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# THE STUDY OF TIN-BASED PEROVSKITE SOLAR CELLS WITH HIGH EFFICIENCY AND STABILITY

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PhD

**The Hong Kong Polytechnic University** 

2021

# The Hong Kong Polytechnic University Department of Applied Physics

# The Study of Tin-Based Perovskite Solar Cells with High Efficiency and Stability

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

September 2020

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\_\_\_\_\_ (Signed)

WANG Tianyue (Name of Student)

## Abstract

Organic-inorganic hybrid perovskite materials have aroused wide research interests due to their superior optical and electrical properties. One successful application of such materials is solar cell, which has recently achieved a power conversion efficiency (PCE) of 25.5%. However, the involvement of toxic lead in common perovskite solar cells (PSCs) may constitute an obstacle for their further commercialization. Less toxic tinbased perovskites are regarded as the most promising alternative among various kinds of lead-free perovskite compounds. It has been found that tin-based PSCs suffer from lower efficiency and stability than their lead analogues because  $Sn^{2+}$  in tin-based perovskites can be easily oxidized to Sn<sup>4+</sup> and induce Sn vacancy defects that lead to severe nonradiative charge recombination in the films. In addition, the rapid crystallization of tin-based perovskites during solution processes can result in poor film morphology and high defect concentration. Moreover, special requirements are needed in charge transport layers of tin-based PSCs to get better energy alignment and interface property. All of the issues make it challenging to achieve high performance tin based PSCs.

In the thesis, antioxidant gallic acid (GA) additive together with excess  $SnCl_2$  were first introduced into FASnI<sub>3</sub> perovskite to improve its stability and the device performance. This coadditive engineering approach enables capping of the perovskite grains with an amorphous  $SnCl_2$ –GA complex and leads to suppressed  $Sn^{2+}$  oxidation and defect

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densities in the perovskite films. Moreover, the bandgap of SnCl<sub>2</sub>-GA complex is decreased and its conduction band is shifted downward compared to SnCl<sub>2</sub>, which facilitates electron transfer from perovskite grains through the complex layer to electron transport layer and reduces recombination loss. By systematically adjusting the amount of coadditives, PSCs based on the inverted structure can attain a PCE of 9.03%. The FASnI<sub>3</sub>-based PSCs also exhibit striking long-term stability, which show no degradation in PCE after being stored in N<sub>2</sub> filled glovebox for more than 1500h. And the unencapsultaed devices can maintain ~80% of the initial efficiency over 1000 h storage upon air exposure (~20% RH).

Second, we have developed a special technique by utilizing liquid-exfoliated twodimensional (2D) transition-metal dichalcogenides as the interlayer for synergistic modulation of perovskite growth and the interfaces in PSCs. Liquid exfoliated MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> flakes (generally referred as MX<sub>2</sub>) were introduced between hole transport layer (NiO<sub>x</sub>) and FASnI<sub>3</sub> perovskite. The smooth and defect-free face of MX<sub>2</sub> can promote van der Waals epitaxial growth of perovskite film with enlarged sizes. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) provide evidence that perovskite films on MX<sub>2</sub> exhibit highly oriented packing of (100) plan in the out-of-plane direction. In comparison with MoS<sub>2</sub> and WS<sub>2</sub>, WSe<sub>2</sub> possesses shallower VBM and is judiciously selected as an efficient charge transport interlayer due to its high hole mobility and good energy alignment with the VBM of HTL and perovskite film. The resultant WSe<sub>2</sub> incorporated PSCs exhibit increased photovoltaic

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parameters in  $J_{sc}$ ,  $V_{oc}$  and FF, which can be attributed to the synergy of enhanced charge transport, less interfacial recombination loss and stronger light absorption. Consequently, a PCE of 10.47% is obtained for the champion device.

Third, perovskite dimensionality manipulation and replacement of PCBM with novel electron transport layer (ETL) were performed simultaneously to reduce the trap density in the perovskite film and optimize band energy alignment. Bulky organic cation phenethylammonium (PEA) was incorporated into FASnI<sub>3</sub>, which effectively generates low-dimensional (LD) perovskite phase in the 3D perovskite. PEA was found to induce superior crystallinity and oriented growth of FASnI3 on NiOx substrates with preferential facet of (100). The high quality LD/3D perovskite with well packing of crystal planes exhibits higher structure robustness than FASnI<sub>3</sub> perovskite, resulting in reduced trap density within the bulk films. Through further using indene-C60 bisadduct (ICBA) with shallower Lowest Unoccupied Molecular Orbital (LUMO) level as the novel ETL, the band energy off-set between LD/3D perovskite and ETL is minimized, leading to enhanced charge extraction and reduced non-radiative recombination at the interface. By adopting these strategies, the V<sub>oc</sub> of the device is increased to more than 0.9V, which is among the highest  $V_{oc}$  reported so far. This work highlights the significance of perovskite compositional engineering and device structure modulation in enhancing the  $V_{oc}$  and efficiency of tin-based PSCs.



## **List of Publications**

(1) Wang, T.; Tai, Q.; Guo, X.; Cao, J.; Liu, C.-K.; Wang, N.; Shen, D.; Zhu, Y.; Lee,

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(2) Wang, T.; Yan, F. Reducing Agents for Improving the Stability of Sn-Based Perovskite Solar Cells. *Chem. Asian J.* 2020, *15*, 1524-1535.

(3) Tai, Q.; Cao, J.; Wang, T.; Yan, F. Recent Advances toward Efficient and Stable Tin-Based Perovskite Solar Cells. *EcoMat* 2019, 1, e12004.

(4) Cao, J.; Tai, Q.; You, P.; Tang, G.; Wang, T.; Wang, N.; Yan, F. Enhanced Performance of Tin-Based Perovskite Solar Cells Induced by an Ammonium Hypophosphite Additive. *J. Mater. Chem. A* **2019**, *7*, 26580-26585.

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# List of Abbreviations

Perovskite solar cells	PSCs
Methylammonium	MA
Formamidinium	FA
Guanidinium	Gua
Ethylenediammonium	EDA or en
Propylenediammonium	PN
Trimethylenediammonium	TN
Ethylammonium	EA
Phenethylammonium	PEA
Trimethylamine	ТМА
Hexafluoro-2-propanol	HFP
2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-	Spiro-
spirobifluorene	OMeTAD
Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate)	PEDOT:PSS
Isopropyl alcohol	IPA
Hypophosphorous acid	HPA
Electron transport layer	ETL
Hole transport layer	HTL

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Transparent conducting oxide	ТСО
Gallic acid	GA
Low-dimension	LD
Indene-C60 bisadduct	ICBA
[6,6]-phenyl-C61-butyric acid methyl ester	PCBM
Lowest Unoccupied Molecular Orbital	LUMO
Conduction band minimum	CBM
Valence band maximum	VBM
Short current density	J <sub>sc</sub>
Open circuit voltage	$V_{oc}$
Fill factor	FF
Power conversion efficiency	PCE
External quantum efficiency	EQE
Scanning electron microscopy	SEM
Steady-state photoluminescence	PL
Time-resolved photoluminescence	TRPL
X-ray diffraction	XRD
Fourier transform infrared spectroscopy	FTIR
Ultraviolet-visible	UV-vis

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Scanning transmission electron microscopy	STEM
Electron energy loss spectroscopy	EELS
Ultraviolet photoelectron spectroscopy	UPS
X-ray photoelectron spectroscopy	XPS
Space charge limited current	SCLC
Electrochemical impedance spectroscopy	EIS
Selected area electron diffraction	SAED
Full width at half maximum	FWHM

#### Chapter 1

## **Chapter 1 Introduction**

## 1.1 Background

Photovoltaics is an important renewable energy technology that can alleviate the energy crisis and avoid environmental pollution in the future.<sup>1-2</sup> Among new generation photovoltaic technologies, PSCs based on novel perovskite materials have aroused great interest recently due to their significantly high efficiency, low cost and facile fabrication process.<sup>3-6</sup> The perovskite materials have a formula ABX<sub>3</sub>, where A is CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (MA), CH(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> (FA) or Cs<sup>+</sup>, B is a metal cation (Pb<sup>2+</sup> or Sn<sup>2+</sup>) and X is a halide anion (I<sup>-</sup>, Br<sup>-</sup> or Cl<sup>-</sup>), and are thus called organic–inorganic metal halide perovskites.<sup>7-10</sup> Various unique physical properties, including the high absorption coefficients in a broad wavelength region, high carrier mobilities, suitable bandgaps and long carrier diffusion lengths, have been observed in perovskite materials, which enables the acquisition of high-performance PSCs.

Miyasaka and co-workers first used the organolead halide perovskite as the absorber material in dye-sensitized solar cells in 2009, which could only attain a PCE of 3.8%.<sup>3</sup> Then, researchers simplified the device design and developed PSCs with an all-solid-state multi-layered structure, which exhibited a PCE of 9.7%.<sup>5</sup> Since then, many efforts have been devoted to this field of research and the device PCE was substantially improved in the past ten years. A record PCE of 25.5% was recently achieved by the institution Ulsan National Institute of Science and Technology.<sup>11</sup> It is noteworthy that

the best research-cell efficiency of PSCs has already surpassed that of multicrystalline Si cells (23.3%), CIGS cells (23.4%) and CdTe cells (22.1%) (**Figure 1.1**). Recently, large-area fabrication techniques for transport materials, perovskite absorbers and counter electrodes are also developing rapidly. The improvement in spray deposition,<sup>12</sup> blade coating,<sup>13</sup> slot-die coating and inkjet printing methods<sup>14</sup> make it potential for the scalable fabrication of PSCs.



Figure 1.1 Best research-cell efficiency chart

Today, the most efficient and stable PSCs contain lead, which is toxic and can pose threat to the environment and reverse effect on human health. Li et al. estimated that a PSC module with a 600-nm-thick MAPbI<sub>3</sub> perovskite layer contains ~0.8 g lead per square meter, and if all the lead is dispersed into soil with the same area, it will increase the concentration of lead in the soil by ~4.0 mg kg<sup>-1</sup>. Such lead contamination can increase the lead concentration of natural soil (with original lead concentration  $\sim$ 36 mg kg<sup>-1</sup> collected from the campus of Fujian Agriculture and Forestry University, China) by  $\sim$ 10%. The effect of bioavailability of lead will be even augmented, since the lead uptake by plants, and the food cycle, increases over 100%.<sup>15</sup> Additionally, the European Union has made strict RoHS standards for restriction of hazardous substances in electrical and electronic equipment. According to the latest directive RoHS 3, the maximum level by weight for lead used in electronic devices is restricted to 0.1%. Unfortunately, the state-of-art halide perovskites used in high-performance PSCs contain more than 10% lead by weight.<sup>16</sup>

Searching for other lead-free metal halide perovskites with identical optoelectronic properties as the alternatives is an effective way to address the issues. Replacement of Pb<sup>2+</sup> with one monovalent cation and one trivalent cation to construct a double perovskite structure is a viable route.<sup>17</sup> Moreover, several divalent cations, such as Sn<sup>2+</sup>, Ge<sup>2+</sup> and Cu<sup>2+</sup> are also promising for Pb<sup>2+</sup> substitution.<sup>18-22</sup> Specifically, tin just sits before lead in the periodic table, which is expected to have similar electronic property to lead and fulfill the requirements (coordination, ionic size, charge balance, etc.) for lead substitution in a genuine perovskite structure. Tin-based perovskites also possess superior electronic and optical characteristics, including narrower bandgaps, high carrier mobilities, and long carrier diffusion lengths. More importantly, tin-based perovskites are less toxic compared to their lead analogues. As a consequence, tin-based perovskites are promising for developing lead-free PSCs. Currently, tin-based PSCs

have already achieved PCE >10%, which is much higher than the efficiency of other lead-free PSCs. Although tin-based PSCs have also acquired rapid development in the past few years, research progress on tin-based PSCs still fall behind that of lead-based PSCs. So far, there are many of challenges about the utilization of tin-based perovskite materials and devices, which needs more efforts devoted by researchers to this field in the future.

## 1.2 Objectives of research

The facile oxidation of  $Sn^{2+}$  to  $Sn^{4+}$  in Sn-based perovskites will result in high density of Sn vacancies, trap defects and p-type metallic behavior of the perovskite films. It is important to find a way to preserve the stability of tin halide perovskites so as to acquire high-performance tin-based PSCs. Adding extra  $SnX_2$  (X=F, Cl, Br) in the precursor solution is an essential strategy to inhibit  $Sn^{2+}$  oxidation. Currently, the reported amount of  $SnX_2$  additive is typically 10%. On the one hand, excess  $SnX_2$  tends to separate out on the surface of perovskite film, which can reduce the anti-oxidation capability and affect the film morphology; on the other hand,  $SnX_2$  as a wide-bandgap semiconductor that envelops the grain boundaries can prohibit charge transfer across the perovskite film. To cope with the problems, antioxidant gallic acid (GA) that contains Lewis-base group (-COOH) is introduced in the FASnI<sub>3</sub> perovskite as the secondary additive with excess  $SnCl_2$ . It is expected that GA restricts separated  $SnCl_2$  aggregates through formation of a  $SnCl_2$ –GA complex that envelops the perovskite grain surface, which can effectively block oxygen diffusion and improve the air stability of FASnI<sub>3</sub> perovskite. Also, the electrical property of SnCl<sub>2</sub> is changed by its coordination with GA, which better facilitates electron transfer from the perovskite to ETL across the complex layer.

The film quality of tin-based perovskite is an important factor that can affect the device performance. However, tin-based perovskite typically crystallizes faster than lead-based perovskite due to the higher acidity of Sn, leading to inferior film quality with rough top-surface and lots of Sn vacancies. Additionally, the interface states and energy level mismatching between tin-based perovskite and common charge transport materials can induce severe non-radiative recombination at the interfaces. Another objective of this thesis is to introduce an interlayer that can synergistically modulate perovskite growth and the interfaces. Liquid-exfoliated 2D transition-metal dichalcogenides with suitable band structures and defect-free surfaces have great potential for interface modification. Here, they are used for modification of the HTL/FASnI<sub>3</sub> perovskite interface under expectation to minimize the interfacial energy loss and promote van der Waals epitaxial growth of perovskite grains with better crystallinity.

Sn-based perovskites suffer from significant  $V_{oc}$  loss. Most Sn-based perovskites have  $V_{oc}$  less than 0.6 V, which generates a  $V_{oc}$ /Eg value lower than 0.5. The low  $V_{oc}$  of Sn-based perovskites can be ascribed to the high defect density in the films and band energy mismatch with conventional charge transport layers. The third objective in this thesis is

to reduce the trap density in the perovskite film and realize band energy alignment through simultaneous perovskite dimensionality manipulation and replacement of PCBM with novel electron transport layer (ETL).

#### **1.3** Outline of thesis

This thesis is organized as follows:

**Chapter 1**: Introduction. In this chapter, the background information of organicinorganic metal halide PSCs is introduced, and the necessity for development of tinbased PSCs is highlighted. The objectives and outline of the thesis are subsequently presented.

**Chapter 2**: Overview of lead-free tin halide PSCs. In this part, the emergence and evolution of tin-based perovskites for photovoltaic application are first presented. Then, the basic properties, such as the crystal structures and physical properties of tin-based perovskites are listed. Next, the deposition methods of tin-based perovskite thin films as well as the device configurations, working principle and characterization methods are summarized. Fourth, strategies to improve the performance of tin-based PSCs, including compositional engineering, additive engineering and interfacial engineering are illustrated in detail. At last, the current challenges like air stability, toxicity of raw materials, and inferior efficiency compared to lead analogues are discussed, as well as the perspective on future development of tin-based PSCs.

**Chapter 3**: Highly air-stable tin-based PSCs through grain-surface protection by gallic acid. In this chapter, antioxidant GA additive together with excess SnCl<sub>2</sub> were introduced into FASnI<sub>3</sub> perovskite to improve its stability and the device performance. This coadditive engineering approach enables capping of the perovskite grains with an amorphous SnCl<sub>2</sub>–GA complex and leads to suppressed Sn<sup>2+</sup> oxidation and defect densities in the perovskite films. Moreover, the bandgap of SnCl<sub>2</sub>-GA complex is decreased and its conduction band is shifting downward compared to SnCl<sub>2</sub>, which facilitates electron transfer from perovskite grain through the complex layer to electron transport layer and reduces recombination loss. By systematically adjusting the amount of coadditives, PSCs based on the inverted structure can attain a PCE of 9.03%. The FASnI<sub>3</sub>-based PSCs also exhibit striking long-term stability, which show no degradation in PCE after being stored in N<sub>2</sub> filled glovebox for more than 1500h. Additionally, the unencapsultaed devices can maintain ~80% of the initial efficiency over 1000 h storage upon air exposure.

**Chapter 4**: Synergistic modulation of perovskite growth and interfaces via a 2D transition-metal dichalcogenide interlayer for high-efficiency tin-based PSCs. In this chapter, liquid-exfoliated 2D transition-metal dichalcogenide with smooth and defect-free surfaces are applied as the epitaxial growth template on the bottom of perovskite film, which regulated perovskite crystallization with enlarged grain size and preferential facet of (100). It is shown that WSe<sub>2</sub> possesses shallower valence band maximum (VBM) than MoS<sub>2</sub> and WS<sub>2</sub>, and is well-aligned with the VBM of Sn-based

perovskite. The NiO<sub>x</sub>/WSe<sub>2</sub>/FASnI<sub>3</sub> layers with a cascade valence band structure facilitate hole extraction at the interface and suppress interfacial charge recombination, leading to improved device performance. The WSe<sub>2</sub> incorporated device shows a power conversion efficiency of 10.47%, which is among the highest of efficiency of FASnI<sub>3</sub>-based inverted PSCs. This work demonstrates the appealing characteristic of 2D transition-metal dichalcogenide for synergistic modulation of perovskite growth and interfaces, which paves a facile way to further improve the performance of Sn-based PSCs.

**Chapter 5**: Efficient lead-free tin halide perovskite solar cells with a record open voltage over 0.9V. Bulky organic cation phenethylammonium (PEA) was used to partially substitute FA cation in 3D FASnI<sub>3</sub> perovskite and generate low-dimensional (LD) perovskite. Addition of 20% PEA is optimal to induce superior crystallinity and oriented growth of FASnI<sub>3</sub> on NiO<sub>x</sub> substrates with preferential facet of (100). The high quality LD/3D perovskite with well packing of crystal planes exhibits higher structure robustness than FASnI<sub>3</sub> perovskite, which effectively reduces the trap density within the bulk films. Moreover, ICBA with higher LUMO level is used in replacement of common PCBM as the ETL. Its minimized energy offset with the CBM of LD/3D perovskite significantly enlarges the  $V_{oe}$  value. Eventually, the device demonstrates a maximum attainable  $V_{oe}$  of 0.96 V, the highest reported so far for Sn-based PSCs. The champion cell delivers a PCE of 9.66% and excellent stability, which retains over 80% of the efficiency after being stored in N<sub>2</sub> for 600 hours without encapsulation.

Chapter 6: Conclusion and future outlook.

#### Chapter 2

# Chapter 2 Overview of lead-free tin halide perovskite solar cells

### 2.1 Introduction

PSCs have aroused tremendous research interest for their high efficiency, low cost and solution processability. However, the involvement of toxic lead in state-of-art perovskites hinders their market prospects. Sn-based perovskites are a highly desirable candidate for the absorber material since they show high carrier mobility, long carrier diffusion length and suitable bandgap (~1.3 eV) that is close to the optimum value of 1.34 eV according to the Shockley–Queisser limit.<sup>23-24</sup> Therefore, Sn-based PSCs can potentially produce higher efficiency than their Pb-based PSCs, and much effort has been exerted to such an emerging photovoltaic technology using lead-free perovksite materials.

Sn-based perovskites in a formula of CsSnX<sub>3</sub> were first synthesised and characterized in 1974.<sup>25</sup> However, Sn-based perovskites were not considered for photovoltaic application in early works since they were found to be metallic.<sup>26</sup> Later, it was found that the metallic nature originates from the self-p type doping caused by tin oxidation, and semiconducting Sn-based perovskites can be obtained by introduction of additional reducing agents. In 2012, Chung et al first reported utilization of Sn-based perovskites in solar cells. They used SnF<sub>2</sub> doped CsSnI<sub>3</sub> as the hole conductor in solid-state dyesensitized solar cells and acquired a PCE of 10.2%.<sup>27</sup> Shortly after the publication of

this work, Chen et al. employed CsSnI3 as the absorbing material in Schottky solar cells, which achieve a PCE of 0.9%.<sup>28</sup> Since then, tremendous efforts have been devoted to developing high-performance Sn-based PSCs. In 2014, Noel et al. and Hao et al. independently reported MASnI3 and MASnI3-xBrx based PSCs fabricated on mesoporous TiO<sub>2</sub> scaffolds with a PCE of 6.4% and 5.73%, respectively.<sup>29-30</sup> Later in 2016, Liao et al. reported the reproduction of efficient FASnI<sub>3</sub> based PSCs with a PCE of 6.22% in an inverted architecture.<sup>31</sup> Thereafter, researchers found that higher efficiency could be attained by introducing of / partially substituting FA cation with other organic molecules in pure FASnI<sub>3</sub> perovskite. For instance, Ke et al. reported fabrication of (en)FASnI<sub>3</sub> based PSCs with a PCE of 7.14% through introduction of en as the additive into FASnI<sub>3</sub> precursor solution.<sup>32</sup> Zhao et al. reported utilization of composite perovskite  $(FA)_x(MA)_{1-x}SnI_3$  as the absorber, which acquired a highest PCE of 8.12% for x=0.75.33 Shao et al. mixed trace amount of 2D Sn perovskite with FASnI3 and further pushed the PCE to 9.0% in planar p-i-n devices.<sup>34</sup> Jokar et al. incorporated guanidinium (Gua<sup>+</sup>) into the FASnI<sub>3</sub> crystal structure together with introduction of ethylenediammonium diiodide (EDAI2) additive, and prepared PSCs with a PCE of 9.6%.<sup>35</sup> More recently, (FA<sub>0.9</sub>EA<sub>0.1</sub>)<sub>0.98</sub>EDA<sub>0.01</sub>SnI<sub>3</sub> based PSCs prepared through mixed cation engineering have achieved a PCE over 13%.<sup>36</sup>

In spite that many groups have been working on Sn-based PSCs, their performances develop much more slowly than Pb-based PSCs. Moreover, the stability of Sn-based PSCs is also inferior in air. To guide the direction for further improving the photovoltaic

performance of Sn-based PSCs, it is necessary to systematically summarize Sn-based perovskites on aspects of material properties, film deposition process and device engineering, etc, and have a comprehensive view of the field.

In this chapter, we will first briefly introduce the crystal structures and physical properties of Sn-based perovskite; the latter includes the band structures, light absorption, carrier mobility, and carrier lifetime and diffusion length. Then, the major deposition methods of Sn-based perovskite films are summarized. In the following part, device architectures and working principles of Sn-based PSCs are introduced to have better understanding of the device performing mechanism. Next, strategies for improving the performance of Sn-based PSCs are presented. Subsequently, current challenges of Sn-based PSCs, including the stability and toxicity of Sn-based perovskite, the inferior device efficiency of Sn-based PSCs compared to its Pb-based counterparts are discussed. Lastly, we will give a perspective and outlook towards further development of Sn-based PSCs.

# 2.2 Structures and properties of tin halide perovskites

#### 2.2.1 Crystal structures

Halide perovskites generally has a crystal unit of ABX<sub>3</sub>, which is composed of a three dimensional corner-shearing [BX<sub>6</sub>] octahedrons, leaving the cuboctahedral cavities
occupied by A site organic or inorganic cations (**Figure 2.1a**).<sup>37-38</sup> For Sn-based perovskites, the B-site is occupied by Sn and their chemical compositions can be tuned by changing the A-site cations ( $MA^+$ ,  $FA^+$ ,  $Cs^+$ ) or X-site anions ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ).<sup>30</sup> Different ionic radii of A site and X site ions will lead to the variation in lattice parameters, the unit cell, and the crystal system. Specifically, the Goldschmidt's tolerance factor (t) can be utilized to roughly estimate the lattice structure of the perovskite. The relation of t with the ionic radius of the A, B and X ions is given by:

$$t = \frac{r_A + r_x}{\sqrt{2}(r_B + r_x)}$$

For t equal to 1, it usually results in an ideal cubic structure, whereas for t in range of 0.7-0.9 or >1, orthorhombic, rhombohedral, or tetragonal structure could be formed.<sup>39</sup> To maintain the stable structure of halide perovskite, t should be lying in the range of 0.813 < t < 1.107.<sup>40</sup> The calculated t-factors for a series of halide perovskites are shown in **Figure 2.1b**.



Figure 2.1 a) Halide perovskite crystal structure.<sup>38</sup> b) Calculated t-factors for a series

of halide perovskites.41

CsSnI<sub>3</sub> perovskite has two distinct polymorphous phases at room temperature, which are 1D double-chain yellow phase (Y) and black orthorhombic phase  $(B-\gamma)$ , respectively. The B- $\gamma$  phase can be converted to Y phase when exposed to air. <sup>42</sup> The instability of CsSnI<sub>3</sub> perovskite structure could be correlated to the small ionic radius of Cs<sup>+</sup>. In contrast, MASnI<sub>3</sub> only forms a stable cubic phase near room temperature.<sup>26,37</sup> It is supposed that MA<sup>+</sup> cation is much bigger than Cs<sup>+</sup>, and can better support the cages. It is interesting that temperature can induce the phase transition of the perovskite. For CsSnI<sub>3</sub> perovskite, the Y phase could be turned to the black cubic phase (B- $\alpha$ ) when heated to 425 K and to the black tetragonal phase (B- $\beta$ ) after the B- $\alpha$  phase is cooled to 351 K.<sup>42</sup> This indicates that elevated temperature is favourable for the phase stability of CsSnI<sub>3</sub> perovskite. As for MASnI<sub>3</sub> perovskite, it can be changed to tetragonal at 275 K and to orthorhombic at 110 K; for FASnI<sub>3</sub> perovskite, it adopts an orthorhombic (Amm2) structure at room temperature, and this structural phase is stable up to 200 °C.<sup>26,43</sup> Smaller X-site ion also benefits the formation of more symmetric and compact structure. For example, Lee et al. found that for  $FASn(Br_xI_{1-x})_3$  perovskite, it keeps a orthorhombic structure for x = 0.08, whereas turned to tetragonal structure for x around 0.17 and eventually cubic structure for x = 1.<sup>44</sup> Similarly, gradually substituting I with Br in CsSnI<sub>3</sub> can turn the orthorhombic phase (for CsSnI<sub>3</sub>) to cubic phase (for CsSnBr<sub>3</sub>).<sup>45</sup>

## **2.2.2** Physical properties

Simulation studies reveal that the conduction band minimum (CBM) of the perovskite is mainly formed by the p orbitals of B-site cation, whereas the valence band maximum (VBM) is formed by s orbitals of B-site cation and X-site p orbitals.<sup>39</sup> Thus, the band structures of Sn-based perovskites are dependent mainly on Sn and halogen. Sn-based perovskites are direct band gap semiconductors and exhibit broader absorption edge than their Pb analogues. Optical characterization of MASnI<sub>3</sub> shows that it has a bandgap of 1.23 eV, with absorption onset at around 1000 nm and a broad photoluminescence peak at 980 nm, whereas its lead analogue MAPbI<sub>3-x</sub>Cl<sub>x</sub>, exhibits absorption edge at 770 nm and much narrower emission.<sup>29</sup> The bandgaps of Sn perovskites can be significantly adjusted by compositional engineering of the X-site ions. Through gradually increasing the Br content in MASnI<sub>x</sub>Br<sub>3-x</sub>, the bandgap can be increased from 1.3 eV for MASnI<sub>3</sub> to 2.15 eV for MASnBr<sub>3</sub>.<sup>30</sup> Similarly, FASnI<sub>3</sub> can be tuned to wider bandgap from 1.4 eV to 1.7 eV with I substituted by 33 mol % Br.44 The A-site cation has little effect on the bandgap, since MASnI<sub>3</sub> has similar bandgap to CsSnI<sub>3</sub> (1.3 eV), whereas the bandgap of FASnI<sub>3</sub> is slightly higher (1.4 eV).

Due to the larger bandwidth for both the valence and conduction bands, Sn-based perovskites have relatively low effective masses of both electrons and holes.<sup>46-47</sup> This contributes to the small binding energies and high charge carrier mobilities of Sn-based perovskites. The exciton binding energies for Sn-based perovskites are in a range similar to Pb-based perovskites (e.g., 18 meV for CsSnI<sub>3</sub>, 31 meV for FASnI<sub>3</sub>, 29 meV

for MASnI<sub>3</sub>, and 2–62 meV for MAPbI<sub>3</sub>).<sup>23</sup> Moreover, it has been reported that MASnI<sub>3</sub> perovskite exhibits remarkably high mobilities, with electron mobility  $\mu_e \approx 2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and hole mobility  $\mu_h \approx 300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . In contrast, MAPbI<sub>3</sub> only shows  $\mu_e \approx 60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Such high mobilites are a unique property, which enables a charge carrier diffusion length of over 500 nm in MASnI<sub>3</sub> films.<sup>48</sup> Wu et al. also reported superior properties for single crystal CsSnI<sub>3</sub> ingots. The time-resolved photoluminescence (TRPL) data shows that the single crystal CsSnI<sub>3</sub> ingots have a bulk carrier lifetime of 6.6 ns. Combined with the doping concentration of  $\approx 4.5 \times 10^{17} \text{ cm}^{-3}$ , the minority-carrier diffusion length can be calculated as approaching 1 µm. However, such superior property is only achieved for large-sized single crystal CsSnI<sub>3</sub>, since further reducing the dimensions of the grains can lead to a significant reduction in the lifetimes. For single crystal CsSnI<sub>3</sub> with 300 nm size grains, they could only get an effective lifetime of  $\approx 3 \text{ ns}$ .<sup>49</sup>

## 2.3 Deposition methods of tin halide perovskite films

Fabrication of high-efficiency Sn-based PSCs has a special requirement for high quality perovskite films with high uniformity, coverage, well crystallinity, etc. Researches have made numerous efforts to develop different methods for deposition of Sn-based perovskite films, including on-step solution method, two-step solution method and vapour deposition method.

### **2.3.1** One-step solution method

One-step solution method was first reported for fabrication of Sn-based perovskite films on mesoporous TiO<sub>2</sub> substrates with reference to fabrication of conventional MAPbI<sub>3</sub> films.<sup>29-30</sup> Typically, organic halides (MAI, FAI, etc.) and tin halide (SnI<sub>2</sub>) are dissolved in solvents such as DMF, GBL or DMSO to prepare the perovskite precursor solution. Then the solution is spin-coated on the substrates and the perovskite films form with the evaporation of solvent driven by centrifugal force. The fabricated Sn-based perovskite films usually need to be thermal annealed at higher temperature to induce better crystallization (**Figure 2.2**a).

Initially, pure DMF was used as the solvent in one-step solution method to fabricate Snbased perovskite films.<sup>29-30</sup> However, Sn-based perovskite films prepared from this method crystallize fast and exhibit rough and discontinuous morphologies. It is acknowledged that the uncontrollable crystallization of Sn-based perovskites results from the high Lewis acidity of Sn<sup>2+</sup>, which reacts fast with the organic halides.<sup>50</sup> Hao et al. thereafter investigated the effects of different solvents, including DMF, GBL, NMP and DMSO, on the crystallization of MASnI<sub>3</sub> perovskite films.<sup>51</sup> They found that the crystallization rate is fastest for DMF, whereas decreases for GBL, DMSO and NMP in sequence. Finally, high quality pin-hole free MASnI<sub>3</sub> perovskite films were obtained from using DMSO solvent, which can be ascribed to the formation of a transitional SnI<sub>2</sub>·3DMSO intermediate phase that retards the film crystallization. So far, pure DMSO or DMF/DMSO mixed solvents are most commonly used for preparation of state-of-art Sn-based PSCs.

For further improvement of the film quality of Sn-based perovskites, the anti-solvent dripping process is included during the one-step solution method. The anti-solvent has poor solubility of the perovskite and is quickly dripped to the rotating wet film to induce saturation of perovskite in DMF or DMSO. The adoption of anti-solvent dripping process can induce fast and homogeneous nucleation of Sn-based perovskite crystallites, leading to uniform and full-coverage final films. The anti-solvent can be chlorobenzene, toluene, diethyl ether, etc. Liu et al. used chlorobenzene as the anti-solvent and acquired dense and uniform FA<sub>0.75</sub>MA<sub>0.25</sub>SnI<sub>3</sub> films processed from DMF/DMSO mixed solution. <sup>52</sup> Xu et al. successfully fabricated oriented quasi-2D Sn perovskite films by employing toluene to extract the excess DMF/DMSO. <sup>53</sup>

#### 2.3.2 Two-step solution method

Two-step solution method is rarely used to fabricate Sn-based perovskite films. There are only a handful of papers reporting such a film deposition technique. Zhu et al reported the deposition of SnI<sub>2</sub> film in the first-step, which was then converted into FASnI<sub>3</sub> perovskite film by dripping FAI/isopropyl alcohol (IPA) solution onto it in the second-step. Notably, trimethylamine (TMA) was introduced as the additive in SnI<sub>2</sub> solution, which can retard the fast reaction between SnI<sub>2</sub> and FAI. <sup>54</sup> Since IPA interacts strongly with SnI<sub>2</sub> to prevent the formation of stable FASnI<sub>3</sub> perovskite film, Shahbazi et al. used cosolvents of hexafluoro-2-propanol (HFP), IPA, and chlorobenzene (CB) to

substitute IPA in the second-step. HFP was introduced to form hydrogen bonds with IPA and FAI to retard FASnI<sub>3</sub> crystallization, and CB was used as the anti-solvent. The schematic of fabrication of FASnI<sub>3</sub> films with two-step solution method is shown in **Figure 2.2**b. As a result, a stable FASnI<sub>3</sub> PSC with a PCE of 6.8% is obtained. <sup>55</sup>



**Figure 2.2** a) Schematic illustration of the one-step solution method <sup>56</sup> and b) two-step solution method for fabrication of Sn-based perovskite films.<sup>55</sup>

### 2.3.3 Vapor deposition method

Sn-based perovskite films can also be prepared by vapour deposition method due to the relative low melting point of the raw precursor materials. Vapor deposition method has many advantages than solution deposition method. For example, it can produce uniform film layers with full-coverage on a large scale. It can also avoid the utilization of polar solvent that is incompatible with Sn-based perovskites. Therefore, many efforts have

been dedicated to fabricate Sn-based perovskite films using vapour deposition method. Xi et al. first fabricated a FAI layer through spin-coating from FAI/PEDOT:PSS solution, and then evaporated SnI<sub>2</sub> on it. The FAI crystals are inhibited to dense tiny seeds due to the introduction of PEDOT:PSS, which offer multichannel interdiffusion between FAI and SnI<sub>2</sub> to form FASnI<sub>3</sub> films (**Figure 2.3**a). Finally, the resultant device shows a PCE of 3.98%.<sup>57</sup> In contrast to the work reported by Xi et al, Weiss et al. thermal evaporated a SnI<sub>2</sub> layer first, and then spin-coated a solution of MAI/IPA on its top surface to convert SnI<sub>2</sub> into full-coverage MASnI<sub>3</sub> perovskite films.<sup>58</sup> Yu et al. reported fabrication of MASnI<sub>3</sub> perovskite films by co-evaporation, as schematically shown in **Figure 2.3**b. 1:1 molar ratio of MAI and SnI<sub>2</sub> used as the organic and inorganic sources respectively were simultaneously evaporated from two separate ceramic crucibles. The as-deposited films are smooth and uniform, leading to a relatively high V<sub>oc</sub> of 494mV for the PSC.<sup>59</sup>

Judging from the current reports, organic-inorganic hybrid Sn-based perovskites fabricated from vapor deposition method typically show lower device PCE than from solution method. However, vapor deposition method finds its potential application in fabricating all-inorganic Sn-based perovskite films. Chen et al. reported the deposition of CsSn<sub>0.5</sub>Ge<sub>0.5</sub>I<sub>3</sub> perovskite films evaporated from its powder synthesized by solid-state reaction (**Figure 2.3**c). The as-fabricated devices in an architecture of FTO/PCBM/ CsSn<sub>0.5</sub>Ge<sub>0.5</sub>I<sub>3</sub>/Spiro-OMeTAD/Au deliver a promising PCE of 7.11%, which is the highest among all-inorganic Sn-based PSCs.<sup>20</sup>



Figure 2.3 a) Two-step interdiffusion process for deposition of FASnI<sub>3</sub> films.<sup>57</sup> b) Dualsource evaporation method for MASnI<sub>3</sub> film preparation.<sup>59</sup> c) Single-source evaporation method for deposition of ultrasmooth  $CsSn_{0.5}Ge_{0.5}I_3$  perovskite thin films.<sup>20</sup>

## 2.4 Device architectures

A PSC is typically a layered structure device comprising a transparent conducting oxide (TCO) film, a light-harvesting perovskite layer, a n-type electron transport layer (ETL), a p-type hole transport layer (HTL) and a metal electrode. Specifically, according to the different positions of ETL and HTL, PSCs can be divided into formal structure (n-i-p) and inverted structure (p-i-n). Sn-based PSCs are initially fabricated in formal structure with a configuration of TCO/compact ETL/mesoporous ETL/perovskite/HTL/metal electrode. This can be also referred as a mesoscopic structure (**Figure 2.4**a).<sup>29-30</sup> Later, some researchers omit the mesoporous ETL in formal structure to simply the fabrication

process, which leads to the generation of planar formal structure (**Figure 2.4**b).<sup>60-61</sup> Snbased PSCs with an inverted structure are usually planar, which are in configuration of TCO/ HTL/perovskite/ETL/metal electrode (**Figure 2.4**c). Normally, TiO<sub>2</sub>, SnO<sub>2</sub>, or phenyl-C61-butyric acid methyl ester (PCBM) is adopted as the ETL in Sn-based PSCs; 2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD), poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) or NiO<sub>x</sub> is used as the HTL.



Figure 2.4 Three main kinds of device configurations of Sn-based PSCs.

So far, most of the high-performance Sn-based PSCs adopt an inverted structure. This can be attributed to several reasons. First, the Spiro-OMeTAD HTL used in formal structure needs oxidation to ensure its high hole mobility, which might accelerate the oxidization of Sn<sup>2+</sup>. Second, lithium salt is widely introduced as the additive in Spiro-OMeTAD, whereas its hygroscopic property could induce device performance degradation. Third, charge separation mainly occurs at the ETL/perovskite interface for

the formal structure while at the perovskite /HTL interface for the inverted structure. Holes are expected to move a long way to the perovskite /HTL interface in formal structure, which have high tendency in reacting with bulk Sn<sup>2+</sup> to Sn<sup>4+</sup>. Fourth, the higher mobility and diffusion length of electrons than holes in Sn-based perovskites favour adoption of an inverted structure.<sup>62</sup>

## 2.5 Working principle and characterization of tin halide perovskite solar cells

The operation of tin halide PSCs is based on the photovoltaic effect. Under illumination, the perovskite layer absorbs the incident photons with energy  $hv \ge Eg$ , which causes electrons in the valence band excited to the conduction band and leaves behind the original sites with holes. The generated electron-hole pairs easily dissociate at room temperature due to the small binding energy. Then, electrons and holes are selectively extracted by corresponding charge transport layers and collected at TCO and metal electrode, resulting in current flow in the external circuit. Since Sn-based perovskite has low Eg, it is expected to exhibit stronger light harvesting capability and thus generate higher current. Nevertheless, the narrower bandgap of Sn-based perovskite can place an upper limit for the device's open voltage.

For a solar cell, PCE is one of the most important parameters, which can be descripted and obtained from its current density–voltage (J–V) curve. The useful part of a typical J-V curve ranges from the short current density ( $I_{sc}$ ) at an output voltage of 0, to the open circuit voltage ( $V_{oc}$ ) with current of 0. The power curve can be derived by multiplying output current density and voltage, and the maximum value ( $P_{MP}$ ) occurs at a voltage of  $V_{MP}$  and a current density of  $J_{MP}$ , where denotes the maximum power generated by the cell. The PCE can be derived from  $P_{MP}$  divided by the indecent light power ( $P_{in}$ ) or from  $V_{oc}$ ,  $J_{sc}$  and fill factor (FF):

$$PCE = \frac{P_{MP}}{P_{in}} = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$

FF can be further determined by:

$$FF = \frac{V_{MP} \times J_{MP}}{V_{oc} \times J_{sc}}$$

# 2.6 Strategies for high performance tin halide perovskite solar cells

## 2.6.1 Compositional engineering

Compositional engineering means chemical modification of the A-, B- and X- sites of the perovskite crystal structure with different cations or anions. It is widely acknowledged as an effective way to tailor the properties of the perovskites and further enhance the efficiency and stability of the PSCs.

#### A-site cations engineering

In section 2.2, Sn-based perovskites with single A site cations are discussed. However, their properties can be further tuned and combine the advantages of mixed A site cations.

Zhao et al. first investigated the effect of partial substitution FA for MA cation in MASnI<sub>3</sub> based perovskite. XRD results reveal that FA and MA cations were evenly distributed in the lattices without formation of different species. While with FA incorporation, the bandgap of  $(FA)_x(MA)_{1-x}SnI_3$  shows a growing trend from 1.26 eV to 1.36 eV. More importantly, FA can improve the film morphology, prolong the PL lifetime and inhibit carrier recombination in the device. With FA amount optimization, the champion PCE of 8.12% and high Voc of 0.61 V were achieved for (FA)<sub>0.75</sub>(MA)<sub>0.25</sub>SnI<sub>3</sub> based inverted devices.<sup>29,33</sup> Ke et al. reported incorporation of ethylenediammonium (en) into 3D FASnI<sub>3</sub> based perovskite. Although en possesses relatively large size, it can be fitted to the perovskite cage by partial replacement of the SnI<sub>2</sub> fragment in the 3D structure, leading to the formation of hollow perovskite. Different from common observations that changes in A site cation only induce small changes in the bandgap, en is capable of achieving marked increase in the bandgap comparable to that of  $ASnI_{3-x}Br_x$  solid solutions. (en)FASnI<sub>3</sub> as the absorber shows reduced background carrier density and better air stability, which can lead to the best PCE of 7.14%.<sup>32</sup> en was also reported effective to improve the performance of MASnI<sub>3</sub> and CsSnI<sub>3</sub> based PSCs, which can achieve a PCE of 6.63% and 3.79%, respectively. <sup>63</sup> Later on, the same author further reported two diammonium cations, i.e., propylenediammonium (PN) and trimethylenediammonium (TN) that can be incorporated into FASnI<sub>3</sub> and enable the formation of 3D hollow perovskites like en does. FASnI<sub>3</sub> perovskite mixed with 10% PN or TN attained a PCE of 5.85% and 5.53%, respectively.<sup>64</sup> Jokar et al. reported Sn-based perovskite containing mixed Gua and FA

cations in the crystal structure. Particular incorporation of GA can increase the bandgap of the perovskite and shift its VBM level with well-alignment with the PEDOT:PSS hole-transport layer. Additionally, fewer defect states are generated in the perovskite film. With optimization, GA<sub>0.2</sub>FA<sub>0.78</sub>SnI<sub>3</sub> perovskite with the presence of 1% ethylenediammonium diiodide (EDAI<sub>2</sub>) additive showed the best performance, which achieved a certified PCE of 8.3%. Such a device was also found stable under continuous 1 sun illumination for 1 h, as well as after being stored in air for 6 days without encapsulation.<sup>65</sup>

Very recently, Nishimura et al. introduced ethylammonium (EA) cation into GeI<sub>2</sub> doped  $FA_{0.98}EDA_{0.01}SnI_3$  and obtained Sn-based perovskites with a chemical composition of  $(FA_{1-x}EA_x)_{0.98}EDA_{0.01}SnI_3$ . Results showed that partial substitution EA for FA can tune the tolerance factor close to 1 and achieve a more stable crystal structure. Moreover, trap densities within the bulk perovskite has been effectively reduced by 1 order of magnitude. Furthermore, EA-substituted Sn-based perovskite has better energy level alignment with charge transport layers and thus the improved built-in potential. These resulted in enhanced device performance with a PCE of 11.75%. Further optimization of the device through surface passivation gave rise to an unprecedented PCE of 13.24 %,  $J_{sc}$  of 20.32 mA cm<sup>-2</sup>, FF of 0.78 and  $V_{oc}$  of 0.84 V. <sup>36</sup>

#### **B-site cations engineering**

Study on B-site cations engineering is quite few. Ge has a similar electronic structure to Sn and is considered as a promising candidate. ITO et al. fabricated perovskites based on mixed Sn and mixed Ge with a composition of FA<sub>0.75</sub>MA<sub>0.25</sub>Sn<sub>1-x</sub>GexI<sub>3</sub>. Such perovskite materials have proper Eg ranging from 1.40 to 1.53 eV. The authors found that Ge at a low concentration can effectively fill the defects and vacancies on the surface of FA<sub>0.75</sub>MA<sub>0.25</sub>SnI<sub>3</sub> perovskite. Finally, the device achieved a PCE of 4.48% with 5% Ge doping, and it increased to 6.9% after 72h. <sup>19</sup> Chen et al alloyed Ge in CsSnI<sub>3</sub> and fabricated CsSn<sub>0.5</sub>Ge<sub>0.5</sub>I<sub>3</sub> perovskite. Once the perovskite films were exposed to air, Ge can be facile oxidized and form a stable native-oxide layer on the surface. XPS results showed that the native oxide contains GeO<sub>2</sub> doped with a small portion of Sn, which effectively encapsulates and passivates the film surface. The champion device based on CsSn<sub>0.5</sub>Ge<sub>0.5</sub>I<sub>3</sub> delivered a PCE of 7.11%. Moreover, the device attained 92% of the initial PCE after 500 h of continuous operation in N<sub>2</sub> atmosphere under one-sun illumination.<sup>20</sup>

Several transition metal ions such as  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  etc. are also potential to be used for modification of B-site cations due to their more stable oxidation state. However, probably the optoelectronic properties and fabrication techniques of transition metal ions incorporated perovskites are no well explored, the corresponding device PCEs are much lower than those of Sn-based perovskites are.<sup>21,66</sup>

#### X-site anions engineering

X-site anions greatly affect the crystal and band structure of the perovskite material. Hao et al. first reported  $CH_3NH_3SnI_{3-x}Br_x$  perovskites via alloying I with Br for high performance PSCs. The absorption onsets of  $CH_3NH_3SnI_{3-x}Br_x$  can be tuned form 954

nm (x=0) to 577 nm (x=3), corresponding to an increased bandgap from 1.3eV to 2.15 eV. Accordingly, with switching from pure I to Br, the Voc can be elevated from 0.68V to 0.88V as a result of the wider bandgap and conduction band shifting to higher energy. Finally, CH<sub>3</sub>NH<sub>3</sub>SnIBr<sub>2</sub> based perovskite exhibited the highest PCE of 5.73%.<sup>30</sup> Lee et al. further introduced Br into FASnI<sub>3</sub> perovskite. Similarly, the bandgap of the perovskite is increased with gradually substituting I with Br. Moreover, the orthorhombic structure of  $FASn(Br_xI_{1-x})_3$  can be converted to symmetric tetragonal structure and eventually cubic structure with all pure I gradually replaced by all Br. Furthermore, Br incorporation was found to play important roles in lowering the carrier density within the perovskite, leading to a PCE of 5.5% and high stability for encapsulated devices under continuous one sun illumination for 1000h.<sup>44</sup> Tsai et al. synthesized tri-halide tin perovskites with a composition of MASnIBr<sub>2-x</sub>Cl<sub>x</sub>. Since Cl and I have large radii difference, continuous solid solutions of MASnI<sub>3</sub>-xCl<sub>x</sub> can't form, whereas stable MASnIBr<sub>2-x</sub>Cl<sub>x</sub> can form at x<1. The presence of Cl in the perovskite can reduce the charge recombination and accumulation, finally leading to a device PCE of 3.1% at an optimal composition of MASnIBr<sub>1.8</sub>Cl<sub>0.2</sub>.<sup>67</sup>

### 2.6.2 Additive engineering

## $SnX_2$ (X = Cl, Br, I) and other $Sn^{2+}$ species

Since intrinsic defects induced by Sn vacancies could easily form in Sn-based perovskites, Sn self-compensation is regarded necessary to make up for the Sn<sup>2+</sup> loss.

Introduction of SnX<sub>2</sub> compound is therefore recognized as an effective way to improve the perovskite material stability.

Among SnX<sub>2</sub> compounds, SnF<sub>2</sub> is a strong reducing agent that is widely used in chemical synthesis. Also, it is a critical additive to ensure efficient photovoltaic performance in Sn-based PSCs. Chung et al. first reported SnF<sub>2</sub> doped CsSnI<sub>3</sub> as the hole conductor in solid-state dye-sensitized solar cells, which exhibited improved J<sub>sc</sub> and PCE than without SnF<sub>2</sub> doping.<sup>27</sup> Inspired by this idea, Kumar et al. explored the viability of using CsSnI<sub>3</sub> as the photoabsorber and tried to control its metallic conductivity via adding SnF<sub>2</sub>. They found that SnF<sub>2</sub> benefit in increasing the Sn chemical potential and formation energy of Sn vacancies. As a result, the background carrier density of CsSnI<sub>3</sub> is reduced with addition of SnF<sub>2</sub>, which further decreases the defects concentration. The champion device was obtained with 20% SnF2 addition, which showed a PCE of 2.02%.68 Subsequently, the same group continued to incorporate SnF<sub>2</sub> into FASnI<sub>3</sub> perovskite. The addition of SnF<sub>2</sub> was found effective in inhibiting the discolouration of  $FASnI_3$  solution and the oxidation of  $Sn^2$  <sup>+</sup>when the solution was left overnight, leading to improved device performance.<sup>69</sup> Later, Liao et al. optimized the amount of SnF<sub>2</sub> in FASnI<sub>3</sub> and obtained devices with PCE up to 6.22%.<sup>31</sup> Considering that 5 mol% SnF<sub>2</sub> has already been effective to reduce the carrier density, 10 mol% SnF<sub>2</sub> is enough for device fabrication since excess SnF<sub>2</sub> can appear as a secondary phase and exert adverse effect on device performance. Similarly, SnF<sub>2</sub> is also beneficial to the property of MASnI<sub>3</sub> perovskite. Ma et al. compared the dynamics of photoexcited MASnI<sub>3</sub> perovskite films without and with SnF<sub>2</sub> doping by time-resolved fluorescence spectroscopy. The pristine MASnI<sub>3</sub> perovskite films show an electron diffusion length of  $279 \pm 88$  nm, and hole diffusion length of  $193 \pm 46$  nm, whereas SnF<sub>2</sub> doped films MASnI<sub>3</sub> films show ~10 times longer fluorescence lifetimes, giving diffusion lengths exceeding 500 nm.<sup>48</sup> The results indicate that SnF<sub>2</sub> is favourable to the photophysics of MASnI<sub>3</sub> perovskite.

SnCl<sub>2</sub> is also a strong reducing agent in chemistry. Different from SnF<sub>2</sub>, it has higher solubility in common solvent like DMF, which is advantageous to process perovskite films. Marshall et al. compared the effect of introducing different additives into CsSnI<sub>3</sub> perovskite, including SnF<sub>2</sub>, SnCl<sub>2</sub>, SnI<sub>2</sub> and SnBr<sub>2</sub>. Results showed that SnCl<sub>2</sub> processed CsSnI<sub>3</sub> film has the highest stability. Meanwhile, the corresponding devices without an electron blocking layer (EBL) exhibit the highest PCE and FF. The authors attributed the improvement of the device performance to that excess SnCl<sub>2</sub> at the surface of CsSnI<sub>3</sub> n-dopes the fullerene layer and forms a Schottky barrier. This can effectively prevent the extraction of electrons from fullerene to ITO electrode through pinholes in the perovskite film, leading to functional devices with no need for EBL.<sup>70</sup>

Additionally, other tin compounds are also used for fabrication of Sn-based PSCs. Song et al. introduced excess  $SnI_2$  into Sn-based perovskite and fabricated  $CsSnI_3$ -based PCSs with a maximum PCE of 4.81%. They found that a wide range of excess  $SnI_2$ does not affect the high surface coverage of  $CsSnI_3$ , but functions as a compensator as well as a suppressor of  $Sn^{2+}$  vacancies to reduce the p-type conductivity in the film.<sup>71</sup> Yokoyama et al. prepared MASnI<sub>3-x</sub>Br<sub>x</sub> films by a low-temperature vapor-assisted solution process. They found that the non-perovskite  $Sn^{2+}$  phases, such as SnO and  $Sn(OH)_2$ , form in the final films, which can compensate  $Sn^{2+}$  vacancies and is beneficial for lowering the hole-doping level and improving the device's air stability.<sup>72</sup>

#### Reductants

The commercially available SnI<sub>2</sub> source, no matter with 99.99% or 99.999% purity, inevitably contains Sn<sup>4+</sup> impurities that are introduced either during synthesis or during storage. To cope with this problem, Gu et al. reported utilization of Sn powder for purification of SnI<sub>2</sub>. They added Sn powder into the initial FASnI<sub>3</sub> precursor solution (prepared from SnI<sub>2</sub> with 99% purity) with a dark red colour. With stirring, the color of the mixture became lighter, and eventually turned to yellow. The authors proposed that the following redox reaction happened after adding Sn powder into the precursor solution:

$$Sn^{4+} + Sn \rightarrow 2Sn^{2+}$$

Since the standard redox potential  $E^{\circ}$  for  $Sn^{2+}/Sn$  is -0.13 V, and for  $Sn^{4+}/Sn^{2+}$  is 0.15 V, thus this reaction is thermodynamically favourable. Here, Sn powder acts as a reductant and, meanwhile, as a compensator via introducing Sn element. Finally, the authors successfully fabricated FASnI<sub>3</sub> based PCSs prepared from SnI<sub>2</sub> with 99% purity with an efficient PCE of 6.75%.<sup>73</sup>

Song et al. dropped hydrazine solution into the spin-coater chamber and created a

reducing vapour atmosphere during the deposition of Sn-based perovskites. During thin film formation, the hydrazine atmosphere can reduce  $Sn^{4+}$  to  $Sn^{2+}$  with the following reduction process:

$$2SnI_6^{2-} + N_2H_4 \rightarrow 2SnI_4^{2-} + N_2 + 4HI$$

XPS analysis showed that the  $Sn^{4+}/Sn^{2+}$  ratios are reduced by more than 20%, which is responsible for the lower level of p-type electrical conductivity and inhibited carrier recombination. This method was found to dramatically increase the PCEs of MASnI<sub>3</sub>, CsSnI<sub>3</sub> and CsSnBr<sub>3</sub>-based PSCs.<sup>74</sup> Li et al. further developed a chemical route to deposit MASnI<sub>3</sub> films in a two-step process. A hydrazinium tin iodide (HASnI<sub>3</sub>) film was first deposited by spin-coating from the HASnI<sub>3</sub> solution, then it was converted into MASnI<sub>3</sub> in a closed vessel with MA gas. This conversion is proceeded via a cation displacement reaction. Hydrazine is released inside the film during film formation, which can provide a more effective approach to in-situ reduce  $Sn^{4+}$  species. Finally, MASnI<sub>3</sub>-based PSCs reached a maximum PCE of 7.13% with good reproducibility.<sup>75</sup> Since hydrazine has the potential to over reduce Sn<sup>4+</sup> to zero-valent Sn, Kayesh et al. introduced a much milder additive, i.e., hydrazinium chloride (N2H5Cl) into the precursor solvent to fabricate FASnI<sub>3</sub> perovskite films. The addition of N<sub>2</sub>H<sub>5</sub>Cl can promote the formation of homogenous FASnI<sub>3</sub> films. Additionally, hydrazine can decompose in the solution and release electrons to suppress  $Sn^{2+}$  oxidation, as shown in the following equation:

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2 + e^-$$

 $Sn^{2+} \Leftrightarrow Sn^{4+} + 2e^{-}$ 

This strategy led to a PCE up to 5.4% and greatly improved stability for the devices.<sup>76</sup>

#### Other additives for morphology optimization

Li et al. added hypophosphorous acid (HPA) into the CsSnIBr<sub>2</sub> precursor solution for solar cells fabrication. The colour of the precursor solution changes from bright yellow to dark brown and its UV-vis absorption spectrum is also changed with addition of HPA solution at a concentration of 0.5  $\mu$ L/mL<sup>-1</sup>, indicative of the generation of new compounds via Sn-O-P-O-Sn coordination bond connection. On the one hand, the coordination between HPA and Sn<sup>2+</sup> stabilizes CsSnIBr<sub>2</sub>, resulting in reduced Sn vacancies and trap densities. On the other hand, the SnF<sub>2</sub> separation phase is avoided with increased content of HPA, because the new compound promotes the growth of perovskite crystals and expelles excess SnF<sub>2</sub> to the surface of perovskite films that sublimates during annealing. The CsSnIBr<sub>2</sub> PSCs with a mesoscopic architecture achieved an impressive stability, which retained 98% of PCE after 9 h continuous thermal treatment at 473 K and exhibited no efficiency loss under ambient condition for 77 days.<sup>77</sup> Later, Tai et al. successfully fabricated air-stable FASnI<sub>3</sub> PCSs by introducing hydroxybenzene sulfonic acid or its salts into the precursor solution along with excess SnCl<sub>2</sub>. They used three representative additives in the study, including phenolsulfonic acid (PSA), 2-aminophenol-4-sulfonic acid (APSA) and potassium salt of hydroquinone sulfonic acid (KHQSA), to illustrate the dual function of the hydroxybenzene group (-OH) and the sulfonate group  $(SO_3)$  in the molecules. The

reducing –OH group can act as an oxygen scavenger; the SO<sub>3</sub><sup>-</sup> group has the coordination ability and can interact with Sn<sup>2+</sup> to eliminate the SnCl<sub>2</sub> phase separation and encapsulate the perovskite grains with a SnCl<sub>2</sub>–additive complex, which greatly improves the oxidation stability of FASnI<sub>3</sub> perovskite films. KHQSA is confirmed to be the most effective additive and can elevate the PCE of devices from ~3% to 6.76%. The unencapsulated device maintained over 80% of the average PCE after being stored in air for more than 500 h.<sup>78</sup> More recently, Meng et al. introduced poly(vinyl alcohol) (PVA) as the additive into the FASnI<sub>3</sub> perovskite. PVA can interact with FASnI<sub>3</sub> via OH...I– hydrogen bonding, which can introduce nucleation sites, slow down perovskite crystallization, and favor the growth orientation of (h00) facet. Moreover, the trap states and iodine ions migration in the perovskite films are reduced. The resultant device exhibited a high PCE of 8.9%, and also worked stably under maximum power point tracking for 400h.<sup>18</sup>

### 2.6.3 Interfacial engineering

Interfacial engineering is an important strategy to enhance the performance of Pb-based PSCs. It can assist perovskite growth, facilitate charge carrier transport, and passivate trap states, etc. Similarly, it is equally significant to Sn-based PSCs and cannot not be neglected. Sn-based perovskites have narrower bandgap than their Pb analogues, which leads to an increase in VBM or a decrease in CBM. As a result, the energy level of Sn-based perovskites is not able to match well with the common transport layers that have been widely used in Pb-based PCSs. Liu et al intercalated PEG into PEDOT:PSS and

successfully reduced the work function of PEDOT:PSS from -5.1 eV to -4.79 eV. The energy level mismatch between PEDOT:SS and the perovskite is therefore reduced, leading to the best device PCE of 5.12% compared to 2.01% PCE of the control device. The devices also attained good stability stored in both ambient condition and N<sub>2</sub> environment.<sup>79</sup> Chen et al. introduced a PEABr layer on PEDOT:PSS before depositing the FASnI<sub>3</sub> perovskite. Results showed that the FASnI<sub>3</sub> perovskite grow better with the PEABr interlayer, and the trap states in the absorber film approaching the interface are significantly reduced. As a result, the device achieved a champion PCE of 7.05% with stabilized power output and negligible hysteresis.<sup>80</sup> More recently, Kamarudin et al. used edamine for post-treatment of the FA<sub>0.98</sub>EDA<sub>0.01</sub>SnI<sub>3</sub> perovskite layer. They proposed that the nonstoichiometric Sn/I ratio in the perovskite is the main reason for charge recombination. Edamine can donate electrons to the undercoordinated Sn in the perovskite, and effectively passivate the dangling bonds. With suppressed charge carrier recombination, PSCs were reported to attain a high PCE of 10.18%. <sup>81</sup>

# 2.7 Current challenges of tin halide perovskite solar cells

#### 2.7.1 Poor air stability of tin halide perovskites

Sn-based perovskites typically exhibit inferior air stability than Pb-based perovskites. As can been seen from **Figure 2.5**a, the light yellow colour of the FASnI<sub>3</sub> perovskite solution quickly turned red after being exposed to air for several hours, indicating that the FASnI<sub>3</sub> perovskite was severely oxidized by air. A comparison of the (100) XRD peak intensity of FASnI<sub>3</sub> and FASn<sub>0.5</sub>Pb<sub>0.5</sub>I<sub>3</sub> perovskites as a function of storage time (85 °C in dry air) clearly demonstrates that Pb incorporation can enhance the air stability of Sn-based perovskite (**Figure 2.5**a).<sup>82</sup> The difference in air sensitivity can be correlated to their different redox potentials. Sn<sup>2+</sup>/Sn has a standard redox potential of -0.14 V, lower than -0.13 V for Pb<sup>2+</sup>/Pb, <sup>83</sup> which accounts for the more facile oxidation of Sn<sup>2+</sup> upon air exposure.

The mechanism of  $\operatorname{Sn}^{2+}$  oxidation to  $\operatorname{Sn}^{4+}$  in Sn-based perovskites in air was investigated by Leijtens et al. They heated the tin halide perovskite at 85 °C in dry air and used in situ X-ray diffraction measurements, thermogravimetric analysis and ultraviolet–visible absorption spectroscopy to identify the decomposition passway and products. They proposed that the following reaction occurs for the pure Sn perovskite exposed to air:

$$2ASnI_3 + O_2 \rightarrow 2AI + SnO_2 + SnI_4$$

where only few S–I bonds are broken, together with equimolecular release of SnI<sub>4</sub> species and generation of SnO<sub>2</sub> compound. They attributed the degradation to an action of cooperative oxidation of multiple adjacent tin iodide octahedral, where the I<sup>-</sup> bonded to one Sn<sup>2+</sup> can be transferred to adjacent Sn<sup>2+</sup> with which the I<sup>-</sup> was shared.<sup>82</sup> This finding is key to the understanding of the oxidation kineticsof Sn-based perovskite in air.



Figure 2.5 a) Photos of FASnI<sub>3</sub> perovskite solutions (with 0 mol% and 5 mol%  $N_2H_5Cl$ ) exposed in air for different periods of time.<sup>76</sup> b) (100) XRD peak intensity of FASnI<sub>3</sub> and FASn<sub>0.5</sub>Pb<sub>0.5</sub>I<sub>3</sub> perovskites as a function of storage time (85 °C in dry air).<sup>82</sup>

## 2.7.2 Toxicity of tin halide perovskites

There also exist debated arguments on substituting toxic lead with less toxic tin in PSCs, because the toxicity of tin-based perovskites is rather complicated.<sup>84</sup> Babayigit et al. compared the environmental impacts of lead and tin-based perovskites through assessing the toxicity of their degradation products. Since MAPbI<sub>3</sub> and MASnI<sub>3</sub> perovskites will be mainly degraded into PbI<sub>2</sub> and SnI<sub>2</sub>, respectively, certain quantities

of PbI<sub>2</sub> and SnI<sub>2</sub> were added to the aquatic environment of zebrafish *Danio rerio* embryos to test their influence on the organisms. As shown in **Figure 2.6**a, the zebrafish larva will respond to intoxication by exhibiting different morphological defects, such as a dorsal curvature tail down ( $T_{down}$ ), hooked tail ( $T_{hook}$ ), heart oedema (HE) and brain haemovascular defect (BH). They found that SnI<sub>2</sub> will degrade into larger amount of hydroiodic acid (HI) in water compared to PbI<sub>2</sub>, which significantly lowers the PH value in the aquatic environment and induces lower survival rate of zebrafish larvas (**Figure 2.6**b-d). As a result, it is concluded that Sn-based perovskites are more lethal than Pb-based perovskites considering intoxication in the form of acidification.<sup>85</sup>

Moreover, Sn present in compound also has biological toxicity. Excess intake of Sn can also induce poisonous symptoms, such as muscle weakness, gastrointestinal irritation and mineral imbalance. However, it must be noted that only Sn present in organic molecules has high toxicity since it can be more easily assimilated into the body compared to the inorganic compound. Then, we may consider the oxidative instability of tin perovskite be an advantage, since SnI<sub>2</sub> will finally decompose into toxicologically inactive Sn<sup>4+</sup> metal oxides.<sup>16,85</sup>



**Figure 2.6** a) Zebrafish larvas in good state or upon intoxication, exhibiting different morphological defects, including a dorsal curvature tail down ( $T_{down}$ ), hooked tail ( $T_{hook}$ ), heart oedema (HE) and brain haemovascular defect (BH). b) PH (brokenlines) and lethality record (full lines) in function of nominal concentration. Nominal concentration–survival curve and concentration–malformation curve for c) SnI<sub>2</sub> and d) PbI<sub>2</sub> treated larva.<sup>85</sup>

### 2.7.3 Low efficiency of tin halide perovskite solar cells

Although Sn-based perovskites possess suitable bandgaps for solar cell application, the PCEs of tin-based PSCs are poorer compared to their lead analogues. So far, only a few research groups are able to fabricate tin-based PSCs with a PCE>10%, and the highest

PCE reported so far is merely over 13%. Considering that Sn-based perovskites have bandgaps close to the optimum according to the Shockley–Queisser limit, theoretically they could generate a maximum PCE of more than 30%. However, the best efficiency achieved currently is far from the theoretical limit, which is mainly due to the low  $J_{sc}$ ,  $V_{oc}$  and FF.

So far, Sn-based PSCs can achieve a J<sub>sc</sub> of about 22-24 mA/cm<sup>2</sup>. Although this value is close to that of Pb-based perovskites, it must be noted that Sn based perovskites possess bandgaps among the range of 1.25-1.40 eV, and can theoretically generate J<sub>sc</sub> up to 30 mA cm<sup>-2</sup>. In contrast, the maximum J<sub>sc</sub> for Pb based perovskites should be lower considering their wider bandgap (typically 1.5 eV). Currently, Pb based perovskites can achieve a certified J<sub>sc</sub> of 24-25 mA cm<sup>-2</sup>, whereas Sn based perovskites generally have lower J<sub>sc</sub>, and no certified Jsc >23 mA cm<sup>-2</sup> has been reported. So the low J<sub>sc</sub> of Snbased perovskites is a critical problem. What's more, Sn-based perovskites suffer from significant V<sub>oc</sub> and FF loss. Most Sn-based perovskites have a V<sub>oc</sub> less than 0.6 V, which generates a V<sub>oc</sub>/Eg value lower than 0.5; and a FF less than 75%. Such low J<sub>sc</sub>, V<sub>oc</sub> and FF are mainly related to the severe recombination in the devices.

 $Sn^{2+}$  can be easily oxidized to  $Sn^{4+}$ , which leaves large amounts of Sn vacancies in the bulk film and therefore inducing deep level defects formation and severe recombination. This problem is particularly significant in polycrystalline Sn-based perovskite films.<sup>49</sup> It was reported that MASnI<sub>3</sub> infiltrated into a mesoporous metal oxide exhibits a recombination rate constant (k1) ~8×10<sup>9</sup> s<sup>-1</sup>, orders of magnitude higher than ~1-250 ×10<sup>6</sup> s<sup>-1</sup> for MAPbI<sub>3</sub>.<sup>86</sup> Since an increase in k1 will decrease the charge-carrier diffusion length L<sub>D</sub>, the potential for Sn-based perovskite film application in single junction device architecture will be limited when L<sub>D</sub> is not sufficiently longer than the absorption depth of sunlight in the perovskite absorber layer. Owing to the short diffusion length in Sn-based perovskites, the absorbers can't be deposited very thick (usually being <400 nm), which will limit the light absorption and J<sub>sc</sub>. The strong recombination within the perovskite film will also decrease the V<sub>oc</sub> and FF directly. What's more, the oxidized perovskite will have deeper valence band, which can lead to mismatched band alignment with the transport layer and cause V<sub>oc</sub> and FF loss.

In comparison with polycrystalline Sn-based perovskite films, single crystal Sn-based perovskites are able to possess superior photophysical properties. Wu et al. synthesized a CsSnI<sub>3</sub> single crystal with bulk carrier lifetimes of about 6.6 ns, doping concentrations of about  $4.5 \times 10^{17}$  cm<sup>-3</sup>, and minority-carrier diffusion lengths approaching 1µm. The optimized CsSnI<sub>3</sub> single crystal PSC is predicated to potentially produce a PCE of ~23%.<sup>49</sup> Nevertheless, there is no report of single crystal tin-based PSCs by now.

## 2.8 Summary and Perspective

Recently, Sn-based PSCs emerge as a black horse in the community of novel lead-free PSCs due to their relatively higher efficiencies. As a result, they are regarded as the most promising alternatives among Pb-free PSCs to conventional Pb-based PSCs. The rapid development of Sn-based PSCs has a pressing need in some fundamental investigations into the their properties from material design to device engineering. This chapter has systematically summarized the crystal structures, physical properties and film fabrication methods of Sn-based perovskites. Moreover, the effects of perovskite composition, additive engineering, interface modification and device configuration on the output efficiencies of PSCs are also broadly reviewed. It can be sure that the PCEs of Sn-based PSCs will be further enhanced if breakthroughs are made in theoretical understanding and technology progress.

Furthermore, to realize commercialization of Sn-based PSCs in the future, some current issues must be solved. For example, the reproducibility and hysteresis problems should be carefully addressed to maximize the actual output power. Long-term stability of Sn-based PSCs should be further improved to meet the practical application requirements for solar cells. Sn-based perovskites are definitely not nontoxic since they can produce acidic decomposition products, therefore, good encapsulation is required to prevent component leakage. Additionally, studies on printing fabrication of absorber films and large-area module integration are rarely reported, which places much room for exploration.

## Chapter 3 Highly air-stable tin-based perovskite solar cells through grain-surface protection by gallic acid

Maintaining the stability of tin halide perovskites is a major challenge in developing lead-free perovskite solar cells (PSCs). Adding extra SnX<sub>2</sub> (X=F, Cl, Br) in the precursor solution to inhibit Sn<sup>2+</sup> oxidation is an essential strategy to improve the device efficiency and stability. However, SnX<sub>2</sub> on the surface of perovskite grains tends to prohibit charge transfer across perovskite films. Here, we report a coadditive engineering approach by introducing antioxidant gallic acid (GA) together with SnCl<sub>2</sub> to improve the performance of tin–based PSCs. The SnCl<sub>2</sub>–GA complex can not only protect the perovskite grains but also more effectively conduct electrons across it, leading to highly stable and efficient PSCs. The unencapsulated devices can maintain ~ 80% of its initial efficiency after 1000 h storage in ambient air with a relative humidity of 20%, which is the best air stability that can be achieved in tin-based PSCs until now.

## 3.1 Introduction

Perovskite solar cells (PSCs) have attracted much attention due to their rapidly improved power conversion efficiency (PCE) from 3.8% to 25.2% in the past decade.<sup>3-5,11,87-88</sup> Generally, PSCs reported so far are mainly based on perovskite materials in a formula of ABX<sub>3</sub>, where A is a monovalent organic or inorganic cation (e.g., CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>

 $(MA^+)$ ,  $CH(NH_2)_{2^+}(FA^+)$ ,  $Cs^+$ ), B is an octahedrally coordinated divalent metal cation (e.g.,  $Pb^{2+}$  or  $Sn^{2+}$ ) and X is a halide anion (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>).<sup>89-90</sup> Although organolead halide perovskites are employed in almost all of the top-performing PSCs due to their excellent optoelectronic properties, the toxicity of lead may prohibit the commercialization of the PSCs.<sup>24,91-93</sup> Therefore, many environmentally friendly cations, such as tin,<sup>18,65</sup> germanium,<sup>94.95</sup> bismuth,<sup>96</sup> and copper,<sup>97</sup> have been explored as alternatives to lead. Specifically, tin is the most promising candidate since tin halide perovskite shows a suitable bandgap ( $E_g$ ) of 1.2–1.4 eV and a high charge mobility.<sup>23</sup> In 2014, Snaith's group first reported MASnI<sub>3</sub> solar cell with a record efficiency of 6.4%.<sup>98</sup> Kanatzidis's group engineered the bandgap of MASnI<sub>3</sub> through chemical substitution of I with Br to obtain MASnI<sub>3-x</sub>Br<sub>x</sub> and realized a PCE of 5.73%.<sup>30</sup> A recent study reported FASnI<sub>3</sub>– based PSCs with a PCE of 9.0%, which contains trace amount of layered tin perovskite in 3D FASnI<sub>3</sub> perovskite.<sup>99</sup> Besides relatively low efficiency, poor long-term stability is a more serious problem for tin-based PSCs in practical applications.

The limited efficiency and poor stability of tin-based PSCs are originated from the chemical instability of  $\text{Sn}^{2+}$ , which tends to convert into more thermodynamically stable  $\text{Sn}^{4+,82,100-101}$  Consequently, the concentrations of  $\text{Sn}^{2+}$  vacancies in tin-based perovskites are increased, leading to high levels of self p-doping and high densities of trap states. To mitigate  $\text{Sn}^{2+}$  oxidation, the introduction of extra  $\text{SnX}_2$  (X=F, Cl, Br) additive becomes a prevailing method in the deposition of tin-based perovskite films.<sup>102-103</sup> SnX<sub>2</sub> acts as both a reducing agent to prevent  $\text{Sn}^{2+}$  oxidation and a tin

compensator to supply the missing Sn<sup>2+</sup>.<sup>23</sup> However, excess SnX<sub>2</sub> presents as a second phase that is prone to aggregate at the grain boundaries or surfaces of the perovskite films, and could therefore deteriorate the film morphology.<sup>54,104-105</sup> Various attempts have been made by coupling  $SnX_2$  with a secondary chelation additive to enable its homogenous spreading in perovskite films. Zhu et al. employed trimethylamine (TMA) additive to constitute SnX<sub>2</sub>-TMA complex in a sequential deposition process to improve the morphology of FASnI<sub>3</sub> film.<sup>54</sup> Lee et al. reported that adding pyrazine into a SnF<sub>2</sub> containing FASnI<sub>3</sub> perovskite precursor could suppress phase separation by forming a SnF<sub>2</sub>-pyrazine complex.<sup>105</sup> More recently, we reported the addition of hydroxybenzene sulfonic acid or salt as an antioxidant additive into perovskite films, leading to a SnCl<sub>2</sub>-additive complex layer that covers the perovskite grains and greatly improves the stability of the perovskite films in air. <sup>78,106</sup> Incorporating PEA molecules into FASnI<sub>3</sub> to generate low-dimensional tin perovskite is also a promising approach to improving the film morphology and device performance.<sup>107-108</sup> Despite the improved film morphology, the wide band-gap  $SnX_2$  (usually with a high amount of ~10 %) or its complex on the surface of perovskite grains tends to prohibit charge transfer across the perovskite film, which is one of the major reasons for the much lower PCE of tinbased PSCs in comparison with lead-based counterparts. Thus, the secondary additive plays an important role on the efficiency and stability of tin-based PSCs.

In this work, we introduced antioxidant gallic acid (GA) as the secondary additive to assist the fabrication of FASnI<sub>3</sub> perovskite films containing excess SnCl<sub>2</sub>. GA helps to

restrict SnCl<sub>2</sub> aggregates through formation of a SnCl<sub>2</sub>–GA complex that envelops the perovskite grain surface. As a result, the inner perovskite is protected from oxidation and less defects are generated in the films. The resultant tin-based PSCs with an inverted planar architecture show PCE up to 9.03%. The devices exhibit striking long-term stability with no degradation in efficiency after storage in N<sub>2</sub> for more than 1500h. More importantly, ~80% of the initial efficiency is maintained in unencapsulated devices exposed to air (relative humidity (RH):20%) for 1000h. In comparison with other additives, we find that GA can decrease the conduction band level and enhance electron transfer in the SnCl<sub>2</sub>–additive complex covering the surface of FASnI<sub>3</sub> perovskite grains, which benefit the improved efficiency in our devices.

## **3.2** Experimental section

*Materials:* Formamidinium iodide (CH(NH<sub>2</sub>)<sub>2</sub>I) was purchased from GreatCell Solar, Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%), SnI<sub>2</sub> (99.999%) and DMF (anhydrous, 99.8%) were purchased from Alfa Aesar. Gallic acid (99%) and SnCl<sub>2</sub> (99%) were purchased from Aladdin. Bathocuproine (BCP, 96%), DMSO (anhydrous, 99.9%) and chlorobenzene (anhydrous, 99.8%) were purchased from Sigma-Aldrich. Phenyl-C71-butyric acid methyl ester (PCBM) was purchased from Nano-C Ltd.

 $NiO_x$  nanocrystals synthesis: NiO\_x nanocrystals were synthesized according to previous report. Briefly, Nickel(II) nitrate hexahydrate (0.05mol) was dispersed in 100ml deionized (DI) water to get a clear green solution. Then, NaOH solution (1M) was

slowly added until the PH value reached 10. After being stirred for 30min, the green precipitations were collected by centrifugation and washed by DI water for three times. The obtained green powders were further dried at 80°C overnight calcined at 270 °C for 2 h to get the final dark NiO<sub>x</sub> nanocrystals.

Solution preparation: NiO<sub>x</sub> solution was prepared by dispersing NiO<sub>x</sub> nanocrystals into DI water at concentration of 6.5mg/ml. Then it was ultra-sonicated for 10min and filtered by a 0.45 $\mu$ m filter. To prepare the perovskite solution with different additives, 0.8 M FASnI<sub>3</sub> precursor comprised FAI, SnI<sub>2</sub>, SnCl<sub>2</sub>, and GA in a molar ratio of 1: 1:0.07:x (x = 0, 0.005, 0.01, 0.02, or 0.03) were mixed in DMF/DMSO (13:1, v/v), and stirred at 70°C for 2h. PCBM solution was prepared by dissolving 20mg PCBM in 1ml chlorobenzene, which was stirred at room temperature for 3h. BCP solution was prepared by dissolving 0.5mg BCP in 1ml isopropyl alcohol.

*Device fabrication:* ITO glasses were cleaned by ultra-sonication with detergent solution, acetone, isopropyl alcohol, and deionized water for 10 min, respectively. The substrates were then dried by nitrogen flow and treated with  $O_2$ -plasma for 5min before use. NiO<sub>x</sub> films were fabricated by spin-coating the NiO<sub>x</sub> solution on ITO at 4000rpm for 30s, followed by heating at 150°C for 30min in air. The coated substrates were then transferred into the N<sub>2</sub>-filled glovebox immediately. To fabricate the perovskite film, the perovskite precursor solution was deposited onto NiO<sub>x</sub>/ITO and spin-coated at 5000rpm for 30s. During the spin-coating, 80 µL of chlorobenzene was poured on top of the substrates. Then the FASnI<sub>3</sub> films were annealed at 70°C for 5min. Next, PCBM

solution was spin-coated at 1500rpm for 30s on the FASnI<sub>3</sub> films, followed by spincoating BCP solution at 4500 rpm for 30 s. Finally, ~80 nm Ag electrode was evaporated on top of the films under vacuum  $<10^{-6}$  mbar.

Characterization: XRD patterns were recorded by Rigaku SmartLab X-ray Diffractometer. Absorption spectra were scanned with Perkin Elmer\_UV-vis-NIR spectrometer. SEM characterizations were conducted on JEOL JSM 6335F SEM. Steady-state and time-resolved photoluminescence spectra were measured using Edinburgh FLS920 fluorescence spectrophotometer with an excitation wavelength of 635nm. EIS measurements were conducted on Zahner electrochemical workstation. FTIR spectroscopy was measured by using Bruker Vertex-70 at the attenuated total reflectance mode. Hall effect measurements were performed with a four-probe Ecopia Hall Effect Measurement System (HMS-5000) in ambient air. The perovskite films were prepared on glass substrates  $(10 \text{ mm} \times 10 \text{ mm})$  and then Au electrodes were thermally evaporated on the four conors of the perovskite films. STEM characterization was performed using JEOL JEM-2100F TEM/STEM operated at 200 kV, using Gatan Enfina electron spectrometer (CA, USA). EELS spectrum imaging was conducted under 200 kV accelerating voltage with an optimal 13 mrad convergence angle. The TEM samples were prepared by direct deposition of the perovskite film on the holey carbon-coated TEM grid. The UPS and XPS spectra were obtained by Thermo Scientific Nexsa system. The J-V curves of PSCs were measured with a source meter (Keithley 2400) under 100 mWcm<sup>-2</sup> AM 1.5G simulated irradiation from a solar simulator (Newport 91160, 300W). The devices were masked to control the active area
at 4.8mm<sup>2</sup>. The EQE characterization was performed on a standard test system equipped with a xenon lamp (Oriel 66902), a Si detector (Oriel 76175\_71580), a monochromator (Newport 66902) and a dual channel power meter (Newport 2931\_C).

### **3.3 Results and discussion**

PSCs based on FASnI<sub>3</sub> with an inverted structure shown in Figure 3.1a were prepared by solution process. GA was introduced in the active layer as an additive to form a SnCl<sub>2</sub>-GA complex that can envelop FASnI<sub>3</sub> grains. As a strong chelating agent and antioxidant, GA can not only modulate the surface morphology of FASnI<sub>3</sub> perovskite film but also retard Sn<sup>2+</sup> oxidation. To evaluate the antioxidant effect of GA on tin components, we prepared FASnI<sub>3</sub> precursor solutions with different additive compositions (w/o additives; with SnCl<sub>2</sub>; and with SnCl<sub>2</sub> and GA) and stored them in air for comparison. All the solutions showed the similar yellow color initially, as shown in Figure 3.2. After being exposed to air for 4 min, the solution without additives quickly turned red as a result of  $Sn^{2+}$  oxidation to  $Sn^{4+}$ , whereas the color of the solution containing SnCl<sub>2</sub> did not change too much. The solution with both GA and SnCl<sub>2</sub> had no change in its color. As the exposure time exceeded 8 min, all the solutions suffered from discoloration. Notably, the rate of discoloration of the solution containing both SnCl<sub>2</sub> and GA was apparently slower compared to the solution with only SnCl<sub>2</sub> additive. This result suggests the potential of GA as a secondary antioxidant to defer Sn<sup>2+</sup> oxidation in FASnI<sub>3</sub> precursor solution. The antioxidant property of GA lies in the reducing hydroxyl groups (–OH) attached to the aromatic ring. When the sample with GA additive is exposed to air, –OH can effectively scavenge oxygen by donating hydrogen atoms and electrons, and finally GA is transferred to quinones derivatives, as illustrated in **Figure 3.1**b.<sup>109</sup> Hence, GA can continuously scavenge oxygen and provide efficient protection of tin-based perovskite against oxidative damage.



**Figure 3.1** a) Schematic illustration of the device configuration of a FASnI<sub>3</sub> PSC with a SnCl<sub>2</sub>–based complex enveloped the perovskite grains. b) Chemical reaction showing the oxidation of GA to quinone when exposed to air. c) Schematic illustration for the preparation of FASnI<sub>3</sub> films and their morphology resulting from different additives. d) Schematic illustration of the interaction between GA and SnCl<sub>2</sub>. Top-view SEM images

of FASnI<sub>3</sub> films processed with excess SnCl<sub>2</sub> and e) 0%, f) 1%, g) 2%, h) 3% GA, the scale bar is 1 $\mu$ m. i) STEM-HAADF images and the STEM–EELS maps of the O, Sn, I, corresponding to the 1% GA, 7% SnCl<sub>2</sub>-modified FASnI<sub>3</sub> film.



**Figure 3.2** Photographs of FASnI<sub>3</sub> solutions with different additive compositions (w/o additives, with 7 mol% SnCl<sub>2</sub> and with 7 mol% SnCl<sub>2</sub> + 10 mol% GA) exposed to air for different periods of time. The bottles were sealed with a cap with a hole (diameter: 1mm) on it.

The perovskite films were fabricated via a one-step spin coating method from precursors of FASnI<sub>3</sub> in a mixture DMF/DMSO solution with 7 mol% excess SnCl<sub>2</sub> and different amounts of GA additive (**Figure 3.1**c), followed by thermal annealing at 70 °C. Due to the Lewis acidity of SnCl<sub>2</sub>, it is inclined to accept lone pairs from donors (such as O atoms in GA) and coordinate with GA. Since GA and SnCl<sub>2</sub> both possess melting points higher than 200 °C,we consider that GA may interact with SnCl<sub>2</sub> and form a SnCl<sub>2</sub>–GA complex in the final perovskite films, as schematically shown in

Figure 3.1d. Therefore, GA can modulate the surface morphology of  $FASnI_3$  perovskite films in the presence of  $SnCl_2$ .

To illustrate the effect of GA on film morphology, we compare the scanning electron microscopy (SEM) images of FASnI<sub>3</sub> films with SnCl<sub>2</sub> and GA additives (FASnI<sub>3</sub>:SnCl<sub>2</sub>:GA=1:0.07:x, x=0, 0.01,0.02 or 0.03). For the perovskite film deposited from the solution with only SnCl<sub>2</sub> additive, excess SnCl<sub>2</sub> tends to aggregate on the film surface and form many needle-like objects, as shown in **Figure 3.1**c and **Figure 3.1**e. Upon addition of 1mol % GA to the above solution, the fabricated FASnI<sub>3</sub> film becomes much smoother with the aggregates almost eliminated (**Figure 3.1**c, f). However, with increasing addition of GA, the perovskite grain size decreases slightly while the distance between individual grains becomes larger (**Figure 3.1**g, h). We speculate that excess GA might impede FASnI<sub>3</sub> crystallization and growth by interacting with Sn<sup>2+</sup> in the perovskite component and ultimately remain at the grain boundaries and surfaces.<sup>110</sup>

To investigate the interaction between GA and SnCl<sub>2</sub>, Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) characterization were conducted on GA and GA–SnCl<sub>2</sub> powders that were prepared by dissolving GA and SnCl<sub>2</sub> together in DMF before being heated to dry. The characteristic C–O stretching vibration for pure GA can be observed at 1258 cm<sup>-1</sup>, while for GA-SnCl<sub>2</sub>, the C–O vibration is shifted to lower wavenumber of 1242 cm<sup>-1</sup> (**Figure 3.3**). Consequently, the –COOH group in GA may coordinate with SnCl<sub>2</sub>. XRD spectra of the films (**Figure 3.4**) indicate that the crystalline SnCl<sub>2</sub> is converted into an amorphous phase when coupling with GA.

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Figure 3.3 FTIR spectra for the powder samples of GA and GA–SnCl<sub>2</sub>.



Figure 3.4 XRD patterns of the samples of SnCl<sub>2</sub> and GA–SnCl<sub>2</sub>.

We notice that the UV–vis absorption spectra of FASnI<sub>3</sub> films prepared with SnCl<sub>2</sub> and varied content of GA exhibit similar absorption edge at around 891 nm (**Figure 3.5**). In addition, the characteristic XRD peaks of FASnI<sub>3</sub> films with SnCl<sub>2</sub> and varied content of GA all match the orthorhombic lattice structure of FASnI<sub>3</sub> (**Figure 3.6**), implying that both SnCl<sub>2</sub> and GA do not affect the crystal phase of FASnI<sub>3</sub> perovskite. Since

SnCl<sub>2</sub> and GA do not participate in perovskite formation, it is reasonable to conclude that GA mainly distributes at grain surfaces and boundaries (GBs), and interacts with excess SnCl<sub>2</sub> to form an amorphous complex.



Figure 3.5 UV–vis spectra of  $FASnI_3$  films prepared with  $SnCl_2$  (7 %) and various amounts of GA additive.



**Figure 3.6** X-ray diffraction (XRD) patterns of FASnI<sub>3</sub> films prepared with SnCl<sub>2</sub> (7 %) and various amounts of GA additive. \* denote to the peaks of ITO.

To further identify the distribution of GA in perovskite films, scanning transmission electron microscopy (STEM) and electron energy loss spectra (EELS) were characterized on a FASnI<sub>3</sub> sample containing 1 mol% GA and 7% mol SnCl<sub>2</sub>. The identification of GA molecules is tracked by its characteristic O element. From the STEM image of a FASnI<sub>3</sub> perovskite grain, and EELS maps of O, Sn, I elements, together with their superposition (**Figure 3.1**i), it can be clearly observed that GA distributes at the perovskite grain surface. Becasue the signal of Cl was too weak in its EELS map, Cl distribution was further confirmed by X-ray photoelectron spectroscopy (XPS). The decreased content for Cl after argon ion etching indicates that SnCl<sub>2</sub> is mainly located on film surface (**Figure 3.7**).



**Figure 3.7** XPS profile of Cl 2p peaks before and after argon ion (2 KeV) sputtering for 30s.

PSCs with a device structure of ITO/NiO<sub>x</sub>/FASnI<sub>3</sub>/PCBM/BCP/Ag were fabricated and the thickness of each layers were characterized by cross-sectional SEM as shown in Figure 3.8a. It is worth noting that SnCl<sub>2</sub> is used as the basic additive with its amount optimized to be 7 mol%, as shown in Figure 3.9. Figure 3.8b shows the J–V curves of the best performing PSCs with the introduction of 0, 0.5, 1, 2, and 3 mol% GA. Notably, the device with the GA addition of 1 mol% demonstrates the best performance. The control device without GA additive exhibits a PCE of 3.38% (2.44%), Voc of 0.33 (0.27) V, J<sub>sc</sub> of 19.33 (19.19) mA/cm<sup>2</sup>, and FF of 53.0% (47.1%) measured under forward (reverse) scan. When 1 mol% GA is introduced in the perovskite layer, J-V curves with negligible hysteresis are achieved and the maximum PCE of 9.03% (8.91%), Voc of 0.64 (0.63) V, J<sub>sc</sub> of 19.75 (19.63) mA/cm<sup>2</sup>, and FF of 71.4% (72.0%) for forward (reverse) scan are obtained. Figure 3.8c shows the external quantum efficiency (EQE) spectra of the control and GA incorporated (1 mol%) device tested from 300nm to 1000 nm. It is obvious that EQE value is increased by GA additive in all the wavelength region. The integrated J<sub>sc</sub> for the GA incorporated device is 19.82 mA cm<sup>-2</sup>, closely matching the measured value from the J–V curve. The integrated J<sub>sc</sub> for the control device (18.03 mA cm<sup>-2</sup>) is much lower than the value (19.33 mA cm<sup>-2</sup>) in its J–V curve probably due to the rapid degradation of the device to some extent in ambient air during the measurements. Steady-state photocurrent and power output of a GA incorporated device were measured in air at a bias of 0.51 V under 100 mWcm<sup>-2</sup> AM 1.5G illumination. A stabilized output of  $\approx 8.3\%$  is achieved (Figure 3.10), which is close to the PCE value obtained from the J-V curve. The PCE statistical histogram of 20 devices

w/o and with 1% GA is presented in **Figure 3.8**d, which verifies the reproducibility of the overall PCE improvement by the GA additive.



Figure 3.8 a) Cross-sectional SEM image of a fabricated inverted FASnI<sub>3</sub> PSC with

SnCl<sub>2</sub>–GA additives; The scale bar is 200nm. b) J–V curves for the best performing PSCs processed with SnCl<sub>2</sub> and 0%, 0.5%, 1%, 2% or 3% GA additive in forward (solid) and reverse scan (hollow). c) EQE spectra, d) PV statistics of PSCs processed w/o and with 1% GA additive. e) PCE evolution of unencapsulated PSCs processed w/o and with 1% GA additive stored in the N<sub>2</sub>-filled glovebox, or f) stored in air with RH  $\approx$ 20%.



**Figure 3.9** J-V curves for FASnI<sub>3</sub> PSCs processed with different amounts of SnCl<sub>2</sub> additive (w/o GA).



Figure 3.10 Steady-state photocurrent density and power output for GA-incorporated device.

The statistical photovoltaic parameters for all conditions are shown in **Table 3.1**. The devices with 1 mol% GA addition exhibit an average PCE of 8.32%, which is much higher than that of the control devices (2.82%). This significant improvement in PCE after the addition of GA is due to the obvious increase in  $V_{oc}$  from 0.28V to 0.61V and FF from 53.9% to 69.4%. The higher  $V_{OC}$  and FF can be attributed to the improved surface morphology of the perovskite film, as observed from the SEM images in Figure **3.1**e-h. Generally, Voc loss can be caused by the non-radiative recombination at trap states within the perovskite bulk or at interfaces.<sup>111</sup> Since GA acts as a strong antioxidant distributed on the surface of perovskite grains, GA can protect the perovskite from oxidation and inhibit the generation of Sn<sup>2+</sup> vacancy defects within the perovskite grain. Moreover, SnCl<sub>2</sub> aggregates could also affect charge collection by lowering the contact area with the Ag electrode. By coupling SnCl<sub>2</sub> with GA, the FASnI<sub>3</sub>/PCBM interface is smoothened and SnCl<sub>2</sub> aggregation is reduced. So the addition of 1 mol% GA can increase Voc and FF of the devices. However, with further increase of the GA concentration to more than 2%, the device PCE and J<sub>sc</sub> are significantly decreased, which can be attributed to the decreased crystallization of the perovskite film induced by GA. The performance of devices with only GA additive was also investigated. The inferior results shown in Figure 3.11 indicate that SnCl<sub>2</sub> is still needed as a moderator for optimal performance.

GA concentration		Voc	Jsc	FF	PCE
(mol %)		(V)	(mA cm <sup>-2</sup> )	(%)	(%)
0	Average	0.28±0.03	19.07±0.70	53.9±3.1	2.82±0.27
	Champion	0.33	19.33	53	3.38
0.5	Average	0.49±0.03	19.61±0.68	66.7±3.4	6.39±0.48
0.0	Champion	0.53	19.42	71.02	7.31
1	Average	0.61±0.02	19.73±0.55	69.4±2.1	8.32±0.36
	Champion	0.64	19.75	71.4	9.03
2	Average	0.53±0.02	16.99±0.84	61.5±4.7	5.50±0.30
L	Champion	0.54	17.23	64.6	6.01
3	Average	0.49±0.03	15.76±0.90	58.8±4.2	4.52±0.38
U U	Champion	0.5	16.34	60.8	4.97

**Table 3.1** Photovoltaic parameters of PSCs with the introduction of excess 7 mol% SnCl<sub>2</sub> and different concentrations of GA in the perovskite film.



Figure 3.11 J-V curves for FASnI<sub>3</sub> PSCs processed with different amounts of GA additive (w/o SnCl<sub>2</sub>).

Poor device stability of tin-based PSCs is a major challenge to their applications. We first monitored the performance evolution of unencapsulated control and GA incorporated devices stored in a N<sub>2</sub>-filled glovebox. The PCE measurement was conducted in ambient air (RH >60%) by taking the devices out of the glovebox. As shown in **Figure 3.8**e, the device with GA shows slowly increased efficiency during the storage within 1500 h while the control device without GA exhibits decreased PCE with increasing storage time. Such a PCE enhancement in the former is associated with the increased values of  $V_{oc}$  and FF (**Figure 3.12**), which is similar to the phenomenon reported in literatures.<sup>65,112</sup> The enhancement can be attributed to the self-healing property or the releasing of crystal strain in the perovskite in the dark. <sup>112-113</sup>



Figure 3.12 Evolution of photovoltaic parameters ( $J_{sc}$ , FF and  $V_{oc}$ ) for a GA-incorporated device stored in N<sub>2</sub>-filled glovebox without encapsulation.

We then tested the stability of unencapsulated devices stored in air with RH  $\approx 20\%$ . As shown in **Figure 3.8**f, the PSC with GA additive shows good long-term stability, which maintains ~ 80% of its initial PCEs after storage for 1000 h, while the control device exhibits a quick decrease of PCE within 200 h. The degradation in both V<sub>oc</sub> and J<sub>sc</sub> of the GA incorporated device is much slower than that of the control device as well, as shown in **Figure 3.13**, indicating that the generation of trap states is slower in the former. We compare our device with the reported tin-based PSCs in terms of stability in ambient air (**Table 3.2**). To the best of our knowledge, the device with GA additive shows much better air stability (RH  $\approx 20\%$ ) than any tin-based PSCs reported before.

Even under a high RH of 60%, only 23% loss of the initial PCE was observed in an unencapsulated GA incorporated device after 120 h storage (**Figure 3.14**a). The durability of device performance under constant light soaking in air (100 mW cm<sup>-2</sup>, RH  $\approx 20\%$ ) was also investigated. Only 30% loss in PCE was observed for the unencapsulated GA incorporated device after 140 min storage (**Figure 3.14**b), which is better than the result in previous report. <sup>63</sup>



Figure 3.13. J-V curves evolution of the control and GA -incorporated devices stored in air at a RH  $\approx 20\%$  without encapsulation.

#### Table 3.2 Summary of the reported stability of $FASnI_3$ based PSCs in ambient

#### environment without encapsulation

Device structure	Best PCE	Storage condition	Lifetime <sup>a)</sup>	Ref
	(%)			
FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /FASnI <sub>3</sub> /TPE/Au	7.23	dark, 15% RH	~ 50 min	114
FTO/SnO <sub>2</sub> /C <sub>60</sub> /FASnI <sub>3</sub> /Spiro-OMeTAD/Ag	4.34	dark, 50% RH	~ 2.5 h	54
ITO/PEDOT:PSS/FASnI3/C60:TBAI/Ag	7.09	dark, 50% RH	~ 3 h	54
FTO/(PEG-)PEDOT:PSS/FASnI <sub>3</sub> /PCBM/BCP/Ag	5.12	dark, 40% RH	~ 6 h	79
ITO/PEDOT:PSS/MA:FASn <sub>1</sub> . xGexI <sub>3</sub> /PCBM/C <sub>60</sub> /BCP/Ag	6.90	dark	< 10 min	115
ITO/PEDOT:PSS/PEA:FASnI3/C60/BCP/Al	9.0	dark, 20% RH	~ 40 h	99
ITO/PEDOT:PSS/Guanidinium:FASnI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	9.6	dark, 20%RH	b)	35
ITO/PEDOT:PSS/Guanidinium:FASnI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	9.6	dark, 60%RH	96 h	35
ITO/PEDOT:PSS/AVA: FASnI <sub>3</sub> /PCBM /BCP/Ag	8.71	dark, 50%RH	< 40 min	116
ITO/NiO <sub>x</sub> /FASnI <sub>3</sub> (KHQSA)/PCBM/Ag	6.76	dark, 20% RH	~ 500 h	
ITO/NiO <sub>x</sub> /FASnI <sub>3</sub> (GA)/PCBM/ BCP/Ag	9.03	dark, 20% RH	~1000h	This work

<sup>a)</sup> For a better comparison, the lifetime was recorded according to the time the device

took to degrade by 20% of the initial efficiency

 $^{\rm b)}$  The device showed almost no degradation after storage for  $\sim 170~h$ 



Figure 3.14 a) Stability of unencapsulated GA –incorporated device stored in air (RH  $\approx 60\%$ ). b) Light soaking test for unencapsulated GA –incorporated device under 100 mw/cm<sup>2</sup> white light illumination in air (RH  $\approx 20\%$ ).

To further illustrate the better air stability for GA incorporated devices, the surface and bulk  $Sn^{4+}$  contents for the control and GA incorporated FASnI<sub>3</sub> films after oxidation were characterized according to the XPS Sn 3d5/2 spectra. Meanwhile, the fresh prepared films before oxidation were also characterized as a reference. As shown in **Figure 3.15**, GA incorporated fresh FASnI<sub>3</sub> film displayed a surface Sn<sup>4+</sup> ratio of 3.2% initially, much lower than that of the control fresh film without GA (8.7%). After exposed to air (RH≈20%) for 12h, the surface Sn<sup>4+</sup> content for the control film reached 65.1%, whereas for GA incorporated FASnI<sub>3</sub> film was only 51.4%. Thus less severe oxidation on the surface for GA incorporated FASnI<sub>3</sub> films was observed. More importantly, we notice that the bulk of the films are well protected by GA. The bulk Sn<sup>4+</sup> ratio of only 0.4% was observed in GA incorporated FASnI<sub>3</sub> film while 5.7% in

the control film after oxidation, which indicates the enhanced effect of SnCl<sub>2</sub>–GA complex in protecting FASnI<sub>3</sub> from oxidation. Moreover, UV-vis absorption spectra of FASnI<sub>3</sub> films containing different additives under air exposure were characterized, as shown in **Figure 3.16**. The film without any additive shows the fastest while the SnCl<sub>2</sub>–GA incorporated one exhibits the slowest change in the absorption spectra. This result also confirms the role of the SnCl<sub>2</sub>–GA complex to improve the film oxidation stability.



**Figure 3.15** XPS Sn 3d5/2 spectra of FASnI<sub>3</sub> films with only SnCl<sub>2</sub> additive w/o GA (a, c, e) and with GA (b, d, f). Specifically, samples (a, b) for measurements were freshly prepared; samples (c, d) were stored in air for 12 h (RH  $\approx$  20%) prior to measurements; samples (e, f) were stored in air for 12 h (RH  $\approx$  20%) and etched with 2 KeV argon ions





**Figure 3.16** UV-vis absorption spectra of FASnI<sub>3</sub> films processed w/o additives a), with only SnCl<sub>2</sub> additive b) and with SnCl<sub>2</sub> –GA coadditives c) as a function of exposure time to air (RH  $\approx$  20%).

To gain insight into the performance enhancement introduced by GA additive, steady state photoluminescence (PL) and time-resolved photoluminescence (TRPL) characterizations were performed on FASnI<sub>3</sub> films (containing 7 % SnCl<sub>2</sub>) w/o and with 1 % GA additive. Both films were processed on ITO substrates, and the laser was irradiated from the ITO side with a wavelength of 636nm. The FASnI<sub>3</sub> film with GA additive shows stronger PL intensity compared to the film w/o GA (**Figure 3.17**a), indicating the decreased density of trap states in the perovskite film induced by GA. The TRPL spectra of the films are presented in **Figure 3.17**b. The TRPL decay is fitted with a biexponential equation:  $Y=A_1exp(-t/\tau_1)+A_2exp(-t/\tau_2)$ , and the fitted parameters are listed in **Table 3.3** in the Supporting Information. The decay process is dominated by the lifetime  $\tau_2$ , which corresponds to non-radiative recombination originated from traps. The introduction of GA can substantially increase the PL lifetime from 0.68 ns to 1.3 ns, which also indicates the decreased defect density in the perovskite film by GA. Therefore, GA can effectively decrease trap densities in the perovskite films by protecting them from oxidation.



**Figure 3.17 a)** Steady state photoluminescence, b) Time-resolved photoluminescence spectra for FASnI<sub>3</sub> perovskite films processed w/o and with 1 % GA additive deposited on ITO/glass. c) I–V curves of electron only devices in three regions, including ohmic, trap-filled limit (TFL) and child regions. d) EIS plots of FASnI<sub>3</sub> based PSCs processed w/o and with 1 % GA additive measured at 0.2V in dark.

Table 3.3	Fitted	parameters	of	TRPL	curves	for	the	FASnI <sub>3</sub>	film	w/o	and	with	GA
additive													

Sample	A <sub>1</sub>	$ au_1(\mathrm{ns})$	<b>A</b> <sub>2</sub>	$ au_2(\mathrm{ns})$	$ au_{avg}(\mathrm{ns})$
w/o GA	$1.88 \times 10^{4}$	4	6.29×10 <sup>14</sup>	0.68	0.68
with GA	1.83×10 <sup>4</sup>	4	6.65×10 <sup>9</sup>	1.3	1.3

To present evidence for the reduction of trap density in FASnI<sub>3</sub> when adding GA, we further conducted space charge limited current (SCLC) measurements on electron-only devices with a device structure of ITO/SnO<sub>2</sub>/FASnI<sub>3</sub>/PCBM/Ag. **Figure 3.17**c displays the I–V curves of the electron-only devices measured in the dark. The plot clearly shows three voltage-dependent regions corresponding to different behaviors, including ohmic region (I  $\propto$  V), trap-filling region (I  $\propto$  V<sup>n</sup>, n>3) and SCLC region((I  $\propto$  V<sup>2</sup>).<sup>80</sup> In the ohmic region, the current shows linear relation to bias voltage and then it increases abruptly when the bias voltage exceeds the kink point, indicating the complete filling of trap states. The voltage at the kink point denotes trap-filled limit voltage (V<sub>TFL</sub>), given by:<sup>101</sup>

$$V_{\rm TFL} = \frac{q n_{\rm t} L^2}{2 \epsilon \epsilon_0} \tag{1}$$

where  $n_t$  is the trap density,  $V_{TFL}$  is the trap-filled limit voltage,  $\varepsilon$  is the relative dielectric constant,  $\varepsilon_0$  is the vacuum permittivity, q is electron charge, L is the thickness of the film. The  $V_{TFL}$  of the pristine FASnI<sub>3</sub> device is 0.23 V, corresponding to a trap density of  $3.63 \times 10^{15}$  cm<sup>-3</sup>; whereas  $V_{TFL}$  is reduced to 0.17V by the GA additive, leading to a lower trap density of  $2.68 \times 10^{15}$  cm<sup>-3</sup>. Electrochemical impedance spectroscopy (EIS) measurement was carried out to investigate the carrier dynamics in PSCs. **Figure 3.17**d shows the Nyquist plots of the FASnI<sub>3</sub> PSCs w/o and with 1 % GA additive measured at a bias voltage of 0.2 V in the dark, and the plots at different bias voltages are presented in Figure S15a,b in the Supporting Information. The corresponding equivalent circuit for fitting the curves is shown in the inset of **Figure 3.17**d, where  $R_s$  is the series resistance,  $R_{rec}$  is the recombination resistance and *C* represents the chemical capacitance. All the PSCs exhibit a main semicircle at low frequency, which can be attributed to the  $R_{rec}$  and *C*. The fitted  $R_{rec}$  values for the GA incorporated device is much larger than the control device at different voltages (**Figure 3.18**). Since the recombination rate is inversely proportional to  $R_{rec}$ , we can conclude that the device with GA additive exhibits a lower recombination rate than the reference device.



**Figure 3.18** EIS spectra of FASnI<sub>3</sub> based PSCs (containing SnCl<sub>2</sub>) processed w/o GA (a) and with 1% GA (b) measured at different bias voltage under dark. (c) Fitted Rec values from EIS analysis at different voltages.

We further investigated the carrier transport property of the perovskite films by hall effect measurement, which was conducted by four contacts Hall bar method.<sup>117</sup> **Table 3.4** shows the information of carrier density and mobility of FASnI<sub>3</sub> films w/o and with 1% GA additive. The GA-added film exhibits a much lower carrier density and a higher hole mobility than the pristine film. Thus, the self-doping effect is clearly alleviated in the GA -added film as a result of the suppressed oxidation of Sn<sup>2+</sup>.

Table 3.4 Hall effect measurement for FASnI<sub>3</sub> perovskite film with SnCl<sub>2</sub> additive

Additive	Carrier density (×10 <sup>16</sup> cm <sup>-3</sup> )	Hole Mobility (cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup> )
SnCl <sub>2</sub>	26.65±11.90	1.05±0.32
SnCl <sub>2</sub> –GA	6.45±1.87	12.71±3.21

and with SnCl<sub>2</sub>–GA co-additives

The error was derived from the results of at least 3 devices.

Besides high-density traps in tin-based perovskite films, another obstacle for achieving high PCE of tin-based PSCs is the SnX<sub>2</sub> layers enveloped on perovskite grains. As shown in Figure 3.1a, SnCl<sub>2</sub> or its complex has a bandgap much larger than that of a FASnI<sub>3</sub> film, which prohibits the transfer of both electrons and holes to the charge transport layers. Hence, the electronic property of the SnCl<sub>2</sub> layer is essential to the device performance. In our previous work, we introduced the potassium salt of hydroquinone sulfonic acid (KHQSA) as an antioxidant additive to passivate FASnI<sub>3</sub> grains. However, the resultant PCE of the devices is much lower than that of the PSCs with GA additive. To make clear this effect, we investigated the band structures of SnCl<sub>2</sub> and its complexes with GA and KHQSA additives. Figure 3.19a shows the light absorption spectra of SnCl<sub>2</sub>, SnCl<sub>2</sub>-GA and SnCl<sub>2</sub>-KHQSA films. According to the absorption edges, the introduction of GA can dramatically decrease the bandgap of SnCl<sub>2</sub> from 3.9 eV to 3.25 eV while KHQSA can slightly decrease the bandgap to 3.8 eV. Such a phenomenon can be correlated to the chemical structure variation and the expanded width of the localized levels after the formation of complex.<sup>118-119</sup> Then the

films were characterized by ultraviolet photoelectron spectroscopy (UPS) measurements (**Figure 3.19**b).<sup>120</sup> To eliminate the influence of unwanted oxidation products on the film surface, the samples were etched by sputtering 2k eV argon ion for 30s prior to measurements. Combining the band gap of FASnI<sub>3</sub> perovskite derived from **Figure 3.5** with the valence band maximum (VBM) derived from **Figure 3.20**, we can obtain the band structures of FASnI<sub>3</sub> and the above three films, as presented in **Figure 3.19**c. We can find that the electron transfer from FASnI<sub>3</sub> to PCBM can be prohibited by all of three films while the SnCl<sub>2</sub>–GA complex shows the lowest barrier height for electron transfer. According to the conduction process in a potential barrier, the tunneling current density *J* can be expressed by<sup>121</sup>:

$$J \sim E^2 exp\left[-\frac{4\sqrt{2m^*(q\phi_B)^{3/2}}}{3q\hbar E}\right]$$
(2)

where E is the electric field, m\* is the effective mass and  $\phi_B$  is the barrier height. Thus, a lower barrier height ( $\phi_B$ ) should enable a higher current through it. To clarify this effect, devices with the three different additives (SnCl<sub>2</sub>, SnCl<sub>2</sub>–1 mol% KHQSA and SnCl<sub>2</sub>–1 mol% GA) were prepared at the same condition and showed the PCE of 3.08%, 6.49% and 8.56%, respectively, as presented in **Figure 3.19**d. Both KHQSA and GA can improve the device performance while the highest PCE is obtained in the GA incorporated devices. The higher improvement in both J<sub>sc</sub> and V<sub>oc</sub> by GA than KHQSA benefits from less recombination loss at the perovskite/PCBM interface induced by decreased conduction band level of SnCl<sub>2</sub>–GA complex and better electron transfer across it.



**Figure 3.19** a) Absorption spectra, b) Near E<sub>f</sub> region and cutoff region in UPS spectra for SnCl<sub>2</sub>, SnCl<sub>2</sub>–GA and SnCl<sub>2</sub>–KHQSA complex. c) Schematic energy level diagram of FASnI<sub>3</sub> perovskite, SnCl<sub>2</sub>, SnCl<sub>2</sub>–GA, SnCl<sub>2</sub>–KHQSA and PCBM layer. d) J–V curves for PSCs processed with SnCl<sub>2</sub> additive, SnCl<sub>2</sub>–GA additives and SnCl<sub>2</sub>– KHQSA additives.



**Figure 3.20** Near  $E_f$  region and cutoff region in UPS spectra for FASnI<sub>3</sub> films with only SnCl<sub>2</sub> additive and with SnCl<sub>2</sub>-GA additives. The samples were etched by sputtering 2k eV argon ion for 30s prior to measurements.

We also measured the electron mobilities of SnCl<sub>2</sub>–GA and SnCl<sub>2</sub>–KHQSA complex by measuring space-charge-limited currents (SCLCs) across the films. **Figure 3.21** in shows the I–V curves for the devices with a structure of ITO/SnO<sub>2</sub>/complex film/ Al. SCLC is given by<sup>101,122</sup>

$$I = \frac{9A\varepsilon\varepsilon_0\mu_e V^2}{8L^3} \tag{3}$$

where *A* is the device area and  $\mu_e$  the electron mobility. The film thickness L = 100nm. The electron mobilities are estimated to be  $5.58 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $1.44 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for SnCl<sub>2</sub>-GA and SnCl<sub>2</sub>-KHQSA films, respectively, indicating that SnCl<sub>2</sub>-GA is more favorable for electron transfer across it. Therefore, the high PCE induced by GA can be attributed to the more suitable electronic property of the SnCl<sub>2</sub>-GA complex in the perovskite films.



**Figure 3.21** Dark I–V curves for capacitor-like device with a structure of ITO/SnO<sub>2</sub>/ SnCl<sub>2</sub>–GA /Al and ITO/SnO<sub>2</sub>/ SnCl<sub>2</sub>–KHQSA /Al. The mobilities of the complex films are calculated through fitting the log(I)–log(V) plots by a line with a slope of 2 (blue).

1

Voltage (V)

10

## 3.4 Summary

1E-5

0.1

In summary, GA additive together with excess SnCl<sub>2</sub> has been introduced into FASnI<sub>3</sub> perovskite films to improve the device photovoltaic performance for the first time. This coadditive engineering approach enables capping of the perovskite grains with an amorphous SnCl<sub>2</sub>–GA complex and leads to suppressed Sn<sup>2+</sup> oxidation and defect densities in the perovskite films. Consequently, the performance of the resultant PSCs is substantially enhanced. We also notice that the large bandgap of SnCl<sub>2</sub> prohibits the transfer of both electrons and holes from FASnI<sub>3</sub> perovskite to charge transport layers while the barrier height for electron transfer is dramatically decreased by formation of complex with GA. Thus, GA can induce higher PCE of PSCs than other antioxidant

additives. More importantly, due to the protection effect of the  $SnCl_2$ -GA complex, our devices exhibit excellent long-term stability both stored in  $N_2$  and in air conditions. This work provides a guideline for the selection of antioxidant additives in tin-based PSCs and paves a way for realizing highly stable tin-based PSCs in the future.

# Chapter 4 Synergistic modulation of perovskite growth and interfaces via a 2D transition-metal dichalcogenide interlayer for high-efficiency tin-based perovskite solar cells

Tin-based perovskites with favorable optoelectronic properties and ideal bandgaps have emerged as promising alternatives to toxic lead-based perovskites for photovoltaic applications. However, it is challenging to obtain high-quality tin-based perovskite films by solution process. Here, liquid-exfoliated two-dimensional (2D) transitionmetal dichalcogenides (i.e. MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub>) with smooth and defect-free surfaces are applied as growth templates for spin-coated FASnI<sub>3</sub> perovskite films, leading to van der Waals epitaxial growth of perovskite grains with a growth orientation along (100). We find that WSe<sub>2</sub> has better energy alignment with FASnI<sub>3</sub> than MoS<sub>2</sub> and WS<sub>2</sub> and results in a cascade band structure in resultant perovskite solar cells (PSCs), which can facilitate hole extraction and suppress interfacial charge recombination in the devices. The WSe<sub>2</sub> -modified PSCs show power conversion efficiency up to 10.47%, which is among the highest efficiency of FASnI<sub>3</sub>-based PSCs. The appealing solution phase epitaxial growth of FASnI<sub>3</sub> perovskite on 2D flakes is expected to find broad applications in optoelectronic devices.

## 4.1 Introduction

Organic-inorganic hybrid halide perovskite solar cells (PSCs) have shown rapid progress in power conversion efficiency (PCE) in the past ten years, which presently has exceeded 25%.<sup>9,11,87</sup> However, the top-performing PSCs are based on toxic lead halide perovskite materials, which are detrimental to the environment. Tin-based perovskites have been recognized as ideal alternatives due to their favorable optoelectronic properties and environmentally friendly characters.<sup>123-125</sup> Notably, tin-based PSCs exhibit the highest performance among the categories of lead-free PSCs, while their performance still lags far behind that of lead-based counterparts.<sup>24,126-129</sup>

The inferior performance of Sn-based PSCs can be ascribed to the following reasons. One critical factor is the poor Sn-based perovskite films with rough surface and highdensity of traps.<sup>51</sup> To achieve high-performance Sn-based PSCs, a uniform and continuous perovskite film with large grain sizes and a preferred orientation is required. Several strategies have been developed to modulate the crystallization of Sn-based perovskites, For example, Meng et al. reported the introduction of pentafluorophenoxyethylammonium iodide (FOEI) into the precursor solution for surface-controlled growth of FASnI<sub>3</sub> perovskites.<sup>130</sup> Yu et al. tuned MA<sub>x</sub>FA<sub>1-x</sub>SnI<sub>3-x</sub>Br<sub>x</sub> perovskites with preferential facet of (001) via compositional engineering.<sup>131</sup> Qiu et al. introduced nbutylamine (BA) and phenylethylamine (PEA) as the intermediate phase suppressor to obtain uniform two-dimensional (2D) Ruddlesden–Popper tin-based perovskites with ordered crystal nucleation.<sup>132</sup> More recently, the solution of n-propylammonium iodide (PAI) was utilized to induce the recrystallization and templated growth of FASnI<sub>3</sub>.<sup>133</sup> Despite the success in modulating the nucleation and crystallization of tin-based perovskites, the obtained perovskite films cannot meet the requirement for high-performance PSCs due to the easy oxidation of  $Sn^{2+}$  to  $Sn^{4+}$  that can induce high levels of p-type doping in perovskite films. Thus reducing agents should be introduced to prohibit the oxidation of the perovskite films, which in turn leads to a less conductive layer unfavorable for charge transfer on grain surfaces.<sup>70,134-135</sup>

Another important factor is the interfacial energy loss that limits the device PCE. The interface states and energy level mismatching between tin-based perovskites and common charge transport materials can induce severe non-radiative recombination and result in low open-circuit voltages ( $V_{oc}$ ) and fill factor (FF).<sup>136-137</sup> To solve this problem, Jokar et al. introduced guanidinium (Gua) cation in the FA/Gua mixed perovskite to match its band structure with PEDOT:PSS and  $C_{60}$ .<sup>65</sup> Thereafter, Nishimura et al. tuned the band structure of GeI<sub>2</sub> -doped (FA<sub>1-x</sub>EA<sub>x</sub>)<sub>0.98</sub>EDA<sub>0.01</sub>SnI<sub>3</sub> perovskite by introducing ethylammonium cation (EA) with different amount to match the energy levels of the transport layers.<sup>36</sup> Very recently, Jiang et al. substituted [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with indene-C60 bisadduct (ICBA) as an electron transport material, which shows a smaller energy level offset with 2D perovskite component due to a higher lowest unoccupied molecular orbital (LUMO) level of the latter.<sup>138</sup> In addition, the energy loss in Sn-based PSCs can be reduced by interface optimization of hole transport layers (HTLs).<sup>79,139</sup>

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Two-dimensional (2D) semiconductors, e.g. transition-metal dichalcogenides, demonstrate unique optoelectronic properties such as high carrier mobilities, tunable band structures and optical transparency,<sup>140-141</sup> making them excellent interlayer materials in PSCs.<sup>6,142</sup> In the present work, we introduced liquid-phase-exfoliated fewlayer MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> (the formula can be referred as MX<sub>2</sub>, where M is a transition metal and X is a chalcogenide) flakes between NiO<sub>x</sub> hole transport layer and FASnI<sub>3</sub> perovskite for achieving high performance inverted PSCs. MX<sub>2</sub> is utilized as a growth template for preparing epitaxial Sn-based perovskite films by spin coating. Perovskite films on MX<sub>2</sub> exhibit (011) and (01 $\overline{1}$ ) oriented growth along the substrate and out-ofplane growth with preferred (100) orientation. We find that the higher valence band maximum (VBM) of WSe<sub>2</sub> than MoS<sub>2</sub> and WS<sub>2</sub> matches well with that of FASnI<sub>3</sub> perovskite, which promotes cascade hole extraction at the interface and suppresses interfacial charge recombination, and the highest PCE of 10.47% is achieved in WSe<sub>2</sub> -incorporated devices.

# 4.2 Experimental section

**Materials**: Formamidinium iodide (FAI) was purchased from GreatCell Solar. Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%) and SnI<sub>2</sub> (99.999%) were purchased from Alfa Aesar. Gallic acid (99%) and SnCl<sub>2</sub> (99.99%) were purchased from Aladdin. Bathocuproine (BCP) was purchased from Sigma-Aldrich. Phenyl-C71butyric acid methyl ester (PCBM) was purchased from Nano-C. **Preparation of MX<sub>2</sub> flakes**: 100 mg of bulk MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> materials were carefully grinded into fine powders and then dispersed in 10 ml isopropanol in a centrifuge tube, respectively. The dispersion was further sealed with parafilm and sonicated with a probe sonic tip for 12h. The temperature of tube was kept at 5°C under ice bath. After that, the dispersion was centrifuged at 2000 rpm for 5 min to extract the unexfoliated materials and the supernatant containing exfoliated flakes was taken for further use.

**Device fabrication**: ITO glass substrates were sequentially washed by acetone, deionized water, and isopropanol. NiO<sub>x</sub> solution (6.5 mg mL<sup>-1</sup> in DI water, synthesis of NiO<sub>x</sub> powder can be referred to our previous report) was spin-coated on ITO substrates at 4000 rpm for 30s then annealed at 150 °C for 20 min. For NiO<sub>x</sub> modification, the asprepared MX<sub>2</sub> flakes in IPA solution were repeatedly spin-coated on it to achieve the desired amount. 0.8 M FASnI<sub>3</sub> perovskite precursor solution containing FAI (1 mmol), SnI<sub>2</sub> (1 mmol), SnCl<sub>2</sub> (0.07 mmol) and Gallic acid (0.01 mmol) in mixed DMF/DMSO solution (v/v=10:1) was spin-coated on the substrates at 5000 rpm for 30s and chlorobenzene was dripped at 13s after starting. The as-spun perovskite films were annealed at 70 °C for 5 min. Afterwards, PCBM (20 mg mL<sup>-1</sup> in chlorobenzene) was spin-coated at 1500 rpm for 30s, followed by spin-coating BCP (0.5 mg mL<sup>-1</sup> in IPA) at 5000 rpm for 30s. The devices were completed by thermal evaporation of 100 nm Ag on the BCP layer.

**Characterizations**: Photocurrent density-voltage (J-V) curves of PSCs were measured using a Keithley 2400 source meter under the illumination of AM 1.5G, 100 mW cm<sup>-2</sup>
solar simulator (Newport 91160, 300W). The external quantum efficiency (EQE) of the PSCs was measured using an EQE system equipped with equipped with a xenon lamp (Oriel 66902), a Si detector (Oriel 76175\_71580), a monochromator (Newport 66902) and a dual channel power meter (Newport 2931\_C). UV-vis spectra were measured with a Perkin elmer\_UV-vis-NIR spectrometer. SEM images were characterized by a field emission scanning electron microscope (Tescan MAIA3). XRD measurements were performed on a Rigaku Smartlab Diffractometer. Ultraviolet photoelectron spectroscopy (UPS) was measured on Thermo Fisher Scientific system. Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were measured using Edinburgh FLS920 fluorescence spectrophotometer. The Raman measurements were performed on a WITEC\_Confocal Raman system. Field emission transmission electron microscopy was performed with a JEOL Model JEM-2100F instrument operated at 200 kV.

#### 4.3 **Results and discussion**

 $MX_2$  (i.e.  $MoS_2$ ,  $WS_2$  and  $WSe_2$ ) flakes were prepared by liquid phase exfoliation of their bulk powders, as schematically shown in **Figure 4.1**a. In brief, 100 mg of the corresponding material powders were added to 10 ml Isopropyl Alcohol (IPA) in centrifuge tubes and then sonicated for 12h in an ice bath. The dispersions were then centrifuged to take the supernatant containing exfoliated flakes. The exfoliated flake samples were characterized with Ultraviolet–visible (UV-vis) and Raman spectroscopies. **Figure 4.1**b shows the image (inset) and Tauc plots of the MX<sub>2</sub> flakes in IPA dispersions. The optical bandgaps of MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> flakes are estimated to be ~1.70 eV, ~1.77 eV, ~1.48 eV, respectively, which are consistent with the values reported in literature.<sup>143-144</sup> **Figure 4.1**c shows the Raman spectra of MX<sub>2</sub> flakes spincoated on Si wafers. Strong characteristic peaks at around 381, 405 cm<sup>-1</sup> for MoS<sub>2</sub>, 350, 415 cm<sup>-1</sup> for WS<sub>2</sub>, and 250 cm<sup>-1</sup> for WSe<sub>2</sub> can be observed, which correspond to the  $E_{2g}^{1}$  and  $A_{1g}$  modes of these MX<sub>2</sub> with a few layer thickness.<sup>145-146</sup> Such MX<sub>2</sub> flakes are typically thin nanosheets as revealed by Transmission electron microscopy (TEM) (**Figure 4.1**d-f). The insets in **Figure 4.1**d-f show the HRTEM images of the corresponding MX<sub>2</sub> flakes. A clear lattice fringe of 0.27 nm, 0.27 nm and 0.28 nm are observed, corresponding to the (100) plane distances of MoS<sub>2</sub> (PDF#65-0160), WS<sub>2</sub> (PDF#08-0237) and WSe<sub>2</sub> (PDF#38-1388), respectively.



Figure 4.1 a) Schematic illustration for preparation of MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> flakes

 $(MX_2)$  via liquid phase exfoliation assisted by sonication. b) The images (shown in the inset) and Tauc plots of  $MX_2$  flakes in IPA dispersions. The Tauc plots are derived from the absorption spectra. c) Raman spectra of  $MX_2$  flakes spin-coated on Si wafers. TEM and HRTEM images of as-exfoliated d)  $MoS_2$ , e) WS<sub>2</sub> and f) WSe<sub>2</sub>, respectively.

PSCs with an inverted structure of ITO/NiOx/MX2/FASnI3/PCBM/BCP/Ag were fabricated. MX<sub>2</sub> interlayers were deposited on the surface of NiO<sub>x</sub> by spin-coating from their IPA solutions. To have a clear observation of film morphology, MX<sub>2</sub> flakes were spin-coated on flat Si substrates and observed under scanning electron microscopy (SEM). The as-deposited MX<sub>2</sub> retain a layered structure and the statistics of the flake sizes are obtained (Figure 4.2). The  $FASnI_3$  perovskite layer was then fabricated on MX<sub>2</sub>/NiO<sub>x</sub> using a one-step anti-solvent dripping method. Top-view SEM images of FASnI<sub>3</sub> films grown on NiO<sub>x</sub> and MX<sub>2</sub>/NiO<sub>x</sub> are shown in **Figure 4.3**a-d. It can be seen that the MX<sub>2</sub> interlayers do benefit the growth of perovskite films and lead to enlarged grain size and less grain boundaries. FASnI<sub>3</sub> perovskites fabricated on  $MoS_2/NiO_x$ , WS<sub>2</sub>/NiO<sub>x</sub> and WSe<sub>2</sub>/NiO<sub>x</sub> exhibit average grain sizes of 607 nm, 575 nm and 669 nm, respectively, which are much bigger than the grain size (286 nm) of the film prepared on pristine  $NiO_x$  layer (see Figure 4.4). This result indicates the role of  $MX_2$  interlayer as a template in regulating the lateral growth of FASnI<sub>3</sub> perovskite crystallites. It has been reported that the smooth and defect-free Van der Waals (vdW) face of MX<sub>2</sub> can provide a growth template and promote perovskite film growth with enlarged grain sizes.<sup>6,147</sup> Thus, it is reasonable to observe larger FASnI<sub>3</sub> perovskite grains grown on big MX<sub>2</sub> flakes.<sup>6</sup>



Figure 4.2 SEM images of as-exfoliated a)  $MoS_2$ , b)  $WS_2$  and c)  $WSe_2$  flakes spincoated on Si-substrates. Lateral size distributions of d)  $MoS_2$ , e)  $WS_2$  and f)  $WSe_2$  flakes extracted from a-c).



**Figure 4.3** Top Top-view SEM images of FASnI<sub>3</sub> perovskite films fabricated on a) NiO<sub>x</sub>, b) MoS<sub>2</sub>/NiO<sub>x</sub>, c) WS<sub>2</sub>/NiO<sub>x</sub>, d) WSe<sub>2</sub>/NiO<sub>x</sub>, respectively. e) TEM image of a WSe<sub>2</sub> flake with a perovskite film grown on it. The SAED patterns of WSe<sub>2</sub> (on the right top) and FASnI<sub>3</sub> perovskite (on right down) corresponding to the areas as indicated. f) XRD and g) UV-vis spectra of FASnI<sub>3</sub> perovskite films grown on pristine and MX<sub>2</sub> -modified NiO<sub>x</sub>/ITO. \* denote to the peaks of ITO. h) Schematic diagram of the growth of the FASnI<sub>3</sub> grain on NiO<sub>x</sub> (left) and vdW epitaxial growth of the FASnI<sub>3</sub> grain on the MX<sub>2</sub> surface (right) from the side view. (i) Schematic diagram for the structures of perovskite



films grown on NiO<sub>x</sub> (left) and MX<sub>2</sub> (right) surfaces.

**Figure 4.4** Statistical grain size distribution of  $FASnI_3$  films deposited on a) NiO<sub>x</sub>/ITO, as well as b) MoS<sub>2</sub>, c) WS<sub>2</sub>, and d) WSe<sub>2</sub> modified NiO<sub>x</sub>/ITO.

To have a scrutiny of the crystallization and growth of FASnI<sub>3</sub> perovskite grains on the surface of MX<sub>2</sub>, MX<sub>2</sub> (i.e. WSe<sub>2</sub>) flakes with perovskite grains on their surfaces were observed under TEM. **Figure 4.3**e shows the image of a FASnI<sub>3</sub>/WSe<sub>2</sub> heterojunction. The selected area electron diffraction (SAED) patterns obtained from two different parts of the heterojunction exhibit a hexagonal pattern (right top) and a square pattern (right down) respectively, corresponding to the hexagonal crystal structure of WSe<sub>2</sub> and the orthorhombic structure of FASnI<sub>3</sub>, which confirms the overlying of a perovskite film on a WSe<sub>2</sub> flake. Two diffraction spots in the square pattern are indexed to (011)

and  $(01\overline{1})$  planes of FASnI<sub>3</sub> perovskite, and the zone axis of [100] can be derived. Such a calibration result shows favorable agreement with the simulated selected area electron diffraction (SAED) pattern from its crystallographic information framework (CIF) file (see **Figure 4.5**). Thus, WSe<sub>2</sub> tends to modulate the growth of perovskite grain with a preferred (100) orientation, with (011) and (01 $\overline{1}$ ) planes grown along the substrate.

Perovskite films on pristine NiO<sub>x</sub> and MX<sub>2</sub>/NiO<sub>x</sub> substrates were characterized by Xray diffraction (XRD). As shown in **Figure 4.3**f, all samples exhibit similar characteristic XRD peak positions, signifying that the MX<sub>2</sub> interlayer did not affect the crystal structure of the upper perovskite layer. Notably, the peak intensities of (100) and (200) increase for perovskite films on MX<sub>2</sub>/NiO<sub>x</sub> substrates and the peak intensity ratio of (100)/(102) increases from 1.19 for NiO<sub>x</sub> to 2.61, 2.43 and 2.68, for MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> modified NiO<sub>x</sub>, respectively. Hence, perovskite films deposited on MX<sub>2</sub>/NiO<sub>x</sub> have better crystallinity and oriented growth along (100) direction.

UV-vis absorption spectra of the perovskite films on pristine NiO<sub>x</sub> and MX<sub>2</sub>/NiO<sub>x</sub> substrates are shown in **Figure 4.3**g. Considerable absorption enhancement is observed for perovskite films with the incorporation of a MX<sub>2</sub> interlayer within the visible wavelength region. Such enhancement is directly related to the enlarged perovskite grains and better crystallinity. UV-vis absorption spectra of NiO<sub>x</sub> substrates processed w/o and with MX<sub>2</sub> interlayer were also characterized (see **Figure 4.6**). The incorporation of MX<sub>2</sub> does not change the optical transmittance, indicating little contribution of MX<sub>2</sub> to the whole absorption of the perovskite films processed on

MX<sub>2</sub>/NiO<sub>x</sub> substrates. Moreover, the slightly higher absorption of perovskite films processed on WSe<sub>2</sub>/NiO<sub>x</sub> than MoS<sub>2</sub>/NiO<sub>x</sub> and WS<sub>2</sub>/NiO<sub>x</sub> is consistent with the results revealed from SEM (**Figure 4.3**a-d) and XRD (**Figure 4.3**f). Based on the above results, the crystal structures and the relative orientations of WSe<sub>2</sub> and FASnI<sub>3</sub> are depicted in **Figure 4.7** and **Figure 4.3**h. The NiO<sub>x</sub> layer composed of random round particles or clusters will not have lattice match with the perovskite and regulate its preferred orientation. WSe<sub>2</sub> flakes have a smooth surface with ordered atom arrangement, where the quadruple distance of the (110) planes in WSe<sub>2</sub> (4d<sub>110</sub>=6.4 Å) is close to the lattice distance of (011) in FASnI<sub>3</sub> (6.33 Å) and thus perfect for the epitaxial growth of FASnI<sub>3</sub> on WSe<sub>2</sub> along (100) direction.



**Figure 4.5** Simulated transmission electron diffraction of FASnI<sub>3</sub> single crystal from view direction of indices [100]. The simulation was performed by CrystalMaker and SingleCrystal Softwares according to the CIF of FASnI<sub>3</sub> (orthorhombic Amm2 space

group).



Figure 4.6 Transmittance spectra of  $NiO_x/ITO/glass$  substrates processed w/o and with  $MX_2$  interlayer.



Figure 4.7 Atomic crystal structure of the (110) plane of WSe<sub>2</sub> from the top view.

Notably, tin-based perovskite grains are encapsulated with an amorphous complex layer made of SnF<sub>2</sub>, SnCl<sub>2</sub> and other additives, which is a general technique that has been developed specifically for tin-based PSCs to prohibit the oxidation of the perovskite grains.<sup>78,134</sup> Here, we fabricated FASnI<sub>3</sub> perovskite films with SnCl<sub>2</sub> and gallic acid

(GA) coadditives, which enables capping of the perovskite grains with an amorphous  $SnCl_2$ -GA complex layer as described in our previous report.<sup>134</sup> However, the complex restricts charge transfer from the grains to the HTL due to its low conductivity. As shown in **Figure 4.3**i, the direct epitaxial growth of a perovskite film on WSe<sub>2</sub> flakes can be favorable for charge transfer from perovskite to the underlying NiO<sub>x</sub> HTL. The perfect interface between perovskite and WSe<sub>2</sub> flakes will enable charge transfer without the influence of the complex layer, which is expected to result in improved device performance.

The potential of using exfoliated MX<sub>2</sub> flakes as an interlayer in PSCs is further evaluated. Considering that the implementation of MX<sub>2</sub> on NiO<sub>x</sub> hole transport layer (HTL) can exert impacts on charge transfer between HTL/perovskite interface,<sup>148</sup> we adjusted their spin-coating times and investigated the corresponding PSC performances. The device performances and PV parameters of the devices with MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> spin-coated for different times can be found in **Figure 4.8** and **Table 4.1**. **Figure 4.9**a shows representative J-V curves of the three MX<sub>2</sub> -modified devices at optimum conditions. The control device exhibits a PCE of 8.03%, a J<sub>sc</sub> of 19.44 mA cm<sup>-2</sup>, a V<sub>oc</sub> of 0.59 V and a FF of 70.0%. The incorporation of MoS<sub>2</sub> increases the PCE to 8.52%, as a result of the significantly enhanced J<sub>sc</sub> to 21.75 mA cm<sup>-2</sup>, although its V<sub>oc</sub> is slightly decreased to 0.57V. Replacing MoS<sub>2</sub> by WS<sub>2</sub> further increases the PCE to 8.75%, with a V<sub>oc</sub> of 0.58V, a J<sub>sc</sub> of 21.44 mA cm<sup>-2</sup> and a FF of 70.4%. The best PCE of 9.90% is achieved for WSe<sub>2</sub> incorporated device, with a considerably improved V<sub>oc</sub> (0.63V), enhanced  $J_{sc}$  (21.82 mA cm<sup>-2</sup>) and FF (72.0%). Therefore, all MX<sub>2</sub> incorporated devices show improved  $J_{sc}$  than the control device, which can be attributed to facile hole transfer from perovskites to HTLs via the 2D MX<sub>2</sub> flakes illustrated in **Figure 4.3**i. Notably, the  $J_{sc}$  differences among MX<sub>2</sub> incorporated devices are not obvious, whereas the V<sub>oc</sub> variation is quite noticeable.



Figure 4.8 Typical J-V curves of the control PSC and MX<sub>2</sub>- incorporated PSCs prepared

by spin-coating MX<sub>2</sub> dispersions for different times.

	V <sub>oc</sub> (v)	J <sub>sc</sub> (mA cm⁻²)	FF (%)	PCE (%)
Control	0.59	19.44	70.0	8.03
MoS <sub>2</sub> -1	0.59	20.02	71.0	8.39
MoS <sub>2</sub> -2	0.58	20.67	70.4	8.44
MoS <sub>2</sub> -3	0.57	21.75	68.7	8.52
MoS <sub>2</sub> -4	0.54	20.40	67.8	7.47
WS <sub>2</sub> -1	0.61	20.32	69.8	8.65
WS <sub>2</sub> -2	0.58	21.44	70.4	8.75
WS <sub>2</sub> -3	0.58	20.71	69.9	8.39
WSe <sub>2</sub> -1	0.61	20.27	70.0	8.66
WSe <sub>2</sub> -2	0.63	21.14	71.9	9.56
WSe <sub>2</sub> -3	0.63	21.85	72.0	9.90
WSe <sub>2</sub> -4	0.62	21.54	72.4	9.67

**Table 4.1** Photovoltaic parameters of  $MX_2$  processed PSCs ( $MX_2$  dispersions were spin-coated for different times) extracted from Figure 4.8.



**Figure 4.9** a) Representative J-V curves of  $MX_2$  incorporated devices at the optimum condition. b) Energy level diagram of the PSC with incorporation of  $MX_2$ . c) PL and d) TRPL spectra of FASnI<sub>3</sub> perovskite films fabricated on pristine NiO<sub>x</sub>/ITO and NiO<sub>x</sub>/ITO substrates modified with  $MX_2$ . Light intensity dependence of e) V<sub>oc</sub> and f) J<sub>sc</sub> of the control and  $MX_2$  incorporated devices.

Ultraviolet photoelectron spectroscopy (UPS) measurements were further conducted to investigate the energy levels of FASnI<sub>3</sub> layer, NiO<sub>x</sub> film w/o and with MX<sub>2</sub>modification, as shown in **Figure 4.10**, **Figure 4.11**. Their VBMs are calculated to be -5.07eV (FASnI<sub>3</sub>), -5.06 eV (NiO<sub>x</sub>), -5.38 eV (MoS<sub>2</sub>), -5.29 eV (WS<sub>2</sub>), -5.06eV (WSe<sub>2</sub>) respectively according to the following equation:<sup>149</sup>

$$E_{VB} = E_{cutoff} - E_F - h\nu \ (h\nu = 21.22 \ eV)$$

where  $E_{cutoff}$  represents the secondary electron cutoff value and  $E_F$  represents the Fermi level. The corresponding conduction band minimum (CBM) can be further derived

from  $E_{CB} = E_{VB} - E_g$ , where Eg is obtained from the absorption edge (see Figure 4.1b, Figure 4.3g). Thus the energy level diagram of the device is depicted in Figure 4.9b. MoS<sub>2</sub> and WS<sub>2</sub> have lower VBM than FASnI<sub>3</sub> perovskite, whereas WSe<sub>2</sub> shows good VBM alignment in the NiO<sub>x</sub>/WSe<sub>2</sub>/perovskite/PCBM multilayer structure. Thus, the incorporation of WSe<sub>2</sub> favors charge transfer and collection at the NiO<sub>x</sub>/perovskite interface and has less voltage loss, which is expected to induce higher device V<sub>oc</sub> than MoS<sub>2</sub> and WS<sub>2</sub>.



Figure 4.10 a) Near  $E_f$  region and b) the secondary electron cutoff region of UPS spectra of the FASnI<sub>3</sub> perovskite film.



Figure 4.11 a) Near  $E_f$  region and b) the secondary electron cutoff region of UPS spectra of the NiO<sub>x</sub> layer and MX<sub>2</sub> modified NiO<sub>x</sub> layers.

To further investigate the effect of  $MX_2$  interlayer on charge dynamic process at the interface of NiO<sub>x</sub>/perovskite, steady state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were characterized on FASnI3 films fabricated on  $MX_2/NiO_x$ /glass substrates. As shown in Figure 4.9c, the samples with the incorporation of MoS<sub>2</sub> and WS<sub>2</sub> exhibit higher PL intensity than the control sample, as a result from the better film quality of the former perovskite films. However, the incorporation of WSe<sub>2</sub> weakens the PL intensity, which can only be accounted by that  $WSe_2$  bridges the energy levels between perovskite film and  $NiO_x$  layer well and therefore boosts charge transfer across the interface. The TRPL results of the corresponding samples are shown in **Figure 4.9**d. The TRPL spectra are assumed in first order decay and fitted by a single-exponential function of  $Y = A^* \exp(-t/\tau) + y_0$ , where A and  $\tau$  represent the amplitude and PL decay lifetime respectively. The FASnI<sub>3</sub> film fabricated on NiO<sub>x</sub> exhibits a characteristic TRPL lifetime of 1.4 ns. With MoS<sub>2</sub> and WS<sub>2</sub>, the PL decay lifetimes are prolonged to 1.55 ns and 1.43 ns respectively. A faster PL quenching (lifetime of 1.3 ns) is observed for the sample with WSe<sub>2</sub>, indicating that WSe<sub>2</sub> is more effective for charge transfer than the pristine NiO<sub>x</sub> as well as MoS<sub>2</sub> and WS<sub>2</sub> modified NiO<sub>x</sub> layers. Therefore, WSe<sub>2</sub> is most favorable for the collection of photo-generated carriers by NiOx and consequently reduces interfacial charge recombination loss.

We also conducted light intensity (P<sub>light</sub>) dependent J-V measurements of the devices to examine the effect of MX<sub>2</sub> interlayer on charge recombination. The dependence of V<sub>oc</sub> on P<sub>light</sub> is plotted according to the relation:  $V_{oc} \propto nkT/q \ln(P_{light})$ , where *n*, *k*, *T*, *q* are ideality factor, Boltzmann constant, temperature in K and elementary charge, respectively. The value *n* reflects the carrier traps assisted recombination in the active layer or at interfaces at open circuit condition.<sup>150-151</sup> As shown in **Figure 4.9**e, the control device shows a slope of V<sub>oc</sub> versus semilogarithmic P<sub>light</sub> of 1.74 kT/q, which is only slightly reduced to 1.66 kT/q for MoS<sub>2</sub> incorporated device and 1.60 kT/q for WS<sub>2</sub> incorporated device. Notably, the lowest slope of 1.47 kT/q is observed for WSe<sub>2</sub> incorporated device, indicating that the trap-assisted recombination losses are greatly suppressed than in other devices. The less trap induced recombination in WSe<sub>2</sub> incorporated device benefits from its proper energy level alignment with NiO<sub>x</sub> and FASnI<sub>3</sub>, which promotes hole transfer from perovskite to HTL.

**Figure 4.9**f plots the dependence of  $J_{sc}$  on  $P_{light}$  on a log-log scale, according to the equation:  $J_{sc} \propto (P_{light})^{\alpha}$ . The exponent  $\alpha$  is close to 1 when all carriers transfer to the electrodes without bimolecular recombination.<sup>101</sup> WSe<sub>2</sub> -incorporated device shows an  $\alpha$  value of 0.98, higher than 0.94 for the control device and 0.95 for both MoS<sub>2</sub> and WS<sub>2</sub> incorporated devices. The results indicate that WSe<sub>2</sub> interlayer can effectively enhance the charge transportation property and reduce the bimolecular recombination.

**Figure 4.12**a presents the J-V curves of the best-performing WSe<sub>2</sub> incorporated device under AM 1.5 one-sun illumination. It displays a  $V_{oc}$  of 0.63 V, a  $J_{sc}$  of 22.71 mA cm<sup>-2</sup>,

a FF of 73.2% and results in a PCE of 10.47% for reverse scan; and a  $V_{oc}$  of 0.64 V, a  $J_{sc}$  of 22.14 mA cm<sup>-2</sup>, a FF of 71.0% and a PCE of 10.06% for forward scan. The negligible hysteresis proves the high quality of the perovskite film with suppressed ion migration as well as efficient interfacial charge transport. **Figure 4.12**b shows the external quantum efficiency (EQE) spectrum for the device.  $J_{sc}$  is integrated to be 22.3 mA cm<sup>-2</sup>, which is close to the value as observed in J-V curves. The stable output of ~ 10.2% is acquired at the maximum power point, as shown in **Figure 4.12**c. Moreover, the histogram of the PCEs of 25 WSe<sub>2</sub> -incorporated devices is presented in **Figure 4.12**d. The narrow distribution of the PCE data further illustrates the reliability and reproducibility of our devices.



**Figure 4.12** a) J-V curves for the champion WSe<sub>2</sub> incorporated device in forward and reverse scans. b) EQE and integrated  $J_{sc}$  curves for the champion PSC with incorporation of WSe<sub>2</sub>. c) Stable photocurrent density and PCE of a WSe<sub>2</sub> incorporated device measured at the maximum power point. d) The statistics of PCEs of WSe<sub>2</sub> incorporated PSCs.

#### 4.4 Summary

In summary, we reported for the first time the introduction of liquid exfoliated  $MX_2$ flakes as an interlayer between NiO<sub>x</sub>/FASnI<sub>3</sub> perovskite to enhance the performance of inverted tin-based PSCs. The  $MX_2$  flakes with smooth vdW faces act as a growth template that can lead to van der Waals epitaxial growth of FASnI<sub>3</sub> perovskite grains with enlarged size and preferred orientation. In comparison with MoS<sub>2</sub> and WS<sub>2</sub>, WSe<sub>2</sub> possesses higher VBM and is judiciously selected as an efficient charge transport interlayer due to its high hole mobility and proper energy alignment with the VBMs of HTL and perovskite film. The resultant WSe<sub>2</sub> incorporated PSCs exhibit increased photovoltaic parameters in J<sub>sc</sub>, V<sub>oc</sub> and FF, which is due to the synergy of enhanced charge transport, less interfacial recombination and stronger light absorption. Eventually, a PCE of 10.47% is obtained for the champion WSe<sub>2</sub>-incorporated device, which is among the highest efficiency for FASnI<sub>3</sub> perovskite film and its interface property, which is also suitable for the preparation of other Sn-based perovskite optoelectronic devices.<sup>117,152</sup>

# Chapter 5 Efficient lead-free tin halide perovskite solar cells with a record open voltage over 0.9V

#### 5.1 Introduction

Organic–inorganic hybrid perovskites are rising as star materials in the field of solar cells due to their superior optoelectronic properties, such as strong optical absorptions, tunable bandgaps, high carrier motilities and long diffusion lengths.<sup>3,153</sup> Lead (Pb-) based PSCs have achieved a record PCE over 25% recently; however, the toxicity of Pb hinders the large-scale application of this new photovoltaic technology.<sup>11,92</sup> Sn is an ideal less toxic element for replacement of Pb, since it just sits before Pb in the periodic table and possesses similar optical and electrical characteristics.<sup>23</sup> Besides, the narrower bandgaps and higher carrier motilities of Sn perovskites compared to their Pb counterparts enable them more suitable for solar cell application.<sup>24</sup> In the past six years, researchers have devoted lots of efforts to develop high performance Sn-based PSCs, and their PCEs have been climbing steadily. However, the efficiency of Sn-based PSCs still falls behind that of their Pb counterparts.

Up to now, state-of art Sn-based PSCs can achieve a decent short current density ( $J_{sc}$ ) of 22~24 mA cm<sup>-2</sup>.<sup>52,128,154</sup> Their inferior PCE is mainly hampered by the low opencircuit voltage ( $V_{oc}$ ) and fill factor (FF).<sup>155</sup> A majority of studies reported Sn-based PSCs with a  $V_{oc}$  at around 0.6 V or below, much lower than the value (~1.1 V) of Pb-

based PSCs.<sup>31,65,132</sup> In principle, Sn-based PSCs with a bandgap ~1.35 eV should generate a maximum Voc >1 V under standard test conditions according to the Shockley–Queisser (SQ) model.<sup>156</sup> The significant voltage loss of real operating devices can be mainly ascribed to the severe recombination both in the bulk of Sn perovskite absorbers and at the interfaces of layered device structures.<sup>81,129</sup> Sn<sup>2+</sup> in the perovskite component can be easily oxidized to Sn<sup>4+</sup>, which will induce elevated Sn vacancies and heavy p-doping in perovskite films. This will accelerate non-radiative recombination and deteriorate the device efficiency. To suppress  $\mathrm{Sn}^{2+}$  oxidation and reduce defect density in the films, various reductants have been employed as the additives, such as SnF<sub>2</sub>,<sup>68</sup> SnCl<sub>2</sub>,<sup>70</sup> Sn powder,<sup>73</sup> hypophosphorous acid,<sup>77</sup> hydrazinium chloride<sup>76</sup> and phenolic compounds.<sup>78,134</sup> Very recently, Nakamura et al. utilized Sn(0) nanoparticles generated by reaction of TM-DHP and SnF<sub>2</sub> for perovskite precursor solution treatment, which leads to Sn(IV)-free perovskite films and devices with a high Voc of 0.76 V.<sup>129</sup> Besides, compositional manipulation is also found effective to enhance the perovskite structural stability and suppress the trap density, finally elevating the device V<sub>oc</sub> to 0.84 V.<sup>36</sup> While these strategies greatly improve the V<sub>oc</sub>, there still exist a great gap with the theoretical value.

Moreover, the unmatched band alignment of Sn-based PSCs results in unfavorable charge transfer and recombination at the interfaces, which limits the  $V_{oc}$  output. Sn-based perovskites typically possess shallower conduction band minimum (CBM) and valence band maximum (VBM) than their lead analogues,<sup>157</sup> while they are commonly

fabricated in similar device structures with little consideration of the energy level differences between Sn perovskite absorbers and charge transport layers. Several works have implemented interfacial modification or work function tuning of hole transport layer,<sup>79-80</sup> or even adopted a new substitute,<sup>158</sup> while the effect to increase the V<sub>oc</sub> is not obvious. Considering that Sn perovskite exhibits high background hole carrier density, the recombination between holes in perovskite and electrons in electron transport layer (ETL) should be a prominent problem. Attending the ETL or Sn perovskite/ETL interface may be another way to minimize the Voc loss, whereas little work has done on this.<sup>81,137</sup>

Here, we reported lead-free tin halide PSCs with an ultrahigh voltage of 0.96 V through simultaneous dimensionally manipulation of 3D formamidinium tin iodide (FASnI<sub>3</sub>) perovskite with phenethylammonium iodide (PEAI) and utilization of indene-C60 bisadduct (ICBA) as the novel ETL. Proper amount of bulky organic cation PEA is incorporated into FASnI<sub>3</sub>, which effectively generates low-dimension (LD) perovskite phase in the 3D perovskite. Results show that addition of 20% PEA is optimal to induce superior crystallinity and oriented growth of FASnI<sub>3</sub> on NiO<sub>x</sub> substrates with preferential facet of (100). The high quality LD/3D perovskite with well packing of crystal planes exhibits higher structure robustness than FASnI<sub>3</sub> perovskite, which effectively reduces the trap density within the bulk films and leads to better air stability. Moreover, ICBA with shallower lowest unoccupied molecular orbital (LUMO) level is used in replacement of common phenyl-C61-butyric acid methyl ester (PCBM) as the ETL. Its minimized energy offset with the CBM of LD/3D perovskite significantly enlarges the  $V_{oc}$  value. Eventually, the device demonstrates a maximum attainable  $V_{oc}$  of 0.96 V, the highest reported so far for Sn-based PSCs. The champion cell delivers a PCE of 9.66% and excellent stability, which retains over 80% of the efficiency after being stored n N<sub>2</sub> for 600 hours without encapsulation.

## 5.2 Experimental section

**Materials**: Formamidinium iodide (FAI) and phenethylammonium iodide (PEAI) were purchased from GreatCell Solar. Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%) and SnI<sub>2</sub> (99.999%) were purchased from Alfa Aesar. SnF<sub>2</sub> (99%) and bathocuproine (BCP) were purchased from Sigma-Aldrich. Phenyl-C71-butyric acid methyl ester (PCBM) was purchased from Nano-C. Indene-C60 bisadduct (ICBA) was purchased from 1-Material.

**Device fabrication**: Cleaned ITO glass substrates were treated with O<sub>2</sub> plasma for 6 min in priority. The NiO<sub>x</sub> solution (prepared according to previous work<sup>78,134</sup>) was spincoated on ITO substrates at 4000 rpm for 30s then annealed at 150 °C for 20 min. 3D FASnI<sub>3</sub> perovskite precursor solution with a concentration of 0.9M was prepared by dissolving FAI, SnI<sub>2</sub>, SnF<sub>2</sub> in the molar ratio of 1:1:0.1 in mixed DMF/DMSO solvents (v:v=4:1). LD/3D perovskite solutions with the compositions of PEA<sub>2</sub>FA<sub>n-1</sub>Sn<sub>n</sub>I<sub>3n+1</sub> were prepared by dissolving PEAI, FAI, SnI<sub>2</sub>, SnF<sub>2</sub> in the molar ratio of 2:n-1:n:0.1n (n=5, 10, 15, 20) in DMF/DMSO solvents (v:v=4:1) with the same concentration. The precursors were spin-coated at 2000 rpm for 3s and 5000 rpm for 60s. Chlorobenzene (CB) was used as the anti-solvent during the spinning process. All the perovskite films were annealed immediately at 70°C for 10min. PCBM or ICBA in the same concentration of 20 mg/ml dissolved in CB was next spin-coated at 1500 rpm for 30s, and annealed at 70°C for 5min. BCP (0.5 mg mL<sup>-1</sup> in IPA) was then spin-coated at 5000 rpm for 30s. Finally, 100 nm Ag was deposited on top of BCP through a mask via thermal evaporation.

**Characterizations**: Photocurrent density-voltage (J-V) curves of PSCs were measured using a Keithley 2400 source meter under the illumination of AM 1.5G, 100 mW cm<sup>-2</sup> solar simulator (Newport 91160, 300W). The external quantum efficiency (EQE) of the PSCs was measured using an EQE system equipped with a Monochromator (Newport 74125). UV-vis spectra were measured with a Perkin elmer\_UV-vis-NIR spectrometer. SEM images were characterized by a field emission scanning electron microscope (Tescan MAIA3). XRD measurements were performed on a Rigaku Smartlab Diffractometer. Steady-state photoluminescence (PL) was measured using Edinburgh FLS920 fluorescence spectrophotometer.

#### 5.3 **Results and discussion**

Perovskite films were prepared using the common anti-solvent assisted one-step spincoating process. PEAI, FAI, SnI<sub>2</sub>, SnF<sub>2</sub> in the molar ratio of 2:n-1:n:0.1n (n=5, 10, 15, 20) were dissolved in DMF/DMSO solvents (v:v=4:1) to get the PEA<sub>2</sub>FA<sub>4</sub>Sn<sub>5</sub>I<sub>16</sub> (n = 5), PEA<sub>2</sub>FA<sub>9</sub>Sn<sub>10</sub>I<sub>31</sub> (n = 10), PEA<sub>2</sub>FA<sub>15</sub>Sn<sub>16</sub>I<sub>49</sub> (n = 15), and PEA<sub>2</sub>FA<sub>19</sub>Sn<sub>20</sub>I<sub>61</sub> (n = 20) perovskites. It is noted that the n value reflects the stoichiometric ratio of PEA in the perovskite precursor solution, not the dimension of perovskite in the final film. 3D FASnI<sub>3</sub> perovskite corresponding to n= $\infty$  was made from precursor solution containing FAI, SnI<sub>2</sub>, SnF<sub>2</sub> in the molar ratio of 1:1:0.1, which acts as a reference in this study.

X-ray diffraction (XRD) patterns were characterized to investigate the effect of PEA incorporation on perovskite structures. Figure 5.1a shows the magnified XRD patterns of FASnI<sub>3</sub> and PEA<sub>2</sub>FA<sub>9</sub>Sn<sub>10</sub>I<sub>31</sub> films. FASnI<sub>3</sub> exhibits an orthorhombic structure as reported in literatures, and the main diffraction peaks at around 14.0°, 24.4°, 28.3°, 31.6° can be indexed to (100), (102), (200), (122) plans.<sup>18,76</sup> In contrast, small diffraction peaks appear in the lower angle region for PEA2FA9Sn10I31 films, indicating the formation of low dimensional perovskite in the 3D component. Figure 5.1b shows the evolution of XRD patterns of PEA<sub>2</sub>FA<sub>n-1</sub>Sn<sub>n</sub>I<sub>3n+1</sub> (n=5, 10, 15, 20, ∞) perovskite films with varied PEAI amounts. The (100) and (200) peak intensities enhance significantly with n decreasing from  $\infty$  to 10, which means that PEA incorporation can induce superior crystallinity and oriented growth of FASnI<sub>3</sub> perovskite films. The above dominant peaks attenuate as n further decreases to 5, as a result of the heavy distortion in 3D lattice induced by excess PEA. It can be seen from Figure 5.1c that the (100) peak of PEA<sub>2</sub>FA<sub>9</sub>Sn<sub>10</sub>I<sub>31</sub> film is more than 80 times to that of FASnI<sub>3</sub> film, with significantly decreased full width at half maximum (FWHM). These results imply high quality perovskite grains with well packing of crystal planes upon PEA incorporation in FASnI<sub>3</sub>. Absorption spectra of FASnI<sub>3</sub> and LD/3D perovskites are presented in **Figure 5.1**d. The absorption onsets are continuously blue shifting with increased PEA incorporation. Tauc plots extracted from absorption spectra demonstrate that the bandgap increases from 1.37 eV to 1.46 eV as n decreases from  $\infty$  to 10. A wider bandgap of 1.69 eV is observed at n=5, which is far away from the optimal bandgap according to the SQ limit (**Figure 5.2**).



**Figure 5.1** a) Magnified XRD patterns of FASnI<sub>3</sub> and PEA<sub>2</sub>FA<sub>9</sub>Sn<sub>10</sub>I<sub>31</sub> films. \* denotes to ITO. b) XRD patterns of PEA<sub>2</sub>FA<sub>n-1</sub>Sn<sub>n</sub>I<sub>3n+1</sub> (n=5, 10, 15, 20,  $\infty$ ) perovskite films. c) FWHM of the (100) peaks of 3D FASnI<sub>3</sub> perovskite and 3D component in LD/3D films with varied PEAI ratio (0, 0.1, 0.133, and 0.2 correspond to n=  $\infty$ , 20, 15, 10

respectively) to SnI<sub>2</sub>, and the (100) peak intensity ratio for LD/3D perovskites to the 3D perovskite . d) Absorption spectra of  $PEA_2FA_{n-1}Sn_nI_{3n+1}$  (n=5, 10, 15, 20,  $\infty$ ) perovskite films.



**Figure 5.2** Tauc plots of PEA<sub>2</sub>FA<sub>n-1</sub>Sn<sub>n</sub>I<sub>3n+1</sub> (n=5, 10, 15, 20,  $\infty$ ) perovskite films.

**Figure 5.3** shows the top-view scanning electron microscopy (SEM) images of perovskite films with incorporation of different amounts of PEAI. The reference FASnI<sub>3</sub> perovskite film shows a compact surface morphology with spherical grains, as observed in **Figure 5.3**a. The grains typically exhibit random sizes in the range of 400-900 nm with sharp grain boundaries. It is highly likely that the nucleation and crystal growth in FASnI<sub>3</sub> perovskite film are random. Additionally, there are several tiny light flakes on the surface of perovskite film, which may be assigned to SnF<sub>2</sub> aggregates that separate out of perovskite component. Introduction of PEA induces significant changes of the film morphology. The grain boundaries are blurred and the film surfaces become flat in

the PEA incorporated films. (**Figure 5.3**b,c). The n=10 film shows the best film morphology with densely packed grains. (**Figure 5.3**d). **Figure 5.3**f shows the cross-sectional SEM image of the perovskite film with n=10. It can be seen that the grains are rectangular from the top to the bottom, indicating the orientated growth of 3D component induced by PEA. However, as the amount of PEAI addition further increases, the large molten film splits into nano-sized triangle islands (**Figure 5.3**e).



Figure 5.3 a-e) Top-view SEM images of  $PEA_2FA_{n-1}Sn_nI_{3n+1}$  perovskite films with n=  $\infty$ , 20, 15, 10, 5. The scale bar is 1µm. f) Cross-sectional SEM image of the perovskite film with n=10.

The oriented growth of PEA incorporated perovskite films benefits in reducing the trap defects within the perovskite films. PL characterization was conducted for the pristine and PEA incorporated perovskite films, as shown in **Figure 5.4**a. PEA incorporated

perovskite film shows stronger PL intensity, indicating less trap density in the film. Space charge limited current characterization was conducted on hole-only devices. We prepared devices in a structure of  $ITO/NiO_x/Perovskite/P3HT/Au$ , and measured their dark I-V curves. As shown in **Figure 5.4**b, the I-V curves exhibit a linear relationship with voltage at low bias, whereas the current abruptly increases as the bias exceeds the kink point, indicating that all the trap states are fully filled. The trap state density (N<sub>t</sub>) can be obtained according to the equation:

$$N_t = \tfrac{2\epsilon\epsilon_0 V_{TFL}}{qL^2}$$

where  $V_{TFL}$  is the trap-filled limit voltage at the kink point;  $\varepsilon$  and  $\varepsilon_0$  are the relative dielectric constant of perovskite and the vacuum permittivity, respectively; q is the elementary charge, L is the thickness of the perovskite film. For n= $\infty$ , we calculated  $N_t$ to be  $3.32 \times 10^{15}$  cm<sup>-3</sup> while for n=10, the value is  $1.25 \times 10^{15}$  cm<sup>-3</sup>. The obvious reduction of the trap density for the latter could be attributed to the better crystallinity and orientation of 3D perovskite induced by LD.



**Figure 5.4** a) Steady state photoluminescence of the perovskite films. b) Dark I-V curves of the hole-only devices.

Solar cell devices were fabricated to illustrate the effect of PEA incorporation on FASnI<sub>3</sub> perovskite. We first prepared PSCs using the architecture of ITO/NiO<sub>x</sub>/perovskite/PCBM/BCP/Ag. Figure 5.5a shows the representative J-V curves of  $n = \infty$  and n=10 based devices. PEA incorporation increases the device PCE from 2.78% to 5.53% with significant enhanced  $V_{oc}$  from 0.22 V to 0.53V. The increase in PCE and Voc indicates that charge carrier recombination within the device is effectively inhibited. This result agrees well with the reduced trap density in LD/3D perovskite film measured through SCLC. We further adopted a new ETL, i.e. ICBA, to better match the energy level of corresponding perovskites. Strikingly, the Voc of PEA incorporated device with ICBA is further elevated to 0.94 V, as well as an enhanced PCE to 8.43%. To find out the reasons for such a prominent improvement, we determined the energy level of perovskites films and ETLs. It can be seen from Figure 5.5b that  $n = \infty$  perovskite exhibits a VBM of -5.10 eV and CBM of -3.73 eV. LD perovskite generation in 3D perovskite could typically induce enlarged bandgap and upward shifting of CBM. Here, a VBM of -5.00 eV and CBM of -3.54 eV are determined for n=10 perovskite. In comparison with PCBM, ICBA shows a shallower LUMO level of -3.74 eV, which better matches with the CBM of n=10 perovskite. It is reported that the device Voc is determined by the quasi-fermi energy level difference of electrons and holes under illumination.<sup>159</sup> When an additional ETL is adopted to extract

electrons from the perovskite, the quasi-fermi energy level of electrons will move downward, which can lead to  $V_{oc}$  loss. As the LUMO of ICBA has smaller energy offset with CBM of n=10 perovskite, it is expected to minimize the recombination loss at the perovskite/ETL interface and give rise to higher  $V_{oc}$ .



Figure 5.5 a) J-V curves of  $n = \infty$  based device using PCBM as the ETL and n=10 based devices using PCBM and ICBA as the ETLs, respectively. b) Band alignment of  $n = \infty$  perovskite, n = 10 perovskite, PCBM and ICBA.

**Figure 5.6**a shows the J-V curves of the best-performing PEA incorporated device using ICBA as the ETL. It achieves a PCE of 9.00% with a V<sub>oc</sub> of 0.96 V, J<sub>sc</sub> of 14.32 mA cm<sup>-2</sup>, and FF of 65.5 when sweeping in forward direction; and a PCE of 9.66% with a V<sub>oc</sub> of 0.96 V, J<sub>sc</sub> of 14.12 mA cm<sup>-2</sup>, and FF of 71.3 when sweeping in reverse direction with negligible hysteresis. Notably, the 0.96 V V<sub>oc</sub> is the highest reported for Sn-based PSCs up till now. The J<sub>sc</sub> measured from J-V curve is in good accordance with that (13.70 mA cm<sup>-2</sup>) integrated from the EQE spectrum (**Figure 5.6**b). The devices also show good reproducibility, with narrow photovoltaic parameters distribution as presented in **Figure 5.6**c. Furthermore, we characterized the shelf-stability of the PEAIincorporated device, as shown in **Figure 5.6**d. The unencapsulated device was stored in N<sub>2</sub> filled glovebox and taken out under ambient air (60% RH) for J-V curves measurements. Such a devices exhibits excellent long-term stability, which maintains more than 80% of the initial performance after 600 h storage.



Figure 5.6 a) J-V curves of the champion PEAI incorporated device using ICBA as the ETL. b) EQE spectrum and the integrated  $J_{sc}$  curve. c) PCE and  $V_{oc}$  distributions of PEA incorporated devices. d) Long-term stability of an unencapsulated PEA incorporated

device stored in N<sub>2</sub>-filled glovebox.

### 5.4 Summary

In conclusion, the low  $V_{oc}$  is a limiting factor that poses a bottle neck for the PCE improvement of Sn-based PSCs. We acquired an ultrahigh  $V_{oc}$  for Sn-based PSCs by dimensionally manipulating 3D FASnI<sub>3</sub> perovskite and introducing ICBA as the new ETL. Incorporation of PEA in FASnI<sub>3</sub> generates LD/3D perovskite with higher crystal structure robustness and better film quality, leading to reduced trap density within the bulk films. ICBA with shallower LUMO level improves the energetics with the perovskite absorber. Eventually, the device demonstrates a maximum attainable  $V_{oc}$  of 0.96 V, the highest reported so far for Sn-based PSCs. The champion cell delivers a PCE of 9.66% and excellent stability, which retains over 80% of the efficiency after being stored n N<sub>2</sub> for 600 hours without encapsulation.

## **Chapter 6 Conclusions and Future outlook**

## 6.1 Conclusions

This thesis presents a comprehensive view of tin halide perovskite solar cells from materials to devices. Family of Sn-based perovskites, basic properties, film fabrication approaches, device architectures, working principles, characterizations, efficiency development, as well as strategies to improve the efficiency and stability of Sn-based PSCs are systematically summarized. All of perovskite composites, film quality, and device design play vital roles in achieving high-performance Sn-based PSCs. So far, Sn-based PSCs exhibit lower efficiency than Pb-based PSCs, which can be ascribed to several challenging issues: i) Poor Sn perovskite film quality due to the rapid crystallization. (ii)Disadvantageous energy level alignment of Sn perovskite with common charge transport layers. (iii) Facile oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup>, which results in high concentration of trap defects and increased nonradiative charge recombination in the perovskite films. This thesis proposes three strategies to solve the above problems. First, GA additive together with excess SnCl<sub>2</sub> are introduced into FASnI<sub>3</sub> precursor solution to significantly improve the air stability of corresponding perovskite films and devices. GA can coordinate with SnCl<sub>2</sub> and form an amorphous SnCl<sub>2</sub>-GA complex through C-O...Sn<sup>2+</sup> Lewis acid and base interaction, which effectively caps the perovskite grain boundaries and surfaces. As a result, the inner perovskite is protected from oxidation and less defects are generated in the films. In comparison with other additives, we find that GA can decrease the conduction band level and enhance electron transfer in the SnCl<sub>2</sub>–additive complex covering the surface of FASnI<sub>3</sub> perovskite grains, which benefit the improved efficiency in our devices. The resultant tin-based PSCs with an inverted planar architecture show PCE up to 9.03%. The devices exhibit striking long-term stability with no degradation in efficiency after storage in N<sub>2</sub> for more than 1500h. More importantly, ~80% of the initial efficiency is maintained in unencapsulated devices exposed to air (relative humidity (RH):20%) for 1000h. This work provides a guideline for the selection of antioxidant additives in tin-based PSCs and paves a way for realizing highly stable tin-based PSCs in the future.

Second, few-layer 2D transition-metal dichalcogenides are introduced as an efficient interfacial layer at the interface of HTL/ perovskite to synergistically modulate the interface and perovskite growth. We have investigated the effects of three kinds of 2D transition-metal dichalcogenides flakes (MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub>) on PSC performance enhancement. All these ultrathin 2D material flakes are prepared by liquid phase exfoliation and facilely deposited on HTLs through spin-coating. The device  $J_{sc}$  is improved with introduction of all 2D material flakes, due to the epitaxial growth of high-quality perovskite films on them with enlarged grain sizes and preferential orientation. In comparison with MoS<sub>2</sub> and WS<sub>2</sub>, the shallower VBM of WSe<sub>2</sub> matches well with that of HTL and perovskite film, which enhances charge transport and supresses recombination loss at the interface and therefore leads to higher V<sub>oc</sub> in the device. Eventually, a PCE of 10.47% is obtained for the champion WSe<sub>2</sub> incorporated

device. This work provide a convenient strategy to control the FASnI<sub>3</sub> perovskite film and interface property, which is likely to be used for preparation of other Sn-perovskite based optoelectronic devices.

Third, perovskite dimensionality manipulation and replacement of PCBM with novel electron transport layer (ETL) were performed simultaneously to reduce the trap density in the perovskite film and optimize band energy alignment. PEA was used to partially substitute FA cation in 3D FASnI<sub>3</sub> perovskite and generate LD perovskite. The resultant LD/3D perovskite exhibits better film quality and lower defect density than its pure 3D counterpart. Through further using ICBA with shallower LUMO level as the novel ETL, the band energy off-set between LD/3D perovskite/ETL is minimized, leading to enhanced charge extraction and reduced non-radiative recombination at the interface. By adopting these strategies, the open voltage ( $V_{oc}$ ) of the device is increased to more than 0.9V, which is among the highest  $V_{oc}$  reported so far. This work highlights the significance of perovskite compositional engineering and device structure modulation in enhancing the  $V_{oc}$  and efficiency of tin-based PSCs.

#### 6.2 Future outlook

Sn-based perovskites possess lots of advantages for fabrication of lead-free PSCs. At present stage, Sn-based PSCs can achieve the best PCE of about 13%. Despite the huge successes achieved, the efficiency and stability of Sn-based PSCs are still inferior compared to Pb-based PSCs. A bottleneck for further increasing the PCE of Sn-based PSCs is their relatively low  $V_{oc}$ . The reported  $V_{oc}$  of Sn-based PSCs in literature shows large deviation. Only Ning's group achieves a record  $V_{oc}$  of 0.94V,<sup>138</sup> another three groups can achieve  $V_{oc}$  among 0.7-0.85V,<sup>36,129,160</sup> and most other groups reported  $V_{oc}$  at around 0.6V or even less. Additionally, the low FF of Sn-based PSCs is also a challenging problem. Only a handful of studies reported FF $\geq$ 75%.<sup>36,127,130</sup> Voc above 1.0 V and FF higher than 75% should be obtained for Sn-based PSCs if their PCE shall be able to compete with Pb-based PSCs. As discussed in this thesis, using mixed tin perovskite material (PEA<sub>2</sub>FA<sub>9</sub>Sn<sub>10</sub>I<sub>31</sub>) and ICBA as the ETL can acquire a  $V_{oc}$  of 0.96V. This highlights the importance of perovskite composites and charge transport layer with optimal energetics for Sn-based PSCs. More work should be done on perovskite composition tailoring,(e.g., incorporating other bulky organic cations) and development of novel charge transport materials for special use in Sn-based PSCs.

How to restrain the oxidation of Sn-based perovskites is another critical research topic. The stability of perovskite material can be affected by its intrinsic structural stability and also structure variation induced by external environment. The common CsSnI<sub>3</sub>, MASnI<sub>3</sub>, and FASnI<sub>3</sub> perovskites have a tolerance factor less than 1, indicating existence of lattice disorder in their crystal structure. It requires tailoring A-, B- and X-sites ions with proper ionic size to tune the tolerance factor to 1 to enhance the intrinsic structural stability. Moreover, there have been questions about the instability of Sn-based perovskites, since phase pure FASnI<sub>3</sub> single crystals with dimensions of 8 mm×6 mm×5 mm can be grown under an ambient atmosphere, and the oxidation state of Sn
in FASnI<sub>3</sub> measured immediately after crystal growth and after exposure to ambient atmosphere for one month remains unchanged.<sup>161</sup> If this can be further verified by more groups, then we may consider that the bulk Sn-based perovskite materials can possess relatively stable property whereas the instability issues originates form the grain boundary effect. Next, fabrication of perovskite film with enlarged grain size and reduced grain boundaries is an important direction to improve its stability. Passivation of the grain boundaries with antioxidant layer is another important way to reduce the trap states and block oxygen diffusion into the bulk perovskite. Both of the strategies should be fully explored in the future.

Besides the performance of Sn-based PSCs, the toxicity of Sn-based perovskite materials should be carefully scrutinized rather than ignored. Although Sn is widely acknowledged to possess low biotoxicity, Sn present in perovskite materials can decompose into high concentration of hydroiodic acid and other soluble side degradation products in water, which is harmful to the aquatic organisms. So far, the impact of tin-based perovskite materials on the environment is rarely investigated, and more work needs to be done in the future

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