Additive Engineering for High-Performance Perovskite Photovoltaics

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Dissertation submitted in partial fulfillment of
the requirements for the degree of Doctor
of Philosophy, in the Department of
Chemistry in the Graduate School
of Duke University

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ABSTRACT

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Abstract

Perovskite photovoltaics has attracted tremendous attention recently due to the advance in the device performance. However, it is still challenging to effectively commercialize the perovskite technology due to several issues including current-voltage hysteresis, stability, complicated device architectures, etc. In this dissertation, we use additives to tailor the properties of the functional layers in perovskite photovoltaic devices, aiming to engineer the interface, film morphology, carrier dynamics and film crystallization process. By using the additive engineering approaches, our goal is to achieve high-performance perovskite photovoltaics with reduced hysteresis, improved stability, versatile processing methods and simplified device architectures.

Perovskite solar cells usually employ p-i-n device architectures and TiO$_2$ is a typical n-type semiconductor widely used in perovskite solar cells. However, perovskite/TiO$_2$ interface is not preferable for the photo-excited carrier collection due to the energy band misalignment, conductivity mismatch, etc. In chapter 2, additive was used to tailor the properties of TiO$_2$ and enable improved interface for perovskite solar cells. With Nb$^{5+}$ as additive in TiO$_2$, the conductivity of TiO$_2$ and interface band alignment were simultaneously improved. Consequently, high-performance perovskite solar cells were successfully obtained with reduced hysteresis by using the Nb-TiO$_2$. 
In addition to the interface, we explored the impact of morphology and carrier dynamics of perovskite films on solar cell performance. In chapter 3, NH$_4$SCN and PbI$_2$ were used as additives to tune the morphology and charge carrier dynamics of perovskite films. Using NH$_4$SCN additive could significantly enlarge the grain size of the polymorph perovskite films while using PbI$_2$ additive could increase charge carrier lifetime of perovskite films. It was found that the open-circuit voltage and fill factor of perovskite photovoltaics were correlative with charge carrier lifetime while short-circuit current density of perovskite photovoltaics were correlative with grain sizes. Using both PbI$_2$ and NH$_4$SCN simultaneously could synergistically improve the quality of perovskite films and performance of perovskite solar cells.

Based on the understanding from chapter 3, a room-temperature process was developed to deposit high-quality perovskite films by using PbI$_2$ and methylammonium thiocyanate (MASCN) as additives in chapter 4. Due to the synergistic effects of the additives, room-temperature-processed perovskite films with micron-size grains and microsecond-range carrier lifetime were successfully obtained for high-performance devices. More importantly, we established the correlation between the crystal grain size in resultant perovskite films and the precursor aggregate size in precursor solutions. The correlation suggested that the perovskite grain sizes from solution process depended on the precursor aggregate sizes.
Following the understanding built in chapter 3, we used the additive engineering method to impact the performance of ETL-free perovskite solar cells. In chapter 5, we found out that the photo-excited carrier injection at the interface was significantly inhibited without the assistance of an ETL, which would compromise the collection of the photo-excited carriers. By using PbI$_2$ as additive to tune the carrier lifetimes in perovskite films, it was found out that increased carrier lifetimes in perovskite films could effectively counterbalance the inferior interface without ETLs and enabled high performance for ETL-free perovskite solar cells. By using perovskite with microsecond carrier lifetime, ETL-free perovskite solar cells were successfully realized with performance comparable to that of ETL-containing perovskite devices. Such results offer the opportunity for the perovskite devices with simplified device architecture.
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1. Introduction

1.1 Recent development of perovskite photovoltaics

Perovskite photovoltaics (PV) is a class of PV devices which employ perovskite materials, mostly hybrid organic-inorganic perovskite as light-absorbers.\textsuperscript{1-3} Perovskite PV has attracted tremendous research interest recently due to their unprecedented device performance. In last few years, the power conversion efficiency (PCE) of perovskite PV has increased from initially 3.8\% to >22\% as shown in the Figure 1.1.\textsuperscript{4} The rapid development of perovskite PV is largely attributed to two factors. The first factor is the unique properties of hybrid organic-inorganic perovskite materials, including high optical absorption coefficient, long carrier diffusion length, shallow point defects, small effective masses for both electrons and holes, suitable energy band positions and benign grain boundaries.\textsuperscript{5-6} The second factor is the versatile processing methods for hybrid organic-inorganic perovskite film deposition.\textsuperscript{7-12} Even though hybrid organic-inorganic perovskite materials have been discovered for many decades, the research for the optoelectronic properties and application of these materials in optoelectronics were started by Dr. David B. Mitzi and his co-workers in 1990s.\textsuperscript{13-32} Their studies were mainly focused on the designs of perovskites and their versatile properties/functions. The application of the hybrid organic-inorganic perovskites in PV field was not initialized until the year of 2009.\textsuperscript{33}
In the year of 2009, the perovskite solar cells were first reported by Miyasaka et al by using methylammonium lead iodide (MAPbI$_3$) and methylammonium lead bromide (MAPbBr$_3$) perovskites, respectively (Figure 1.2). In their work, both MAPbI$_3$ and MAPbBr$_3$ were used as dyes and the typical dye-sensitized solar cell architecture was used. In the device, a thin layer of hybrid organic-inorganic perovskite materials (e.g., MAPbI$_3$ and MAPbBr$_3$) was deposited on the mesoporous TiO$_2$ which serves as the scaffold, and then the photoelectrode was dipped into the organic electrolyte. By using such device structure, the PCE of 3.8% was achieved at that time. However, due to the corrosion effect of the electrolyte, solar cells could not last long.
To address the stability issue, Park et al developed solid-state perovskite PV devices (Figure 1.3) in 2012. In their solid-state perovskite solar cells, the electrolyte was replaced by a solid hole-transport material (HTM), 2,2’,7,7’-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9’-spirobifluorene (Spiro-OMeTAD). By using such solid HTM, the 9.7% PCE of perovskite solar cells was obtained with significantly improved device stability.

Figure 1.2: The first perovskite-based dye-sensitized solar cells reported by Miyasaka et al. The figure is adapted from Ref [35] with permission.
Based on the solid-state device design, new progress of perovskite solar cells was made in 2013. Snaith et al. reported planar heterojunction perovskite solar cells (Figure 1.4). In the planar structure, planar TiO$_2$ layer was used without the mesoporous TiO$_2$ scaffold and 15.4% PCE of the planar perovskite solar cells was achieved in their work. At the same year, the perovskite solar cells based on typical “organic solar cell” device architecture was also illustrated (Figure 1.5).
The progress of perovskite solar cells in 2013 made perovskite technology one of the hottest research topics, which attracted many researchers and resources in this field.
In addition to device architecture evolution, the versatile deposition methods of perovskite films were brought in including two-step solution method and vapor deposition method.\textsuperscript{7-8} Perovskite solar cells with these processing methods achieved decent \textit{PCE} values.\textsuperscript{7-8, 35} In addition, the investigation of the properties (e.g., optical, electronic properties, etc) of hybrid organic-inorganic lead-halide perovskites (e.g., MAPbI\textsubscript{3}, MAPbI\textsubscript{x}Cl\textsubscript{3-x}) was also hot topics.\textsuperscript{36-38}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_6.png}
\caption{Optical absorption spectra of FAPbI\textsubscript{3} film (red curve) and MAPbI\textsubscript{3} film (black curve). The figure is adapted from Ref [41] with permission.}
\end{figure}

In 2014, another hybrid organic-inorganic lead-halide perovskite material, formamidinium lead iodide (FAPbI\textsubscript{3}) was incorporated in the perovskite solar cells.\textsuperscript{39} FAPbI\textsubscript{3} was reported to have smaller bandgap (e.g., \textasciitilde 1.48 eV) than that of MAPbI\textsubscript{3} (Figure 1.6), offering promise for enhanced light absorption and higher performance in
perovskite solar cells. In the year of 2015, new breakthrough came. Seok et al demonstrated an intramolecular exchange method (as shown in Figure 1.7) to fabricate perovskite solar cells by using FAPbI₃ as perovskite light-absorber. By using such method, perovskite solar cells with PCE of 21.0% was achieved. The 21.0% PCE of perovskite solar cells reported by seok et al was the first PCE value exceeding 20%.

![Figure 1.7: The schematics of the intramolecular exchange process for FAPbI₃ formation from PbI₂(DMSO), and FAI. The figure is adapted from Ref [42] with permission.](image)

The world-record PCE of single-junction perovskite solar cells was further pushed to 22.1% in 2016 and 22.7% in 2017. The development of the device performance makes perovskite technology one of the fastest advancing technology in this decade. Even though the great and rapid development in device performance was achieved for perovskite solar cells, issues arose simultaneously including film quality,
interface, hysteresis, stability issues and so on. Great efforts were made to address these issues such as solvent engineering, interface engineering, material compositional engineering, additive engineering, etc. For example, the mixed-cation lead mixed-halide perovskite (e.g., CsxFAyMA1-x-yPbIBr3-z) was used to replace MAPbI3 or FAPbI3 to enhance the PV device stability (Figure 1.8). Moreover, new ETMs (e.g., SnO2, BaSnO3, etc) and HTMs (e.g., NiO, etc) were used to tailor the device interface, leading to significantly improved device stability (Figure 1.9).

Figure 1.8: The operational stability test of the perovskite devices by using Cs-containing perovskite film (red curve) and Cs-free perovskite film (black curve). The figure is adapted from Ref [54] with permission.
1.2 Perovskite materials

1.2.1 Perovskite structure

Perovskite refers the crystal structure same as three-dimensional (3D) structure of the mineral calcium titanium oxide (CaTiO₃). The general chemical formula of perovskite crystal structure is ABX₃, in which “A” and “B” are cations and “X” is anion. Figure 1.10 shows the ABX₃ structure. In the typical hybrid organic-inorganic perovskites for high-performance photovoltaics, “A” is usually an organic cation (e.g., MA⁺ and FA⁺) or large inorganic cation (e.g., Cs⁺). “B” is a divalent metal cation (e.g., Pb²⁺ and Sn²⁺) while “X” is a halide (I, Br and Cl). The perovskite structure involves a BX₆ octahedral framework with the “A” cations in 12-fold cuboctahedral coordination.
Figure 1.10: ABX₃ perovskite structure. The figure is adapted from Ref [61] with permission.

The relative radii of ions “A”, “B” and “X” in the ABX₃ structure are of vital importance to sustain the perovskite structure. According to the Goldschmidt Tolerance Factor equation, $t = (R_A + R_X)/\sqrt{2}(R_B + R_X)$, the appropriate value for $t$ is between 0.8 and 1, empirically. Based on the concept, in the hybrid organic-inorganic lead-halide perovskites, substitution or incorporation of functional ions into the perovskite structure is limited. For example, motivated by solving the stability issue, attempts were made to incorporate the inorganic cation into the ABX₃ structure to replace organic cations in the organic-inorganic lead-halide perovskites. However, study shows most of the inorganic cations are not satisfied the criterion to sustain photoactive perovskite structure. To date,
only Cs\(^+\) and Rb\(^+\) can be used to substitute or partially substitute the organic cations (e.g., MA\(^+\) and FA\(^+\)) without violating the structure in lead-halide perovskites (Figure 1.11). \(^{60}\)

![Figure 1.11: Tolerance factor of APbI\(_3\) with A as Li, Na, K, Rb, Cs, MA and FA ions. Perovskite materials with a tolerance factor value between 0.8 and 1.0 show a photoactive phase, empirically. The figure is adapted from Ref [62] with permission.](image)

### 1.2.2 Optical property

Optical property of hybrid organic-inorganic perovskites is one of the keys for the high performance in the corresponding PV devices. Hybrid organic-inorganic perovskites have proper direct bandgap for light harvesting. For example, the bandgap of MAPbI\(_3\) is ~1.58 eV and that of the FAPbI\(_3\) is ~1.48 eV. The Shockley-Queisser Efficiency Limit indicates that the light absorber with bandgap in between 1.1 eV and 1.6
eV would lead to maximum PCE of solar cells, theoretically (Figure 1.12). Fortunately, the bandgap of the commonly used hybrid organic-inorganic lead-halide perovskite light-absorbers are in this range, thereby resulting in the sufficient absorption of sunlight. Another advantage is tunability of the optical bandgap. For example, by simply incorporating Br into MAPbI$_3$, the bandgap can be significantly shifted, as shown in Figure 1.13. The tunable bandgap property is useful, particularly for building tandem solar cells to overcome the Shockley-Queisser Efficiency Limit. Due to the easily tunable bandgap of lead-halide perovskites, design and developing efficient all-perovskite tandem solar cells become a promising research direction.

![Figure 1.12](image)

Figure 1.12: The dependence of ultimate power conversion efficiency ($u(x_g)$) upon the energy bandgap ($V_g$) of the semiconductor absorber. The figure is adapted from Ref [63] with permission.
In addition to the bandgap, lead-halide perovskites have extremely high optical absorption coefficients. Figure 1.14 shows the optical absorptions and calculated maximum PCE of commonly light-absorbers as a function of film thickness.\(^6\) The ultrahigh optical absorption coefficients of lead-halide perovskites enable the sufficient light harvesting by using ultrathin films.\(^5\) The small thickness of light-absorber films can lead to effective photo-excited carrier collection before the carriers undergo recombination.
Figure 1.14: a, The optical absorption spectra of MAPbI$_3$, CsSbI$_3$ and GaAs. The maximum power conversion efficiency of solar cells as function of the thickness of the light-absorbers used in the solar cells. The figure is adapted from Ref [6] with permission.

1.2.3 Electronic property

In thin film solar cells, the deep energy levels of defects in the forbidden bandgaps would be the recombination centers, mostly causing the nonradiative recombination of photo-excited carriers. These defects are expected to result in low open-circuit voltage ($V_{oc}$) of the PV devices. Fortunately, the formation energies of the intrinsic point defects in commonly used hybrid organic-inorganic lead-halide perovskites are low. These shallow point defects will not cause the significant loss of $V_{oc}$ in perovskite PV devices, theoretically. Figure 1.15 illustrates the formation energies of the intrinsic defects for MAPbI$_3$ obtained from calculation in literature. From Figure 1.16, it can be seen that the dominant defects have low formation energies including energy levels of $V_{MA}$ (MA vacancies), $V_{Pb}$ (Pb vacancies), $V_I$ (I vacancies), $I_i$ (I interstitials),
MAi (MA interstitials), PbMA (Pb at MA site), MA\textsubscript{Pb} (MA at Pb site) and MAi (MA at I site). These shallow point defects give great opportunities for lead-halide perovskite solar cells. The excellent defect properties of the lead-halide perovskites are possibly due to the strong $sp$ orbital coupling at valence band maximum edges.

![Diagram of Conduction and Valence Bands](image)

**Figure 1.15:** The calculated formation energies of point defects in MAPbI\textsubscript{3}. The figure is adapted from Ref [6] with permission.

From solution process, the perovskite films are typically polycrystalline. The grain boundary density in the solution-processed perovskite films is significant. At the grain boundaries, it is expected that high densities of dangling bonds, extra bonds and wrong bonds exist, giving rise to high defect levels.\textsuperscript{6} In conventional PV materials, the defects created at the grain boundaries are with energy levels deep in bandgaps, usually leading to the severe nonradiative recombination of photo-excited carriers.\textsuperscript{62-65} However, recent study indicates that the grain boundaries in the hybrid organic-inorganic lead-
halide perovskites are intrinsically benign. The benign grain boundaries are explained with two factors. The first factor is that the chemical environment of the atoms at grain boundaries is similar to that of the atoms in the crystal grains. The second factor is that the formation energies for the point defects in lead-halide perovskites are relatively low. Therefore, dominant defects at the grain boundaries are also shallow point defects so that the grain boundaries in perovskite films will not cause significant loss of the charge carrier collection.

### 1.3 Perovskite film processing methods

One of the reasons for the rapid development of perovskite technology in solar cells is the simple film deposition process. Solution process is the most popular for perovskite film deposition. In the solution process, the typical route is to coat the perovskite precursor solutions onto the substrates and then anneal the wet films to obtained resultant perovskite films for PV applications. Based on the typical route, recent years witness versatile processing methods have been developed to obtained high-quality perovskite films including one-step methods, sequential methods (also called two-step methods), scalable methods, room-temperature methods, etc.


### 1.3.1 One-step method

One-step method is the most popular method for perovskite film deposition. In the typical one step method, the perovskite precursors (e.g., MAPbI$_3$, FAPbI$_3$, Cs$_x$FA$_{y}$MA$_{1-x-y}$PbI$_{3-z}$Br$_{z}$, etc) are dissolved in the solvents. The widely used solvents include dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), γ-butyrolactone (GBL) and the mixture of these solvents. With aging the precursor solutions for certain time, the precursor solutions are coated on substrates as the wet films and the typical equipment for the wet film deposition is spin-coater. To obtain high-quality perovskite films, solvent engineering methods are usually used. In the process, highly polar mixed solvents (e.g., DMF/DMSO, DMF/GBL, etc) are used to dissolve the perovskite precursor, aiming to retard the fast nucleation and crystallization process. When the films are deposited, the antisolvent (e.g., chlorobenzene, diethyl ether) treatment is applied on the perovskite precursor during and/or after wet film coating, to induce the formation of perovskite intermediate films. Then, thermal annealing treatment is applied to the perovskite intermediate films to remove the residual solvent and enhance the crystallinity to obtain the resultant perovskite films (Figure 1.16). Antisolvent treatment process is usually necessary when the highly polar solvents (e.g., DMSO, NMP, GBL, etc) are used. The important function of the antisolvent treatment is to induce the nucleation sites in the perovskite precursor and precipitate the intermediate phase (perovskite precursor-solvent complexes).
Without the antisolvent treatment, the films may not be continuous, and the perovskite grains will become isolated islands on the substrates.

Figure 1.16: Schematics of one-step method for compact perovskite film deposition with ant-solvent dripping process reported by Seok et al. The figure is adapted from Ref [9] with permission.

Similar to antisolvent treatments, some useful methods are also developed, especially in the scalable film deposition process, to induce the nucleation formation. For example, as shown in Figure 1.17, N₂ gas flow is used to blow the perovskite precursor to evaporate solvent for nucleation during the film coating process. Potentially, by controlling the N₂ flow rate, the solvent evaporation rate could be well controlled. Moreover, the air-blow process is compatible to the roll-to-roll manufacturing in industry. This fact makes the air-blow or similar process advantageous over the antisolvent treatments towards effective commercialization of perovskite technology.
1.3.2 Sequential method

The sequential method is also called two-step method. Typically, the perovskite films are obtained by using the lead halide films (e.g., PbI₂) to react with the organic halide solution (FAI, MAI, MABr, etc) to form the resultant perovskite films. Figure 1.17 shows the sequential method for the perovskite film deposition. In the sequential method, two precursor solutions need to be prepared. One is the lead halide precursor solution. The lead halide precursor is usually dissolved in highly polar solvents such as DMF, DMSO, NMP or their mixture to form a transparent solution. Another one is the organic halide solution. The organic halide precursor is usually dissolved in isopropyl alcohol (IPA). To deposit perovskite films, the lead halide precursor solution is first deposited on the substrates. Then, organic halide solution is poured onto the as-deposited lead halide films to react with the lead halide. Similarly, dipping the as-deposited lead halide films into the organic halide solution is also a common way. After
the reaction, the films are annealed on the hotplate to obtain the resultant perovskite films.

**Figure 1.18:** The sequential method for compact perovskite film deposition. The figure is adapted from Ref [73] with permission.

Since organic halide solution needs to penetrate to lead halide films for the reaction. Therefore, the solution concentration and reaction time are very important. Lack of well control of the reaction time or solution concentration will lead to inferior film quality including incomplete conversion of lead halide to perovskite, pinholes, etc.71 Compared with one-step method, one of the advantages of sequential method is that antisolvent treatments are not necessary for achieving high-quality films. This provides convenience for high-quality perovskite film deposition. However, stoichiometry of the perovskite films from sequential method is difficult to determine. This property makes
sequential method not suitable for the research in which the specific chemical composition of perovskite films is needed.

One-step method and sequential method for perovskie film deposition have their own advantages, respectively. For the perovskite PV devices, both methods can provide high-quality for high-performance devices and no one is inferior.

1.4 Perovskite photovoltaics architectures

1.4.1 p-i-n device architectures

The performance of the perovskite solar cells not only depends on the properties of the perovskite materials, but also depends on the device architectures. Study shows that the hybrid organic-inorganic lead-halide perovskites are intrinsic semiconductors (i-type), in which the Fermi level is approximately at the middle of their bandgap. The p-i-n device architectures are usually employed in perovskite solar cells. In the p-i-n structure, the n-type and the p-type semiconductors are used to extract electrons and holes, respectively, which are photo-generated in perovskite films.
In the last decade, the device architectures of perovskite PV devices gradually evolve from the dye-sensitized structure (Figure 1.19a) to the mesoscopic structure (Figure 1.19b) and planar structures (Figure 1.19c and Figure 1.19d). In the dye-sensitized-structured device (Figure 1.19a), the perovskite material is treated as dye and only a very thin layer of perovskite materials is coated on the metal oxide (usually TiO₂) scaffold. However, the perovskite layer is too thin to sufficiently harvest sunlight, limiting the output of the devices. To increase the light absorption, the mesoscopic device architecture is developed (Figure 1.19b). In this type of architecture, a relatively thicker perovskite capping layer is deposited on metal oxide scaffold with one end of the
perovskite layer well penetrating to the porous scaffold. Sufficient light absorption is achieved with the thicker perovskite capping layer. Combined with the increased interfacial contact between perovskite and metal oxide scaffold for good carrier collection, the performance of perovskite PV devices is significantly enhanced.

With deep investigation, it is found that the hybrid organic-inorganic lead-halide perovskites have superior defect properties and carrier properties (low defect formation energy level, benign grain boundaries, long diffusion length, etc). These superior properties suggest that the mesoporous scaffold layer is not necessary in perovskite PV devices. Therefore, the planar device architecture is designed (Figure 1.19c and Figure 1.19d). It is proved that the planar device architecture can provide perovskite PV devices with performance as good as that of devices with mesoscopic architecture. This understanding greatly facilitates the development of perovskite device architecture designs since n-type semiconductor used is not only limited to TiO₂.
In the perovskite device architecture, the heterojunctions formed at the interface are important for the collection of photo-excited carriers, directly determining the operational output of the PV devices\textsuperscript{73-75} Therefore, designing device interface is the key for efficient device architectures. For good interface, many factors should be considered. One of the most important factors is the energy band alignment. For a good band alignment, the conduction band minimum (CBM) edge of n-type semiconductor should be closed to the CBM edge of i-type semiconductor and the valence band maximum (VBM) edge of p-type semiconductor should be closed to the VBM edge of i-type semiconductor (Figure 1.20a).\textsuperscript{73} The closed energy band positions can guarantee efficient photo-excited carrier collections at the interface during operation under illumination.
If the energy band positions are misaligned, the significant photo-excited carrier loss would be severe at the interface, which detrims the performance of devices (Figure 1.21).

Selection of materials with proper energy band positions is an effective method to build efficient interface for perovskite solar cells. Based on the band alignment concept, many n-type and p-type semiconductors are used in the perovskite solar cells to study the interface properties. Figure 1.22 and Figure 1.23 show the energy band information for some n-type and p-type semiconductors, respectively, and the interface band alignment with perovskite films.
1.4.2 Carrier-transport layer-free architectures

It is worth mentioning that the device architectures without electron-transport layers (ETLs, n-type layers) or hole-transport layers (HTLs, p-type layers) are also designed and studied, in addition to p-i-n structures.\textsuperscript{45, 77-84} For example, in 2014, Kelly et
al reported the ETL-free perovskite solar cells with the architecture shown in Figure 1.24.\textsuperscript{77}

![Diagram of device architectures with and without ETL](image)

**Figure 1.24:** a, Schematics of the device architectures with ETL (ZnO) and without ETL. b, Energy band diagram of the device architectures with ETL (ZnO) and without ETL. The figure is adapted from Ref [79] with permission.

The carrier-transport layer-free (e.g., ETL-free and HTL-free) architectures have several advantages over the p-i-n configurations. Firstly, the carrier-transport layer-free configurations are much simpler. Inclusion of numerous layers in PV devices is not desired for manufacturing. Since the fabrication yield of a device is the multiplication of the yields of each layer in the device. Simpler structures with fewer layers can greatly enhance the fabrication yield and reproducibility. Secondly, cost could be significantly reduced with carrier-transport layer-free architectures. For the typical metal oxide used for ETLs, high temperature is usually required for the film processing (e.g., 500 °C for TiO$_2$, 500 °C for BaSnO$_3$, etc). The high temperature condition would significantly compromise the low-temperature advantage for perovskite film deposition. Meanwhile, some organic p-type semiconductors are expensive (e.g., Spiro-OMeTAD). These factors
will remarkably increase the payback time of projected perovskite PV devices, which is not for effective commercialization. Finally but most importantly, some of most widely used carrier-transport materials can cause the fast degradation of perovskite PV devices, such as TiO₂, Li-doped Spiro-OMeTAD, etc. The fast degradation would make the perovskite technology lose the opportunity to compete the traditional Si-based devices. These advantages make the carrier-transport layer-free configurations attractive, especially for industrialization.

Figure 1.25: The energy band diagram of the ITO/MAPbI₃ interface with band bending. The interface allows the electrons to transfer from MAPbI₃ to ITO but doesn’t allow the hole to transfer from MAPbI₃ to ITO. The figure is adapted from Ref [88] with permission.

There are several reasons why the carrier-transport layer-free (e.g., ETL-free and HTL-free) perovskite PV devices are working. Recent study demonstrated that the exciton binding energy for hybrid organic-inorganic lead halide perovskites is relatively
low (~50 meV). The photo-excited excitons could easily dissociate to be free carriers (e.g., electrons and holes) at room temperature. The separation of charge carriers from excitons does not need the assistance from interface. Moreover, since hybrid organic-inorganic lead halide perovskites are intrinsic semiconductors, the working function of typical transparent metal oxide (TCO) electrodes is relatively higher than the Fermi level of hybrid organic-inorganic lead halide perovskites. Therefore, at the ETL-free interface, the energy band bending situation at the TCO/perovskite is beneficial for the electron extraction and hole repelling. Figure 1.25 shows an example for the ETL-free interface. Similar situation could be achieved for perovskite/metal electrode interface. By controlling the working function of metal electrodes, the HTL-free interface could be engineered for hole extraction and electron repelling. Based on these factors, the carrier-transport layers are not necessary in the perovskite PV devices theoretically. Unfortunately, in the published results, the performance of the carrier-transport layer-free (either ETL-free or HTL-free) PV devices are significantly lower than that of carrier-transport layer-containing PV devices. Terribly, the reasons why the carrier-transport layer-free perovskite solar cells suffer from inferior performance and meanwhile no effective methods were reported to impact on their performance. Such situation hinders development of carrier-transport layer-free device configurations in perovskite PV devices. Luckily, in my research, we figure out possible reasons for the low performance
of ELT-free perovskite solar cells and develop an effective additive-engineering approach to improve the device performance. The details will be discussed later.

1.5 opportunities and challenges

Each year, the solar power that irradiates earth is near $3.8 \times 10^{24}$ J. The energy amount produced by the solar illumination in one hour is more than that the world consumes in one year. Based on this fact, solar cells, which convert sunlight into electricity, offer the opportunities to collect the unlimited solar energy to power our society. However, to date, solar energy is only a small fraction of our energy portfolio and the dominant energy resource is still the traditional fossil fuel. The small contribution of solar energy to our energy consumption could be largely attributed to a critical issue, difficulty in collecting the solar illumination and transforming it to a conveniently useable energy form, electricity, with an affordable cost. To reduce the cost of the solar energy, high-performance solar cells with low processing cost is the key.

Recent development of perovskite technology makes the perovskite photovoltaics one of the most efficient energy conversion devices. In addition to the high performance, the manufacturing of the perovskite devices is also advantageous. The processing methods for the perovskite films deposition do not require high temperatures. The processing temperatures for perovskite films are typically $\leq 150$ °C. Compared with the Si-based devices, such low temperatures for film processing can
significantly reduce the payback time of the PV devices. These advantages make perovskite solar cells a promising alternative for the market-dominant Si-based devices, and also offer a great opportunity for cost-effective solar energy supply.

While perovskite technology is promising, there are still challenging to realize the commercialization of perovskite optoelectronics. One big challenge is the long-term stability of the perovskite solar cells. It is reported that the moisture, oxygen, heating and ultraviolet light can induce the fast degradation of perovskite films and the corresponding devices. Studies show that the instability of the perovskite device could originate from the high solubility of hybrid organic-inorganic perovskites in water, volatile nature of the organic group, ion migration, lattice distortion, high density of grain boundaries, easy oxidation, ultraviolet light response of ETLs, moisture absorption of HTLs, etc. Many efforts have been made to address the stability issues of perovskite films/devices, including encapsulation, full or partial substitution of organic ions with inorganic ions, bromide alloying, designing new device architectures, using new ETLs and HTLs, using additives, etc. Certain improvement of stability is achieved. However, the improved stability reported in literatures by using these methods is only for several hundred hours or several thousand hours and the stability evaluation usually happens in mild conditions (e.g., in N2-filled glovebox, no ultraviolet light, stabilized temperature, etc). For effective commercialization, long-term stability (e.g., for decades) measured under hashing
conditions is highly demanded for the market. Therefore, further enhancing the stability of perovskite devices is necessarily required and it is still a long way to go.

Another big issue is the current-voltage hysteresis behavior. During current-voltage characterizing, different voltage-scanning directions, voltage-scanning speeds and voltage-scanning times can lead to significant different device performance.\textsuperscript{94-100} Such phenomenon makes it difficult to correctly evaluate the performance of perovskite devices. Recent research attributes the hysteresis behavior to the ion migrations, defects, interface, etc.\textsuperscript{94-100} Many methods have been developed to reduce or fully eliminate the hysteresis behavior.\textsuperscript{42, 47, 94-100} However, hysteresis is also dependent on the measurement process. To date, the standard protocol to quantitatively evaluate the hysteresis of perovskite devices is still not built up. Consequently, to a certain extent, the reported hysteresis results in literatures have no generalized meanings, especially in industry which requires a standardized and general evaluation criterion.

The toxicity of is also a big issue. The commonly used perovskite light absorbers contains toxic element, Pb. Lack of well handling or protecting will cause severe heavy metal contamination. Recently, Pb-free perovskite solar cells have been studied, aiming to address this toxicity issue.\textsuperscript{101-107} However, the performance of Pb-free perovskite solar cells is remarkably low than that of Pb-containing perovskite devices to date.\textsuperscript{101-107} These issues shown above are the main obstacles for perovskite solar cells for effective
commercialization. To address these issues, establishing deep and comprehensive understanding of perovskite materials is needed.
2. Perovskite Solar Cells by Employing Nb-TiO$_2$ as Electron Transport Layers

Qiwei Han conceived the idea and led the project. Qiwei Han carried out the film deposition, device fabrication and characterization. We acknowledge Prof. Ian Hill and Jon-Paul Sun from Dalhousie University for measuring the XPS and UPS and analyzing the data. Prof. Jie Liu and Prof. David Mitzi supervised the project.

2.1 Introduction

Hybrid organic-inorganic perovskite materials have attracted notable attention in recent years due to their excellent properties for solar cells, including proper band-gap, high optical absorption, extremely long diffusion length, benign grain boundary and dominant shallow point defects.$^{5,6}$ The power conversion efficiency (PCE) of perovskite-based solar cells has rapidly increased from initially 3.8% to exceeding 20% over last several years.$^{4,7,33-34,52,108}$ The rapid development of the perovskite solar cells benefits not only from the novel properties of perovskite materials, but also from the solution-based process for perovskite film deposition at low temperature (e.g., 25~150 °C).$^{12,42}$ In addition to the advantageous properties of materials, the device architectures are also of vital importance for perovskite solar cells to delivery high PCE. Typically, p-i-n or n-i-p sandwich structures are widely used for perovskite solar cells. The electron-transport layers (ETLs) and hole-transport layers (HTLs) are employed for reliable separation and
collection of photo-excited carriers. As one of typical n-type semiconductors, TiO$_2$ are widely used as ETLs in solar cells.$^7,^{33-34, 40, 47}$

To date, most of the high-performance perovskite solar cells employ TiO$_2$ in the device architectures as ETLs.$^{40, 52}$ However, the hysteresis behaviors are severe in TiO$_2$-based perovskite solar cells. Typically, the forward voltage-scanning $PCE$ is significantly lower. The interface issues in the perovskite devices could be one of the reasons for the loss of the $PCE$. Recently, investigation indicates that the property mismatch/misalignment exists at the TiO$_2$/perovskite interface.$^{44, 73, 109-111}$ For example, it is reported that the conduction band minimum edge of TiO$_2$ is relatively higher than that of the perovskite materials (e.g., MAPbI$_3$ and MAPbI$_3-x$Br$_x$, where MA = CH$_3$NH$_3$), so that an energy barrier is induced at the TiO$_2$/perovskite interface.$^{109-111}$ Such energy band misalignment is not beneficial for the injection of photo-excited charge carriers at the interface due to the formation of energy barrier.$^{73, 109}$ In addition, the conductivity of TiO$_2$ is inferior to that of its counterpart HTLs (e.g., Spiro-OMeTAD).$^{44, 112}$ Such conductivity mismatch can cause electrons to be stacked at the TiO$_2$/perovskite interface without extraction and eventually undergo the recombination.$^{109-110, 112}$ In short, the band misalignment and electric property mismatch at the TiO$_2$/perovskite interface is not beneficial for the charge carrier injection and eventually lead to the insufficient charge carrier collection and loss of device performance. Based on these observations,
engineering the interface in perovskite device to enable efficient charge carrier injection/collection is a key for the performance and hysteresis behavior of perovskite solar cells.

In this chapter, we demonstrate an interface engineering method to tailor the electron injection property at the TiO₂/perovskite interface by using niobium ions (Nb⁵⁺) as additive in TiO₂ compact layer. By well controlling the Nb⁵⁺ level in TiO₂ compact films, the electron injection at the TiO₂/perovskite is significantly tailored by improving conduction band alignment between perovskite/TiO₂ and the conductivity of TiO₂ compact layers. With the improved electron injection rate at the interface, the short-circuit current-density (Jₘ) of perovskite solar cells is substantially increased, thereby leading to enhanced device performance. Meanwhile, the hysteresis behavior of the perovskite solar cells is reduced by tuning the interfacial properties. Our result provides a feasible method to impact the interface property in perovskite solar cells and suggest that electron injection rate at the interface is an important role for device performance and hysteresis behaviors.

2.2 Experimental section

2.2.1 Preparation of Nb-TiO₂ precursor solutions and films

To prepare the precursor solutions for Nb-TiO₂ compact layers, 0.25 mol titanium butoxide, 0.25mol ethanolamine and niobium ethoxide was added into 1ml 2-methoxyethanol and then the solutions were stirred at 70 °C for 1 hour. After the stirring,
the solutions were aged for 24 hours to form a sol-gel. To obtain the compact Nb-TiO$_2$ films, the precursor solutions were spin-coated on the FTO substrates with 3000 r.p.m for 30s, and then the as-deposited films were annealed in air at 500 °C for 1 hour.

### 2.2.2 Device Fabrications

To fabricate perovskite solar cells, fluorine-doped tin oxide (FTO) substrates were washed by using soapy water, deionized (DI) water, acetone and isopropyl alcohol (IPA) with sonication treatment for 10 min, respectively. Then, the substrates were baked in air at 500 °C for 1 hour before further use.

With the cleaned FTO substrates, the compact Nb-TiO$_2$ compact layers were deposited by following the methods shown above. Then, mesoporous TiO$_2$ scaffolds were deposited on the Nb-TiO$_2$ compact layers. The TiO$_2$ paste solution in ethanol (1:5 w.t%) was spin-coated on the compact films with 6000 r.p.m for 30s and then annealed in air at 500 °C for 1 hour. After cooling down, the substrates were transfer into glovebox for perovskite film deposition.

The perovskite films were deposited by a two-step method. PbI$_2$ precursor solution was prepared by dissolving 1.7g PbI$_2$ in 2.0 ml DMF and 0.4ml DMSO and the precursor solution was stirred in glovebox at room temperature for 3h. Then, the PbI$_2$ precursor solution was spin-coated on the prepared substrates at room temperature with a speed of 3000 r.p.m for 30s. Immediately after the PbI$_2$ deposition, methylammounium
iodide (MAI) solution (50mg/mL in IPA) was put on the PbI₂ films to react with PbI₂ for 15 s. Then, the remaining MAI solution was removed by spin-coating with a speed of 3000 r.p.m for 15s. Finally, the films were annealed at 150 °C for 20 min to form resultant MAPbI₃ films.

To complete the devices, Li-doped Spiro-OMeTAD was spin-coated on the MAPbI₃ films as the hole transport layer (HTL). A solution consisting of 75 mg Spiro-OMeTAD, 28.8 μL 4-tert-butylpyridine, 17.6 μL Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520mg Li-TFSI in 1mL acetonitrile) and 1 mL chlorobenzene was employed with a spin speed of 3000 r.m.p for 30s. Finally, Au was thermally evaporated on the HTL, with thickness of ~60 nm as the electrode.

2.2.3 Characterizations

Morphologies of the MAPbI₃ films were imaged with a scanning electron microscope (SEM, FEI XL30 SEM-FEG). Optical absorption measurements were performed on a Shimadzu UV-3600 spectrophotometer. The ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS), were conducted using as-loaded samples and after receiving different length sputtering treatments (i.e., Ar ion source with an extractor voltage of 3000 V and a beam current of 5 μA, rastered over a 10 mm × 10 mm area). The analysis chamber was equipped with a hemispherical energy analyzer (Specs Phoibos 150) for UPS and XPS studies. UPS measurements were
performed using a He I ($h\nu = 21.22$ eV) source and XPS measurements were conducted using both Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) sources. The UPS and XPS measurements were performed in the isochromat mode using a homemade spectrometer with a resolution of approximately 0.6 eV as determined by the width of the Fermi edge of clean polycrystalline silver. The positions of the Fermi edge were used to align the UPS energy scales. The charge carrier lifetimes were characterized via time-resolved photoluminescence (TRPL) experiments using a Hamamatsu C4780 picosecond fluorescence lifetime measurement system (instrument response function ~150 ps). This system employs a Hamamatsu Streakscope C4334 as the photon-counting detector, and a Hamamatsu C4792-01 synchronous delay generator that electronically generates all time delays. A Hamamatsu 405 nm diode laser was utilized as the excitation source. The current density-voltage (J-V) characteristics and steady-state output were measured using a Keithley 2400 source meter. The illumination source was a Newport Oriel 92192 solar simulator with an AM1.5G filter, operating at 100 mW cm$^{-2}$. All devices were masked with area of 0.1 cm$^2$ aperture to define the active areas. A standard silicon solar cell from Newport Corp. was used as reference for J-V and EQE measurements. All measurements were performed under ambient condition with relative humidity level of 35–55%. 
2.3 Results and discussion

2.3.1 Characterizations of energy bands for compact Nb-TiO$_2$ films

To study the impact of Nb$^{5+}$ addition on the TiO$_2$ film quality, 0%, 1%, 2%, 3%, 4% and 5% (mol%, relative to Ti$^{4+}$) Nb$^{5+}$ precursor (niobium ethoxide) was added to the TiO$_2$ precursor solutions. Then, the Nb-TiO$_2$ precursor solutions were deposited on the glass/FTO substrates to form compact Nb-TiO$_2$ films. To study the chemical composition of the Nb-TiO$_2$ films, the X-ray photoelectron spectroscopy (XPS) measurements were performed on the surface of Nb-TiO$_2$ films. For simplifying the measurements, only Nb-TiO$_2$ films with 0%, 1%, 3% and 5% Nb$^{5+}$ in precursor solutions (labeled as S0, S1, S3 and S5) were measured.

![Figure 2.1: XPS region spectra of Nb-TiO$_2$ with Nb$^{5+}$ addition levels of 0%, 1%, 3% and 5% (labeled as S0, S1, S3 and S5) for (a) O 1s peaks and (b) Ti 2p peaks.](image-url)
Figure 2.1 shows the XPS region spectra for the Ti and O elements in the resultant Nb-TiO$_2$ films. From the spectra, it is seen that the locations of the Ti 2p3/2 are 459.27 eV, 459.27 eV, 459.28 eV and 459.28 eV (± 0.01 eV) and the locations of the O 1s are 530.51 eV, 530.51 eV, 530.53 eV, 530.53 eV (± 0.01 eV) for the S0, S1, S3 and S5, respectively. In addition, the peak intensity for Ti 2p3/2 and O 1s are similar. These results suggest addition of Nb$^{5+}$ into the TiO$_2$ films does not change the properties of Ti$^{4+}$ and O$^{2-}$ in the TiO$_2$ films significantly.

Figure 2.2: XPS region spectra of Nb-TiO$_2$ with Nb$^{5+}$ addition levels of 1%, 3% and 5% (labeled as S1, S3 and S5) for Nb 3d peaks.

From Figure 2.2, we can observe that the XPS spectra signal of the Nb 3d gradually increase from S1 to S5, indicate that the amount of Nb$^{5+}$ in the resultant Nb-TiO$_2$ films increases, as the addition level of niobium ethoxide in TiO$_2$ precursor solutions increases. By extracting from the XPS spectra in Figure 2.2, the amount of Nb$^{5+}$ in resultant Nb-TiO$_2$ films are $1.4 \pm 0.2 \%$, $4.1 \pm 0.4 \%$, $6.8 \pm 0.8 \%$ for S1, S3 and S5. The
values of Nb\(^{5+}\) level from XPS spectra is slightly higher than the niobium ethoxide addition levels in TiO\(_2\) precursor solutions, which suggests that the Nb\(^{5+}\) may migrate to the top surface of resultant compact Nb-TiO\(_2\) films after thermal annealing treatment.

Figure 2.3: a, UPS He I emission onset for Nb-TiO\(_2\) with Nb\(^{5+}\) addition levels of 0\%, 1\%, 3\% and 5\% (labeled as S0, S1, S3 and S5). b, UPS spectra of sample S0, S1, S3 and S5 for the VBM values relative to the Fermi levels.

To understand the energy band positions of the Nb-TiO\(_2\) films at the top surface, the ultraviolet photoelectron spectroscopy (UPS) and optical absorption measurements were performed on the Nb-TiO\(_2\) films (e.g., S0, S1, S3 and S5) to evaluate the valence band maximum (VBM) edges and optical bandgaps of the Nb-TiO\(_2\) films. From Figure 2.3a, the UPS He I emission onset for the sample S0, S1, S3 and S5 is 17.49 eV, 17.42 eV, 17.43 eV and 17.40 eV (± 0.01 eV), respectively. As shown in the Figure 2.3b, the UPS spectra show that the VBM values relative to the Fermi levels are 3.21 eV, 3.22 eV, 3.22 eV and 3.25 eV (± 0.01 eV) for S0, S1, S3 and S5, respectively. The optical
absorption spectra in Figure 2.4a indicate that the absorption onset of Nb-TiO$_2$ films blue shifts with increase of the Nb$^{5+}$ addition level. By using Tauc plots (Figure 2.4b), the extracted bandgaps of the S0, S1, S3, S5 are 3.30 eV, 3.31 eV, 3.40 eV and 3.45 eV. The Tauc plots illustrate that adding Nb$^{5+}$ into the TiO$_2$ can lead to the wider bandgaps of TiO$_2$ films. The reason for the wider bandgaps is that the Nb$^{5+}$ promotes the formation of anatase phase over rutile phase in the TiO$_2$ films, which is indicated by the literature.\textsuperscript{113}

![Figure 2.4: a, Optical absorption spectra of Nb-TiO$_2$ with Nb$^{5+}$ addition levels of 0%, 1%, 3% and 5% (labeled as S0, S1, S3 and S5). b, Tauc plots of Nb-TiO$_2$ with Nb$^{5+}$ addition levels of 0%, 1%, 3% and 5% (labeled as S0, S1, S3 and S5) for bandgap information extraction.](image)

With the information from UPS and absorption results, the energy diagrams of the Nb-TiO$_2$ films S0, S1, S3 and S5 are constructed as shown in Figure 2.5. It is seen that Nb$^{5+}$ addition can shift down the VBM edges of TiO$_2$ compact films as well as increase the bandgaps. Compared with bare TiO$_2$ compact film, by adding 1% Nb$^{5+}$, the VBM edges of Nb-TiO$_2$ compact film shift down remarkably but bandgap of Nb-TiO$_2$ compact
film does not change significantly. The situations make the CBM edge of Nb-TiO$_2$ (1% Nb$^{5+}$) obviously lower than that of bare TiO$_2$. However, with high levels of Nb$^{5+}$ (e.g., ≥3%), significantly wider bandgaps of Nb-TiO$_2$ films are induced, which offsets the shifting of the VBM edges, eventually leading to the situation that the CBM edge of Nb-TiO$_2$ with ≥3% Nb$^{5+}$ are higher than that of bare TiO$_2$. It is reported that the CBM edge of bare TiO$_2$ is relatively higher than that of perovskites (e.g., MAPbI$_3$ or MAPbI$_{3-x}$Br$_x$). An energy barrier may be induced at the perovskite/TiO$_2$ interface, leading to inferior carrier injection. Therefore, further increase of the CBM edge of TiO$_2$ should be avoided and Nb$^{5+}$ addition level need to be well controlled at low level (e.g., <3%).
2.3.2 Electrical property of compact Nb-TiO$_2$ films

In previous section, the energy band positions of the Nb-TiO$_2$ films were evaluated and discussed. Here, we discuss the electrical property of the Nb-TiO$_2$ films. To evaluate the conductivity of the Nb-TiO$_2$ film at the direction perpendicular to the film, devices with architecture of glass/FTO/Nb-TiO$_2$/Au (schematics shown in Figure 2.5: Schematics of energy band information for the Nb-TiO$_2$ films with 0%, 1%, 3% and 5% Nb$^{5+}$ addition levels.)
2.6) were fabricated. The thickness of the Nb-TiO\textsubscript{2} films was controlled with 30 nm and the thickness of Au was controlled with 60 nm.

![Figure 2.6: Schematics of the device architecture for conductivity/resistance measurements for Nb-TiO\textsubscript{2} films](image)

The current-density-voltage (J-V) characteristics of these devices obtained at dark condition are shown in Figure 2.7a. From these J-V characteristics, one can observe that adding Nb\textsuperscript{5+} in the TiO\textsubscript{2} films can enhance the conductivity of the TiO\textsubscript{2} films at the vertical direction. In Figure 2.6b, the resistance of the Nb-TiO\textsubscript{2} films at vertical direction is extracted from their J-V characteristics. From Figure 2.7b, it is obviously that adding 1\% Nb\textsuperscript{5+} can significantly reduce the resistance of the TiO\textsubscript{2} films. Moreover, even though further addition of Nb\textsuperscript{5+} (e.g., 2–5\%) can gradually decrease the film resistance, the decrement of the resistance becomes smaller and smaller.
Figure 2.7: a, J-V characteristics measured at dark condition of the devices with architectures of glass/FTO/Nb-TiO$_2$/Au as shown in Figure 2.6. The Nb$^{5+}$ addition level in Nb-TiO$_2$ is 0%, 1%, 2%, 3%, 4% and 5%, respectively. b, the resistance of the Nb-TiO$_2$ films (extracted from their corresponding J-V characteristics in Figure 2.7a) as function of Nb$^{5+}$ addition level in Nb-TiO$_2$.

The results discussed in this section indicate that adding small amount of Nb$^{5+}$ in TiO$_2$ films can enable better film conductivity at the direction perpendicular to the film. The impact of Nb$^{5+}$ on the performance of perovskite solar cells will be illustrated in next section.

### 2.3.4 Perovskite solar cells with compact Nb-TiO$_2$ films as ETLs

It was shown in previous sections that adding Nb$^{5+}$ in TiO$_2$ films leads to improvement of film conductivity which is beneficial for the enhanced interface property. Low Nb$^{5+}$ addition level (e.g., 1%) could decrease the CBM edge of TiO$_2$ compact film. However, the CBM edges of TiO$_2$ gradually shift up with high levels of
Nb$^{5+}$ (e.g., $\geq$3%), which is not wanted at the TiO$_2$/MAPbI$_3$ interface. Therefore, balancing the influence of Nb$^{5+}$ at different aspects is required to obtain the optimal device performance in perovskite solar cells. Based on these results, 1~2% Nb$^{5+}$ additive level may lead to optimal perovskite/TiO$_2$ interface property. To understand the effect of Nb$^{5+}$ in TiO$_2$ films on the perovskite solar cell performance, the solar cells with device architectures of glass/FTO/compact Nb-TiO$_2$/mesoporous TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au were fabricated. The details for the fabrication are illustrated in the Experimental section. The Nb$^{5+}$ addition level in the TiO$_2$ film will be controlled as 0%, 1%, 2%, 3%, 4% and 5%.

Figure 2.8: a, Top-view SEM image of a MAPbI$_3$ film deposited by using two step method. b, XRD pattern of a MAPbI$_3$ film deposited by using two step method.

Figure 2.8a showed the top-view scanning electron microscope (SEM) image of the MAPbI$_3$ film obtained from the two-step deposition method. From the SEM image, it
can be seen that the grain size of the MAPbI₃ films is in the range of 0.3~1.0 µm. In addition, the MAPbI₃ film is a pinhole-free film. Since the film compactness/coverage is of vital importance for the performance of the thin-film solar cells, our pinhole-free film provides a precondition for the performance of the perovskite solar cells. The X-ray diffraction (XRD) pattern of the MAPbI₃ film (Figure 2.8b) indicates that the MAPbI₃ film is well crystallized. In addition to crystallinity of the film, it can be observed that extra PbI₂ exists in MAPbI₃ film. The extra PbI₂ in the MAPbI₃ is beneficial for the electronic properties of MAPbI₃ films and thereby the device performance.¹¹⁴⁻¹¹⁵ The details about the advantage of extra PbI₂ in MAPbI₃ will be discussed in next chapter.

Figure 2.9: a, Optical absorption spectrum of a MAPbI₃ film deposited by using two step method. b, Tauc plot of a MAPbI₃ film deposited by using two step method.

Figure 2.9 shows the absorption spectra and Tauc plot of the MAPbI₃ film obtained from the two-step method. It is seen that the bandgap is ~1.6 eV which is
consistent with the reported result.\textsuperscript{3} The SEM image in Figure 2.10 shows the cross-section of a perovskite solar cell with the device architecture we mentioned above. From the SEM image, it can be identified that the thickness of compact Nb-TiO\textsubscript{2} film is \( \sim \)30 nm, the thickness of mesoporous TiO\textsubscript{2} is \( \sim \)150 nm, the thickness of MAPbI\textsubscript{3} capping layer is \( \sim \)400 nm, the thickness of Spiro-OMeTAD is \( \sim \)100 nm and the thickness of Au is \( \sim \)60 nm. In addition to the thickness, we can see that the MAPbI\textsubscript{3} film well penetrate to the mesoporous TiO\textsubscript{2} scaffold which increases interfacial contact. Also, there are no shunting paths in the device so the performance loss from shunting can be well avoided.

![SEM Image](image)

**Figure 2.10:** SEM image of the cross-section of a perovskite solar cell by using the architecture of glass/FTO/compact Nb-TiO\textsubscript{2}/mesoporous TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro-OMeTAD/Au.

The statistical results of device performance are shown in Figure 2.11. To obtain such statistical distribution for device performance, 20 devices for each Nb\textsuperscript{5+} addition level were fabricated. From the PCE distribution, it can be observed that 1% Nb\textsuperscript{5+} addition in TiO\textsubscript{2} films leading to significant increase of photovoltaic parameters of our
perovskite solar cells including PCE, short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$) and fill factor (FF). From Figure 2.5 and Figure 2.7, we see that using 1% Nb$^{5+}$ addition in TiO$_2$ film can significantly decrease the CBM edge of TiO$_2$ film and enhance the film conductivity at same time. Such property should enable improved charge carrier injection at the TiO$_2$/MAPbI$_3$. To provide evidence, the photoluminescence (PL) quenching measurements were performed to evaluate the charge carrier injection property at the interface. The MAPbI$_3$ films were deposited on the glass, glass/compact TiO$_2$/mesoporous TiO$_2$ and glass/compact Nb-TiO$_2$/mesoporous TiO$_2$ substrates. Here, Nb-TiO$_2$ film with 1% addition level was used in PL quenching measurements. From Figure 2.12, it is obvious that the PL signal of the MAPbI$_3$ film quenched much faster on the compact TiO$_2$ film with 1% Nb$^{5+}$, clearly indicating improved charge carrier injection at the interface.
Figure 2.11: Distributions of the photovoltaic parameters for perovskite solar cells.
The solar cells employ the device architecture of glass/FTO/compact Nb-TiO$_2$/mesoporous TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au. The Nb$^{5+}$ addition level in Nb-TiO$_2$ is 0%, 1%, 2%, 3%, 4% and 5%, respectively.

When compact Nb-TiO$_2$ films with 2~5% Nb$^{5+}$ addition levels were employed in our solar cell devices, the $PCE$, $J_{sc}$, $V_{oc}$ and $FF$ gradually decrease, comparing with the devices with 1% Nb$^{5+}$ in TiO$_2$. The decrease trend could be due to the formation of wider bandgap of TiO$_2$ caused by high concentrations of Nb$^{5+}$. From Figure 2.5, it is obviously seen that the CBM edges of TiO$_2$ are increased with wider bandgaps. Given that CBM edge of pristine TiO$_2$ is higher than that of MAPbI$_3$, the further increased CBM edges of
Nb-TiO$_2$ would enlarge the energy barrier at the interface. With the formation of larger energy barrier, the charge carrier injection is inhibited, leading to the insufficient collection of photo-excited charge carriers and severe carrier recombination. Since the $J_{sc}$ is correlative with charge carrier collection and $V_{oc}/FF$ are correlative with charge carrier recombination, the $J_{sc}$, $V_{oc}$ and $FF$ are therefore decreased with high levels of Nb$^{5+}$.

![Graph showing TRPL spectra of MAPbI$_3$ films deposited on glass substrate, glass/compact TiO$_2$/mesoporous TiO$_2$ substrate and glass/compact Nb-TiO$_2$/mesoporous TiO$_2$ substrate, respectively. The Nb$^{5+}$ level in Nb-TiO$_2$ film is 1%.

Figure 2.12: TRPL spectra of MAPbI$_3$ films deposited on glass substrate, glass/compact TiO$_2$/mesoporous TiO$_2$ substrate and glass/compact Nb-TiO$_2$/mesoporous TiO$_2$ substrate, respectively. The Nb$^{5+}$ level in Nb-TiO$_2$ film is 1%.

The device results shown above indicate that adding right amount of Nb$^{5+}$ (1%) in compact TiO$_2$ films can significantly tailor the band alignment and conductivity of TiO$_2$ films at interface, which enable improved charge carrier injection at the TiO$_2$/MAPbI$_3$ interface. With the enhanced interfacial properties, high performance perovskite solar cells are achieved.
2.3.4 Hysteresis behaviors

It is reported that the performance of perovskite solar cells is correlative with the voltage-scanning directions. To evaluate the scanning-direction-dependent hysteresis, the best-performing perovskite device by using Nb-TiO₂ film with 1% Nb⁵⁺ addition level was evaluated with both forward and reverse voltage-scanning directions. The voltage-scanning speed was controlled at 10 V/s. Figure 2.13a shows the J-V characteristics with both forward and reverse voltage-scanning directions for this best-performing device. With reverse (forward) scanning direction, the device yields PCE of 17.67 (17.48) %, Jₛ of 22.14 (21.74) mA cm⁻², Vₒc of 1.007 (1.002) V and FF of 79.86 (79.65) %.

We can see that the hysteresis is very small in the device. As comparison, the best-performing perovskite device by using pristine compact TiO₂ film was also evaluated with forward and reverse voltage-scanning directions with 10 V/s scanning speed. The J-V characteristics for this device are shown in Figure 2.13b. It is obvious that significant discrepancy of photovoltaic parameters exists in J-V characteristics of device using pristine TiO₂ film from forward and reverses scanning directions. These results illustrate that the improved charge carrier injection at interface can not only facilitate the device performance, but also reduce the hysteresis behavior of perovskite solar cells.
It is reported that the device performance also depends on the voltage-scanning speed. To evaluate the scanning-speed-dependent hysteresis behavior, the best-performing perovskite device by using Nb-TiO₂ film with 1% Nb⁵⁺ addition level was evaluated with voltage-canning speed of 10 V/s, 5 V/s and 0.5 V/s. Figure 2.14 shows the J-V characteristics with the voltage-canning speed of 10 V/s, 5 V/s and 0.5 V/s by using reverse scanning direction.
Figure 2.14: J-V characteristics of best-performing perovskite solar cells by using compact Nb-TiO$_2$ (Nb$^{5+}$ addition level is 1%) in device architecture. The J-V characteristics were obtained by using different scanning speeds, 10 V/s, 5.0 V/s and 0.5 V/s, with reverse scanning direction.

From the results in Figure 2.15, the hysteresis for the best-performing device with 1% Nb$^{5+}$ in TiO$_2$ with slow scanning speed (e.g., 5.0 V/s and 0.5 V/s) is still smaller than that of best-performing device using pristine TiO$_2$ film with fast scanning speed (e.g., 10 V/s). These results suggest that the improved charge carrier injection at the interface can reduce the scanning-speed-dependent hysteresis behavior.
Figure 2.15: J-V characteristics of best-performing perovskite solar cells by using compact Nb-TiO₂ (Nb⁵⁺ addition level is 1%) in device architecture. The J-V characteristics were obtained by using scanning speed of 5.0 V/s and 0.5 V/s, respectively, with both forward and reverse scanning direction.

2.4 Conclusions

In conclusion, we demonstrate adding Nb⁵⁺ in TiO₂ films can increase the film conductivity films while bandgaps of the films become wider if the Nb⁵⁺ concentration is relatively higher. By well controlling the Nb⁵⁺ addition level, the charge carrier injection can be significantly improved at the TiO₂/MAPbI₃ through increase of film conductivity and better conduction band alignment. With the enhanced charge carrier injection at the interface, the MAPbI₃ solar cells using compact Nb-TiO₂ ETLs show high performance with significantly reduced hysteresis behavior. Our results indicate tailoring the interface property can lead to improved perovskite device performance and hysteresis behavior.
3. Insight into the Role of Morphology and Charge Carrier Dynamics in Perovskite Photovoltaics

Qiwei Han conceived the idea and led the project. Qiwei Han carried out the film deposition, device fabrication and characterization. We acknowledge Prof. Kenan Gundogdu and Dr. Bhoj Gautum from North Carolina State University for measuring TRPL. Prof. Jie Liu and Prof. David Mitzi supervised the project.

3.1 Introduction

Recently, hybrid organic-inorganic perovskite (HOIP) based solar cells have attracted notable attention due to their rapid development and high power conversion efficiency (PCE) exceeding 22%.\textsuperscript{4, 33, 40, 52, 111} Current research attributes the high PCE to advantageous properties of the Pb-based perovskites, including suitable bandgap, large absorption coefficient, small effective masses with extremely long diffusion lengths for both electrons and holes, shallow point defects, and benign grain boundaries.\textsuperscript{1-2, 5-6, 34, 36-38, 116} These outstanding properties theoretically promise an ~30% PCE without the need of a tandem structure.\textsuperscript{1-2, 5-6, 34, 36-38, 61, 116-117} With the addition of facile film manufacturing using low-temperature solution processing, perovskite photovoltaics (PV) offer a potentially lower-cost alternative to traditional Si-based solar cells, which currently dominate the PV market.\textsuperscript{1-2, 117} However, it is also well-recognized that the stability and reproducibility of HOIP PV remains a challenge and associated performance heavily relies on the fabrication and characterization methods.\textsuperscript{38, 46, 76, 90, 118-119} Unacceptably, large
electrical hysteresis during the solar cell operation represents another critical issue for HOIP solar cells, and this problem is especially severe for planar interface PV structures. These issues currently render HOIP PV less attractive for commercialization.

One possible explanation of the hysteresis correlates with defect-assisted trapping processes. Ion migration has also been demonstrated as a possible origin of the hysteresis, which may correlate with the density of grain boundaries. Recent efforts to improve the HOIP film quality, such as enhanced crystallinity/grain size and passivation of bulk/surface defects have led to obvious improvement in HOIP solar cell performance and hysteresis. In our previous work, we also observed improvement in solar cell performance and reduction in hysteresis by engineering the MAPbI\textsubscript{3} grain sizes and grain boundaries through the use of Pb(SCN)\textsubscript{2} additive in MAPbI\textsubscript{3} precursor solutions. Results shows that addition of Pb(SCN)\textsubscript{2} simultaneously increases the MAPbI\textsubscript{3} grain sizes and induces thin layers of PbI\textsubscript{2} at the grain boundaries for defect passivation, thereby significantly increasing overall performance. However, this work does not differentiate whether the performance and film quality correlate with presence of excess Pb\textsuperscript{2+} ion or the SCN\textsuperscript{-} ion, or whether both are required. Also it does not distinguish if the improvement comes as a result of enhanced grain size or due to grain boundary passivation. To address these
questions, the effect of Pb and SCN ions on the film quality and performance need to be analyzed separately.

In this chapter, we gain insight in the importance of MAPbI\(_3\) film morphology and charge carrier dynamics on PV characteristics, through the separated addition of NH\(_4\)SCN and PbI\(_2\) additives, as part of a single step deposition process. We illustrate that addition of NH\(_4\)SCN to MAPbI\(_3\) precursor can increases MAPbI\(_3\) grain sizes and improves their crystallinity that subsequently improve the charge carrier collection, while not significantly impacting the charge carrier lifetime. These modifications primarily lead to the statistically significant enhancement of short-circuit current density (\(J_{sc}\)) and fill factor (\(FF\)), but only slightly influence open-circuit voltage (\(V_{oc}\)).

Interestingly, using NH\(_4\)SCN does not introduce significant NH\(_4^+\) or SCN\(^-\) impurity within the final films. Meanwhile, we also illustrate that adding extra PbI\(_2\) to the MAPbI\(_3\) precursor solution can tailor the charge carrier lifetime of MAPbI\(_3\) films but does not contribute significantly to grain size or crystallinity improvement. The impact of PbI\(_2\) addition mainly improves \(V_{oc}\) and \(FF\) but does not substantially shift \(J_{sc}\). By combined addition of these two different additives in the pristine MAPbI\(_3\) solution, synergistic effects yield larger grain sizes and good interface passivation that resulted in longer charge carrier lifetimes than that can be achieved with a single additive. The PV performance is significantly enhanced and the hysteresis nearly eliminated as a result of these additions. After systematic optimization, films obtained with both NH\(_4\)SCN and
PbI$_2$ added into the traditional precursor solutions, in devices with a glass/FTO/TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au planar architecture, could routinely yield PCE >17% with negligible hysteresis.

### 3.2 Experimental section

#### 3.2.1 Device Fabrications

The FTO glasses were cleaned in soapy water, deionized water, acetone and isopropanol with sonication and then all the substrates were baked at 500 °C in air for 1 hour for further use.

To prepare the TiO$_2$ electron transport layers (ETLs), a precursor solution containing 2 mL ethanol and 4 mL titanium diisopropoxide bis(acetylacetonate) solution (75% wt. in isopropanol) was stirred at room temperature in air for 1 hour. Then the TiO$_2$ precursor solution was used to deposit TiO$_2$ ETL by using hot pray pyrolysis method at 450 °C. Finally, the TiO$_2$ compact films were annealed in air at 500 °C for 1 hour.

The MAPbI$_3$ thin films were deposited by one-step method with solvent washing process. 1.25 M PbI$_2$ and 1.25 M MAI were dissolved in DMF/DMSO co-solvent with volume ratio of 9:1 to form pristine MAPbI$_3$ precursor solution. To study the additives’ impact on final thin films, NH$_4$SCN and extra PbI$_2$ with specific concentration (mol% relative to MAPbI$_3$) were added to the pristine MAPbI$_3$ precursor solutions before MAPbI$_3$ film deposition. Then, the precursor solution was spin-coated on
glass/FTO/TiO$_2$ substrates at speed of 5000 r.m.p for 30s. During the spinning, chlorobenzene was applied on the MAPbI$_3$ thin films for washing process. Finally, the thin films were annealed at 100 °C for 10 min to obtain the resultant MAPbI$_3$ thin films.$^{42}$

To complete the devices, the Li-doped Spiro-OMeTAD was spin-coated on MAPbI$_3$ thin films as hole transport layers (HTLs) at speed of 3000 r.m.p for 30s by using solution consisting of 75 mg Spiro-OMeTAD, 28.8 µL tBp, 17.6 µL Li-TFSI solution (520mg Li-TFSI in 1mL acetonitrile) and 1 mL chlorobenzene.$^{42,53}$ Finally, Au was thermally evaporated to deposit on HTLs as electrodes.

### 3.2.2 Characterizations

Morphologies of MAPbI$_3$ thin films were imaged with scanning electron microscope (SEM, FEI XL30 SEM-FEG). The atomic force microscopy (AFM) images were characterized by scanning probe microscope (Digital Instruments Dimension 3100). X-ray diffraction (XRD) measurements were carried out on a PANalytical Empyrean powder X-ray diffractometer under ambient conditions using CuKα radiation. The charge carrier lifetime of MAPbI$_3$ thin films on glass were characterized with time-resolved photoluminescence (TR-PL) using a tunable Ti:sapphire femtosecond-pulsed laser (150 fs pulse, 4 MHz). The surface composition of MAPbI$_3$ thin films were examined with X-ray photoelectron spectrometer (XPS, Kratos Analytical Axis Ultra). Optical absorption measurements were performed on a Shimadzu UV-3600
spectrophotometer. The current density-voltage (J-V) characteristics and steady-state output were measured using a Keithley 2400 source meter. The illumination source was a Newport Oriel 92192 solar simulator with an AM 1.5G filter, operating at 100 mW/cm². The active area of each solar cell was 0.1 cm². A standard silicon solar cell was used to calibrate the light intensity.

### 3.3 Results and discussion

#### 3.3.1 Morphology control of perovskite films

![SEM images of MAPbI₃ films with 0~50% NH₄SCN addition in precursor solutions](image)

Figure 3.1: Top view SEM images of the MAPbI₃ films with 0~50% NH₄SCN addition in precursor solutions. All images use a 1 μm scale bar.
To explore the influence of NH₄SCN on MAPbI₃ films, 0%, 10%, 20%, 30%, 40% and 50% (mol% relative to MAPbI₃) NH₄SCN were added to the MAPbI₃ precursor solutions during a one-step film deposition process on glass/FTO/TiO₂ substrates (described in detail in the Experimental section). By checking the top-view scanning electron microscope (SEM) images (Figure 3.1) of the resulting films, we find that without NH₄SCN addition, the average MAPbI₃ grain size is ~0.2 µm and by adding NH₄SCN with concentration of 10% to 50%, the average MAPbI₃ grain size increases to >1.0 µm. In addition, we can see that pinholes start to appear in the film with high NH₄SCN concentration. To further clarify this point, 70% NH₄SCN is added to the MAPbI₃ precursor solution. The top-view SEM image of this film (Figure 3.2) shows that the MAPbI₃ grains become totally isolated on the substrate. Such results illustrate that NH₄SCN addition can enhance the grain size but too much NH₄SCN would lead to the fragmentation of the MAPbI₃ films.

Figure 3.2: Top view SEM images of the MAPbI₃ films with 70% NH₄SCN addition in precursor solution. The images use a 5 µm scale bar.
X-ray diffraction (XRD) measurement was performed on MAPbI₃ films with NH₄SCN addition to understand the chemical composition and film crystallinity. The associated XRD patterns (Figure 3.3a) illustrate that the NH₄SCN addition does not produce additional XRD peaks related to NH₄SCN, indicating that SCN-related compounds don’t residue in the resultant MAPbI₃ films. This phenomenon can be attributed to the volatile nature of NH₄SCN additive, which is discussed in literature.⁴²

As shown in Figure 3.3b, the trend of full width at half maximum (FWHM) values of the MAPbI₃ (110)-peak exacted from XRD patterns indicates that using NH₄SCN as additive can enhance the crystallinity of MAPbI₃ films significantly. The FWHM reaches the minimum value with 40% NH₄SCN.

Figure 3.3: a, XRD patterns of the MAPbI₃ films with 0-50% NH₄SCN addition in precursor solutions. b, The FWHM value of MAPbI₃ (110) peaks as function of NH₄SCN addition level in precursor solutions.
Figure 3.4: TRPL spectra of the MAPbI₃ films with 0~50% NH₄SCN addition in the precursor solutions. b, The extracted carrier lifetime of MAPbI₃ films with 0~50% NH₄SCN addition in precursor solutions.

Time-resolved photoluminescence (TRPL) was then used to study the impact of NH₄SCN on carrier dynamics of MAPbI₃ films. The MAPbI₃ films were deposited on glass substrates with addition of 0~50% NH₄SCN as shown in Figure 3.5. The excitation wavelength was 400 nm and 760 nm emission was monitored. By using bi-exponential equation to fit the TRPL spectra (Figure 3.4a), charge carrier lifetime of MAPbI₃ films (Figure 3.4b) gradually increases with addition of NH₄SCN and 40% NH₄SCN leads to the optimal charge carrier lifetime. The carrier lifetimes are correlative with inverse of FWHM values of the MAPbI₃ films. This results suggest that the carrier lifetime of MAPbI₃ films depends on the film crystallinity.
Figure 3.5: Top-view SEM images of the MAPbI$_3$ films with 0-50% NH$_4$SCN addition in precursor solutions. The films are deposited on glass substrates for TRPL measurements. All images use a 1 µm scale bar.
3.3.2 Tuning carrier lifetime of perovskite films

Figure 3.6: Top view SEM images of the MAPbI₃ films with 0~7.5% extra PbI₂ addition in precursor solutions. All images use a 1 µm scale bar.

In this section, we discuss the function of extra PbI₂ additive and its impact on the carrier lifetime of perovskite films. For comparison, 0%, 2.5%, 5.0% and 7.5% extra PbI₂ was added into pristine MAPbI₃ precursor solutions (no NH₄SCN addition) for film deposition. The top-view SEM images in Figure 3.6 illustrate that the adding extra PbI₂ does not change the grain size of perovskite films. The XRD patterns in Figure 3.7a shows that PbI₂ phase exists in this set of films; From the SEM image in Figure 3.6, the PbI₂ phase is randomly inserted as flakes or particles predominantly at grain boundaries.
as secondary phase. The FWHM values of the MAPbI$_3$ (110) peaks slightly increases as a function of extra PbI$_2$ addition (Figure 3.7b), implying that adding a small amount of extra PbI$_2$ (≤7.5%) does not improve crystallinity within the MAPbI$_3$ films.

![Figure 3.7: a. XRD patterns of MAPbI$_3$ films with 0–7.5% extra PbI$_2$ addition. b, The FWHM values of (110) MAPbI$_3$ peaks as function of extra PbI$_2$ addition amount.](image)

To understand the impact of extra PbI$_2$ on carrier dynamics of MAPbI$_3$ films, the MAPbI$_3$ films with extra PbI$_2$ deposited on glass substrates were examined with TRPL. The SEM images for these films are shown in Figure 3.8. From the TRPL spectra in Figure 3.9, it can be observed that addition of extra PbI$_2$ can significantly enhance the charge carrier lifetime of MAPbI$_3$ films. Here, 5% extra PbI$_2$ appears to be the optimal concentration. Similar results have been observed in published work.$^{42, 115, 130}$ By examining FWHM values (Figure 3.7b) and carrier lifetime (Figure 3.9b), we can see that the mechanism of extra PbI$_2$ to improve carrier lifetime is not to enhance the film
crystallinity. The possible reason for the improved charge carrier lifetime via adding extra PbI$_2$ is existence of extra PbI$_2$ at the grain boundaries. Since defect density at the grain boundaries are far higher than that inside the grain, the existence of the extra PbI$_2$ at the grain boundaries may suppress the carrier loss from defect trapping.$^{115,130}$ In addition, comparing with the results shown in Figure 3.4b, adding extra PbI$_2$ is a more efficient method than adding NH$_4$SCN for the carrier lifetime enhancement.

Figure 3.8: Top-view SEM images of MAPbI$_3$ films with 0-7.5% extra PbI$_2$ addition deposited on glass substrates for TRPL measurement. All images use a 1 µm scale bar
These results above suggest that extra PbI₂ addition can effectively improve carrier lifetime of perovskite films. This improvement is not from the enhanced film crystallinity but from the passivation function of extra PbI₂ at grain boundaries.

### 3.3.3 Synergistic impact of additives on perovskite films

In previous sections, we separately studied the impact of the NH₄SCN and extra PbI₂ on the properties on MAPbI₃ films. We find out that the mainly function of NH₄SCN is to enlarge grain size and improve the crystallinity while the main function of extra PbI₂ addition is to enhance carrier lifetime. In this section, the synergistic effect of both NH₄SCN and PbI₂ will be studied. As mentioned, 5.0% is the optimal level for extra PbI₂ in term of charge carrier lifetime. To simplify the study of synergistic effect of both
additives, the addition level of PbI$_2$ will be fixed at 5.0% and the addition level of NH$_4$SCN is varied from 0~50%.

![Top-view SEM images of the MAPbI$_3$ films with 0~50% NH$_4$SCN and 5% extra PbI$_2$ addition in precursor solutions. All images use a 1 µm scale bar.](image)

**Figure 3.10:** Top-view SEM images of the MAPbI$_3$ films with 0~50% NH$_4$SCN and 5% extra PbI$_2$ addition in precursor solutions. All images use a 1 µm scale bar.

From the SEM images in Figure 3.10, it is seen that adding NH$_4$SCN and extra PbI$_2$ simultaneously can significantly enlarge the grain size of MAPbI$_3$ films and at same time, thin layers of secondary phase are induced to coat at the grain boundaries conformally. Based on the additives we used, the secondary phase could consist NH$_4$SCN or PbI$_2$. To identify the chemical composition of the secondary phase, the X-ray photoelectron spectroscopy (XPS) measurements were performed on this set of MAPbI$_3$ films, as shown in Figure 3.11. From comparison, the XPS measurement was also conducted on the pristine MAPbI$_3$ film (i.e., no NH$_4$SCN or extra PbI$_2$ addition). The
region spectra for N 1s in the range of 410–392 eV show that only one type of N in the MAPbI₃ samples even though NH₄SCN addition levels varied from 0% to 50%. Such results indicate that the secondary phase at the grain boundaries is not consisting of NH₄⁺ ions. Additionally, the region spectra of S 2s and S 2p in the ranges of 245–220 eV and 172–158 eV, respectively, show no sulfur residue on the surface of these MAPbI₃ films, illustrating that the secondary phase at the boundaries is not consisting of SCN⁻ ions or sulfur-related compounds. These XPS results suggest that the secondary phase coating at the grain boundaries is PbI₂.
Figure 3.11: XPS spectra of pristine MAPbI₃ film, MAPbI₃ film with 5% extra PbI₂ and MAPbI₃ films with 10~50% NH₄SCN and 5% extra PbI₂ dual addition in precursor solutions.

From the SEM and XPS results, it can be observed that the simultaneously using NH₄SCN and extra PbI₂ lead to large grain size and extra PbI₂ grain boundaries. However, by only using extra PbI₂ as additive, the extra PbI₂ are inserted at the grain boundaries randomly. Different from the situation that only extra PbI₂ was used, in the
MAPbI$_3$ films with dual additives, the extra PbI$_2$ is coated at grain boundaries conformally. This conformal coating makes the extra PbI$_2$ attach the MAPbI$_3$ grain termination much more efficiently. As shown in Figure 3.9, extra PbI$_2$ at the grain boundaries could facilitate the carrier lifetime. By using dual additive, this conformal coating of extra PbI$_2$ may greatly enhance the carrier lifetime of MAPbI$_3$ films.

Figure 3.12: Top-view SEM images of the MAPbI$_3$ films with 0-50% NH$_4$SCN and 5% extra PbI$_2$ addition in precursor solutions. The films are deposited on glass substrates for TRPL measurements. All images use a 1 µm scale bar.
To verify our hypothesis and understand the synergistic impact of the dual additives on the charge carrier lifetime of perovskite films, the TRPL measurements were performed on the MAPbI₃ films deposited on the glass substrates (Figure 3.12). From the TRPL results of the MAPbI₃ films with addition of 5% extra PbI₂ and 0-50% NH₄SCN (Figure 3.13), we can observe that adding NH₄SCN together with extra PbI₂ make the carrier lifetime of MAPbI₃ film much longer than that of MAPbI₃ films with only NH₄SCN or only extra PbI₂ addition. The TRPL results indicate that there is synergistic effect of NH₄SCN and PbI₂ additives on charge carrier lifetime of perovskite films. The synergistic effect should be attributed to the formation of PbI₂ conformally at grain boundaries.

Figure 3.13: a, TRPL spectra of the MAPbI₃ films with 0-50% NH₄SCN and 5% extra PbI₂ addition in precursor solutions. b, The extracted carrier lifetime of MAPbI₃ films with 0-50% NH₄SCN and 5% extra PbI₂ addition in precursor solutions.
Figure 3.14: a, Optical absorption spectra of the MAPbI$_3$ films with 0~50% NH$_4$SCN and 5% extra PbI$_2$ addition in precursor solutions. b, Roughness of the MAPbI$_3$ films with 0~50% NH$_4$SCN and 5% extra PbI$_2$ addition in precursor solutions. The roughness values are extracted from the AFM images shown in Figure 3.15.

For evaluating the optical properties of the MAPbI$_3$ films with dual additives, the optical absorption measurements were conducted on the MAPbI$_3$ films with addition of 5% extra PbI$_2$ and 0~50% NH$_4$SCN. The optical absorption spectra Figure 3.14a illustrate that relatively low addition levels of NH$_4$SCN (e.g., 10~30%) could enhance the film absorption but high concentration of high addition levels of NH$_4$SCN (e.g., 40~50%) reduce the film absorption. The reduction of the optical absorption could be due to the fragmentation of the MAPbI$_3$ films induced by high NH$_4$SCN addition level, which is discussed in previous section.
Figure 3.15: AFM images of the MAPbI$_3$ films with 0~50% NH$_4$SCN and 5% extra PbI$_2$ addition in precursor solutions.

In addition to the optical absorption, the top-surface roughness of the MAPbI$_3$ films were examined with atomic force microscope (AFM). Figure 3.15 shows the top-view AFM images of the MAPbI$_3$ films with addition of 5% PbI$_2$ and 0~50% NH$_4$SCN. The average roughness values (shown in Figure 3.14b) indicate that increase of NH$_4$SCN addition level would induce rougher top surface of MAPbI$_3$ films. The increased top-surface roughness can be attributed to enlarged grain sizes and fragmentation of the films especially when NH$_4$SCN level is >30%.

To explore how these properties of MAPbI$_3$ films impact on the PV device performance, perovskite solar cells were fabricated by employing MAPbI$_3$ films with addition of 5% extra PbI$_2$ and 0~50% NH$_4$SCN. A device architecture of
glass/FTO/TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au was used and the fabrication method is illustrated in Experimental section in detail. To obtain the statistical results, for each NH$_4$SCN addition level, 20 devices were prepared. The statistical performance is shown in Figure 3.16. From the statistical results in Figure 3.16, it can be seen that high addition levels of NH$_4$SCN can reduce the $V_{oc}$ and $FF$. By analyzing the TRPL, optical absorption and roughness results shown above, the decrease trend of $V_{oc}$ and $FF$ could be attributed to the significantly increased roughness with high concentration of NH$_4$SCN addition. With increased top-surface roughness of MAPbI$_3$ films, the contact at the MAPbI$_3$/Spiro-OMeTAD is enhanced, which could lead to increased interfacial recombination rate at the interface. Therefore, $V_{oc}$ and $FF$ are reduced due to the interface.
Figure 3.16: The distributions of the photovoltaic parameters of perovskite solar cells by using the MAPbI₃ films with 0-50\% NH₄SCN and 5\% extra PbI₂ addition in precursor solutions.

From the results shown in this section, we can know that using dual additives, NH₄SCN together with PbI₂ can synergistically impact on the morphology and charge carrier dynamics. By comprehensively considering morphology and charge carrier lifetime, 5\% and 10\% are the optimal addition levels for extra PbI₂ and NH₄SCN, respectively, in term of PV device performance.
3.3.4 Role of morphology and carrier dynamics on performance of perovskite photovoltaics

In previous section, it is found that the 10% NH$_4$SCN together with 5% extra PbI$_2$ used as additives can optimize the device performance of perovskite solar cells. Based on the results, how the morphology and carrier dynamics impact on the performance of perovskite photovoltaics will be discussed. 10% and 5% are chosen as the addition levels for NH$_4$SCN and extra PbI$_2$, respectively. To decouple the functions of carrier lifetime and grain size in terms of photovoltaic performance, additional devices were fabricated, consisting of 20 devices with pristine MAPbI$_3$ films (no additives) and 20 devices with 10%-NH$_4$SCN-added MAPbI$_3$ films. The SEM images of device cross-section in Figure 3.17 indicate that the thicknesses of the layers (e.g., TiO$_2$, MAPbI$_3$, Spiro-OMeTAD and Au) in each type of devices are well controlled in the same ranges. The statistical results from measurements made on these devices are shown in Figure 3.18, along with results for devices with 5% extra PbI$_2$ addition and devices with 5% PbI$_2$ and 10% NH$_4$SCN dual addition.
Figure 3.17: SEM images of the cross section of perovskite solar cells by using pristine MAPbI$_3$ film, MAPbI$_3$ film with only 5% extra PbI$_2$, MAPbI$_3$ film with only 10% NH$_4$SCN and MAPbI$_3$ films with both 5% extra PbI$_2$ and 10% NH$_4$SCN. The images employ 500 nm scale bar.

As shown in Figure 3.18, pristine MAPbI$_3$ devices give the $V_{oc}$ in ranges from 0.840 to 1.062 V (0.922 V average value), $J_{sc}$ in ranges from 16.03 to 20.65 mA/cm$^2$ (18.58 mA/cm$^2$ average), $FF$ broadly in ranges from 22.38% to 65.57% (48.65% average) and $PCE$ in range of 4.15% to 13.93% (8.77% average). When 5% extra PbI$_2$ is added to the MAPbI$_3$ films, the devices exhibit $V_{oc}$ in ranges from 0.985 to 1.034 V (1.012 V average), $J_{sc}$ slightly in ranges from 19.28 to 20.24 mA/cm$^2$ (19.82 mA/cm$^2$ average), $FF$ in the ranges from
61.71% to 74.26% (67.68% average) and PCE in ranges from 11.54% to 15.09% (13.44% average). Meanwhile, when NH₄SCN (10%) is separately used as additive, the devices show the Vₖ in ranges from 0.957 to 1.025 V (0.994 V average), the Jₑ in the ranges from 20.36 to 22.43 mA/cm² range (21.13 mA/cm² average), the FF in ranges from 57.60% to 70.63% (63.72% average), PCE in ranges from 13.37% to 15.16% (14.08% average). When both PbI₂ (5%) and NH₄SCN (10%) are used, the devices show the Vₖ in ranges from 0.989 to 1.065 V (1.020 V average), the Jₑ in ranges from 20.42 to 22.43 mA/cm² (21.10 mA/cm² average), the FF in ranges from 71.87 to 81.50% (76.06% average) and the PCE in ranges from 15.32% to 17.82% (16.35% average).
The device performance results in Figure 3.18 illustrate that extra PbI₂ addition mainly improves $V_{oc}$ and $FF$. Given that the function of extra PbI₂ is to increase the charge carrier lifetime, this result indicates the $V_{oc}$ and $FF$ of perovskite device are correlative with charge carrier lifetime of perovskite films. Meanwhile, it is seen that NH₄SCN as additive mainly enhances the $J_{sc}$ of perovskite solar cells. By checking the
optical absorption spectra in Figure 3.19, adding 5% extra PbI₂ and 10% NH₄SCN separately and simultaneously do not change the optical absorption of MAPbI₃ films significantly. Therefore, the improvement of $J_{sc}$ in perovskite solar cells should benefit from the large grain size. It is known that the grain boundaries can scattering charge carriers, which would result in the loss of photo-excited carrier during the carrier diffusion process. With large grain size, the grain boundaries are significantly eliminated, especially these grain boundaries paralleling to the junction interface. The photo-excited charge carriers can be sufficiently collected from the perovskite films and contribute to the $J_{sc}$.

![Absorption Spectra](image)

Figure 3.19: Optical absorption spectra of pristine MAPbI₃ film, MAPbI₃ film with only 5% extra PbI₂, MAPbI₃ film with only 10% NH₄SCN and MAPbI₃ films with both 5% extra PbI₂ and 10% NH₄SCN.
The results above illustrate that the charge carrier lifetime in perovskite films is an important role for perovskite solar cells which can significantly impact on the $V_{oc}$ and $FF$ of the solar cells. Meanwhile, large grain size in the perovskite films would benefit the charge carrier transfer/collection, leading to improved $J_{sc}$ in solar cells.

### 3.3.5 Hysteresis and steady-state output

To understand the impact of additives on device hysteresis, $J$-$V$ characteristics of champion devices made with pristine MAPbI$_3$ films and those with extra 5% PbI$_2$ and 10% NH$_4$SCN dual addition were compared under forward and reverse scans with the voltage-scanning speeds of 1.0 V/s, 0.5 V/s and 0.1 V/s (Figure 4.20). For device with dual additives (Figure 4.20a), the variances of $V_{oc}$, $J_{sc}$, $FF$ and $PCE$ obtained from forward and reverse scanning directions are quite small under the three voltage scanning speeds and the degree of its hysteresis is therefore negligible. By comparison, the champion device with pristine MAPbI$_3$ absorber does not function as well with regards to hysteresis (Figure 3.20b).
Figure 3.20: The J-V characteristics of best-performing perovskite solar cells by using (a) MAPbI$_3$ films with 5% extra PbI$_2$ and 10% NH$_4$SCN dual addition and (b) pristine MAPbI$_3$ films. The J-V characteristics were evaluated by using both forward and reverse voltage scanning directions with voltage speed of 10 V/s.

Apart from the J-V scanning, steady-state output profiles for both devices were also measured with bias voltage of 0.875 V for more than 200 s. Figure 3.21 displays the steady-state output current density ($J$) of the pristine device at ~13.8 mA/cm$^2$ and that for the device with dual additive in the precursor at ~19.9 mA/cm$^2$. The steady-state output efficiencies are calculated to be ~12.8% and 17.4%, respectively. The efficiencies achieved from J-V scanning and steady-state output agree for the device with dual additives, but not for the pristine device. In addition to the efficiency difference, the device with dual...
additive responds essentially immediately. By contrast, the illumination response of the pristine device is much slower, taking ~30 s to reach the maximum current value.

![Graph showing the steady-state output efficiency of best-performing perovskite solar cells with and without additives. The graph displays two curves: one for no additive and another for 5% PbI₂ + 10% NH₄SCN dual addition. The curve with additives reaches a peak at ~19.9 mA/cm² with a PCE of ~17.4%, while the curve without additives reaches a peak at ~13.8 mA/cm² with a PCE of ~12.1%. The voltage (V) is 0.875 V.]

Figure 3.21: The steady-state output efficiency of best-performing perovskite solar cells by using MAPbI₃ films with 5% extra PbI₂ and 10% NH₄SCN dual addition and pristine MAPbI₃ films.

From the results shown above, the device with dual additives exhibits not only better photovoltaic performance under different scanning direction and scanning speed, but also negligible hysteresis and fast illumination response. It has been demonstrated that trap-assisted defects in perovskite absorbers are one of main origins of device hysteresis. Moreover, grain boundaries have been also demonstrated to give rise to hysteresis because of ion migration along the boundaries. Therefore, low density of defects and large grains are desirable for a hysteresis-free device. In our
method, dual addition of extra PbI$_2$ (5%) and NH$_4$SCN (10%) reduces the density of defects (i.e., longer minority carrier lifetime) and grain boundaries simultaneously—presumably giving rise to the reduction in hysteresis, as well as promoting the higher device performance.

### 3.4 Conclusions

In conclusion, we study the role of morphology and charge carrier dynamics in MAPbI$_3$-based photovoltaics through additives of NH$_4$SCN and PbI$_2$. A broad range of techniques have been used to explore relations between grain size, crystallinity, surface roughness, chemical composition, optical absorption, charge carrier lifetime, charge carrier generation, charge carrier collection, photovoltaic performance and hysteresis behaviors. Separately, adding NH$_4$SCN in the MAPbI$_3$ precursor significantly impacts MAPbI$_3$ grain size, crystallinity and hence charge carrier generation and collection, without introducing a substantial impurity into the film. Meanwhile separately adding extra PbI$_2$ to the MAPbI$_3$ precursor can significantly tune the charge carrier lifetime by more than an order of magnitude. Introduction of both PbI$_2$ and NH$_4$SCN can synergistically reinforce material properties, yielding larger grains and better charge carrier dynamics than can be achieved by separately using NH$_4$SCN or PbI$_2$. Then, the optimal concentrations of additives to maximize the $PCE$ in dual addition are identified from TRPL for PbI$_2$ and photovoltaic performance for NH$_4$SCN. Further, the functions of
these two additives on device performance are decoupled and studied at their optimal concentration. From device performance statistics, both additives are able to give rise to overall device performance improvement; however, they contribute to the improvement differently. PbI₂ addition benefits $V_{oc}$ and $FF$, while NH₄SCN addition improves $J_{sc}$. The results also indicate that $V_{oc}/FF$ preferably correlates with charge carrier lifetime as suggested by TRPL. $J_{sc}$ is more related with charge carrier generation and collection impacted by morphology. The hysteresis behaviors from champion device with dual addition at optimal additive levels and champion device without additives are shown and compared under different measuring condition. The results indicate that dual addition of NH₄SCN and PbI₂ is an effective approach to elimination of hysteresis through effective reduction of trapping defects and grain boundaries.
4. Additive Engineering for High-Performance Room-Temperature-Processed Perovskite Absorbers with Micron-Size Grains and Microsecond-Range Carrier Lifetimes

The content of this chapter is adapted from our publication (Energy & Environmental Science 2017, 10, 2365-2371). Qiwei Han and Prof. David Mitzi conceived this project. Qiwei Han carried out the film deposition, device fabrication and characterization including SEM, XRD, optical absorption, PL, J–V and DLS, and analyzed data. Yusong Bai performed the TRPL measurement. Jie Liu (student) assisted in fabricating devices. Ke-zhao Du provided simulated XRD patterns for selected crystal structures and helped to identify prospective impurities within the films discussed in this manuscript. Tianyang Li performed the full-profile Pawley fitting of the X-ray diffraction data to determine the unit cell parameters and FWHMs. Dong Ji performed the IR measurement. Yihao Zhou conducted the AFM measurement. Changyong Cao drew the schematic flow diagram for the room-temperature process. Jie Ding performed the XPS depth profiling. All authors discussed the results and commented on the manuscript. Prof. Jie Liu and Prof. David Mitzi supervised the project. We acknowledge our co-authors’ contribution to this work.
### 4.1 Introduction

In recent years, perovskite photovoltaics (PV) have achieved remarkable advances in device performance, from initial 3.8% power conversion efficiency (PCE) in 2009 to over 22% PCE in 2016.\textsuperscript{4, 33-34, 40, 44, 52, 134} However, current highest-performance perovskite film deposition requires annealing at elevated temperatures (e.g., 100–150 °C) to obtain suitable crystallization and to remove solvent.\textsuperscript{52, 134} Due to the sensitivity of perovskite films to annealing conditions, inaccurate annealing time/temperature leads to perovskite film degradation, resulting in decreased device performance and processing yield.\textsuperscript{88, 91, 135-136} When fabricating more complex devices such as all-perovskite tandem PVs, annealing temperatures used to prepare top perovskite cells can cause degradation of well-prepared perovskite layers within bottom cells,\textsuperscript{136-140} thereby hindering fabrication of tandem PVs targeting ultra-high PCE (e.g., >25%). High annealing temperatures can also lead to the melting or deformation of flexible (e.g., polymer-based) substrates and impede the application of perovskite technology in flexible devices. Moreover, added heating steps increase the payback time and ultimately cut into the economic viability of perovskite technology for large-scale production. More recently, several room-temperature approaches have been reported for perovskite film deposition.\textsuperscript{11, 68-69, 141-145} Nevertheless, perovskite film quality from current room-temperature processing approaches underperforms the analogous films obtained with thermal anneals in terms of persistent residual solvent, small grain size (≤300 nm) and/or
short charge carrier lifetimes. These issues arise from the lack of effective mechanisms to positively impact the film crystallization process. In addition to film quality, the film deposition steps for current room-temperature approaches are not generally suitable for device structures involving multiple perovskite layers, as in all-perovskite tandem PVs. For example, the required dipping steps (e.g., in diethyl ether or methylammonium iodide/isopropanol solutions) in current room-temperature processes can cause the degradation or cross-reaction of well-deposited layers in bottom cells during preparation of top perovskite layers.\textsuperscript{68, 141-142} To fully benefit from the room-temperature process, the film quality and deposition process requirements should be simultaneously considered.

In this chapter, we demonstrate an additive engineering approach to deposit high-quality methylammonium lead iodide (MAPbI\textsubscript{3}) films at room temperature. By using methylammonium thiocyanate (MASCN) as an additive to the precursor and a rapid vacuum-based drying approach, high quality MAPbI\textsubscript{3} films are achieved. Despite the absence of heating, such MAPbI\textsubscript{3} films possess high crystallinity, large grains (>2 μm) and long charge carrier lifetimes ($\tau_1 = 931.94 \pm 89.43$ ns; $\tau_2 = 320.41 \pm 43.69$ ns), which represent the best overall results among reported room-temperature film processing approaches\textsuperscript{11, 68-69, 141-143} and also comparable characteristics to state-of-the-art MAPbI\textsubscript{3} films deposited with annealing steps.\textsuperscript{42} Unlike previously reported room-temperature approaches, our process requires no extended dipping steps that could cause
degradation and cross-reaction during preparation of more complex devices structures, including all-perovskite tandem PVs. Moreover, our room-temperature MAPbI₃-based PVs exhibit a best PCE of 18.22% (16.9%, average), with significantly reduced hysteresis and improved environmental stability over 1000 hours without encapsulation. To understand the origin of the outstanding film properties from the additive-based approach, dynamic light scattering (DLS) and scanning electron microscopy (SEM) measurements have been used to reveal that the average grain size in room-temperature-processed perovskite films strongly correlates with solution precursor aggregate size and that micron-sized grains originate from similar-scale MASCN-facilitated aggregates in the precursor solution. The obtained high film quality coupled with room-temperature processing points to the potential for reduced costs and increased versatility for fabrication of high-performance perovskite optoelectronic devices.

4.2 Experimental section

4.1.1 Film deposition

To prepare the pristine (no additives) precursor solution for MAPbI₃ films, 1.25 mmol methylammonium iodide (MAI) and 1.25 mmol lead iodide (PbI₂) were dissolved in 1 mL solvent containing N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), with the volume ratio of DMF:DMSO = 9:1. To obtain the optimal MAPbI₃ films
for high device performance at room temperature (i.e., RT-MAPbI₃), 40% MASCN and 5% extra PbI₂ (both are mol% relative to MAPbI₃) were added to the pristine precursor solution. The films were then deposited by spincoating the precursor solution using a spin speed of 5000 r.m.p for 30 s, with a solvent dripping process (chlorobenzene used for the dripping step). The spin coating was performed in a nitrogen-filled glovebox with oxygen and water levels maintained below 0.1 ppm. The asdeposited MAPbI₃ films were dried in the glovebox anti-chamber at reduced pressure (Edwards RV12, maximum achievable vacuum is 2X10⁻³ mbar) for 20 min, to form the resultant films. For comparison, pristine MAPbI₃ (i.e., P-MAPbI₃) films were also prepared. The pristine MAPbI₃ precursor solution (no MASCN or extra PbI₂) was deposited with similar steps. After spin-coating, P-MAPbI₃ films were annealed on a hotplate at 100 °C for 10 min. To study the impact of MASCN level on room-temperature films, 0~50% MASCN together with 5% extra PbI₂ was added to the pristine MAPbI₃ precursor and the MAPbI₃ films were deposited with similar steps to those described above.

4.2.2 Device Fabrication

The FTO-coated glass substrates were cleaned in soapy water, deionized water, acetone and isopropanol with sonication and then all the substrates were baked at 500 °C in air for 1 hour before further use. To prepare the TiO₂ electron transport layers (ETLs), a precursor solution containing 2 mL ethanol and 4 mL titanium diisopropoxide bis(acetylacetonate) solution (75% wt. in isopropanol) was stirred at room temperature
in air for 1 hour. The TiO\textsubscript{2} precursor solution was used to deposit the \(\sim 50\ \text{nm}\) TiO\textsubscript{2} ETL by the hot spray pyrolysis method at 450 \(\degree\text{C}\). The TiO\textsubscript{2} compact films were annealed in air at 500 \(\degree\text{C}\) for 1 hour. Then, the substrates were immersed in 0.02 M TiCl\textsubscript{4} water solution at 70 \(\degree\text{C}\) for 10 min. After the TiCl\textsubscript{4} treatment, substrates were dried by house compressed air and finally annealed at 500 \(\degree\text{C}\) in air for 1 hour. The MAPbI\textsubscript{3} films were deposited on the glass/FTO/TiO\textsubscript{2} substrates by following the procedure mentioned above. To complete the devices, Li-doped Spiro-OMeTAD was spin-coated on the MAPbI\textsubscript{3} films as the hole transport layer (HTL). A solution consisting of 75 mg Spiro-OMeTAD, 28.8 \(\mu\text{L}\) 4-tert-butylpyridine, 17.6 \(\mu\text{L}\) Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520mg Li-TFSI in 1mL acetonitrile) and 1 mL chlorobenzene was employed with a spin speed of 3000 r.m.p for 30s. Finally, Au was thermally evaporated on the HTL, with thickness of \(\sim 80\ \text{nm}\), to serve as the electrode.

### 4.2.3 Characterizations

Morphologies of the MAPbI\textsubscript{3} films were imaged with a scanning electron microscope (SEM, FEI XL30 SEM-FEG). Atomic force microscopy (AFM) images were characterized using a scanning probe microscope (Digital Instruments Dimension 3100). X-ray diffraction (XRD) measurements were carried out on a PANalytical Empyrean Powder X-ray diffractometer using Cu K\(\alpha\) radiation. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALab220i-XL electron spectrometer (VG Scientific) using 300W Al K\(\alpha\) radiation. Transmittance Infrared (IR)
measurements were carried out employing a Fourier Transform Infrared (FTIR)
spectrometer (Thermo Scientific Nicolet 380). The charge carrier lifetimes were
characterized via time-resolved photoluminescence (TRPL) experiments using a
Hamamatsu C4780 picosecond fluorescence lifetime measurement system (instrument
response function ~150 ps). This system employs a Hamamatsu Streakscope C4334 as the
photon-counting detector, and a Hamamatsu C4792-01 synchronous delay generator
that electronically generates all time delays. A Hamamatsu 405 nm diode laser was
utilized as the excitation source. Optical absorption measurements were performed on a
Shimadzu UV-3600 spectrophotometer. The Tindall effect was tested with a commercial
laser pen with red beam light (Beboncool RF 2.4 GHz). Dynamic light scattering (DLS)
measurements were performed on a Zetasizer (Nano-ZS, Malvern Instruments). The
external quantum efficiency (EQE) was taken using a QE-R instrument from Enlitech
without bias voltage or illumination. The current density-voltage (J-V) characteristics
and steady-state output were measured using a Keithley 2400 source meter. The
illumination source was a Newport Oriel 92192 solar simulator with an AM1.5G filter,
operating at 100 mW cm$^{-2}$. All devices were masked with area of 0.1 cm$^2$ aperture to
define the active areas. A standard silicon solar cell from Newport Corp. was used as
reference for J-V and EQE measurements. All measurements were performed under
ambient condition with relative humidity level of 35-55%.
4.3 Results and discussion

4.3.1 Growth and characterization of room-temperature processed films

Figure 4.1: a, Top-view SEM image of a RT-MAPbI₃ film. The scale bar shows 1 µm length. b, Top-view SEM image of a RT-MAPbI₃ film at large scale. The scale bar shows 10 µm length.

The top-view SEM image of a RT-MAPbI₃ film (Figure 4.1a) reveals that the film grain size exceeds 2 µm—i.e., a value that exceeds other room-temperature processing approaches¹¹,¹⁸⁶-¹⁸⁹,¹⁴¹-¹⁴³ and is as large as the grains in state-of-the-art MAPbI₃ films obtained with annealing processes.⁴² In addition, the RT-MAPbI₃ films exhibit good coverage without pinholes (Figure 4.1a and Figure 4.1b). According to atomic force microscopy images (Figure 4.2a), the surface of the RT-MAPbI₃ film has a roughness on the order of 20 nm. This flat surface and resulting reduced interfacial area should benefit device performance by reducing interfacial recombination loss.
Figure 4.2: a, Atomic force microscope (AFM) image of a RT-MAPbI₃ film. The extracted arithmetic average roughness is 21.80 nm. Film was deposited on a glass/FTO/TiO₂ substrate. b, XRD pattern for a RT-MAPbI₃ film using Cu Kα radiation.

The XRD pattern (Figure 4.2b) shows strong intensity for the MAPbI₃ peaks, pointing to good crystallinity of the RT-MAPbI₃ films. Furthermore, no extra peaks could be found beyond those for MAPbI₃ and the substrate, indicating no solvent inclusion or SCN-related compounds in the resulting films. SCN⁻ is a volatile species and expected to be removed during processing (the proposed mechanism is discussed further below). To verify this point, X-ray photoelectron spectroscopy (XPS) depth profiling spectra (Figure 4.3) show no detectable residual sulphur within the RT-MAPbI₃ film, indicating that SCN⁻ and DMSO are effectively removed during the vacuum pump process, despite 40% MASCN and DMSO being added into precursor solution.
Figure 4.3: XPS depth profiling results for the RT-MAPbI₃ film with 40% MASCN addition, in which the Pb 4f and S 2p peak are monitored at each etching thickness. The Pb 4f results are used to monitor when the back surface of the RT-MAPbI₃ has been reached. The S 2p results are used to indicate whether residual SCN⁻ and/or DMSO exist in the RT-MAPbI₃ film.

Figure 4.4: Infrared (IR) spectra of RT- and A-MAPbI₃ films. The nearly overlapping spectra for the two films indicate the identical chemical bonding in these two samples.
Moreover, a transmittance infrared (IR) measurement was performed on the RT-MAPbI₃ film, along with (for comparison) a spectrum for pristine MAPbI₃ (no MASCN addition) with annealing treatment (referred to as P-MAPbI₃). As shown in Figure 4.4, IR spectra of RT-MAPbI₃ and P-MAPbI₃ are essentially identical, further confirming that no SCN⁻ anions or solvent remain in the RT-MAPbI₃ films (or associated concentrations fall below the detection limit of the measurement). These results illustrate that the SCN⁻ /DMSO is depleted from the RT-MAPbI₃ films after low vacuum treatment, which is different from analogous reports that do not employ a vacuum-treatment process.⁴³, ¹⁴⁴ Complete removal of solvent and SCN⁻ anions in the RT-MAPbI₃ films is beneficial because residuals of these species may influence film quality, leading to losses of optical absorption and conductivity, and also negatively impact film stability.

Figure 4.5: a, UV-Vis (red curve) and PL (blue curve) spectra of RT-MAPbI₃ film (PL excitation wavelength is 442 nm); b, TRPL spectrum of RT-MAPbI₃ film (TRPL excitation wavelength is 405 nm).
For optoelectronic characterization of RT-MAPbI₃ films, ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectroscopy were performed (Figure 4.5a), revealing good correspondence between UV-Vis absorption and PL emission features. From the time-resolved PL (TRPL) spectrum of a RT-MAPbI₃ film (Figure 4.5b), an average charge carrier lifetime ($\tau_{\text{avg}}$) of $613.47 \pm 65.61$ ns is obtained from the relative amplitudes of the long-lived ($\tau_1 = 931.94 \pm 89.43$ ns; $A_1 = 47.92\%$), and short-lived ($\tau_2 = 320.41 \pm 43.69$; $A_2 = 52.08\%$) components of the charge carrier lifetime.¹³¹,¹⁴⁵-¹⁴⁶ For comparison, under the same characterization conditions, SEM, XRD, UV-Vis and PL measurements were also performed on the P-MAPbI₃ film (Figure 4.6). We can see that the $\tau_{\text{avg}}$ of RT-MAPbI₃ exceeds the analogous value for P-MAPbI₃ by ~500 fold. The minority charge carrier lifetimes also fall into the same microsecond timeframe as the analogous values for state-of-the-art MAPbI₃ films processed with annealing steps.⁴² The long charge carrier lifetime can be attributed to the synergistic impact of improved crystallinity from MASCN addition and extra PbI₂ passivation.⁴²,¹¹⁴-¹¹⁵
Figure 4.6: a, Top-view SEM image of the P-MAPbI$_3$ film deposited on a glass substrate for PL/TRPL measurements. The image employs a 1 µm scale bar; b-c, UV-Vis (b) and PL (c) spectra of the RT-MAPbI$_3$ and P-MAPbI$_3$ films; d, TRPL spectra of the P-MAPbI$_3$ film. The excitation wavelength for the PL spectrum is 442 nm and the excitation for TRPL is 405 nm. The charge carrier lifetimes ($\tau_1$ and $\tau_2$) and their corresponding contributions ($A_1$ and $A_2$) are extracted by fitting the PL decay curves with a biexponential equation.
4.3.2 Photovoltaic performance, hysteresis and stability

To evaluate PV performance of devices fabricated using the RT-MAPbI$_3$ films, solar cells were fabricated with a planar device architecture of glass/FTO/TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/ Au (see the Experimental section for details). The typical thickness of MAPbI$_3$ layers is ~400 nm (Figure 4.7).

Figure 4.7: SEM image of device cross-section with RT-MAPbI$_3$ film. Scale bar is 500 nm.

Histograms of PV performance (Figure 4.8) illustrate that the PCE, short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$) and fill factor (FF) by forward scanning, over 28 devices with RT-MAPbI$_3$ films, vary from 15.81% to 18.22% (16.92% average), 21.16 to 23.20 mA cm$^{-2}$ (22.32 mA cm$^{-2}$ average), 0.998 to 1.064 V (1.029 V average) and 70.09% to 76.94% (73.67% average), respectively. The best device yields PCE of 18.22%, $J_{sc}$
of 22.29 mA cm$^2$, $V_{oc}$ of 1.064 V and $FF$ of 76.83%. This performance level closely matches state-of-the-art MAPbI$_3$ solar cells achieved with annealing steps with planar device structure,\textsuperscript{42} attesting to the fact that the RT-MAPbI$_3$ films are of similar quality as state-of-the-art films prepared using thermal annealing methods.

![Graphs of PCE, J$_{sc}$, V$_{oc}$, and FF](image_url)

**Figure 4.8:** Statistical PCE, J$_{sc}$, V$_{oc}$ and FF of devices prepared using RT-MAPbI$_3$ films. The $J$-$V$ measurement was conducted in air (relative humidity of 35~55\%), with 0.1 V s$^{-1}$ voltage scanning rate and forward scanning direction.
Figure 4.9a and Figure 4.9b show the $J$-$V$ hysteresis of the best-performing devices employing RT-MAPbI$_3$ and P-MAPbI$_3$ films, using the same device structure. We can see that employing RT-MAPbI$_3$ helps to reduce the $J$-$V$ hysteresis, presumably due to the enhanced grain size and long charge carrier lifetime. The external quantum efficiency (EQE) spectrum in Figure 4.10a indicates high quantum yield for the RT-MAPbI$_3$ device, resulting in an integrated $J_{sc}$ value of 21.98 mA cm$^{-2}$, which is in good agreement with $J_{sc}$ from the $J$-$V$ result. The steady-state output profile (Figure 4.10b) shows output current, $J$, of ~20.7 mA cm$^{-2}$ and steady-state output $PCE$ of ~18.1% under bias of 0.875 V for this best-performing device. The efficiencies from $J$-$V$ scanning and steady-state output are consistent, further confirming the reduced hysteresis behavior (Figure 4.9a).

![Figure 4.9](image)

**Figure 4.9**: a, $J$-$V$ characteristics of the best-performing device achieved with a RT-MAPbI$_3$ film. b, $J$-$V$ characteristics of the best-performing device achieved with a P-MAPbI$_3$ film. The $J$-$V$ characteristics were obtained by both forward and reverse scanning direction with 0.1 V s$^{-1}$ scanning rate.
To test the environmental stability of the RT-MAPbI\textsubscript{3} devices, the best-performing device was stored in air, under relative humidity of \(\sim\)20-25\%, for 1000 hours without encapsulation. For comparison, the stability of the best-performing P-MAPbI\textsubscript{3} device was also tested under the same conditions. Device performances as a function of time are shown in Figure 4.11. The unencapsulated device with a RT-MAPbI\textsubscript{3} film maintains a PCE of 16.34\% after 1000 hours, which is \(\sim\)89.7\% of its initial PCE value. By contrast, the unencapsulated device with P-MAPbI\textsubscript{3} film only survives for \(\sim\)150 hours. Given that degradation of MAPbI\textsubscript{3} films likely originates at defect sites/grain boundaries\textsuperscript{90}, the newly-developed room-temperature process simultaneously reduces the grain boundary density and defect density, thereby leading to significantly enhanced stability in MAPbI\textsubscript{3} films and their devices.
Figure 4.11: PCE, \( J_{sc} \), \( V_{oc} \) and FF of best-performing devices prepared using RT-MAPbI\(_3\) and P-MAPbI\(_3\) films, as a function of time. The devices were stored without encapsulation under relative humidity of 20~25\%. The \( J-V \) measurement was conducted with 0.1 V s\(^{-1}\) voltage scanning rate and forward scanning direction.

### 4.3.3 Effects of additive on film quality and device performance

To gain insight into the role of additives on film microstructure and resulting PV performance, the impact of the additive level was examined. As shown in previous work, 5\% extra PbI\(_2\) was found to be optimal in terms of device performance.\(^{42}\) To obtain the best MASCN addition level, different MASCN levels were added to the MAPbI\(_3\).
precursor and these solutions were spin-coated using the same room-temperature procedure. Figure 4.12 shows top-view SEM images of these RT-films with 0 to 50% MASCN (mol% relative to MAPbI₃) in the precursor solution. The grain size for 0-50% MASCN additive level increases over the range of 0.1-2.0 µm, indicating that the MASCN additive plays an important role in the increased grain size.

Figure 4.12: Top view SEM images of RT-MAPbI₃ films with addition of 5% extra PbI₂ and 0-50% MASCN to the precursor. The scale bar for the SEM images is 1 µm.
According to XRD patterns (Figure 4.13a), the unit cell parameters determined from full-profile Pawley fitting (Figure 4.14 and Table 4.1) indicate only minor lattice parameter variation, on the level of ~0.2%, with no obvious systematic trend over the range of additive levels considered. The absence of significant change in unit cell parameters illustrates that addition of MASCN doesn’t significantly impact the MAPbI₃ crystal structure.
Figure 4.14: The unit cell parameters (determined from full-profile Pawley fitting) as a function of MASCN additive level to the MAPbI$_3$ film precursor solution.

Table 4.1: The unit cell parameters list (determined from full-profile Pawley fitting) as function of MASCN additive level to the MAPbI$_3$ film precursor solution.

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<th>MASCN addition level (%)</th>
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<th>c axis (Å)</th>
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Figure 4.15: The FWHMs of RT-MAPbI₃ films as function of MASCN additive level, extracted from the XRD patterns for the specified peaks.
Figure 4.15 shows the FWHMs of RT-MAPbI₃ films as a function of MASCN addition level, indicating that the 40% MASCN additive level yields films with the best crystallinity. By comparing the XRD patterns in Figure 4.2b, Figure 4.13a and Figure 4.13b, we find that (MA)₂[(PbI₃)₂PbI₂]•2DMSO (structure shown in Figure 4.16) exists in the RT-MAPbI₃ films with 0–30% MASCN addition, but this phase does not appear for ≥40% MASCN addition levels. These results and the corresponding XPS (Figure 4.3) and IR results (Figure 4.4) suggest that MASCN can facilitate the removal of solvent for MASCN additive levels exceeding 30% (possible mechanism to be discussed later).

Figure 4.16: Schematics of (a) the packing structure of (MA)₂[(PbI₃)₂PbI₂]•2DMSO and (b) the 1D structure of [(PbI₃)₂PbI₂]⁻ along different crystallographic directions. The corresponding simulated XRD pattern for (MA)₂[(PbI₃)₂PbI₂]•2DMSO is shown in Figure 4.13b.

Complete removal of solvent is important in room-temperature-processed films because solvent residue can lead to optical and electrical losses. Specifically, Figure 4.17a shows that DMSO remaining in the MAPbI₃ films correlates with optical absorption loss.
Figure 4.17b shows the \( J-V \) characteristics of solar cells based on RT-MAPbI\(_3\) films with 0–50% MASCN addition in the precursor solution (parameters are listed in Table 4.2). We can see that \( J_{sc}, V_{oc} \) and \( FF \) are simultaneously enhanced with increased addition of MASCN. Such PV improvement correlates with the removal of solvent, increased grain size and improved crystallinity.

**Table 4.2**: The photovoltaic parameters of the best-performing solar cells prepared using RT-MAPbI\(_3\) films with 5% extra PbI\(_2\) and 0–50% MASCN addition to the MAPbI\(_3\) precursor solution. All \( J-V \) measurements were conducted with 0.1 V s\(^{-1}\) voltage scanning rate and forward scanning direction.
4.3.4 Proposed mechanism for RT-MAPbI$_3$ film formation

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Figure 4.18: Top view SEM images of RT-MAPbI$_3$ films formed by using (a) 40% extra MAI and (b) 40% NH$_4$SCN to replace MASCN as an additive in the precursor solutions.

To understand the independent effects of MA$^+$ and SCN$^-$ from MASCN on the room-temperature MAPbI$_3$ grain formation, methylammonium iodide (MAI) and ammonium thiocyanate (NH$_4$SCN) were used independently as additives. Figure 4.18a and Figure 4.18b show the top-view SEM images of MAPbI$_3$ films deposited with addition of extra 40% MAI or 40% NH$_4$SCN in the precursor solution. Adding extra MAI does not change the grain size, while adding NH$_4$SCN results in grain sizes exceeding 1
µm with uniform film surface morphology. This result indicates that the SCN⁻ anion, rather than the MA⁺ cation, plays the critical role in increasing grain size at room temperature. Furthermore, grain size progressively increases with increased NH₄SCN addition level (Figure 4.19), confirming the relevance of the SCN⁻ ion to grain size enlargement.

![Figure 4.19: Top-view SEM images of the room-temperature MAPbI₃ films with 5% extra PbI₂ and 0-50% NH₄SCN addition to the MAPbI₃ precursor solutions. All films were deposited on glass/FTO/TiO₂ substrates and all images employ a scale bar of 1 µm.](image)

Given that there is no post-annealing step to accomplish thermally-assisted MAPbI₃ grain growth, the significant film morphology change upon SCN⁻ anion
addition may directly originate from changes taking place within the precursor solutions. Since the perovskite precursor solution consists of precursor aggregates formed by molecular self-assembly\textsuperscript{71,147} and SCN\textsuperscript{−} is a strong bridging group for coordination bonding,\textsuperscript{148-149} we propose SCN\textsuperscript{−} can coordinate with Pb\textsuperscript{2+} to facilitate enlargement of the precursor aggregates up to the microscale before spin-coating.\textsuperscript{71,147} During the film deposition, these enlarged precursor aggregates arrange in an orderly and compact fashion on the substrates. With the assistance of gentle vacuum, the precursor aggregates crystallize and convert into the final grains, as solvent and volatile SCN\textsuperscript{−} species are removed (Figure 4.20 illustrates the proposed film formation mechanism).

![Diagram of the film formation process](image)

**Figure 4.20:** Schematic flow diagram of the room-temperature process to deposit MAPbI\textsubscript{3} films and illustration the film formation mechanism.

To verify this mechanism, Tindall-effect tests and DLS measurements were performed for MAPbI\textsubscript{3} precursors containing 0-50% MASCN additive. All precursor solutions display the Tindall effect, while the solvent alone does not, illustrating that the Tindall effect is induced through the MAPbI\textsubscript{3} precursor with additives (Figure 4.21). DLS
spectra (Figure 4.22a) quantitatively display the size distribution of the precursor aggregates in each MAPbI$_3$ precursor solution, from which the average aggregate size (distribution peak) ranges from 0.3~2.5 µm with 0~50% MASCN addition. The correlation of the precursor aggregate size with grain size (Figure 4.22b) demonstrates that grain size in the final films strongly follows from the precursor aggregate size. Meanwhile, the coordination of SCN⁻ ligands may possibly reduce the activation energy for the grain crystallization,\textsuperscript{141,142} thereby enabling the precursor aggregates to transform to high crystallinity during a mild room-temperature vacuum pumping process.

![Figure 4.21: Tindall test of DMF/DMSO solvent and MAPbI$_3$ precursor solutions with 5% extra PbI$_2$ and 0~50% MASCN addition. The DMF/DMSO solvent does not show the Tindall effect, but all the MAPbI$_3$ precursor solutions do show the Tindall effect. The red laser illuminates from the bottom of the vials.](image)
In addition to the grain size/crystallinity effects, we previously mentioned that MASCN can facilitate solvent removal and that SCN$^-$ anions don’t remain in the final films. At sufficiently high concentration, SCN$^-$ likely reduces the interaction between Pb$^{2+}$ ions and DMSO through Pb$^{2+}$ ion coordination (i.e., SCN$^-$ out-competes DMSO for coordination sites), enabling more facile DMSO removal under mild vacuum conditions. In turn, we propose that SCN$^-$ reacts with MA$^+$ to form volatile CH$_3$NH$_2$ and HSCN gases. Under vacuum conditions, these volatile gas species form and are continuously removed from the system, thereby disturbing the chemical equilibrium and finally causing MAPbI$_3$ films to be depleted of SCN$^-$ during the vacuum pumping step. Another prospective pathway involves SCN$^-$ reacting with MA$^+$ to form CH$_3$SCN and NH$_3$ gases. These gases are also volatile and can be readily depleted during the vacuum
pump step. With one or both of these processes occurring, the precursor aggregates lose the solvent/SCN\(^-\) and eventually form crystalline grains.

### 4.4 Conclusions

In conclusion, we demonstrate an additive engineering approach to deposit high-quality MAPbI\(_3\) films at room temperature, employing a simple low-vacuum processing step (compatible with low-cost processing). The as-deposited MAPbI\(_3\) films exhibit micron-sized grains and microsecond-range charge carrier lifetimes, high crystallinity and flat uniform surfaces. With such excellent film characteristics, the corresponding MAPbI\(_3\) solar cells show high performance (best \(PCE=18.22\%\) and average \(PCE=16.92\%\)) with low hysteresis and good environmental stability over 1000 hours. In addition, we establish the size dependence between perovskite precursor aggregates and crystal grains in solution-processed perovskite films and, through this understanding, propose a general additive-based mechanism for engineering grain size. Even though we only discuss the additive engineering approach for MAPbI\(_3\) films and room temperature processing, given the flexibility to independently tailor excess Pb\(^{2+}\) and SCN\(^-\) levels using both PbX\(_2\) (X = Cl, Br, I) and MASCN addition, the approach should also be transferrable to alternative perovskite systems and film deposition conditions (e.g., perovskites with mixed anions, films processed with gentle annealing-based approaches). The additive engineering approach should therefore provide a new pathway towards more versatile,
low-cost processing of high-performance devices with complex structures, including all-perovskite tandem PVs and flexible optoelectronic devices.
5. Carrier Dynamics Engineering for High-Performance Electron-Transport Layer-Free Perovskite Photovoltaics

The content of this chapter was used to prepare a manuscript which have been submitted to *Chem, Cell Press*. Qiwei conceived the project and prepared the manuscript. Qiwei Han and Jie Ding carried out the film deposition and device fabrication. Qiwei Han carried out the characterizations including SEM, XRD, UV-Vis, PL, TRPL and J-V, and analysed data. Yusong Bai performed the TRPL fitting and analysis. Yihao Zhou, Jing-Yuan Ma, Yao-Xuan Chen, Jie Liu (student), Jie Chen and Qianqing Ge assisted in film characterizations. All authors discussed the results and commented on the manuscript. Prof. Jie Liu, Prof. David Mitzi and Prof. Jinsong Hu supervised the project. We acknowledge all the authors’ contribution to this work.

5.1 Introduction

Perovskite photovoltaics (PV) has attracted tremendous attention due to recent advances in power conversion efficiency (PCE) and diverse processing options.\(^4, 9, 33-34, 40\) Other than high performance, the factors of good stability, simpler device configuration and low processing cost should be considered in next-generation perovskite PV. Currently, high-performance (e.g., >19% PCE) perovskite solar cells exclusively employ p-i-n device architectures,\(^40, 52, 134\) wherein distinct electron transport (n-type) and hole transport (p-type) layers are generally viewed as critical components.
for reliable photogenerated carrier extraction. However, the deposition processes to construct a p-i-n architecture, especially for inorganic electron-transport layers (ETLs), typically require high-temperature conditions (e.g., ~500 °C for TiO₂, ~500 °C for BaSnO₃, and ~250 °C for ZnO). Such high temperature steps compromise the low-cost advantage of solution-based approaches for perovskite film deposition (e.g., generally performed at 25–100 °C), leading, for example, to increased projected payback time for perovskite PV and other optoelectronics. Additionally, in building more complex optoelectronic devices, such as all-perovskite tandem solar cells, the high temperatures to process ETLs in top cells can damage the perovskite and/or other temperature-sensitive films in bottom cells. The high temperatures can also melt prospective flexible substrates and/or cause ion migration from substrates, limiting the application of perovskite technology in versatile optoelectronics. More importantly, the existence of some ETLs themselves can detrimentally impact the perovskite devices. For example, ZnO ETLs can cause the decomposition of perovskite layers during annealing and TiO₂ ETLs can induce degradation of perovskite films under illumination. Regardless of performance issues, the inclusion of more numerous layers in devices is not desired for effective commercialization. In short, these ETL-induced issues lead to prospects of lower processing yields, increased payback times, faster degradation and difficulties in constructing more versatile/complex perovskite optoelectronics. To address these issues, building solar cells without distinct ETLs in the architectures is a
promising direction for next-generation perovskite PV. In fact, studies have demonstrated that perovskite films possess superior properties for charge-carrier dissociation\textsuperscript{85} and transport,\textsuperscript{36-37} and that the transparent electrodes (e.g., fluorine-doped tin oxide glass (FTO) and tin-doped indium oxide glass (ITO)) themselves are typically n-type semiconductors. Therefore, distinct ETLs should not theoretically be necessary for high-performance perovskite PV. Unfortunately, all current-generation ETL-free perovskite solar cells suffer from low $PCE$ (e.g., $< 15\%$), with relatively large hysteresis and inferior stability.\textsuperscript{45, 77-80, 100, 152-154} In this regard, creating deeper understanding and developing effective approaches to improve the performance are keys for the success of ETL-free perovskite PV.

In this chapter, we reveal that the carrier injection process is significantly inhibited at the interface in the absence of an ETL, which leads to insufficient carrier collection and severe interfacial carrier recombination. The recombination decreases the external quantum efficiency (EQE) in both short- and long-wavelength ranges and thereby compromises the performance for ETL-free perovskite PV. Moreover, we demonstrate that improving the intrinsic carrier lifetimes in perovskite films can counterbalance the inferior device interfaces and suppress the carrier recombination at the ETL-free interface. Such an approach can remarkably tailor the carrier collection efficiency, enabling the carrier dynamics in ETL-free perovskite PV to approach that in ETL-containing devices, and thereby remedy the poor EQE/performance. Benefiting
from this discovery, ETL-free perovskite PV devices are successfully realized with best $PCE$ of 19.5% (18.48% in average), nearly eliminated hysteresis and good stability, through the use of perovskite films with microsecond carrier lifetimes. Such high $PCE$ is comparable to the analogous values (20.7%) achieved for ETL-containing solar cells prepared using analogous perovskite films, and the $PCE$ is also the best result among all reported ETL-free perovskite solar cells to date. Our research provides insight into ETL-free solar cells and points out a promising direction for perovskite PV and analogous optoelectronic devices, offering simultaneously high performance, simplified processing and better prospects for ultra-low cost device fabrication.

5.2 Experimental section

5.2.1 Perovskite film deposition

For deposition of the baseline MAPbI$_3$ films, precursor solutions were prepared with 1.2 M PbI$_2$ and 1.2 M MAI in the DMF/DMSO co-solvent ($V_{DMF}:V_{DMSO} = 9:1$). Extra PbI$_2$ with levels of 0%, 2.5%, 5% and 7.5% (mol%, relative to stoichiometric MAPbI$_3$) was added into the MAPbI$_3$ precursor solutions, respectively, to tune the carrier lifetimes in the MAPbI$_3$ films. For each system, the precursor solutions were stirred at ~25 °C for 24 hours and filtered with a 0.45 µm PTFE syringe filter before further use. The MAPbI$_3$ films were then deposited by spin-coating the precursor solution using a spin speed of 5000 r.p.m for 30 s. 1.5 mL chlorobenzene was poured on the surface of the MAPbI$_3$ film
~5 s after commencing spin-coating. The as-deposited MAPbI$_3$ films were annealed at 100 °C for 10 min to form the resultant films. For the Cs$_{0.05}$FA$_{0.80}$MA$_{0.15}$PbI$_{2.55}$Br$_{0.45}$ (CsFAMA) films, a 1.2 M precursor solution was prepared with 0.06 M CsI, 0.96 M FAI, 0.18 M MABr, 1.02 M PbI$_2$ and 0.18 M PbBr$_2$ dissolved in DMF/DMSO co-solvent (V$_{DMF}$:V$_{DMSO}$ = 4:1) and 10% extra PbI$_2$ (mol%, relative to CsFAMA) was added to the CsFAMA precursor.$^{52, 155}$ The precursor solution was stirred at ~25 °C for 24 hours and filtered with a 0.45 µm PTFE syringe filter before further use. To obtain the CsFAMA film, the CsFAMA precursor solution was spin-coated on the substrates (glass, glass/ITO or glass/ITO/SnO$_2$) using a spin speed of 2000 r.p.m for 10 s and 4000 r.p.m for 20 s. During the second spinning step, 1.5 mL of chlorobenzene was poured on the top surface of the CsFAMA film ~5 s before the end of the spinning cycle. Then, the as-deposited films were annealed on a hotplate at 100 °C for 10 min to form the resultant CsFAMA films. All the preparation and deposition steps were performed in a nitrogen-filled glovebox.

5.2.2 Device fabrications

ITO-coated glass substrates (10 ohm/sq) were cleaned in soapy water, deionized water, acetone and isopropanol with sonication. The ITO-coated glass substrates were then subjected to ultraviolet-ozone (UVO) treatment for 10 min. For the ETL-free perovskite solar cells, the perovskite films were directly deposited on the ITO substrates
by following the procedure mentioned above. Then, Li-doped Spiro-OMeTAD was spin-coated as the HTL on the perovskite films. A solution consisting of 72.5 mg Spiro-OMeTAD, 28.8 µL 4-tert-butylpyridine, 17.6 µL Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 mL acetonitrile) and 1 mL chlorobenzene was employed with a spin speed of 3000 r.p.m for 30s. To complete the device, Au was thermally evaporated on the HTL to serve as the electrode. For the device with SnO$_2$ ETL, the SnO$_2$ ETL was deposited by spin-coating a SnO$_2$ suspension (15 wt.% in H$_2$O) in air on the UVO-treated ITO substrates and then annealing on a hotplate at 150 °C for 20 min to form an ~20-nm-thick ETL in air.$^{54}$ Then, the glass/ITO/SnO$_2$ substrates were treated with UVO for 10 min. Finally, the perovskite layer, Li-doped Spiro-OMeTAD and Au were sequentially deposited to complete the ETL-containing perovskite solar cells, by following the procedures described above for the ETL-free device.

5.2.3 Characterizations

Morphologies of the CsFAMA and MAPbI$_3$ films were imaged with a scanning electron microscope (SEM, FEI XL30 SEM-FEG). Atomic force microscopy (AFM) images were characterized using a scanning probe microscope (Digital Instruments Dimension 3100). X-ray diffraction (XRD) measurements were carried out on a PANalytical Empyrean Powder X-ray diffractometer using CuKα radiation. The charge carrier lifetimes were characterized via time-resolved photoluminescence (TRPL) experiments.
using an Edinburgh FLS980 fluorescence spectrometer with excitation wavelength of 510 nm. The stationary PL was also measured with the Edinburgh FLS980 fluorescence spectrometer with excitation wavelength of 510 nm. Optical absorption measurements were performed on a Shimadzu UV-3600 spectrophotometer. The external quantum efficiency (EQE) was taken using a QE-R instrument from Enlitech without bias voltage or illumination. The current density-voltage (J-V) characteristics and steady-state output were measured using a Keithley 2420 source meter. The illumination source was a Newport Oriel 92192 solar simulator with an AM1.5G filter, operating at 100 mW cm\(^{-2}\). All devices were masked with area of 0.09 cm\(^2\) aperture to define the active areas. All the J-V characteristics of perovskite solar cells were evaluated with voltage scanning speed of 1.0 V/s. A standard silicon solar cell from Newport Corp. was used as a reference for J-V and EQE measurements. All measurements were performed under ambient conditions with relative humidity level below 30%.

### 5.3 Results and discussion

#### 5.3.1 ETL-free and ETL-containing PV

To identify the difference between typical ETL-free and ETL-containing PV, pristine CH\(_3\)NH\(_3\)PbI\(_3\) (MAPbI\(_3\)) perovskite films are used as absorbers. The pristine MAPbI\(_3\) films are deposited by a one-step method, using a precursor solution containing a 1:1 molar ratio of MAI and PbI\(_2\) (i.e., no extra PbI\(_2\) added). ITO-coated glass is used as
the transparent electrode substrate. In the ETL-containing PV devices, SnO₂ is chosen as the ETL due to the wider bandgap of SnO₂ (e.g., compared to TiO₂), such that the distinct ETL would at most minimally impact the light absorption within the perovskite films during device operation (as discussed later).⁵⁴ The full details for film deposition are described in the Methods section. Top-view scanning electron microscope (SEM) images in Figure 5.1a and Figure 5.1b present the morphologies of typical pristine MAPbI₃ films on glass/ITO and glass/ITO/SnO₂ substrates, respectively, from which one can deduce that the MAPbI₃ films share similar film morphologies and compactness on both substrates. From X-ray diffraction (XRD) patterns (Figure 5.1c), the MAPbI₃ films exhibit similar structural properties on both substrates. The optical absorption spectra (Figure 5.1d) illustrate that the MAPbI₃ films also have similar optical features (E₈ = ~1.60 eV). These results indicate that glass/ITO and glass/ITO/SnO₂ substrates do not impact the basic structural/optical properties of MAPbI₃ films. In many respects, this observation is not surprising, given that both SnO₂ and ITO present a tin-oxide-based surface.
Figure 5.1: a-b, Top-view SEM images of pristine MAPbI$_3$ films deposited on glass/ITO substrate (a) and glass/ITO/SnO$_2$ substrate (b), respectively. Images employ a 1 µm scale bar. c, The XRD patterns of pristine MAPbI$_3$ films on glass/ITO/SnO$_2$ and glass/ITO substrates, respectively. d, The optical absorption spectra of pristine MAPbI$_3$ films on glass/ITO/SnO$_2$ and glass/ITO substrates, respectively.

To examine the PV performance for such MAPbI$_3$ films in devices, ETL-free and ETL-containing perovskite PV devices were fabricated with the device architectures of glass/ITO/MAPbI$_3$/2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD)/Au and glass/ITO/SnO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au, respectively. Figure 5.2a presents the statistical distributions of PCE values, from which the ETL-free
devices yield $PCE$s of from 7.70% to 11.40% (8.68% in average) over 24 devices, while ETL-containing devices yield $PCE$s of from 15.78% to 17.99% (16.97% in average) over 24 devices. The statistical results indicate that the $PCE$ of a typical ETL-free PV device is significantly lower than the analogous value for ETL-containing PV, when using the pristine MAPbI$_3$ films, which is consistent with earlier reports.\textsuperscript{77,80} To figure out the reasons for the compromised $PCE$, the EQE was compared for ETL-free and ETL-containing perovskite PV.

![Figure 5.2: a, PCE distributions for ETL-free and ETL-containing PV. b, EQE spectra for the ETL-free and ETL-containing PV.](image)

From the EQE spectra (Figure 5.2b), the EQE response of the ETL-free device falls significantly lower than that for the analogous ETL-containing device, especially in the short (300-400 nm) and long (500-750 nm) wavelength ranges. Such results indicate that carrier collection is less effective in ETL-free devices (e.g., due to enhanced recombination
in the ETL-free device structures). Since the glass/ITO and glass/ITO/SnO$_2$ substrates have nearly the same optical absorption features (Figure 5.3) and the perovskite films have similar grain structures, the reduced carrier collection in ETL-free devices likely derives from the different interface.

![Image](image_url)

**Figure 5.3**: The optical absorption spectra of glass/ITO/SnO$_2$ and glass/ITO substrates, respectively.

To understand the impact of interface on photogenerated carriers, photoluminescence (PL) quenching measurements were performed. Figure 5.4a presents the stationary PL spectra for the MAPbI$_3$ films on quartz, glass/ITO and glass/ITO/SnO$_2$, respectively, from which we can observe that the PL signal quenches less on the ETL-free substrates. The quenching results evidently illustrate that the interfacial carrier injection process is substantially inhibited without the assistance of a distinct ETL.
Figure 5.4: a, The stationary PL spectra of pristine MAPbI₃ films deposited on quartz, glass/ITO and glass/ITO/SnO₂ substrates, respectively. b, The TRPL spectrum of pristine MAPbI₃ films deposited on quartz substrate. The average carrier lifetime (τavg) is obtained by considering the long-lived component (τ₁) and short-lived component (τ₂) and their corresponding amplitudes (A₁ and A₂).

At the interface, we expect carrier injection and defect-trapping/recombination processes to compete with each other. When the electron injection process slows down, the defect-trapping/recombination process may dominate. From the TRPL result (Figure 5.4b), the pristine MAPbI₃ films used in typical ETL-free PV exhibit short average carrier lifetimes (τavg = 1.17 ± 0.02 ns). We refer to such lifetimes as “intrinsic” lifetimes since they are measured for films on quartz substrates rather than for films within device structures, wherein built-in electric fields will impact the values measured. The photogenerated carriers with such short intrinsic lifetimes will more readily recombine at the interface if they cannot make it rapidly across the interface to the contact. To reduce the carrier recombination near the low-injection-rate interface, the typical
approach involves adding an additional layer at this poor interface to improve the rate of electron extraction (ultimately, before recombination). However, this approach adds extra layers to the ETL-free architectures and creates an architecture that is essentially identical to that for the ETL-containing devices. Logically, if we are not able to improve the interfacial band alignment to enhance the injection, then the next best thing would be to improve the intrinsic minority carrier lifetimes within the perovskite, so that the photoexcited carriers can survive long enough to make it across the less effective interface. Based on this analysis and expectation, long lifetimes are highly desired for ETL-free PV (even more so than in ETL-containing PV). In the following section, we will explore the effect of carrier lifetimes on the performance of ETL-free PV devices.

### 5.3.2 Impact of carrier lifetimes on PV performance

![Figure 5.5: Top-view SEM images of MAPbI₃ films with addition of 2.5%~7.5% extra PbI₂, respectively. The images employ a scale bar of 1 µm.](image)

For exploring the effect of the intrinsic carrier lifetime on the performance of ETL-free perovskite PV, extra PbI₂ was introduced into the MAPbI₃ films to tune the film
carrier lifetimes. Top-view SEM images (Figure 5.5) show that the MAPbI$_3$ films with 2.5%, 5.0% and 7.5% extra PbI$_2$ on glass/ITO substrates have similar grain size to that in the pristine MAPbI$_3$ film as shown in Figure 5.1a. From the atomic force microscope (AFM) images in Figure 5.6, the MAPbI$_3$ films share similar surface roughness, within the range of 6 to 8 nm, illustrating that adding extra PbI$_2$ to the MAPbI$_3$ films does not significantly impact film morphology. The optical absorption spectra for the MAPbI$_3$ films with 0–7.5% extra PbI$_2$ (Figure 5.7) indicate that adding extra PbI$_2$ does not remarkably affect the absorption characteristics of the MAPbI$_3$ films (over the limited range of PbI$_2$ added).

Figure 5.6: AFM images of the MAPbI$_3$ films with addition of 0–7.5% extra PbI$_2$. The arithmetic average roughness ($R_a$) of MAPbI$_3$ films with 0%, 2.5%, 5.0% and 7.5% extra PbI$_2$ is 6.0 nm, 7.2 nm, 7.3 nm and 7.8 nm, respectively.
TRPL was performed for the MAPbI₃ films on quartz substrates to evaluate the optoelectronic properties of the MAPbI₃ films with extra PbI₂. By comparing the TRPL spectra in Figure 5.8a-c and Figure 5.4b, it can be observed that adding extra PbI₂ significantly enhances the intrinsic carrier lifetimes of the MAPbI₃ films, from several nanoseconds to several hundred nanoseconds. To further pursue this point, stationary PL measurements were also performed on the MAPbI₃ films (Figure 5.8d), showing significant intensity enhancement with extra PbI₂ addition, which is consistent with the TRPL results.
In addition to the intrinsic carrier lifetimes, we also measured the stationary PL for the MAPbI$_3$ films with extra PbI$_2$ on glass/ITO substrates, to understand whether extra PbI$_2$ in MAPbI$_3$ films may change the carrier injection rate (as shown in Figure 5.9). Since the PL intensity of the MAPbI$_3$ films significantly differ with varied PbI$_2$ levels, we define a PL quenching rate metric (QR$_{PL}$) — i.e., $QR_{PL} = (I_{1} - I_{2})/I_{1}$, where $I_{1}$ is the PL...
intensity of the MAPbI₃ film on quartz, while I₂ is the analogous value on ITO—to better evaluate the carrier injection at the ITO/perovskite interface.

![Figure 5.9: The stationary PL spectra of MAPbI₃ films with 0~7.5% extra PbI₂ on quartz and glass/ITO substrates, respectively.](image)

By Comparing the QR_{PL} values (Figure 5.10), it is seen that the extra PbI₂ in MAPbI₃ films does not enhance the electron injections at the ITO/perovskite interface in term of PL quenching. This result is reasonable since the relative conduction band position of PbI₂ is higher than that of perovskite materials so that the extra PbI₂
accumulation at the ITO/MAPbI$_3$ interface would not improve the band alignment for electron injection.\textsuperscript{14} Taken together, the TRPL and PL results indicate that addition of extra PbI$_2$ significantly improves the carrier lifetimes in the MAPbI$_3$ films but does not facilitate the electron injection at the ITO/MAPbI$_3$ interface.\textsuperscript{12, 42}

![Graph showing PL quenching rate (QR$_{PL}$) as a function of PbI$_2$ addition level. The equation $QR_{PL} = \frac{I_1 - I_2}{I_1}$ is provided, where $I_1$ is the PL intensity of MAPbI$_3$ on quartz, and $I_2$ is the PL intensity of MAPbI$_3$ on ITO.]

Figure 5.10: The PL quenching rate (QR$_{PL}$) of the MAPbI$_3$ films with 0–7.5% extra PbI$_2$. The QR$_{PL}$ values are calculated by using the stationary PL intensity from Figure 6.9.

To show the correlation between the intrinsic carrier lifetimes and performance for ETL-free perovskite PV, solar cells using extra-PbI$_2$-added MAPbI$_3$ films were fabricated with the same ETL-free architecture (glass/ITO/MAPbI$_3$/Spiro-OMeTAD/Au) described above. For each PbI$_2$ addition level, 24 devices are used for the statistical results shown in Figure 5.11. It can be observed that the trend of the PV parameters is similar to the trend of carrier lifetimes as the PbI$_2$ addition level changes, illustrating
close correlation between the device performances and the intrinsic carrier lifetimes and that long carrier lifetimes substantially benefit the ETL-free device performance.

Figure 5.11: Distributions of the PV parameters for ETL-free perovskite solar cells. The ETL-free perovskite solar cells employ the device architecture of glass/ITO/MAPbI\textsubscript{3}/Spiro-OMeTAD/Au. The MAPbI\textsubscript{3} used in the devices are with 0~7.5% extra PbI\textsubscript{2}, respectively.

For comparison, ETL-containing PV devices were also fabricated. From the PCE distributions shown in Figure 5.12, the intrinsic carrier lifetimes are also seen to effect the performance of ETL-containing PV. To explore the degree to which the carrier lifetimes can impact on the ETL-free and ETL-containing perovskite solar cells,
respectively, the correlations between extra PbI₂ addition levels and average PCE values are presented. From Figure 6.13, it is found that the performance of ETL-free devices is far more sensitive to the intrinsic carrier lifetimes relative to ETL-containing PV.

![Graphs showing correlations between PbI₂ addition levels and PCE, Voc, Jsc, and FF.]

Figure 5.12: Distributions of the PV parameters for ETL-containing perovskite solar cells. The ETL-containing perovskite solar cells employ the device architecture of glass/ITO/SnO₂/MAPbI₃/Spiro-OMeTAD/Au. The MAPbI₃ used in the devices are with 0–7.5% extra PbI₂, respectively.
The EQE was also measured on the ETL-free and ETL-containing PV devices for better understanding the impact of carrier lifetimes on photogenerated carrier collection. It can be observed that, as carrier lifetimes increase, both the short- and long-wavelength spectral responses substantially improve for ETL-free PV, while only the long-wavelength range increases for ETL-containing PV. For ETL-containing PV (Figure 5.14a), the EQE increase in the long-wavelength range can be attributed to the reduction of bulk-defect-induced recombination, enabling more long-wavelength-excited carriers...
to travel through the perovskite films for extraction. For ETL-free devices (Figure 5.14b), the additional enhancement of short-wavelength EQE could be due to reduced carrier recombination at the ETL-free interface, leading to increasing number of short-wavelength-excited carriers being effectively collected at the ITO/perovskite interface. The EQE spectra explain the result that the performance of ETL-free PV is more sensitive to carrier lifetimes.

**Figure 5.14:** a, EQE spectra of the ETL-containing PV by using MAPbI$_3$ films with addition of 0–7.5% extra PbI$_2$. b, EQE spectra of the ETL-free PV by using MAPbI$_3$ films with addition of 0–7.5% extra PbI$_2$.

Moreover, comparing the EQE spectra shown in Figure 5.15, we see that the EQE values for the ETL-free PV progressively converge to that for ETL-containing PV for long carrier lifetimes, totally different from the situation for short carrier lifetimes (Figure 5.2b). Long carrier lifetimes in perovskite films therefore appear to be important for obtaining high-performance ETL-free PV. In addition, these results also suggest that
use of distinct ETLs is beneficial for the device performance if the intrinsic carrier lifetimes in the associated perovskite absorbers are relatively short.

![EQE spectra of the ETL-free and ETL-containing PV by using MAPbI₃ films with addition of 5% extra PbI₂.](image)

Figure 5.15: EQE spectra of the ETL-free and ETL-containing PV by using MAPbI₃ films with addition of 5% extra PbI₂.

### 5.3.3 Perovskite Films with Microsecond Carrier lifetimes

For further boosting the PCE of ETL-free PV, mixed-cation lead halide perovskite films (Cs₀.₀₅FA₀.₈MA₀.₁₅PbI₂.₅Br₀.₄₅, referred to as CsFAMA, where FA = formamidinium) with microsecond carrier lifetimes were used as the light absorbers in devices (see the Methods section for deposition details).¹⁰ The top-view SEM image of an CsFAMA film on glass/ITO substrate (Figure 5.16a) reveals that the grain size is ~500 nm, with good compactness and coverage over relatively large area (Figure 5.16b). Based on the AFM image (Figure 5.16c), the CsFAMA films exhibit flat surfaces, with roughness on the
order of 20 nm. The relatively flat surface reduces the contact area at the CsFAMA/Spiro-OMeTAD interface, leading to reduced interfacial recombination and therefore benefiting the device performance.

Figure 5.16: a, Top-view SEM image of CsFAMA perovskite film. The scale bar is 1 µm. b, Top-view SEM image of CsFAMA perovskite film at large scale. The image employs a scale bar of 2 µm. c, AFM image of CsFAMA perovskite film. The Rₐ for the film is 18.2 nm; d, The XRD pattern of CsFAMA perovskite film. The XRD pattern (Figure 5.16d) for a CsFAMA film on glass/ITO substrate demonstrates that the CsFAMA film contains only the photoactive perovskite α-phase (black phase), and no non-perovskite δ-phase (yellow phase) exists to negatively impact
the optoelectronic properties. To evaluate the optical properties of the CsFAMA film, optical absorption and stationary PL measurements were performed (Figure 5.17a) and demonstrate that the optical absorption onset and PL peak are consistent ($E_g = -1.59$ eV).

To understand the charge carrier dynamics, TRPL measurement was performed on a CsFAMA film on quartz substrate. The intrinsic charge carrier lifetimes extracted from the PL dynamics (Figure 5.17b) are $1231.9 \pm 27.7$ ns for $\tau_1$ and $301.9 \pm 28.3$ ns for $\tau_2$ with their corresponding $A_1 = 71.4\%$ and $A_2 = 28.6\%$, respectively ($\tau_{avg}$ is $966.4 \pm 27.9$ ns). Such microsecond carrier lifetimes, approximately three times the value achieved for the previously discussed MAPbI$_3$ devices with 5% extra PbI$_2$ added, are expected to substantially boost the performance of ETL-free perovskite PV, as discussed above.

Figure 5.17: a, The optical absorption spectrum and PL spectrum of a CsFAMA perovskite film. b, The TRPL spectrum of a CsFAMA perovskite film. The film for optical absorption measurement was deposited on a glass/ITO substrate. The film for PL and TRPL measurements was deposited on a quartz substrate.
5.3.4 High-Performance ETL-free Devices

Given the above results, ETL-free perovskite solar cells were fabricated with the device architecture ITO/CsFAMA/Spiro-OMeTAD/Au. From SEM device cross-section analysis (Figure 5.18a), the thicknesses of the CsFAMA, Spiro-OMeTAD and Au layers are seen to be ~ 650 nm, ~150 nm and ~80 nm, respectively. The statistical distributions of PCE values (reverse scanning direction) for 24 ETL-free devices (Figure 5.18b) vary from 17.85 to 19.52% (18.48% in average). For comparison, analogous ETL-containing perovskite solar cells with structure ITO/SnO\textsubscript{2}/CsFAMA/Spiro-OMeTAD/Au yield similar performance levels (Figure 5.18b), with PCE values varying from 19.60 to 20.72% (20.03% average). Such performance levels for the ETL-free devices approach record metrics for any type of perovskite device and represent the best PCE performance level among all currently reported ETL-free perovskite solar cells.

![Cross-section SEM image of an ETL-free perovskite solar cell with device architecture glass/ITO/CsFAMA/Spiro-OMeTAD/Au. The image employs a 500 nm scale bar.](image1)

![PCE distributions for ETL-free and ETL-containing perovskite solar cells prepared with CsFAMA films.](image2)
Table 5.1: Summary of ETL-free perovskite solar cells, noting the publication year, perovskite material used, device architecture and best PCE (to the best of the author’s knowledge) for each configuration. The results from the current work are also included for comparison.

<table>
<thead>
<tr>
<th>Year</th>
<th>Perovskite Material</th>
<th>Device architecture</th>
<th>Best PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014(^{77})</td>
<td>MAPbI(_3)</td>
<td>ITO/MAPbI(_3)/Spiro-OMeTAD/Ag</td>
<td>13.5%</td>
</tr>
<tr>
<td>2015(^{45})</td>
<td>MAPbI(_3)</td>
<td>ITO/MAPbI(_3)/Spiro-OMeTAD/Ag</td>
<td>11.4%</td>
</tr>
<tr>
<td>2015(^{153})</td>
<td>FAPbI(<em>{CL</em>{3-x}})</td>
<td>ITO/FAPbI(<em>{CL</em>{3-x}})/Spiro-OMeTAD/Au</td>
<td>12.7%</td>
</tr>
<tr>
<td>2015(^{50})</td>
<td>MAPbI(<em>{CL</em>{3-x}})</td>
<td>FTO/MAPbI(<em>{CL</em>{3-x}})/Spiro-OMeTAD/Au</td>
<td>14.14%</td>
</tr>
<tr>
<td>2016(^{154})</td>
<td>MAPbI(<em>{CL</em>{3-x}})</td>
<td>FTO/MAPbI(<em>{CL</em>{3-x}})/Spiro-OMeTAD/Au</td>
<td>10.67%</td>
</tr>
<tr>
<td>2016(^{152})</td>
<td>MAPbI(<em>3):C(</em>{70})</td>
<td>FTO/MAPbI(<em>3): C(</em>{70})/Spiro-OMeTAD/Au</td>
<td>13.6%</td>
</tr>
<tr>
<td>2016(^{78})</td>
<td>MAPbI(_3)</td>
<td>ITO/MAPbI(_3)/diketopyrrolopyrrole-based copolymer/MoO(_3)/Ag</td>
<td>10.8%</td>
</tr>
<tr>
<td>2016(^{79})</td>
<td>MAPbI(_3)</td>
<td>FTO/MAPbI(_3)/Spiro-OMeTAD/Au</td>
<td>11.07%</td>
</tr>
<tr>
<td>Current work</td>
<td>MAPbI(_3)</td>
<td>ITO/MAPbI(_3)/Spiro-OMeTAD/Au</td>
<td>17.64%</td>
</tr>
<tr>
<td></td>
<td>CsFAMA</td>
<td>ITO/MAPbI(_3)/Spiro-OMeTAD/Au</td>
<td>19.52%</td>
</tr>
</tbody>
</table>

To evaluate the hysteresis behavior, the best-performing devices were measured using both forward and reverse voltage scanning directions. From the reverse (forward) scan, the best-performing ETL-free device (Figure 5.19a) yields PCE of 19.52 (18.84) %, \(V_{oc}\) of 1.061 (1.069) V, \(J_{sc}\) of 23.61 (23.39) mA cm\(^{-2}\) and FF of 77.79 (75.37) %. The best-performing ETL-containing device (Figure 5.19b) yields PCE of 20.72 (20.51) %, \(V_{oc}\) of 1.100 (1.100) V, \(J_{sc}\) of 23.75 (23.51) mA cm\(^{-2}\) and FF of 79.28 (79.23) %. From this comparison, we can see that the ETL-free device hysteresis approaches that of the ETL-containing device.
Figure 5.19: a, J-V characteristics of the best-performing ETL-free perovskite solar cell prepared with a CsFAMA film. b, J-V characteristics of the best-performing ETL-containing perovskite solar cell prepared with a CsFAMA film. J-V characteristics are evaluated with reverse and forward voltage scanning directions.

The steady-state output profile (Figure 5.20a) shows that the best performing ETL-free device has a steady-state output current density ($J$) of $\sim21.37 \, \text{mA cm}^{-2}$ under 0.89 V applied bias, corresponding to a stabilized $PCE$ value of $\sim19.02\%$—i.e., showing good agreement with the $J$-$V$ measurement $PCE$ value. The EQE spectrum of the best-performing ETL-free device (Figure 5.20b) illustrates high quantum efficiency for energies above the band gap, leading to an integrated $J_{sc}$ of $23.39 \, \text{mA cm}^{-2}$, which is consistent with the results from the $J$-$V$ characteristics.
Figure 5.20: a, Steady-state output profile for the best-performing ETL-free perovskite solar cell, prepared with a CsFAMA film, under a bias voltage of 0.89 V. b, EQE and integrated $J_{sc}$ of the best-performing ETL-free perovskite solar cell with a CsFAMA film.

The PCE of the best-performing ETL-free device remains ~19.1% (from $J$-$V$ measurement) after 1000 hours of storage (temperature of ~25 °C and relative humidity of ~25% in the dark), illustrating that the ETL-free devices have good environmental stability (Figure 5.21a). The photo-stability of the best-performing ETL-free perovskite solar cells was also measured using continuous light soaking (one sun) under ambient conditions (temperature of ~25 °C and relative humidity of ~25%) without encapsulation (Figure 5.21b). Such stability tests suggest that ETL-free PV with CsFAMA perovskite films could be made with reasonable stability during operation.
Figure 5.21: a, The environmental stability of the best-performing ETL-free perovskite solar cell with a CsFAMA film. The device was stored in dark condition without encapsulation at ~25 °C with relative humidity of ~25%. The PCE value of the device were evaluated with reverse scanning direction. b, The photo-stability of the best-performing ETL-free perovskite solar cell. The PCE value of the device were evaluated with reverse scanning direction at ~25 °C with relative humidity of ~25%.

Finally, the correlation between carrier lifetime and device performance is examined for ETL-free/ETL-containing PV (Figure 5.22) with the carrier lifetimes ranging from nanosecond scale to microsecond scale. Such results indicate PCE discrepancy between ETL-free and ETL-containing perovskite solar cells is significantly reduced as the minority carrier lifetime increases and they further suggest that extending the carrier lifetimes of perovskite films (e.g., >>1 µs) may boost the PCE of associated ETL-free perovskite solar cells to the same level as ETL-containing perovskite solar cells.
Figure 5.22: Correlations between carrier lifetimes of perovskite films and average PCE for ETL-free and ETL-containing perovskite photovoltaics.

5.4 Conclusions

In conclusion, we use EQE to reveal that typical ETL-free perovskite PV devices with relatively low minority carrier lifetime exhibit more substantial photogenerated carrier loss compared with ETL-containing devices. PL quenching experiments show that the injection of carriers from the perovskite to the transparent conducting oxide contact (ITO) is less effective for ETL-free devices. To address this interface issue without changing the ETL-free design, we tailor the carrier lifetimes of the perovskite films by addition of extra PbI₂ during the film deposition process and by transitioning to a mixed MA/Cs cation stoichiometry. We demonstrate that improved carrier lifetimes can suppress the carrier recombination and enhance the carrier collection efficiency at the low-injection-rate interface, making the carrier dynamics in ETL-free devices.
essentially as good as that in ETL-containing devices. Based on such understanding, by using perovskite films with microsecond carrier lifetimes, ETL-free perovskite solar cells exhibit a best $PCE$ of 19.52% with nearly-eliminated hysteresis and good stability. Such high-performance ETL-free perovskite solar cells are comparable to the analogous ETL-containing devices ($PCE: 20.72\%$). These results offer new opportunities for versatile perovskite PV with simple processing, low cost and high performance. Our results also provide a general approach to improve the performance of PV with low-injection-rate interfaces, not only limited to the perovskite PV family.
6. Conclusion

In conclusion, we studied the impact of band alignment, grain size, carrier injection, carrier lifetime, film crystallization process and device architecture on the performance, hysteresis behaviors and stability of perovskite solar cells by different additives. By using Nb$^{5+}$ addition in TiO$_2$ ETL, the conductivity and CBM edges of the Nb-TiO$_2$ ETL were successfully tuned. By using Nb-TiO$_2$ ETLs in perovskite solar cells, it was found that the interfacial energy band alignment could significantly impact on the performance and hysteresis of perovskite solar cells. When the discrepancy of CBM edges of perovskite films and Nb-TiO$_2$ ETL was minimized, the carrier injection at the interface could be significantly enhanced, which enables improved device performance and reduced hysteresis of the perovskite solar cells.

In addition to the interface, the impact of morphology and carrier dynamics of perovskite films on solar cells was explored by using NH$_4$SCN and PbI$_2$ as additives. It was illustrated large grain size of perovskite films could benefit the carrier transport/injection, leading to improved short-circuit current density of perovskite photovoltaics while long carrier lifetime of perovskite films could lead to significant enhancement of the open-circuit voltage and fill factor of perovskite photovoltaics. These results established correlations between the perovskite film properties and perovskite device performance. Benefiting from the understanding, additive (MASCN) was designed and used to develop a room-temperature process method for perovskite
films deposition. Due to the effect of the additives, room-temperature-processed perovskite films with micron-size grains and microsecond-range carrier lifetime were successfully obtained for high-performance devices. More importantly, we established the correlation between the crystal grain size in resultant perovskite films and the precursor aggregate size in precursor solutions. The correlation suggested that the perovskite grain sizes from solution process depended on the precursor aggregate size.

Finally, the additive engineering method was used to impact on the ETL-free perovskite solar cells benefiting from the understanding we built. In ETL-free perovskite solar cells, we found out that the photo-excited carrier injection at the interface was significantly inhibited without the assistance of an ETL, which would compromise the collection of the photo-excited carriers. The possible reason for the low-injection interface could be that the work function different at the interface could not provide strong band bending/interfacial built-in electric field for the carrier drifting and collection. To compensate the interior interface, long carrier lifetime could be helpful which increases the ability for photo-excited carriers to diffuse. By using additive PbI₂ to tune the carrier lifetimes in perovskite films, it was found out that increased carrier lifetimes in perovskite films could effectively counterbalance the inferior interface without ETLs and enabled high performance for ETL-free perovskite solar cells. Based on the understanding, by using perovskite with microsecond carrier lifetime, ETL-free perovskite solar cells were successfully realized with performance comparable to that of
ETL-containing perovskite devices. Such results offer the opportunity for the perovskite devices with simplified device architecture.
References


Biography

Qiwei Han was born in Changshun City, Guizhou Province, P. R. China, in August 1990. In June 2013, He received his B.S. degree from Nankai University in Tianjin, China.

In August 2013, he went to Duke University in North Carolina, USA as a graduate student. Qiwei worked in Jie Liu’s Lab (Department of Chemistry) and David Mitzi’s Lab (Department of Mechanical Engineering and Materials Science) as a Ph.D. student. In Duke University, Qiwei’s research is about additive engineering for high-performance perovskite solar cells. By using additives, it is aimed to tailor the functional layers in perovskite solar cells and study the effects of interface, carrier dynamics, morphology, film crystallization, device configuration, etc on the perovskite photovoltaics performance, hysteresis behaviors and stability. His work in Ph.D. has given rise to one first-author publication and seven co-author publications. In addition, three more first-author manuscripts have been submitted to high-level journals and another two manuscripts are to be submitted soon. Qiwei has previously been awarded GPNANO Fellowship, Paul M. Gross Fellowship, MRSEC Fellowship and Charles Bradsher Fellowship in Duke University.