring of perovskite crystallite grains.

Figure 4.12 Cross-sectional view of field electric scanning electron microscope (FE-SEM) images of perovskite solar cells without and with Cs-oleate treatment.

4.4.1 Device Performance

The influence of passivation on open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) was studied, which are summarized in Figure 4.13a-d. Cs-oleate passivated devices generally exhibit higher V_{oc} and FF, resulting in higher PCE as compared to standard devices. The gradual increase of V_{oc} as concentration of Cs-oleate increases up to 10 mM is believed due to passivation effect towards surface defects of the perovskite layer that leads to reduced interfacial recombination.

Figure 4.13 Statistical representation of devices for the standard and Cs-oleate-treated devices for parameters (a) Open circuit voltage (V_{oc}), (b) Short-circuit current (J_{sc}), (c) Fill factor (FF), and (d) Power conversion efficiency.

Interestingly, the J_{sc} of Cs-oleate-passivated devices are not greatly affected by the passivation up to 20 mM. This can be achieved due to the undisrupted structure of 3D perovskite upon passivation as no bulky organic cation is used. The charge transport is only compromised when the passivation is increased to

40 mM which is possibly due to the insulating nature of oleate chains that is lying in between the perovskite/spiro-OMeTAD interface.

The device fabricated with a standard triple-cation perovskite yielded an average PCE of 17.58% with an average V_{oc} , J_{sc} , and FF of 1.10 V, 21.15 mA cm⁻², and 75.35%, respectively. The device fabricated with 10 mM modification gave an average PCE of 18.01% with a V_{oc} of 1.12 V, J_{sc} of 21.11 mA cm⁻², and FF of 76.34%. Consistent with the statistical data presented earlier, the passivated device exhibits better V_{oc} and FF, while retaining good J_{sc} . The current-voltage (I-V) characteristics of best performing devices of Cs-oleate passivated (10 mM) and pristine perovskites measured under a simulated air mass (AM) of 1 sun illumination (100 mW cm⁻²) are depicted in Figure 4.14.

Figure 4.14 Current–voltage (J – V) curves of standard and 10 mM Cs-oleate-treated film devices subjected to forward and reverse bias scan direction.

Additionally, comparing the reverse and forward scans of both devices. The device fabricated with 10 mM Cs-oleate-treated films exhibited a V_{oc} of 1.12 V,

J_{sc} of 21.33 mA cm^{-2} , FF of 76.44%, and PCE of 18.31%, observed in the reverse scan direction, and a V_{oc} of 1.09 V, J_{sc} of 21.64 mA cm^{-2} , FF of 66.67%, and PCE of 15.70% in the forward scan direction, whereas the standard device exhibited a V_{oc} of 1.10 V, J_{sc} of 21.56 mA cm^{-2} , FF of 74.41%, and PCE of 17.65% in the reverse scan direction and V_{oc} of 1.09 V, J_{sc} of 21.64 mA cm^{-2} , FF of 69.53%, and PCE of 16.34% in the forward scan direction under 1 sun illumination. The reverse scan shows enhanced V_{oc} , FF, and PCE when compared to forward scan for 10 mM Cs-oleate-treated and standard devices.

Figure 4.15 Incident photon-to-current conversion efficiencies (IPCE) of best performing perovskite solar cells without and with Cs-oleate treatment (1 sun; AM 1.5G).

The relatively unchanged current collected from device upon Cs-oleate passivation is reflected in the accompanying incident photon-to-current conversion efficiency (IPCE) spectra shown in Figure 4.15 where no major difference can be observed in comparison to that of control. The IPCE spectra

shows devices treated with different concentrations of Cs-oleate and non-passivated device.

Figure 4.16 Nyquist plots of perovskite devices with and without Cs-oleate passivation. Measurement was done with 0.85 V bias under constant illumination.

The impedance of perovskite devices with and without passivation is shown in the Nyquist plots in Figure 4.16. The single semicircle of the plots represents the charge recombination resistance. The diameters of the semicircle of Cs-oleate passivated device is larger than that of control device, which reveals that the passivated perovskite device has higher recombination resistance.

4.4.2 Device Stability

Figure 4.17a shows the stabilized photocurrent density measured as a function of time to compare the performance of Cs-oleate passivated device and the control device. It was found that device passivated with Cs-oleate displays better stability towards long-term light soaking as compared to control device.

Figure 4.17 a) Stabilized photocurrent density at the maximum power point (PP_{max}) vs time for the unsealed standard and 10 mM Cs-oleate-treated devices. b) Evaluation of photovoltaic power conversion efficiencies of unsealed mesoporous devices that were stored under $\sim 55\%$ relative humidity and dark conditions.

To demonstrate the benefit of having Cs-oleate as the perovskite capping layer toward moisture, the shelf stability studies of complete devices based on 10 mM is also carried out and compared with the standard under ambient environments at room temperature under relative humidity (RH) of $\sim 55\%$ without any encapsulation. The Cs-oleate passivated device retained 88% of its original

power conversion efficiency after 720 hours while that of control device was dropped to ~69%, which is unsatisfied for practical working condition (Figure 4.17b). Therefore, the Cs-oleate significantly improved the moisture and thermal stabilities of perovskite solar cells in agreement with improved stability features of perovskite films discussed prior.

4.5 Conclusion

In summary, efficient and moisture-stable perovskite solar cells are fabricated by passivating the perovskite film with a layer of cesium oleate. Cs-oleate as the passivator shows unique advantages over other passivators mainly in two aspects. First of all, the small Cs cation in Cs-oleate is able to diffuse into perovskite lattices, passivating the cuboctahedral vacancies of the host 3D perovskites due to its size and mobility. The resulted Cs-riched perovskite film also shows enhanced thermal stability.

In addition, the carboxyl group in oleate anchored the organic chain to Pb-X framework, significantly improving the moisture tolerance of perovskite. The water contact angle increased from 76.7 degree to 107.4 degree, indicating that the surface property changed from hydrophilic to hydrophobic. For the device performance, V_{oc} and fill factor improved with Cs-oleate treatment due to the passivation of defects. The overall efficiency also increased with smaller deviation compared to the control devices. Device efficiency of passivated device retained close to 90% of its initial PCE over 720 hours under 55% RH at room temperature. Therefore, surface passivation using Cs-oleate is a feasible way to improve the moisture stability of perovskite solar cells with improved performance.

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Chapter 5 Mix-dimensional Perovskite for Flexible Photodetector

This chapter is devoted to improve the stability of perovskite optoelectronic devices using mix-dimensional perovskite. A hot casting method is used to fabricate the mix-dimensional perovskite films, and the film quality is subsequently compared with the one fabricated by normal spin coating method. The hot casted mix-dimensional perovskite film shows better moisture stability, and the device exhibits longer lifetime compared with 3D perovskite-based device. The mix-dimensional perovskite is also employed as the active material in flexible photodetector which shows impressive performance with long-term stability.

5.1 Introduction

Organic-halide perovskite is an emerging material system for optoelectronic applications, such as photovoltaics, light emitting diodes (LED), and photodetectors, from the confluence of many promising properties, including tunable band gap^{1,2}, high optical absorption coefficient in visible range³⁻⁵ and long carrier diffusion length⁶⁻⁸. Due to its solution-processability and abundant raw materials, perovskite materials are employed in photovoltaics reducing cost of solar cells⁹⁻¹³. Though performance of PSCs might be expiring, the problems of these devices are also serious, including the toxicity and instability. The instability of perovskite devices can be caused by light, thermal, oxygen and moisture, which limits the application of perovskite devices¹⁴⁻¹⁶.

2D perovskites, by substituting A-site with bulky organic ammonium cations, is convinced to be one of the solutions to improving the air stability of 3D PSCs¹⁷. Due to the larger size of the bulky organic ammonium cation, the network of BX_6 are expanded and thus separated, becoming layered structure¹⁸. By mixing layered structured perovskite with 3D perovskite, the dimensionality can be tuned and named mix-dimensional perovskites¹⁹. In Figure 5.1, mix-dimensional perovskite based solar cells provide a facile approach to improving stability of PSCs and aroused more interests^{18,20}. The organic layers insulate moisture from degrading of perovskites, therefore mix-dimensional perovskites have become a stable alternative material for optoelectronic applications²¹⁻²³.

Figure 5.1 a) Crystal structure of 3D and 2D perovskites. b) XRD peaks of 2D perovskite (1) and 3D perovskites (2a & 2b) over 46 days¹⁸.

Perovskites are also an inspiring material in photodetection applications. Photodetectors are essential devices in various applications, such as sensing, communication systems, and environmental monitoring^{24–27}. Perovskite also offers the opportunity of large-area and flexible photodetector devices, which can be applied in wearable devices, displays for electronics, and biosensors^{25,28–30}.

Figure 5.2 a) Schematic diagram showing the working principle of MAPbI_3 based flexible photodetector. b) Energy diagram of perovskite active material and electrodes.³¹

In Figure 5.2, the first work in flexible perovskite photodetector was demonstrated in 2014, with simple configuration of $\text{ITO}/\text{MAPbI}_3/\text{ITO}$ ³¹. The

device shows a photo-responsivity of 3.49 A W^{-1} at 365 nm, and 0.0367 A W^{-1} at 780 nm. However, the on/off ratio of the device at 8 V was only 20, and the sensitivity is not high enough. Research works on improving the performance of perovskite based photodetectors are carried out over the years. Besides, 3D perovskite is known to be unstable in ambient environment. Therefore, 2D perovskite as active material provides a solution to improve the stability of devices. 2D perovskites also show promising capability for photodetection, which benefit from its anisotropic structure. 2D perovskites consist of alternating layers of inorganic framework and bulky organic cations, which act as wells and barriers respectively. The intra-well charge conductive channels allows charge transport across the organic layers^{23,32–36}. In addition, due to the spatial confinement effect, the carrier lifetime is prolonged in 2D perovskites.

However, it still remain challenge to selectively suppress dark current and enhance photocurrent along charge transport direction. Recently, 2D Ruddlesden-Popper perovskite was discovered to have exotic edge states, which are able to dissociate bound excitons rapidly³⁴. The discovered edge feature may create new opportunities to crosslink the intra-well exciton formation to orthogonal free-carrier edge conduction.

5.2 Material Synthesis

Here, mix-dimensional perovskites is applied in flexible photodetector as an active material. The mix-dimensional perovskites have a general molecular formula of $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$, where $n=1, 2, 3, 5$. In this chapter, 2:1, 2:2, and 2:4 refer to the molar ratio of PEA^+ and MA^+ , which represent $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively.

The phenethylammounium iodide (PEAI) was synthesized by adding 12.6 ml of phenyl ethylamine into a mixture of ethanol (15 ml) and DI water (15 ml) in round-bottom flask soaking into ice/water bath. Around 14.51 ml of HI was added to the flask dropwise and the color turned brownish. After stirring for 10

min in an ice/water bath, the solution was taken out from the ice bath and cooled down to room temperature. Rotary evaporator was used to remove the solvent at 45 °C, followed by recrystallization. The crystals were later dissolved in large amount of ethyl acetate mixed with 10 ml ethanol, then the solution was heated up to 80 °C while stirring until no remnant. Crystals were precipitated out by cooling down the solution and filtered after shaking the bottle gently, followed by drying in vacuum oven overnight at 60 °C.

Zn₂SnO₄ nanoparticle, as the electron transporting material, was synthesis at low temperature (< 100 °C) as described in ref³⁷, and the colloidal was dispersed in ethanol. The Zn₂SnO₄ nanoparticle solution was deposited on pre-etched ITO/glass or ITO/PET substrates by spin coating at 3000 rpm for 30 seconds, followed by annealing at 150 °C for 2 hours.

The mix-dimensional perovskite films were prepared through hot casting method²³. The perovskite precursor (1.2 M) and substrates were preheated to 70 °C and 100°C, respectively. The hot precursor was span onto the hot substrate and started spin coating immediately (2000 rpm for 30 sec), followed by annealing at 120 °C for 20 min. A solution of PTAA of 10 mg/ml in toluene was spin coated on the perovskite film at 3000 rpm for 60 sec. Au electrodes (~100 nm) were thermally evaporated on samples with the size of 0.2 cm x 0.2 cm using a shadow mask.

The quality of mix-dimensional perovskite films deposited through hot casting method and normal spin coating method is compared using X-ray diffraction. The peak position and intensity can be used to analyze the phase and crystal size of the perovskite, as shown in Figure 5.3. The peak at 5.4° belongs to pure 2D perovskite, PEA₂PbI₄, which can also be observed in the mix-dimensional perovskite (PEA₂MA₁Pb₂I₇ and PEA₂MA₂Pb₃I₁₀) in Figure 5.3a. This indicates that the mix-dimensional films contain a mixture of 2D and 3D phases in normal spin-coating method. While in Figure 5.3b, there is no peak at 5.4°, which shows that the hot casting method can reduce phase separation in mix-dimensional perovskite.

Figure 5.3 XRD profiles of PEA_2PbI_4 and mix-dimensional perovskite films through a) normal spin coating method, and b) hot casting method. (PEA, 2:1, 2:2, 2:4 represents PEA_2PbI_4 , $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively)

According to previous study, layered perovskite films are found to be a mixture of layered and three dimensional (3D)-like phases with phase separations at micrometer and nanometer scale in both vertical and lateral directions. This was explained by the surface initiated crystallization process and the competition of

the crystallization between 3D-like and layered perovskites. As such, the difference of resulting films produced by normal spin coating and hot casting can be attributed to variation in relative abundance between different perovskites species (and presumably, their distribution) in the final films. The intense GAXRD peaks of $2\theta = 14.2^\circ$ and 28.45° presented in Figures 5.3a and b can be attributed to the (110) and (220) crystallographic planes from 3D perovskite MAPbI₃. While those peaks are solely observed in hot casted samples, additional peaks are found in GAXRD pattern of the normal spin coated sample. Although growing of single crystals of the corresponding pure phases is needed for confirmation, we ascribe the aforementioned extra peaks to perovskite phases of low dimensionalities (e.g. $n = 2, 3$, or 4). This implies that hot casting method was able to yield perovskite films with more dominant 3D perovskite phase in comparison to that of normal spin coating

The intensity ratio of peak at 5.4° over peak at 14.2° is calculated in Figure 5.4a. The control represents the perovskite films deposited through normal spin coating method, while the other one fabricated through hot casting method. For hot casting method, the intensity ratio is always smaller than 0.1, which means only a small portion of phase separation occurs in the film. In addition, the value is much smaller than that of normal spin-coated films, especially for PEA₂MA₁Pb₂I₇ and PEA₂MA₂Pb₃I₁₀ (2:1 and 2:2). Therefore, less phase separation can be achieved through hot casting method.

Figure 5.4 a) Full width at half maximum (FWHM), and b) intensity ratio of 5.4°/12.4° of mix-dimensional perovskite films through normal spin coating method and hot casting method. (PEA, 2:1, 2:2, 2:4 represents PEA_2PbI_4 , $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively)

To reveal the crystal size of the film, the Full Width at Half Maximum (FWHM) of the peak around 14.2° is compared, which belongs to the mid-dimensional perovskite. For $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, the FWHM is comparable between the two methods, while for $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$, the hot-casted film shows a higher FWHM than normal spin-coated film, indicating a larger crystal size in the film.

5.3 Film Characterization

The absorption spectra of mix-dimensional perovskite films, as shown in Figure 5.5, are used to characterize the optical bandgap and exciton peaks. The multiple excitonic absorption peaks around 515 nm, 565 nm and 610 nm indicates a mixture of multiple phases within the films.

Figure 5.5 Absorption spectra of PEA_2PbI_4 and mix-dimensional perovskite films. (PEA, 2:1, 2:2, 2:4 represents PEA_2PbI_4 , $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively)

The absorption edge of 2D perovskite (PEA_2PbI_4) and mix-dimensional perovskite ($\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$) are used to obtain the optical bandgap (Figure 5.6). The bandgap of PEA_2PbI_4 is found to be 2.33 eV, which is in good agreement with the reported values of layered perovskite. However, the derived bandgap of $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ (1.52 eV) is similar to the bandgap of MAPbI_3 . The results show that the MAPbI_3 phase co-exist in the film.

Figure 5.6 Tauc plots of a) PEA_2PbI_4 , and b) $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ at the absorption edge.

Figure 5.7 SEM top view images of a) & b) PEA_2PbI_4 , c) & d) $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, e) & f) $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and g) & h) $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$.

The morphology of mix-dimensional perovskites is characterized by SEM as shown in Figure 5.7. The surface of 2D perovskite is very rough, while the mix-dimensional perovskite films are relatively smooth. $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$ and $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ films look more uniform and with little pinholes. However, as the MA^+ ratio increasing, the perovskite film shows more pinhole formed and less uniform.

5.4 Device Performance

The performance of mix-dimensional perovskite-based photodetector is first characterized on rigid substrates (glass/ITO). The photodetector is in vertical structure, with a configuration of ITO/ Zn_2SnO_4 /perovskite/PTAA/Au, as shown in Figure 5.8.

Figure 5.8 Device configuration of perovskite photodetector, with Zn_2SnO_4 as electron-transporting material and PTAA as hole-transporting material.

The logarithmic current-voltage (I - V) characteristics of photodetectors based on PEA_2PbI_4 and mix-dimensional perovskite are shown in Figure 5.9, where 2:1, 2:2, 2:4 refer to the molar ratio of PEA^+ and MA^+ , and represent $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively.

Figure 5.9 Logarithmic I - V characteristics of PEA_2PbI_4 and mix-dimensional perovskite devices a) in the dark, and b) under illumination (55 mW/cm^2). (PEA, 2:1, 2:2, 2:4 represents PEA_2PbI_4 , $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively)

In Figure 5.9a, the dark current of PEA_2PbI_4 is extremely low. For 2:1 and 2:2 devices, the dark current at 1 V increases to few tens of nano ampere (nA), due to the enhanced conductivity by 3D perovskite layers. Further increase the MA^+ ratio in mix-dimensional perovskite, the dark current of 2:4 device rises to hundred nA. Due to the higher ratio of small organic cations (MA^+) in the film,

the carriers could find a pathway through the connected 3D blocks. Therefore, the dark current dramatically increases. In Figure 5.9b, the photocurrent of mix-dimensional perovskites are all enhanced compared with 2D perovskite, while the difference between 2:2 and 2:4 devices is not very significant. Therefore, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ (2:2) device demonstrates suppressed dark current and selectively enhanced photocurrent, which gives the best overall performance among the photodetectors.

The photoresponse of each device is measured under various irradiance from 100 mW/cm^2 to 0.13 mW/cm^2 . The results of PEA_2PbI_4 , $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ based devices are shown in Figure 5.10, 5.11, 5.12, and 5.13 respectively.

Figure 5.10 Logarithmic I - V curve of PEA_2PbI_4 , under dark and various irradiation.

Figure 5.11 Logarithmic *I-V* curve of PEA₂MA₁Pb₂I₇, under dark and various irradiation.

Figure 5.12 Logarithmic *I-V* curve of PEA₂MA₂Pb₃I₁₀, under dark and various irradiation.

Figure 5.13 Logarithmic I - V curve of $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$, under dark and various irradiation.

Table 5.1 The on/off ratio of each perovskite photodetector under various irradiance at 1 V bias.

Irradiance (mW cm^{-2})	on/off ratio			
	PEA_2PbI_4	$\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$	$\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$	$\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$
100	468	2819	11712	1603
55	307	1846	6829	893
25	206	1072	3492	511
12	148	679	1987	320
5.3	85	370	987	190
3	66	263	619	131
1.6	46	167	339	79
0.9	34	115	207	50
0.65	25	77	163	35
0.44	20	56	104	23
0.32	15	35	53	14
0.13	12	23	32	9

The on/off ratio at 1 V for each composition is compared in Table 5.1. Firstly, the mix-dimensional perovskite devices show higher on/off ratio compared with 2D perovskite (PEA_2PbI_4) except $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ at extremely low irradiance. As increasing the ratio of MA^+ in the composition, it first shows enhanced on/off ratio and then drop for the 2:4 ratio device, which is consistent with the I - V characteristics discussed previously. Therefore, the 2:2 ratio device demonstrates the best performance in terms of photodetection sensitivity. At even low irradiance of 5.3 mW/cm^2 , the on/off ratio of $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ photodetector is up to three orders of magnitude.

The photocurrent against irradiance is plotted under double log scale, and the results are fitted with a linear curve. For most of photodetector applications, it is necessary to extract the irradiance of the light based on the photocurrent values. Therefore, a linear relation of current density with irradiance is important for such applications. In Figure 5.14a, the photocurrent is fit with a linear curve and each perovskite device exhibits linear photoresponse to the irradiance.

The responsivity of each device is calculated using the equation: $R = I_{ph}/P$, where I_{ph} refers to the photocurrent and P represents the irradiance power³⁸. In Figure 5.14b, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ photodetector shows an almost constant responsivity, which is important in characterizing the light intensity range based on the photocurrent.

Figure 5.14 a) Photocurrent and b) responsivity as a function of irradiance.

The IPCE of flexible perovskite based on PEA₂MA₂Pb₃I₁₀ is measured under 0.5 and 1 V bias in Figure 5.15. The device under 1 V bias shows the highest IPCE around 450 nm, and the EQE is up to 150%. The EQE shows a gradually decrement as the wavelength increase from 450 nm to 800 nm.

Figure 5.15 IPCE of $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ flexible photodetector under 0.5 V and 1 V bias.

5.5 Stability of Films and Devices

The moisture stability of mix-dimensional perovskites is compared with 3D perovskite (MAPbI_3). The perovskite films were exposed to ambient lab condition with relative humidity of 70% at 25 °C. After 4 days, MAPbI_3 film totally degrade since perovskite peak at 14 degree disappear and moisture complexation crystals form^{39,40}. In comparison, 2D perovskite $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ film is stable without any other phase formation.

Figure 5.16 XRD profiles of as prepared MAPbI₃ and PEA₂MA₂Pb₃I₁₀ films and after exposed to ambient lab condition for 4 days.

Figure 5.17 Device stability of PEA₂MA₄Pb₅I₁₆, exposed to ambient lab environment with relative humidity of 70%, at 25 °C.

After exposed to ambient environment for 10 days, photodetector based on 3D perovskite shows no functional behavior, while the mix-dimensional perovskite device based on PEA₂MA₂Pb₃I₁₀ shows excellent on/off ratio, as shown in Figure

5.17. The dark current almost remain unchanged, while photocurrent shows a small drop at 1 V, which probably due to little degradation of the perovskite film. Overall, the device is still in good working condition with on/off ratio more than two orders of magnitude.

Figure 5.18 The current vs time (I-t) curves of a) PEA_2PbI_4 , and b-d) mix-dimensional perovskite devices under light pulse (55 mW/cm^2 , 1 V bias). (PEA, 2:1, 2:2, 2:4 represents PEA_2PbI_4 , $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, and $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ respectively)

The stability of photodetector at working state is also tested under 1 V bias. Upon a continuous light pulse, the current changes over time are recorded for each perovskite. 2D perovskite photodetector shows very stable output signals, while as increasing the MA^+ ratio in the mix-dimensional perovskite, it shows a trend of decreasing photocurrent, which is obvious in the $\text{PEA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ (2:4) device.

On the other hand, for $\text{PEA}_2\text{MA}_1\text{Pb}_2\text{I}_7$ (2:1) device, the dark current tends to rise. In comparison, the $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ (2:2) device maintains a high on/off ratio, meanwhile it exhibits a relatively stable dark current and the photocurrent maintains at same level. Therefore, the overall performance of $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ (2:2) device is the best among the devices with stable signal output.

5.6 Bending Test

Figure 5.19 Flexible photodetector based on $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ under a) flat, and bending radius of b) 0.81 cm, c) 0.73 cm, d) 0.58 cm. d) I - V curves of device under each bending condition. e) on/off ratio of each condition vs bending radius.

The flexible perovskite photodetector is tested under various bending radius (0.81 cm, 0.73 cm, 0.58 cm), as shown in Figure 5.19. The dark currents remains unchanged for each condition, while only a small drop of photocurrent at 1 V compared with flat sample, can be observed. The on/off ratio under each condition is plotted in Figure 5.19e, all the values are more than two orders of magnitude, which shows no significant effect on the device performance.

Figure 5.20 I - V curve of flexible photodetector based on $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ after bending for 60 cycles, with bending radius of 1.3 cm.

The cyclability of the flexible photodetector based on $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ is measured after bending for 60 cycles with bending radius of 1.3 cm. The I - V curve is shown in Figure 5.20, and the inset image shows the device during the test. From the I - V curve, there is no significant sign of degradation in performance. Therefore, the $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ based photodetector would be stable for flexible applications.

To investigate the effect of bending on the signal output of flexible photodetector, the current of the device is continuously monitored during the change from flat to bending states. The photocurrent shows no significant affect from the shape states of the device, except the negligible distortion at the moment of deformation. Therefore, the flexible photodetector demonstrates a stable signal output regardless the shape states.

Figure 5.21 The current of flexible perovskite is monitored during the bending process (I - t curve). The bending radius is 1.3 cm.

5.7 Conclusion

In summary, another method to improve the stability of 3D perovskite optoelectronic devices is to introduce bulk organic spacer into the crystal structure. Mix-dimensional perovskites, $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=1, 2, 3$, or 5), have successfully demonstrated enhanced moisture stability, showing no significant sign of degradation after 4 days exposure to ambient lab environment with 70% RH at 25 °C.

The mix-dimensional perovskite, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, has been applied as the active material in flexible photodetector, with a device configuration of ITO/ Zn_2SnO_4 /perovskite/PTAA/Au. The device shows suppressed dark current and selectively enhanced photocurrent, results in a high on/off ratio more than four orders of magnitude. The flexible photodetector is bended at bending radius of 0.81 cm, 0.73 cm, 0.58 cm, and showing no significant sign of performance degradation. In addition, the device survived from the cyclability test (1.3 cm bending radius

for 60 cycles). Therefore, mix-dimensional perovskite based flexible photodetector has been successfully demonstrated, and exhibit enhanced stability compared with 3D perovskite.

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Chapter 6 Conclusion and Future Outlook

In this chapter, the scientific insights gained during this project to enhance the stability of three-dimensional perovskite and its optoelectronic devices are presented. Suggestions for future work related to integrated system to protect perovskite devices in practical application is proposed.

6.1 Conclusion

In this thesis, two methods of improving the intrinsic stability of organic-inorganic perovskites are demonstrated, and the enhanced performance of their optoelectronic devices are also discussed. The first method is through surface passivation of cesium oleate on three-dimensional perovskite in photovoltaics. The other method is by employing 2D/3D mix-dimensional perovskites as the alternative to 3D perovskite in photodetectors.

6.1.1 Surface Passivation of Cesium Oleate

In summary, efficient and moisture-stable perovskite solar cells are fabricated by passivating the perovskite film with a layer of Cs-oleate. Cs-oleate as the passivator shows unique advantages over other passivators mainly in two aspects. First of all, the small Cs cation in Cs-oleate is able to diffuse into perovskite lattices, passivating the cuboctahedral vacancies of the host 3D perovskites due to its size and mobility¹. The resulted Cs-riched perovskite film also shows enhanced thermal stability. Compared with other passivators that have ammonium groups, Cs-oleate passivation avoids destroying the crystal structure of perovskites, thus it is able to retain the performance of photovoltaics (PCE over 18%).

In addition, the carboxyl group in oleate anchored the organic chain to Pb-X framework, significantly improving the moisture tolerance of perovskite. The water contact angle increased from 76.7 degree to 107.4 degree, indicating that the surface property changed from hydrophilic to hydrophobic. For the device performance, V_{oc} and fill factor improved with Cs-oleate treatment due to the passivation of defects. The overall efficiency also increased with smaller deviation compared to the control devices. Device efficiency of passivated device retained close to 90% of its initial PCE over 720 hours under 55% RH at room temperature. Therefore, surface passivation using Cs-oleate is a feasible way to

improve the moisture stability of perovskite solar cells with improved performance.

6.1.2 Mix-Dimensional Perovskite

In chapter 5, another method to improve the stability of 3D perovskite optoelectronic devices is discussed by introducing bulky organic spacer into the crystal structure. Mix-dimensional perovskites, $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=1, 2, 3, 5$, or ∞), have successfully demonstrated enhanced moisture stability, showing no significant sign of degradation after 4 days exposure to ambient lab environment with 70% RH at 25 °C.

The mix-dimensional perovskite, $\text{PEA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, has been applied as the active material in flexible photodetector, with a device configuration of ITO/ Zn_2SnO_4 /perovskite/PTAA/Au. The devices show suppressed dark current and selectively enhanced photocurrent, results in a high on/off ratio more than four orders of magnitude. The flexible photodetector is bended at bending radius of 0.81 cm, 0.73 cm, 0.58 cm, and showing no significant sign of performance degradation. In addition, the device survived from the cyclability test (1.3 cm bending radius for 60 cycles). Therefore, mix-dimensional perovskite based flexible photodetector has been successfully demonstrated, and exhibit enhanced stability compared with 3D perovskite.

6.2 Future Perspective

Bio-inspired self-protection of perovskite based energy harvesting system is proposed in this chapter. In this system, it can achieve a self-protection movement of perovskite solar cell upon environmental stimuli, such as sunlight and weather. The system includes two parts, one being sensory unit, the other one being action unit. The sensory unit employs perovskite photodetector as sensor to the environment, while the action unit includes soft actuator and perovskite

solar cell. At night or during cloudy days, the system will close up to protect perovskite solar cell. Thus, it can realize a self-protection of perovskite photovoltaics.

The integrated energy harvesting system is inspired by the nastic movement of plants that occurs in response to environment stimuli, which is a fast self-protection movement by plants². For instance, the prayer plants open up their leaves in daytime to maximize exposure to sunlight for photosynthesis, and close the leaves at night to reduce water loss, shown in Figure 6.1.

Figure 6.1 Demonstration of nastic movement. Prayer plant a) in daytime, and b) at night.

The designed self-protection integrated system is shown in Figure 6.2, including a sensory unit and an action unit. The sensory unit could be the stalk of the plant and is made of perovskite photodetector that used to detect the intensity of sunlight, thus distinguishes sunny days, cloudy days or nights. The action unit could be the leaves of the plant, and consists of perovskite solar cell integrated on soft actuator. The movement of actuator can carry the solar cell. In Singapore, the humidity is generally much higher at night or in cloudy days compared to sunny days³. During nights or cloudy days, the perovskite solar cells are not in working condition nor working efficiently. The leaves of actuators will move inwards, and the solar cells are being protected by the leaves to reduce exposure

time to the humid environment. This self-protection integrated system can be the first line of defence of perovskite solar cells to minimize moisture- and photo-degradation.

Figure 6.2 Concept design of the bio-inspired self-protection energy harvesting system. The yellow shaded area refers to the action unit, which includes perovskite solar cell and soft-actuator. The blue shaded area refers to the sensory unit, which consists of perovskite photodetector.

There are two states of the system, which is achieved by the movement of actuator. The resting state (Figure 6.3a), happens during nights or cloudy days, where the leaves are closed together and create a relatively isolated environment, thus protect the perovskite solar cell from exposure to the high humidity environment. The working state (Figure 6.3a and b) is happened during sunny days. The open of the leaves (with solar cells on top) can maximize the sunlight exposure.

Figure 6.3 The design of bio-inspired self-protection of energy harvesting system. a) Resting state and b) working state of the system. c) The circuit design of the system including sensory unit and action unit.

The circuit design to achieve environmental stimuli modulated movement of actuator is realized through the circuit shown in Figure 6.3c. The sensory unit and the action unit are connected through a relay. In the sensory unit, it consists of an electrical bridge with R1, R3 of normal resistors, and R2, R4 of flexible perovskite photodetectors. Two ends of the electrical bridge are connected to a 3 V power source, while the other two ends are connected to the relay for signal output.

The resistance of perovskite photodetector under light or dark are very different. By connecting resistors of certain resistance value, it is able to change the output signal direction. Here, mix-dimensional perovskite flexible photodetector is used

in the sensory unit. The resistance of the photodetector under light and dark are around 40 kΩ, and 30 MΩ respectively. Therefore, the resistor R1 and R3 are chosen to be 400 kΩ. Using the equation 6.1 shown below, the theoretical output voltage can be calculated. U is the output voltage that connects to the relay, while U₀ is the 3 V power source. The output voltage in dark is calculated to be 2.99 V, and the one under light is -2.45 V.

$$U = \frac{R_2 R_4 - R_1 R_3}{(R_1 + R_2)(R_3 + R_4)} U_0 \quad (\text{Equation 6.1})$$

The signal output from the electrical bridge is measured using multi-meter, as shown in Figure 6.4. The output voltage is 2.2 V in dark condition, and -2.6 V under light. The opposite direction of output voltage is desired to trigger the switch of relay.

Figure 6.4 output voltage measured from the electrical bridge a) in dark and b) under light.

Once the relay is switched, the direction of voltage applied to actuator is changed, which is able to induce the movement of actuator towards different direction. Here, the soft actuator is fabricated in a sandwich structure, as shown in Figure

6.5a. The electrodes are made by drop casting a solvent of multiwall carbon nanotube (MWCNT), PVDF and electrolytes, followed by the evaporation of gold (Au) layer. A separator layer of PVDF and electrolyte is sandwiched by two electrode layers to form the soft actuator. In Figure 6.5b, the current of actuator under applied voltage pulse is monitored, accompanied by the bending movement of actuator in opposite directions.

Figure 6.5 a) Configuration of soft actuator. b) Current measured through the actuator under voltage pulse.

Figure 6.6 a) Flexible perovskite solar cells. b) Device architecture of flexible perovskite solar cell.

Flexible perovskite solar cell is integrated on soft actuator. The bending of actuator will carry the movement of flexible solar cell. The current of flexible

perovskite solar cell is monitored during the bending and straighten process of actuator under opposite voltage bias applied. It shows that upon +3 V bias, the bending of actuator can maximize the sun exposure of solar cell for efficient energy harvesting. Upon -3 V bias, the actuator is straightened. With multi actuator integrate together like leaves, the close up of the actuators will create a relatively isolated environment to protect the perovskite solar cell from moisture attack.

Figure 6.7 Current density of flexible perovskite solar cell is monitored during the movement of actuator under +/- 3 V bias.

In conclusion, the bio-inspired self-protection perovskite based energy harvesting system is a promising and smart integrated system that can be responsive to the environment, thus it can possibly achieve an improved extrinsic stability and prolonged the lifetime of perovskite photovoltaics.

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APPENDIX

In Chapter 4, the distribution of cesium element is studied in cross-sectional EDX in Figure A.1.

Figure A.6 a) and b) Cross-sectional EDX showing the distribution of elements (cesium, lead, iodine, bromine) in control and 40 mM Cs-oleate-treated perovskite films. (Purple represents cesium La1; cyan represents lead Ma1; green represents iodine La1; red represents bromine La1) c) comparison of Cs⁺ distribution in control (yellow) and 40 mM Cs-oleate-treated (purple) perovskite films.

The bandgap is derived from the tauc plots in Figure A.2.

Figure A.7 Bandgap and Tauc plot for control perovskite film (a) and with Cs-oleate passivation of 5 mM, 10 mM, 20 mM, and 40 mM (b-e).

Figure A.8 Valence band position of control perovskite film (a) and with Cs-oleate passivation of 5 mM, 10 mM, 20 mM, and 40 mM (b-e).

Figure A.9 Energy levels of control and Cs-oleate-treated perovskite films of different concentrations.

Table A.2 The dimensions of oleate, BA and PEA.

	Oleate	Butylammonium	Phenethylammonium
Minimum projection area	56.87 Å ²	20.67 Å ²	24.96 Å ²
Maximum projection area	107.89 Å ²	34.40 Å ²	46.76 Å ²
Minimum projection radius	6.38 Å	2.97 Å	3.37 Å
Maximum projection radius	10.32 Å	4.58 Å	5.03 Å

Effect of Cs⁺ on thermal stability

To understand the effect of Cs on stability, we synthesize MA-oleate and use it for passivation on triple cation perovskite and study the thermal stability of MA-oleate passivated film. The pristine film and 10 mM MA-oleate passivated film were annealed at 85 °C under inert environment for 8 hours. The XRD profile of these films are recorded and shown in Figure A.5. The results show that no significant improvement in thermal stability was observed after annealing for 8 hrs. This has highlighted the importance of Cs-rich perovskite surface for enhanced thermal stability.

Figure A.10 Thermal stability of pristine perovskite and 10 mM MA-oleate passivated films (85 °C, 8 hr).