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Photophysics and solar cell devices of two dimensional perovskites

PhD student
Qingqian Wang

Supervisor
Prof. Michele Saba

Coordinator of PhD school
Prof. Paolo Ruggerone
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Chapter 1. Introduction

1. Introduction

The organic-inorganic trihalide perovskites have attracted much attention for their amazing achievements in the application for solar cells.[1-4] The power conversion efficiency (PCE) of perovskite solar cells has increased from 3.8% to more than 25% in the past ten years.[5-10] They have been proved to be great active materials for different optoelectronic devices.[11-17] With tunable bandgap, high absorption coefficient, long carrier lifetime and the low cost, easy processing procedures for thin film devices, perovskites are very potential for the next generation photovoltaics.[18-27]

In this thesis, I summarize the evolution of perovskite solar cells concisely and demonstrate the research results on two dimensional perovskites. First part shows the orientation and phase control about the 2D lead perovskite PEA$_2$MA$_4$Pb$_5$I$_{16}$, and novel hole transport layer that is beneficial for solar cell devices. The PCE of this perovskite solar cell achieves beyond 14%. Then ultrafast spectroscopy and pump-probe researches on 2D tin perovskite BA$_2$MA$_{n-1}$Sn$_n$I$_{3n+1}$ with $n=1$ and 2 are revealing the carrier behavior in these samples. Results show in $n=1$ sample, the carriers are mainly excitons whereas in $n=2$ sample, the carriers are mainly free carriers.
1.1. Perovskite structure

Perovskite, initially representing the metal oxide compound calcium titanium oxide (CaTiO$_3$), was named after Russian mineralogist Lev Perovski. Now, all the compounds with the formula ABX$_3$ could be called perovskites.[28] Figure 1.1 shows the ideal structure. In this case, the crystal structure is perfectly cubic with B cation surrounded by six X anions, forming [BX$_6$]$^{4-}$ octahedron. Those octahedra connect each other in all three dimensional directions enclosing A cation in the centre of eight octahedra.

Two factors are necessary to maintain this unique structure. One is Goldschmidt tolerance factor $t$ given by the equation below,

$$ t = \frac{R_A + R_X}{\sqrt{2} (R_B + R_X)} $$

where $R_A$, $R_B$ and $R_X$ are radii of A, B and X ions respectively; the other is octahedron factor, $\mu = R_B/R_X$. Only when $t$ ranging from 0.81 to 1.11 and $\mu$ ranging from 0.44 to 0.90 are both satisfied, the perovskite structure could be stable with little distortion. If $t$ is valued in the range of 0.89-1.0, the structure will be cubic and lower $t$ values lead to tetragonal or orthorhombic structures.[29-32]

For metal halide perovskites, X is selected from Cl$^-$, Br$^-$ and I$^-$, while Cs$^+$, methylammonium (CH$_3$NH$_3^+$, MA) and formamidinium (HC(NH$_2$)$_2^+$, FA) could be used as A cations. Thus the B cation should be bivalent, it can be selected from 14 different elements (rare earth, alkaline earth and IV main group), most commonly are Pb$^{2+}$ and Sn$^{2+}$.[33-37]

1.2. Tunable bandgap ($E_g$)

Since there are several different choices for A, B and X, by substituting or mixing of
them, perovskite with very a wide range of bandgap (from 1.24 eV to 3.10 eV, which is the light range from 400 nm to 1000 nm, in Figure 1.2) could be achieved.[38-48]

With given A and B cations, the bandgap decreases with the increasing of X anion radii, that is $E_g$(Cl) > $E_g$(Br) > $E_g$(I). By mixing different X anions, perovskite with different bandgaps could be obtained. For instance, the bandgap of MAPbBr$_3$ is about 2.3 eV, but introducing Cl and I in, the bandgap could vary from 1.57 eV to 3.17 eV, corresponding to MAPbBr$_{3-a}$I$_a$ and MAPbCl$_b$Br$_{3-b}$ (a and b ranging from 0 to 3).[49, 50] Owing to this excellent feature, perovskite could be fabricated with bandgaps varying in almost whole visible light spectrum. Besides, for MAPbI$_3$ perovskite, by

\textbf{Figure 1.1} Perovskite structure, the big pink spheres represent A cations, the green spheres inside octahedra are B cations, small red spheres are X anions and the blue octahedra are $[BX_6]$. 


changing MA cation, from Cs, MA, to FA, the radius increases, from 1.81, 2.70 to 2.79, the correlated bandgap decreases (\(E_g(\text{Cs}) = 1.73\) eV, \(E_g(\text{MA}) = 1.55\) eV, \(E_g(\text{FA}) = 1.48\) eV).[51, 52] The last way to regulate the bandgap is substituting B, metal cation. Pb can be doped or replaced by Sr, Ca, Cd, Sn, Ge and so forth. Both calculation and experimental studies demonstrate the decrease of bandgap.[53-55]

1.3. High absorption coefficient

For the first and second generation solar cells, to collect most of the light from the sun, the light absorber layers should be around 300 \(\mu\)m and 2 \(\mu\)m respectively.[56, 57] Figure 1.3 demonstrates the optical absorption mechanism of different solar cells. For Si, the first generation, although the absorption at band edge is from Si \(p\) orbitals to Si \(p\) and \(s\) orbitals, the indirect bandgap nature determines low absorption coefficient and very thick absorber layer to utilize majority of sunlight.
Chapter 1. Introduction

GaAs, as one of the second generation, possesses direct bandgap, which is beneficial for light absorber. However, the conductive band minimum is composed by s orbitals of Ga and As, leading to lower electronic density of states. Thus, the optical absorption is still not so high.

Differently, perovskites have direct bandgap and the conductive band minimum is derived from Pb p orbitals. With higher density of states, the absorption coefficient is 2 to 4 times higher than GaAs at visible light range. MAPbI$_3$ has the absorption coefficient at order of 2*10$^5$ cm$^{-1}$ at 500 nm, which means 300 to 500 nm thickness of MAPbI$_3$ could absorb the excitation light thoroughly. This thinner absorber layer also means less material cost for solar cells.[58]

1.4. Charge recombination

In metal halide perovskites, the initial decay at low excitation carrier density is approximately monoexponential corresponding to monomolecular decay.[59, 60] But
with the increasing of excitation carrier density, the initial decay time becomes shorter.[61] This dynamics can be depicted by the equation of time dependent carrier density $n$:

$$\frac{dn}{dt} = -k_1n - k_2n^2 - k_3n^3$$

where $k_1n$ is monomolecular recombination with rate $k_1$, $k_2n^2$ is bimolecular recombination with rate $k_2$ and $k_3n^3$ is Auger recombination with rate $k_3$. Table 1 summarizes the results of $k_1$, $k_2$ and $k_3$ through global fitting of different materials.[62]

The monomolecular recombination is defined by a process generated by a single particle which can be an electron in CB, a hole in VB (trap-assisted recombination) or an exciton meaning bounded electron-hole pair (excitonic recombination). Bimolecular recombination, depending on both electrons and holes, can be viewed as intrinsic photon-radiative recombination correlated to the reverse process of light absorption. Auger recombination process involves three carriers, energy coming from the recombination of electron and hole is absorbed by third carrier, leading to the excitation of this carrier to higher energy level. Then the carrier relaxes to the bottom

<table>
<thead>
<tr>
<th>perovskite$^a$</th>
<th>deposition method$^b$</th>
<th>film architecture$^c$</th>
<th>charge-carrier mobility$^d$ [cm$^2$ (V s)$^{-1}$]</th>
<th>$k_1$ [s$^{-1}$]</th>
<th>$k_2$ [cm$^3$ s$^{-1}$]</th>
<th>$k_3$ [cm$^6$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPb$_{1-x}$Cl$_x$</td>
<td>solution</td>
<td>meso Al$_2$O$_3$</td>
<td>12</td>
<td>$5 \times 10^6$</td>
<td>$0.9 \times 10^{-10}$</td>
<td>$1.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>MAPb$_{1-x}$Br$_x$</td>
<td>2-source vapor</td>
<td>flat film</td>
<td>33</td>
<td>$12 \times 10^6$</td>
<td>$1.1 \times 10^{-10}$</td>
<td>$0.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>MAPb$_3$</td>
<td>solution</td>
<td>meso Al$_2$O$_3$</td>
<td>8</td>
<td>$14 \times 10^6$</td>
<td>$9.2 \times 10^{-10}$</td>
<td>$1.3 \times 10^{-13}$</td>
</tr>
<tr>
<td>MAPI</td>
<td>solution</td>
<td>flat film</td>
<td>35</td>
<td>$15 \times 10^6$</td>
<td>$0.6 \times 10^{-10}$</td>
<td>$1.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>FAPbI$_3$</td>
<td>solution</td>
<td>flat film</td>
<td>27</td>
<td>$7 \times 10^6$</td>
<td>$1.1 \times 10^{-10}$</td>
<td>$0.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>FAPbBr$_3$</td>
<td>solution</td>
<td>flat film</td>
<td>14</td>
<td>$21 \times 10^6$</td>
<td>$11 \times 10^{-10}$</td>
<td>$1.5 \times 10^{-13}$</td>
</tr>
<tr>
<td>MASnI$_3$</td>
<td>solution</td>
<td>meso TiO$_2$</td>
<td>1.6</td>
<td>$8 \times 10^6$</td>
<td>$14 \times 10^{-10}$</td>
<td>$1.5 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Table 1 aChemical formulae, where MA is CH$_3$NH$_3$ (methylammonium) and FA is HC(NH$_2$)$_2$ (formamidinium). bThrough a solution precursor or via dual-source vapor deposition under vacuum. cPerovskite flat films or infusions into a mesoporous metal oxide matrix. dCharge-carrier mobility at terahertz frequencies. eMonomolecular rate constant. fBimolecular rate constant. gAuger rate constant.


of conductive band with thermalization process. Figure 1.4 depicts the scheme of the three different recombinations.

Generally, at very low carrier density, most of the perovskite materials make the monomolecular recombination the dominant process. However, with carrier density of $10^{17}$-$10^{18}$ cm$^{-3}$, the recombination is mainly bimolecular recombination. Auger recombination can only be observed at very high carrier density $>10^{19}$ cm$^{-3}$.[63-67] It is noticeable that the photophysics of perovskite films is very different from of perovskite solar cell devices. Actually, the recombination lifetime of perovskite film can reach to several microseconds whereas the lifetime measured in perovskite device is sub-microsecond, even in optimized devices with PCE$>20%$.[68] This is mainly
attributed to the separation of photo-generated electrons and holes caused by charge transport layers. As a result, the photoluminescence is really so weak that cannot be accurately measured by TRPL measurements. Considering the commonly observed correlation between the lifetime and device PCE, TRPL lifetime is still a reasonable parameter for defect density and suitability for solar cells. [69]

1.5. Metal halide perovskite solar cells

In 2009, Miyasaka and coworkers firstly applied MAPbBr$_3$ and MAPbI$_3$ as light absorbers in solar cells. Efficiency reached to 3.13% and 3.81% respectively.[5] Subsequently, Park and colleagues improved the PCE to 6.54% with MAPbI$_3$ quantum dots as light sensitizer in 2011. But the perovskite could dissolve into the redox electrolyte gradually, leading to about 80% degradation in 10 min.[70]
To improve the stability, liquid electrolytes must be substituted. In 2012, Park, Grätzel and coworkers introduced a solid state hole transport layer (HTL), spiro-OMeTAD, which increased PCE to 9.7% and significantly enhanced device stability.[71] Simultaneously, Snaith and colleagues found perovskite itself might transport electrons effectively, then they substituted TiO$_2$ electron transport layer (ETL) by insulating Al$_2$O$_3$. The results exhibited an increased PCE of 10.7% and lower energy loss, 1.1V open circuit voltage with 1.55eV band gap. On this basis, they employed vapor deposition method to fabricate perovskite in a planar heterojunction device structure and achieved PCE of 15.4%.[72, 73]

After those pioneer works, more and more researches sprung up and the PCE of perovskite solar cells increased rapidly.[74-79] In 2014, Seok and coworkers boosted the PCE to 16.2% with no hysteresis by a solvent-engineering technology for depositing extremely uniform perovskite film.[80] Soon after, Yang and colleagues suppressed the carrier recombination in absorber by controlling formation of perovskite and careful choice of other charge transport layers. The PCE of their devices achieved to 19.3%.[81]

More recently, this year in 2019, You and coworkers added PEAI salt on FA-MA mixed perovskite films and found reduced defects and suppressed non-radiative recombination. The PCE of their devices reached to 23.32%.[82] Only several months later, from the newest NREL statistics, the record PCE has increased to 25.2%, accomplished by KRIST/MIT shown in Figure 1.5. All these breakthroughs are showing the bright prospects for the industrialization of perovskite photovoltaics.[83, 84]

However, despite the quickly increased PCE of devices, stability is a big issue that limits the industrialization.[85] As can be seen in Figure 1.5, only perovskite solar
cell is denoted as “not stabilized”. Moisture, either rain or water vapor can lead to the degradation, the mechanism can be described as below:[86]

\[4(\text{MAPbI}_3 \cdot \text{H}_2\text{O}) \leftrightarrow \text{MA}_4\text{PbI}_6 \cdot 2\text{H}_2\text{O} + 3\text{PbI}_2 + 2\text{H}_2\text{O}\]

\[\text{MA}_4\text{PbI}_6 \cdot 2\text{H}_2\text{O} \leftrightarrow 4(\text{MAI}) + \text{PbI}_2 + 2\text{H}_2\text{O}\]

Another factor is high temperature, some studies imply that at temperature higher than 100°, the surface of \(\text{MAPbI}_3\) decomposes to \(\text{PbI}_2\), \(\text{CH}_3\text{I}\) and \(\text{NH}_3\). Finally, \(\text{Pb}^{2+}\) will be easily oxidized to \(\text{Pb}^{4+}\) when exposed to ambient condition.[87, 88]

Additionally, the toxicity level of \(\text{Pb}^{2+}\) is even higher than conventional \(\text{Cd}^{2+}\) in \(\text{CdTe}\). Due to the stability in ecosystem, once the lead and its compounds are releasing into the environment, the harm will be almost eternal.[54, 89] To protect environment and implement sustainable development, it is necessary to replace lead by other non-toxic, environment friendly metal element.

1.6. Two dimensional hybrid perovskite

Since the instability is an inevitable constraint for perovskite solar cells, developing stable perovskite attracts more and more attention.[90-93] One of the methods is to reduce the dimension of perovskites. For \(\text{MAPbI}_3\) perovskite, \([\text{PbI}_6]^{4-}\) octahedra are
connected to each other in all the three dimensions thus it is called 3D perovskite.

Table 2 Reported different large organic cations for 2D perovskite structure.[50]
When some of the MA are exchanged by much larger organic cations, then the octahedra will separate, leading to a lower-dimensional structure, including 2D, 1D and even 0D.[94, 95]

Among the different structures, 2D perovskites are very good candidates for solar cells. The formula of those kind of 2D perovskites is $A'^2A_{n-1}B_nX_{3n+1}$, where A, B and X are the same with their 3D counterparts, while $A'$ is an organic cation much larger than A, such as phenethylammonium (PEA, $C_6H_5CH_2CH_2NH_3^+$) and butylammonium (BA, $CH_3CH_2CH_2CH_2NH_3^+$).[96, 97] Different kinds of $A'$ are summarized in Table 2.[98] Thus, by regulating the molar ratio of the precursors, different 2D perovskites with n layers $[BX_6]^{4-}$ octahedra separated by 2 layers $A'$ cations could be obtained, from pure 2D ($n = 1$) to 3D ($n = \infty$), depicted in Figure 1.6.[99]

The large organic cation layers confine the charge transport between different octahedral $[BX_6]^{4-}$ layers, acting as natural insulating “barriers” and the octahedra

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**Figure 1.7** Absorbance of different 2D perovskite ($BA_2MA_{n-1}Pb_nI_{3n+1}$) and 3D perovskite ($MAPbI_3$), the bandgap decreases with the increase of n number.[51]
layers as conductive “wells”. This special structure leads to much broader bang gap \( \sim 2.6 \) eV than 3D one 1.5 eV for low n, which is not a suitable band gap for solar cells. Differently, from \( n = 4 \), high n members possess narrower band gap \( \sim 1.7 \) eV (Figure 1.7) and better stability in the air environment. [97, 100]

Those quasi-2D perovskites are investigated extensively for light absorption materials in solar cell applications in recent years. [101] In 2014, Smith et al firstly employed a 3-layer PEA\(_2\)MA\(_2\)Pb\(_3\)I\(_{10}\) perovskite as light absorber in solar cells, in a n-i-p device structure, with TiO\(_2\) as electron transport layer (ETL) and Spiro-OMeTAD as hole transport layer (HTL). [102] Enhanced stability resulted, but only 4.73% of PCE. Soon after, Cao et al used BA as large organic cation using the same device structure and made \( n=1 \) to 4 perovskite solar cells with the highest PCE at 4.02%. [100] Those pioneering attempts show the critical issue that is the multiple-quantum-well structure is a great obstacle for out-of-plane charge transport. Thus, to control the growth orientation of “wells”, to make them perpendicular to ETL and HTL is highly

**Figure 1.8** Promising metal substitutions for lead free organic inorganic hydrid perovskites.[57]
advantageous for charge transport and electron-hole separation. To achieve this goal, several methods have been developed. Tsai et al applied hot-casting method when depositing BA\textsubscript{2}MA\textsubscript{3}Pb\textsubscript{4}I\textsubscript{13} (n=4) thin films on substrates, before deposition of perovskite thin films, the substrates are preheated to a temperature of \(\sim 150^\circ\text{C}\). They successfully fabricated oriented 2D thin films and increased the PCE to 12.52%.[103] Other efforts, such as Cesium doping, adding additive in perovskite precursor solution and so forth, also achieved some excellent results.[104-107] All these achievements imply that 2D perovskites are promising substitutions for solar cells.[108, 109]

1.7. Lead free hybrid perovskite

Not many choices can be select to replace Pb in perovskites, not only because the tolerance factor constraint, but also the electronic structure of Pb. Pb is rather important to stabilize the structure according to theoretical calculation studies. To date,
only Sn, Ge, Cu and some double perovskites are proved that can be potential candidates (Figure 1.8).[110]

As in the same main group, Sn is similar to Pb. The radii of Sn and Pb are 1.35 Å and 1.49 Å respectively, which encourages to be a substitution. [111-113] Snaith et al firstly reported MASnI$_3$ solar cells in 2014.[114] Studies exhibit that MASnI$_3$ possess highly symmetrical $\alpha$-phase of $P4mm$ group even at room temperature. The absorption edge is much broader than MAPbI$_3$, approximate to 1000 nm with bandgap estimated at 1.23 eV. But the PCE is much lower compared to Pb counterpart, only 6.4%. Almost the same time, Kanatzidis et al developed mixed MASnI$_{3-x}$Br$_x$ as light absorber material.[115] With the increasing of $x$, the absorption blue shift from 950nm (MASnI$_3$) to 577nm (MASnBr$_3$), leading to the film color changing form dark brown to bright yellow. The best PCE is achieved by MASnIBr$_2$ solar cells, which is 5.73%. Since the low PCE of pure tin perovskite, lots of people start to research on Sn-Pb mixed perovskites. However, more recently, Loi et al applied FASnI$_3$ as active
layer for solar cells. By inducing a small amount of 2D tin perovskite, the perovskite thin film showed high crystallinity and preferable orientation. Compare to the pristine 3D thin film, this 2D/3D thin films got reduced number of grain boundaries, suppressed tin vacancies and longer carrier lifetimes. As a result, device with PCE of 9.0% was achieved, which is the highest PCE of tin perovskite solar cells so far.[116]

Ge (germanium), is another similar element that may replace Pb for perovskites. The radius of Ge$^{2+}$ is 0.73 Å, and the tolerance factor of MAGeCl$_3$, MAGeBr$_3$ and MAGeI$_3$ are 1.005, 0.988, and 0.965 respectively, which are all in ideal range for perovskite structure.[117, 118] Stoumpos et al reported a series of Ge perovskite, CsGeI$_3$, MAGeI$_3$, FAGeI$_3$ etc in 2015.[117] Studies exhibited that the bandgap is strongly affected by the A cations, ranging from 1.63 to 2.8 eV. Bandgaps of CsGeI$_3$, MAGeI$_3$, FAGeI$_3$ are 1.63, 2.0 and 2.35 eV, as shown in Figure 1.9.[119] Although Ge is suitable for ideal tolerance factor, but it is so small that cannot fit the [GeI$_6$]$^{4-}$

![Schematic representation of double perovskite structure and the variety of different metal elements, normal 3D perovskite as comparison.](image-url)
octahedron well, leading to structural distortions. So far, very few studies have been reported because of the instability of Ge\(^{2+}\), even worse than Sn\(^{2+}\). The PCE of works done by Krishnamoorthy et al and Kopacic et al are all less than 1%.\(^{119, 120}\) Further researches still need to be carried on for revealing material properties and improving solar cell PCE of Ge perovskites.

Recently, Karunadasa et al reported a double perovskite, Cs\(_2\)AgBiBr\(_6\), incorporating Bi\(^{3+}\) in a 3D perovskite framework for the first time in 2016.\(^{121}\) This is a new line of thoughts to solve the issues of mostly studied Pb perovskites. The absorption region of Cs\(_2\)AgBiBr\(_6\) starts from 1.8 eV and at 2.1 eV there is a sharp increase. The Tauc plot exhibits that it possess an indirect bandgap of 1.95 eV with phonon energy 0.12 eV, which may be useful for tandem solar cells (Figure 1.10). With different permutation and combination of B\(^{1}\) and B\(^{III}\) elements, different double perovskite can be obtained (Figure 1.11).\(^{122, 123}\) The biggest advantage is this kind of perovskite is rather stable. Woodward et al synthesized Cs\(_2\)AgBiBr\(_6\) and Cs\(_2\)AgBiCl\(_6\) perovskite and found that they were rather stable to light irradiation or moisture.\(^\text{[124]}\) However, the indirect bandgap nature again implied future use for tandem solar cells. Giustino et al reported direct bandgap double perovskite, Cs\(_2\)AgInCl\(_6\).\(^\text{[125]}\) The measured optical bandgap is 3.3 eV with a very weak absorption at 2.1 eV. And it is very interesting that there is a reversible color changing from white to orange under UV light irradiation. After these pioneer researches on double perovskite material properties, some solar cell devices were fabricated. However, same as Ge perovskite solar cells, the PCE is very low, which is not higher than 3%, not the stability, the main constraint is the not suitable bandgap. Future works should be focused on this issue.

1.8. Scope of this thesis

In this thesis, considering the two disadvantages of perovskite, efforts were made on
stability and non-toxicity.

First of all, quasi-2D lead perovskite (n=5, PEA₂MA₄Pb₅I₁₆) solar cells were fabricated. Vacuum assisted method was employed to deposit the perovskite thin films. Since it is not easy to obtain pure n=5 perovskite, XRD (X-ray diffraction) and GIWAXS (grazing incident wide angle X-ray scattering) measurements were performed to confirm the phases of the perovskite thin film and the crystal grow orientation. Results shows that films deposited by conventional method show much n=2 phase at the bottom side which is not beneficial to charge transport, whereas films deposited by vacuum method show mainly n=5 phase with little n=2 phase. The vacuum-films also exhibit more compact morphology with less grain boundaries and cracks. Then, by introducing a novel, pH neutral hole transport layer into the devices, PCE increases to above 14%.

Secondly, 2D tin perovskite thin films were fabricated (n = 1, 2, 3, BA₂MAₙ₋₁SnₙI₃ₙ₊₁). With conventional method for film deposition, it is fine to get rather pure n=1 and 2 samples, but not for n=3. Still by using vacuum assisted method single phase of n=3 can be achieved. Then TRPL (time-resolved photoluminescence) and pump-probe spectroscopy measurements were carried on to detect the behavior of photo generated carriers in the samples. The results of TRPL exhibit in n=1 sample, the photo generated carriers are mainly excitons while in n=2 sample, the carriers are free carriers. The n=3 sample is not really clear because of the low reproducibility which made the results unreliable. In addition, pump-probe results furtherly confirmed the results of TRPL measurements. Besides the fast degradation of the samples in the air may also be one of the reason for uncertainty for n=3 sample, all the samples degraded more than 50% within 30 min.
Chapter 2. Synthesis and characterization

2. Synthesis and characterization

2.1. Perovskite thin film deposition

Perovskite thin film deposition is very important in making solar cell devices.\cite{126, 127} The quality of film directly determines the PCE of the devices.\cite{128} A smooth, compact with less grain boundaries thin film is beneficial to solar cell devices. Various methods have been developed to achieve this goal.

2.1.1. Spin-coating method

Spin-coating may be the most widely used method to deposit perovskite thin films.\cite{129-133} This technique includes one-step, two-steps and anti-solvent method, scheme depicted in Figure 2.1.

**One-step spin-coating.** This should be the easiest for operation. For instance, to deposit MAPbI$_3$ film, first of all, precursor chemical MAI and PbI$_2$ are dissolved in DMF (Dimethylformamide), DMSO (Dimethyl sulfoxide) or GBL ($\gamma$-Butyrolactone) solvent. After the precursors dissolve in the solvent homogeneously, for a 3×3 cm substrate, 2 or 3 drops (80-120 μL) will be enough for spin-coating. Then by regulating the spin speed, film with different thickness will be fabricated. Besides, the concentration and solvent type will also affect the thickness. After the deposition, the as prepared film should be heated to ~100° for further crystallization. Films fabricated in this way usually has an issue of coverage, besides the film morphology is also not with high quality.

**Two-steps spin-coating.** This method is separated in two steps. First, PbI$_2$ in DMF is deposited on the substrate at specified temperature, after cooling down, the substrate with PbI$_2$ thin film is soaked in MAI/IPA solution to react to MAPbI$_3$ thin film.
Another way is still spin-coating MAI on the substrates following the PbI$_2$ deposition step. Finally, same as one-step, the film is annealed at $\sim$100°.

**Anti-solvent method.** Anti-solvents can change the supersaturation, the nucleation and also the crystal growth rates, thereby they will strongly affect the crystallization kinetics and final morphology. Generally, this method is processed in two spin-coating speed, a very short time for low speed (within 2 s) and a long time for high speed (up to 60 s). Anti-solvent is added at high speed. Proficiency of adding anti-solvents is important in this process, because too fast leading to washed away of perovskite in the center of the thin films while too slow leading to very large cracks of the final thin film that can be seen by eyes.[134] Crystallization starts when
anti-solvent is added, by annealing is still necessary for totally crystallization.

Comparing the three solution-process methods, one-step is the easiest one for operation, but thin films fabricated in this way are difficult to form uniform morphology and high coverage. In contrast, two-steps and anti-solvent method are preferable to get smooth, compact films, but they need higher proficiency level for operation, especially the anti-solvent method.[135-137]

2.1.2. Vapor deposition

Scalable and highly reproducible fabrication is indispensable for industrialization, comparing to the uncertainty with solution processing methods, vapor deposition can completely satisfy those requests. In double sources vapor deposition, MAI and PbI$_2$ are evaporated to compacted TiO$_2$ at 120° and 325° in high vacuum degree (~10$^{-7}$ mbar) chamber simultaneously. Different from solution processing, the homogeneity of the final films is remarkably improved.[73] Yang et al modified the procedure and avoid high temperature and high vacuum. They spin-coated PbI2 on compacted TiO2, followed by heating the substrate inside MAI vapor with nitrogen. By this way, they achieved good morphology for films and 12.1% PCE for solar cells.[138]

2.2. X-ray diffraction (XRD)

In 1912, on the basis of theoretical prediction, Laue confirmed that the atoms at a distance from tens to hundreds picometers to each other in crystal materials are periodically arranged. This periodically arranged structure can become diffraction gratings for X-ray and the experiment becomes the first milestone of X-ray diffraction. When a beam of monochromatic X-rays is incident on the crystal, since the crystals are composed of unit cells which are regularly arranged by atoms, the distance between these regularly arranged atoms is the same order of magnitude as the X-ray diffraction analysis of the incident X-ray wavelength, so it is scattered by different atoms. The X-rays interfere with each other and produce strong X-ray diffraction in
some special directions. The orientation and intensity of the diffraction lines in the spatial distribution are closely related to the crystal structure. The diffraction patterns produced by each crystal reflect the atoms arrangement rules inside the crystal. This is the basic principle of X-ray diffraction, scheme in Figure 2.2.[139]

The diffraction can be described by Bragg’s Law, \(2d \sin \theta = n \lambda\), where \(d\) is the distance of diffraction planes, \(\theta\) is the angle of incident X-ray and diffraction planes, \(n\) is any integer, and \(\lambda\) is the wavelength of the X-ray. The angle of incidence of X-ray and transmission is \(2\theta\). Different diffraction planes can be denoted by \(d_{hkl}\), where \(hkl\) are called Miller Indices. With different \(\theta\), X-ray can be diffracted by all the planes (if there is the plane growing in the crystal). Then, after comparing the \(hkl\) from experiments with standard reference patterns, we can determine the phase of the samples.

**2.3. Optical absorption**

Absorption spectrum is commonly used for bandgap determination of semiconductor materials. When the incident light photon energy is larger than the bandgap of the semiconductor, the light will be absorbed by the semiconductor, leading to the
electron transition from the valence band to conduction band. The basic principle is given by Beer-Lambert law, \( A = \varepsilon l c \), where \( A \) is the absorbance, \( \varepsilon \) is the molar attenuation coefficient, \( l \) is the optical path length, that is how long does the light pass in the sample, and \( c \) is concentration of the attenuating species.[140]

Absorption spectra of 2D tin perovskite films are measured with a UV/Visible Perkin Elmer Lambda 950 spectrometer. Using this spectrometer, absorbance data can be measured directly, and then after the film thickness is measured, we can get the Tauc plot.

2.4. Time-resolved photoluminescence (TRPL)

TRPL is one of the measurements of ultrafast spectroscopy and the core of the measurement is the laser.[141, 142] The first question is how to change continuous wave laser to ultra short laser pulse. Depending on the duration and energy of the pulses we want to produce, two engineering solutions are available: Q-switch or a
variable attenuator inside the laser cavity (usually resulting in high energy pulses with the duration of several nanoseconds); mode-locking of the light modes inside the laser cavity (for obtaining pico- and femtosecond pulses). In the case of this thesis, mode-locking is applied to generate laser pulse and the laser is from Ti:Sapphire oscillator.

After generated laser pulse, we need to amplify the laser pulse since the laser come from the oscillator has very high repetition and narrow tuning range. To obtain higher pulse energies, a technique called chirped pulse amplification is employed (Figure 2.3). In this technique, the initial short laser pulse is stretched in time by a factor of a thousand through a pair of gratings. Then the power of the pulse is amplified. Finally, a second pair of gratings reverses the stretching process and compresses the pulse.

Now we have the last question, the tuning range is only from 700-1000 nm. The next is to amplify the energy range. Optical parametric amplification is used for this process.

First of all, the laser beam (denoted as pump) with frequency $\omega_p$ is split into two beams with frequency $\omega_s$ and $\omega_i$ which are signal and idler. The relation is given by equation $\omega_p = \omega_i + \omega_s$. This effect is achieved using a non-linear crystal. The wavelengths of the signal and idler are determined by the phase matching condition, which can be modified by changing the angle between the incident pump laser and the optical axes of the crystal. This means that signal’s wavelength can be tuned just turning the crystal using a stepper motor. In the special case of $\omega_s = \omega_i$, we have the exact reverse of the second-harmonic generation, which is called degenerate parametric amplification.

After the signal has been produced, the OPA will amplify it, using again nonlinear processes in crystals. A pump photon excites the system to a virtual energy level, whose decay is stimulated by a signal photon. Therefore, another photon is emitted...
with the same direction, energy and phase of the signal one. Since we are interested in a monochromatic beam, the idler is filtered and only the signal can escape the OPA. Due to the conservation of energy, it follows that it is impossible to obtain a signal with a wavelength lower than the pump. This can be obtained doubling the signal using second-harmonic generation. Now we have the laser that can perform TRPL measurements.

2.5. Pump-probe spectroscopy

The diagram of a general pump-probe measurement is shown in Figure 2.4.[143] In pump-probe system, the laser pulse is split to two pulse by a beam splitter. The two split beams are called pump pulse and probe pulse, generally the pump pulse is much more powerful than the probe pulse and also has a larger size of beam spot that can totally cover probe beam spot. There is a time delay system to regulate the time delay between pump and probe and the two laser beams must be temporally coincident on the sample. The strong pump excites the sample and changes the state of the sample, then the weak probe detects the perturbation changes.[142, 144] By measuring the differential transmission with different delay time, we can know the dynamic process of the material. In this experiment, the $\Delta T/T$ is measured. The experiment set up is shown in Figure 2.5.
There are three phenomenon can be observed in this measurement. First one is named ground state photobleaching, with the spectral shape of ground state absorption after thermalization. In this case, the pump pulse reduces the number of absorbing molecules in the ground state inducing an absorption decrease at probe frequencies equal or higher than the ground state absorption. The result is the increasing of $\Delta T/T$.

The second one is stimulated emission, which leads to an increasing of photons with the same direction, wavelength and phases. The pump pulse populates the excited state, the probe photon can stimulate it to emit back to the ground state. In this case the $\Delta T/T$ is still increased. The third one is called photoinduced absorption, that is in this case, the probe excited electron from excited state to higher excited level. Thus, the transmission is decreased and $\Delta T/T$ shows a negative value.
3. Quasi-2D lead perovskite solar cells

2D perovskites are being studied by more and more researchers since their stability. Various film processing methods were developed to improve the device PCE. But the device structure has not been optimized so much, especially for the hole transport layer. Generally, solar cells are employing spiro-OMeTAD or PEDOT: PSS as hole transport layer (HTL) in solar cells and they are also the most commonly used in 2D perovskite solar cells. But the drawbacks are apparent, the conductivity of spiro-OMeTAD is really low (~10^{-5} \text{ S cm}^{-1}), and in this kind of structure TiO_2 or other metal oxides will be used as electron transport layer (ETL) which need very high temperature (~300°C) for deposition. PEDOT: PSS is widely used in p-i-n structure which has easy device fabrication process and possess higher conductivity (~1.35 \times 10^{-3} \text{ S cm}^{-1}).[84, 88, 102, 145] But it’s not a pH neutral material, the acidity is corrosive to the anode which may cause device defect, decreasing the device performance.[146] Thus, a suitable HTL with pH neutral, high conductivity and matched work function is needed for improving the solar cell performance.[147, 148]

Herein, we report on how the different HTL affect the device of p-i-n 2d perovskite (PEA_2MA_4Pb_5I_16) solar cells.

In this part, we prepared quasi-2D lead perovskite and by XRD, absorption spectroscopy and GIWAXS measurements confirmed the composition phases of the film. By a different processing method, the orientation of film growth was controlled to charge transport preferable direction. PCP-Na[149] (structure in Figure A7) was employed as the HTL for solar cells and PEDOT: PSS was chosen as the control experiment. PCP-Na possesses an electrical conductivity (1.66 \times 10^{-3} \text{ S cm}^{-1}) a little bit higher than PEDOT: PSS. The HOMO level of PCP-Na (-5.22 eV) is closer to the valence band of PEA_2MA_4Pb_5I_16 perovskite (-5.3 eV) comparing to PEDOT: PSS (-5.11 eV) which results in the enhancement of open circuit voltage of solar
3.1. Experimental section

3.1.1. Film deposition and device fabrication

**Materials.** PEDOT: PSS water dispersion (Clevios VP AI 4083) was acquired from Heraeus. PEAI, MAI (>98%) and PbI$_2$ (>99.99%) were purchased from TCI EUROPE N.V. PCBM was purchased from Solenne BV. C$_{60}$ (>99.9%), BCP (99.99%), DMF (99.8%), and DMSO (99.8%) were purchased from Sigma Aldrich. All the materials were used as received without further purification. PCP-Na was synthesized following a previously reported method.[149]

**Perovskite film deposition.** The precursor solution was mixed by 0.4 mmol PEAI, 0.8 mmol MAI, 1 mmol PbI$_2$ and 0.4 mmol ammonium thiocyanate (NH$_4$SCN) in 1 mL DMF solvent or DMF/DMSO mixed solvent with ration of 1:2. The 2D perovskite precursor solution in pure DMF was deposited at a speed of 5000 rpm for 45 s followed by 100 °C annealing for 10 min on the hotplate. The solution with mixed solvent was deposited at a speed of 5000 rpm for 20 s, The above films were immediately annealed at 100 °C for 10 min (conventional method) or put in vacuum for 5 min and then annealed at 100 °C for 10 min (vacuum assisted method). The as-prepared films on glass were for further characterizations.

**Device fabrication and Characterizations.** ITO glasses were cleaned in soap water ultrasonication, followed by washing with water, acetone, isopropyl alcohol in sequence. Then the substrates were treated by UV-ozone for 10 min to remove organic residues which may affect the deposition of hole transport layers. PEDOT: PSS was spin-coated on the cleaned ITO substrates at a speed of 3000 rpm for 60 s. PCP-Na was dissolved in solvent mixture of water and methanol with the volume ratio of 3:7 and was spin-coated on the substrates at a speed of 3000 rpm for 30 s. The
HTL coated substrates were dried at 140 °C for 15 min. Then the substrates were transferred to a glove box filled with nitrogen. On those substrates, PEA2MA4Pb5I16 films were deposited in the same way above. Then PCBM solution in chlorobenzene of 20 mg mL\(^{-1}\) was deposited at a speed of 1000 rpm for 60 s. 20 nm of C\(_{60}\), 6 nm BCP and 100 nm aluminum were sequentially evaporated on top of PCBM layer under vacuum degree <10\(^{-7}\) mbar. The \(J-V\) curves of the devices were measured at 295 K using a Keithley 2400 source meter under simulated AM 1.5 G solar illumination using a Steuernagel Solar constant 1200 metal halide lamp in a nitrogen-filled glove box. The light intensity was calibrated to be 100 mW cm\(^{-2}\) by using a Si reference cell and correcting the spectral mismatch. A shadow mask (0.04 cm\(^2\)) was used to exclude lateral contributions beyond the device area.

3.1.2. Film characterizations

**Absorbance, XRD patterns and SEM measurements.** The absorbance of the perovskite films was recorded on Shimatzu UV–vis–NIR spectrophotometer (UV 3600). XRD patterns were recorded in air on a Bruker D8 Advance X-ray diffractometer with a Cu K\(\alpha\) source (\(\lambda = 1.54\) Å) and a Lynxeye detector. SEM images of perovskite films were taken in vacuum on an FEI NovaNano SEM 650 with an acceleration voltage of 5 kV.

**GIWAXS measurement.** Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed using a MINA X-ray scattering instrument built on a Cu rotating anode source (\(\lambda = 1.5413\) Å). 2D patterns were collected using a Vantec500 detector (1024x1024 pixel array with pixel size 136x136 microns) located 93 mm away from the sample. The perovskite films were placed in reflection geometry at certain incident angles \(\alpha_i\) with respect to the direct beam using a Huber goniometer. GIWAXS patterns were acquired using an incident angle of 2° in order to probe the thin film structure at an X-ray penetration depth of the entire film thickness. For an ideally flat surface, the value of the X-ray penetration depth (i.e. the depth into the
material measured along the surface normal where the intensity of X-rays falls to 1/e of its value at the surface) depends on the X-ray energy (wavelength $\lambda$), the critical angle of total reflection, $\alpha_c$, and the incident angle, $\alpha_i$, and can be estimated using the relation:

$$\Lambda = \frac{\lambda}{4\pi} \sqrt{\frac{2}{(a_i^2-a_c^2)^2 + 4\beta^2 - (a_i^2-a_c^2)}}$$

where $\beta$ is the imaginary part of the complex refractive index of the compound. The direct beam center position on the detector and the sample-to-detector distance were calibrated using the diffraction rings from standard silver behenate and Al$_2$O$_3$ powders. All the necessary corrections for the GIWAXS geometry were applied to the raw patterns using the FIT2D and the GIXGUI Matlab toolbox. The reshaped GIWAXS patterns, taking into account the inaccessible part in reciprocal space (wedge-shaped corrected patterns), are presented as a function of the vertical and parallel scattering vectors $q_z$ and $q_r$. The scattering vector coordinates for the GIWAXS geometry are given by:

$$q = \left\{ \begin{array}{lcr} 
q_x &=& \frac{2\pi}{\lambda} (\cos(2\theta_f) \cos(\alpha_f) - \cos(\alpha_i)) \\
q_y &=& \frac{2\pi}{\lambda} (\sin(2\theta_f) \cos(\alpha_f)) \\
q_z &=& \frac{2\pi}{\lambda} (\sin(\alpha_i) + \sin(\alpha_f)) \end{array} \right. \quad [151]$$

where $2\theta_f$ is the scattering angle in the horizontal direction and $\alpha_f$ is the exit angle in the vertical direction. The parallel component of the scattering vector is thus calculated as $q_r = \sqrt{q_x^2 + q_z^2}$.\[151\]

**PL measurement.** The samples were excited at laser wavelength 400 nm by the second harmonic of a mode-locked Ti:sapphire (Mira 900) laser delivering pulses of 150 fs. The laser repetition rate is 76 MHz; a pulse picker was inserted in the optical path to reduce the repetition rate. A 150 mm focal length lens was used to focus the beam, and the emission was collected by a spectrometer with a 50 lines mm$^{-1}$ grating. The steady-state PL was recorded with a CCD camera from Hamamatsu (Hamamatsu, Japan). Time-resolved PL was measured with the streak camera.
3.2. Results and discussion

3.2.1. Solar cells with different hole transport layers

3.2.1.1. Film morphology and structure

![Diagram of solar cell structure](image)

**Figure 3.1** (a) device structure of the solar cells, (b) work function of different layers correlated to device structure, (c,d) XRD patterns and UV-vis absorption of the different samples.

The device structure is shown in **Figure 3.1a** and **Figure 3.1b** shows the related work function respectively. X-ray diffraction (XRD) patterns are shown in **Figure 3.1c**. Diffraction patterns for both the thin films on PEDOT: PSS and PCP-Na demonstrate oriented growth. The two main peaks at 2\(\theta\) around 14.17° and 28.54° are assigned to (110) and (220) facets respectively. The small peaks in PCP-Na sample at 3.96°, 7.88°, 11.82°, 15.74°, 19.72°, 23.70°, 27.73° and 31.77° are correlated to (002), (004), (006),
(008), (0010), (0012), (0014) and (0016) facets, indicating the presence of n=2 member. The optical absorbance of thin films grown on different HTLs is shown in Figure 3.1d. The small ripples at 564 nm, 608 nm and 643 nm belong to low n=2, 3, and 4 members respectively, indicating different phases exist in the thin films.

The pattern for the thin film on PCP-Na exhibits higher crystallinity than on PEDOT: PSS, indicating PCP-Na as supporting layer is better for 2d perovskite crystallization. To furtherly confirm the growth orientation of the thin films, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were carried on. Results are shown in Figure 3.2, with all the panels showing sharp, discrete Bragg spots. At the lowest incident angle of 0.25°, probing the first several tens of nanometers on the top surface of the thin films, the images of thin films grown on PEDOT: PSS (Figure 3.2a) and PCP-Na (Figure 3.2c) are very similar. The Brag spot at around $q_y=1$ Å$^{-1}$ represents the (110) plane grown along in-plane direction which is much stronger than $q_y=1$ Å$^{-1}$ representing (110) plane grown along out-of-plane direction. It means that the (110) plane is mainly growing along in-plane direction indication the $[\text{Pbl}_6]^{4-}$
Chapter 3. Quasi-2D lead perovskite solar cells

octahedron layers are perpendicular to the substrates. The results measured at highest incident angle of 2°, probing the last several tens of nanometers on the bottom surface of the thin films, are shown in Figure 3.2b (PEDOT: PSS) and 3.2d (PCP-Na). Still they are very similar but in Figure 3.2b, at around $q_z=0.75 \text{ Å}^{-1}$, there appears a small Debye-Scherrer ring indexed as the (006) plane of n=2 phase. But the Debye-Scherrer ring means that at this part of the thin films, the “wells” and “barriers” are growing randomly way lead to form defects determined to charge transport from bottom to upper layers.

The morphology of the thin films grown on PEDOT: PSS and PCP-Na were measured by scanning electron microscope (SEM). As shown in Figure 3.3a, PEA$_2$MA$_4$Pb$_5$I$_{16}$ grown on PEDOT: PSS substrate has some large pinholes and obvious grain boundaries on the film, which may cause current leakage by forming shunts and trap-assisted recombination. Furthermore, the HTL and ETL may contact each other directly through pinholes, short-circuiting the device. On the other hand, in Figure 3.3b, the film grown on PCP-Na shows much better quality, less pinholes and more uniform surface which may help to reduce trap states.

3.2.1.2. Photoluminescence measurements

To further understand the charge recombination process in perovskite thin films,
steady state and time-resolved photoluminescence (TRPL) measurements were performed on pristine perovskite on glass and on different HTLs. Results are shown in Figure 3.4. Steady state PL (Figure 3.4a, b) intensity, measured from the two different sides of the samples, is reduced in the presence of HTLs, indicating efficient charge transfer from perovskite to HTL. In Figure 3.4b, the spectra measured from backside display weak peaks at 526 nm and 581 nm which are corresponding to \( n=1 \) and \( n=2 \) phase (details in semilogarithmic plots of Figure A1). The TRPL spectra measured from frontside (Figure 3.4c) are very similar to samples on different HTLs. The lifetime are 26.7 ns for PEDOT: PSS sample and 24.9 ns for PCP-Na sample. But the PL decay measured from backside, the lifetime for PCP-Na sample is 49.4 ns.
which is significantly longer than PEDOT: PSS sample 35.0 ns. This effect may attribute to the less oriented growth of PEDOT: PSS film, leading to the low efficient charge transport and more recombination of charge carriers.

**Figure 3.5** (a) $J-V$ curves, (b) IPCE spectra, (c) Max power point track, and (d) PCE distribution of devices using different HTL.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$FF$</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT: PSS F</td>
<td>1.09</td>
<td>14.30</td>
<td>0.61</td>
<td>9.62</td>
</tr>
<tr>
<td>PEDOT: PSS R</td>
<td>1.07</td>
<td>14.16</td>
<td>0.58</td>
<td>8.76</td>
</tr>
<tr>
<td>PCP-Na F</td>
<td>1.15</td>
<td>15.54</td>
<td>0.79</td>
<td>14.12</td>
</tr>
<tr>
<td>PCP-Na R</td>
<td>1.14</td>
<td>16.17</td>
<td>0.72</td>
<td>13.35</td>
</tr>
</tbody>
</table>

Table 3. Performance parameters of devices using different HTL.
3.2.1.3. Device performance

To investigate the solar cell performance, a p-i-n architecture was employed, namely ITO/(PEDOT: PSS or PCP-Na)/Perovskite/PCBM/C_{60}/BCP/Al. Figure 3.5a shows the $J$-$V$ curve of the solar cells using different HTLs and the relevant parameter details are summarized in Table 3. The best performance is obtained for the device using PCP-Na as HTL, with a $V_{OC}$ value of 1.15 V, a $J_{SC}$ of 15.54 mA cm$^{-2}$, a FF of 0.79 and a PCE of 14.12% in forward scan. In reverse scan, the device shows a $V_{OC}$ of 1.14 V, a $J_{SC}$ of 16.17 mA cm$^{-2}$, an FF of 0.71 and a PCE of 13.35%. As a comparison, the device using PEDOT: PSS as HTL shows a $V_{OC}$ of 1.09 V, a $J_{SC}$ of 14.30 mA cm$^{-2}$, a FF of 0.61 and a PCE of 9.62% in forward scan and a $V_{OC}$ of 1.07 V, a $J_{SC}$ of 14.16 mA cm$^{-2}$, a FF of 0.58 and a PCE of 8.76% in reverse scan. The tracks of max power point of the devices are shown in Figure 3.5b, the steady state PCE are 13.44% and 9.42% for PCP-Na and PEDOT: PSS, respectively. Figure 3.5c shows the external
Chapter 3. Quasi-2D lead perovskite solar cells

Quantum efficiency spectra of the different devices. The current density integrated from the spectra are 15.97 mA cm$^{-2}$ and 14.70 mA cm$^{-2}$ corresponding to PCP-Na and PEDOT: PSS respectively, which closely match the $J_{SC}$ value obtained by $J-V$ curves.

Dark current refers to the reverse direct current generated when the P-N junction is under reverse bias conditions with no incident light. It is generally caused by the diffusion of carriers or defects on the surface and inside of the device and impurities. The principle of diffusion is that inside the P-N junction, there are many electrons in the N region, and there are many holes in the P region. Because of the difference in concentration, electrons in the N region are diffused into the P region, and holes in the P region are diffused into the N region, despite the P-N junction. The built-in electric field prevents this diffusion, but in reality, the diffusion has been going on, only to achieve a dynamic equilibrium, which is the formation of diffusion current. In addition, when there are defects on the surface and inside of the device, the defect level acts as a recombination center. When electrons and holes are captured by the defect level, the movement of carriers forms an electric current. The impurity also functions as a recombination center in the device, with the same principles as defects. The dark $J-V$ curves (Figure 3.6) are showing under dark condition, PCP-Na device generates dark current much smaller than PEDOT: PSS samples. This indicates that the PCP-Na device has less defect density than PEDOT: PSS one which is

Figure 3.7 Light intensity dependence of $J_{SC}$ (a) and $V_{OC}$ (b) of the devices using different HTL.
corresponded to the SEM and GIWAXS measurements.

To further understand the recombination in presence of different HTL, we measured the light-intensity dependence of $J_{SC}$ and $V_{OC}$. The results are shown in Figure 3.7. In Figure 3.7a, the $J_{SC}$ to light intensity plot of PCP-Na has a slope closer to 1, and Figure 3.7b shows the semilogarithmic plots of the $V_{OC}$ to light intensity of the devices, the PCP-Na device exhibits a much smaller slope (1.35 kT/q) than PEDOT: PSS device (1.93 kT/q). These results indicate more equal trapping recombination of electrons and holes occurs in PEDOT: PSS device, which is corresponded to the SEM and GIWAXS measurements. The air stability of the thin films was also evaluated. In Figure A2, after 80 days in the air, the thin films still remain good crystallization and the images of the thin films exhibit one edge of the film on PEDOT: PSS turn yellow while the film on PCP-Na is still dark brown.

In addition, I also applied this new HTL in 3D lead perovskite to see if it could improve the performance of solar cell devices. $(\text{FAPbI}_3)_{0.87}(\text{MAPbBr}_3)_{0.17}$ was employed as the active perovskite layer. The device performance is improved from PCE of 12.32% (PEDOT: PSS) with $J_{SC}$ 19.75 mA cm$^{-2}$, $V_{OC}$ 0.87 V, FF 0.72 to PCE of 15.73% (PCP-Na) with $J_{SC}$ 21.03 mA cm$^{-2}$, $V_{OC}$ 0.99 V, FF 0.75 ($J-V$ curves in Figure A3).

3.2.2. Comparison of two deposition methods for mixed solvent

3.2.2.1. Film morphology and structure
In the conventional method, the wet films were put on a hot plate at 100 °C immediately after spin-coating, and they turned dark red after 10 seconds due to fast evaporation of the solvent (Figure 3.8a). These films appear very rough, non-uniform and not very reflective to the eye. In vacuum assisted method, the films were placed in vacuum immediately after the same spin-coating procedure, after 5 minutes in the chamber they appear as dark red, uniform and very reflective (Figure 3.8b). The films were then put on the hot plate at 100 °C for 10 min. The morphology of the thin films is shown in Figure 3.8c, d. The conventional sample film (denoted as M1) forms large grains but also with very large cracks and pinholes, resulting open grain boundaries and increased defect densities. Differently, vacuum sample film (denoted as M2).

The absorption spectra of the thin films in Figure 3.9 exhibit an absorption onset at around 780 nm resembling of 3D MAPbI₃ films. They show several higher energy
peaks due to strong excitonic absorption associated with 2D phases. These features suggest that the quasi-2D films consist of multiple perovskite phases. Perovskite M1 film exhibits much stronger absorption corresponding to the n=2 phase at 569 nm and weak absorption consistent with the n=1 phase at 514 nm. Perovskite M2 film displays a much weaker absorption from the n=1 and 2 phases, but absorption corresponding to the n=3 (609 nm), 4 (640 nm) and 5 (663 nm) phases are observed. Such distinctive features in the absorption spectra imply the presence of domains of different phase composition in these RPP films.

The two type of perovskite films display rather distinct X-ray diffraction (XRD) patterns (Figure 3.10). M1 film exhibits two intense diffraction peaks at $2\theta = 14.15^\circ$ and $28.48^\circ$, which are assigned to the (110) and (220) crystallographic planes, respectively. It also exhibits several evenly spaced peaks at $2\theta = 3.96^\circ$, $7.88^\circ$, $11.82^\circ$, $15.76^\circ$, $19.72^\circ$, $23.70^\circ$ and $27.725^\circ$, which are indexed as the (002) (004)...to (0014) planes of the n=2 phase. In addition, another two very weak peaks at low reflection angles ($2\theta = 5.48^\circ$ and $10.72^\circ$) are assigned to the (002) and (004) planes of the n=1 phase. The n=3, 4, 5 phases do not show any peaks at low diffraction angle ($2\theta <$
14.15\(^\circ\), most probably due to their preferential orientation. M2 film exhibits two dominant peaks from the (110) and (220) planes, indicating preferential orientation of the perovskite domains. Diffraction peaks from the n=1 and 2 phases are visible but very weak due to their small volume fractions. Similar to the M1 film, the 5≥n≥3 phases have the same preferential orientation, exhibiting dominant (110) and (220) planes.

In order to probe the orientation of the perovskite phases with respect to the substrate, we carried out grazing incidence wide-angle X-ray scattering (GIWAXS) measurements at incident angles of 0.25\(^\circ\) and 2\(^\circ\) (Figure 3.11). Both M1 and M2 films show remarkably sharp Bragg spots at different X-ray penetration depths. Indexing the intense Bragg spot at q\(_z\)=0.89 Å\(^{-1}\) confirms that the infinity ≥n≥ 3 phases in these films are oriented with their (110) planes packing in the out-of-plane direction, thus the octahedron layers are perpendicular to the substrate. The Bragg spot at q\(_y\)=0.89 Å\(^{-1}\) assigned to the in-plane-oriented (110) plane is much weaker than that at q\(_z\)=0.89 Å\(^{-1}\), indicating the dominant vertical orientation of the infinity ≥n≥ 3 phases. This is a common feature of the M1 and M2 films.
The M1 film shows intense Bragg spots at \( q_z \approx 0.25 \, \text{Å}^{-1}, 0.54 \, \text{Å}^{-1} \) and \( 0.78 \, \text{Å}^{-1} \) in the entire film, which are indexed as the (002), (004) and (006) planes of the \( n=2 \) phase with octahedron layers parallel to the substrate (Figure 3.11a-c). In addition, a Bragg spot at \( q_z \approx 0.39 \, \text{Å}^{-1} \) is observed belonging to the (002) plane of the \( n=1 \) phase parallel to the substrate. Since PEA organic double layers is a potential barrier for charge transport, such preferential parallel alignment of the \( n \leq 2 \) phases inhibits charge transport and collection of charges in the vertical direction of the solar cells. The M2 film does not show any diffraction spots from \( n=1 \) and 2 phases at shallow X-ray penetration depth (Figure 3.11d-f). Very weak diffraction signal of the \( n=2 \) phase is observed in the out-of-plane direction at the bottom of the film (Figure 3.11e) due to its small volume fraction. Therefore, the vertically oriented octahedron layers in M2 film, facilitate charge transport and collection in the corresponding solar cells.

**Figure 3.11** GIWAXS images of M1 film (a,b) and M2 film (c,d), measured on 0.25 and 2, which is on bottom and top of the film, respectively. Structure illustration of M1 film (c) and M2 film (f).
### 3.2.2.2. Device performance

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$/V</th>
<th>$J_{SC}$/mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT_M1 F</td>
<td>0.81</td>
<td>7.97</td>
<td>0.37</td>
<td>2.40</td>
</tr>
<tr>
<td>PEDOT_M1 R</td>
<td>0.74</td>
<td>7.93</td>
<td>0.30</td>
<td>1.79</td>
</tr>
<tr>
<td>PEDOT_M2 F</td>
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<td>15.50</td>
<td>0.65</td>
<td>10.57</td>
</tr>
<tr>
<td>PEDOT_M2 R</td>
<td>1.06</td>
<td>15.82</td>
<td>0.66</td>
<td>11.07</td>
</tr>
<tr>
<td>PCP-Na_M1 F</td>
<td>0.99</td>
<td>6.31</td>
<td>0.53</td>
<td>3.31</td>
</tr>
<tr>
<td>PCP-Na_M1 R</td>
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<td>6.63</td>
<td>0.57</td>
<td>3.65</td>
</tr>
<tr>
<td>PCP-Na_M2 F</td>
<td>1.10</td>
<td>17.09</td>
<td>0.73</td>
<td>13.70</td>
</tr>
<tr>
<td>PCP-Na_M2 R</td>
<td>1.10</td>
<td>17.52</td>
<td>0.73</td>
<td>14.14</td>
</tr>
</tbody>
</table>

**Table 4.** Devices with perovskite films M1 and M2 on different hole extraction layers under one sun condition.

**Figure 3.12.** $J$-$V$ curves of devices using different hole transport layers, PEDOT: PSS (a) and PCP-Na (b). M1 device film shown in black and M2 film device shown in red.

The device structure is same with the one shown in **Figure 3.1a.** Both M1 and M2 are employed in PEDOT: PSS and PCP-Na devices. Results are obvious that M2 devices
possess higher PCE than M1 devices (Figure 3.12). In PCP-Na devices, device with M2 film exhibits a $V_{OC}$ valued of 1.10 V, a $J_{SC}$ of 17.09 mA cm$^{-2}$, an FF of 0.73 and a PCE of 13.70% in forward scan. In reverse scan, the device shows a $V_{OC}$ of 1.10 V, a $J_{SC}$ of 17.52 mA cm$^{-2}$, an FF of 0.73 and a PCE of 14.14%. While the M1 device shows a $V_{OC}$ of 0.985 V, a $J_{SC}$ of 6.31 mA cm$^{-2}$, a FF of 0.53 and a PCE of 3.31% in forward scan and a $V_{OC}$ of 0.959 V, a $J_{SC}$ of 6.63 mA cm$^{-2}$, a FF of 0.57 and a PCE of 3.65% in reverse scan. In PEDOT: PSS devices, they show the same trend with M2 device PCE 10.57% (11.07%), much higher than M1 2.40% (1.79%). Detailed data of J-V curves are summarized in Table 4.

3.2.2.3. Conclusion

In this chapter, we developed a vacuum-assisted fabrication method for quasi-2D perovskite (PEA$_2$MA$_4$Pb$_5$I$_{16}$) thin films which is rather useful to improve the film morphology with mixed solvent precursors. Films deposited in this method have shown very smooth and reflective surface with compact and less grain boundary morphology. It also can improve the phase distribution and growth orientation to become more preferable for charge transport at in-plane direction. The stability of those thin films can be up to more than 2 months with little degradation. Meanwhile, a novel hole transport layer, PCP-Na was employed to replace PEDOT: PSS. PCP-Na is pH neutral and possess an electrical conductivity ($1.66 \times 10^{-3}$ S cm$^{-1}$) a little bit higher than PEDOT: PSS ($1.35 \times 10^{-3}$ S cm$^{-1}$). The HOMO level of PCP-Na (-5.22 eV) is closer to the valence band of PEA$_2$MA$_4$Pb$_5$I$_{16}$ perovskite (-5.3 eV) comparing to PEDOT: PSS (-5.11 eV) which results in the enhancement of open circuit voltage of solar cells. With these improvements, PCE of solar cells was improved beyond 14%.
4. Photophysics of 2D tin perovskite

Different from the lead counterpart, studies on tin perovskite are not so many. Although the approximate 10% has appealed plenty of studies, there still exists various issues need to be solved and the photophysics needs to be elucidate.[152-157] In this part, 2D tin perovskites $\text{BA}_2\text{MA}_{n-1}\text{Sn}_n\text{I}_{3n+1}$ with different $n$ numbers were fabricated and the photogenerated carriers were studied through ultrafast systems to understand the carrier behaviors in the perovskite.

4.1. Experimental section

4.1.1. Synthesis of $\text{BA}_2\text{MA}_{n-1}\text{Sn}_n\text{I}_{3n+1}$ thin films

The thin films were deposited by spin-coating method. Stoichiometric MAI, BAI and SnI$_2$ were dissolved in DMF, that is 0:2:1 for $\text{BA}_2\text{SnI}_4$ ($n=1$), 1:2:2 for $\text{BA}_2\text{MASn}_2\text{I}_7$ ($n=2$) and 2:2:3 for $\text{BA}_2\text{MA}_2\text{Sn}_3\text{I}_{10}$ ($n=3$). The concentration of Sn$^{2+}$ was 0.5 M. The glass substrates were cleaned by soap water with ultrasonic at 50°C for 10 min, then washed by deionized water. After that, the substrates were washed by acetone and isopropanol with ultrasonic for 10 min subsequently. The precursor solutions were then heated to 70°C for 30 min and spin-coated at a speed of 3000 rpm for 30 s with an acceleration of 1500 rpm/s. Then the thin films were annealed at 75°C for 10 min.

4.1.2. Film characterization

X-ray diffraction. X-ray diffraction measurement was carried at room temperature using a Bruker D8-Discover diffractometer (Bragg-Brentano geometry) for crystals with parallel beam geometry and Cu Ka wavelength ($\lambda=1.5418\text{Å}$), operated at 40 kV and 40 mA using a step size of 0.05° and a time per step of 1 s. For $n=1$ sample, the Bragg angle was scanned from 5 to 40. For $n=2$ sample, it was 3 to 40 and 2 to 40 for $n=3$ sample.
AFM and UV-vis absorption. Film morphology and thickness is roughly measured.
by atomic force spectroscopy with a NT-MDT Solver P47H-Pro in semicontact mode by a high-resolution non-contact silicon tip. Absorption spectra of perovskite films are measured with a UV/Visible Perkin Elmer Lambda 950 spectrometer. The wavelength range is from 350nm to 1100nm.

**Time-resolved photoluminescence.** Since tin perovskites are even more unstable than lead perovskites, all the samples were measured in vacuum circumstance. Samples were excited with a regenerative amplified laser (Coherent Libra) delivering 130-fs-long pulses at a repetition rate of 1 KHz. Photoluminescence was dispersed with a grating spectrometer (Princeton Instruments Acton SpectraPro 2300i equipped with a 50 gr mm$^{-1}$ grating blazed) and detected by a streak camera (Hamamatsu).

### 4.2. Results and discussion

#### 4.2.1. Synthesis for single phase

Generally, for 2D perovskites, it is rather tough to get a very pure phase of target material. The n=1 sample, since there is only large organic cation, can be pure phase. When trying to increase the n number, as described in chapter 3, the n=5 sample is actually a mixture of 3D and different 2D phases. Here, in this experiment, first of all, all the films were deposited by the normal method and XRD results are shown in Figure 4.1.

The n=1 is obvious pure material, and the peaks at $2\theta$ of 6.5°, 12.9°, 19.35°, 25.9° and 32.5° can be indexed as the (002), (004), (006), (008) and (0010) planes respectively. In n=2 sample, things become different. The main peaks at 4.55°, 9.05°, 13.55°, 18° and 27.1° belong to (002), (004), (006), (008) and (0012). Besides, there are also some weak peaks, only the two ripples at 22.55° and 31.7° are (0010) and (0014) of n=2 material. Other ripples are peaks from n=1 or maybe because randomly growth orientation reflectivity. Considering the limit of detection of XRD is 2% and the intensity of the ripples, we can consider the n=2 as a 97% pure material. But for the n=3 sample, the XRD pattern shows many irregular peaks of this film through this
deposition method. Despite the (00l) planes of n=3 phase, some peaks of n=1 and 2 phases are also observed, implying the film is a mixture of different phases.

### 4.2.2. Optical absorption and free energy

For thin films samples, there is an equation to describe the absorption:

\[
I_d = I_0 e^{-\alpha d} \quad (4.1)
\]

where \(I_d\) is the transmission light, \(I_0\) is the incident light, \(\alpha\) is the absorption coefficient of the material, \(d\) is the thickness of the film, that is the distance of light passing the sample. As seen in Figure 4.2, the Y axis is absorbance, which is given by \(\log_{10} (I_0/I_d)\). The shift up of n=2 sample from 750 to 1100 nm might be the roughness of the film (Figure B1). The light scatters when arriving on the surface of the film. Since the n=3 sample is a mixture, 2 very small shoulder peaks can be seen at the same wavelength of n=1 and 2 samples which also confirms the mixture phases of the sample. Figure 4.3 shows the degradation of the samples, from the absorption spectra,
we can see all the samples degrades very fast in the air circumstance. Within 30 min, the absorption of all the samples degrade more than 50%.

Figure 4.3. Optical absorption degradation of 3 different samples. Blue is fresh sample, black is after TRPL measurement in vacuum, others are exposed to air.
To determine the bandgap of the materials, Tauc to Energy plot of the samples are extracted from the absorbance data.[158] The Tauc and Davis-Mott relation can be written by

\[(\alpha h \nu)^n = K(h \nu - E_g)\] (4.2)

This relation is usually used to probe the optical bandgap energy for materials. In this equation, \(\alpha\) is the absorption coefficient, \(h \nu\) is the photon energy, \(K\) is an energy independent constant, \(E_g\) is the optical bandgap energy and \(n\) represents the nature of transition. Its value is fixed, 2 for direct allowed transition, 0.5 for indirect allowed transition, 2/3 for direct forbidden transition and 1/3 for indirect forbidden transition.

For the Y axis, \((\alpha h \nu)^n\), \(h \nu\) can be given by 1240/wavelength with unit eV; \(\alpha\), with the Beer-Lambert absorption equation, can be given by 2.303*absorbance/d with unit cm\(^{-1}\), and for these 2D tin perovskite samples, the \(n\) is 2. The X axis is just \(h \nu\). Thus, we extract the Tauc plot data from absorbance data. Figure 4.4 shows the Tauc plot of

![Tauc plot from absorption of n=1 and 2 samples.](image)

**Figure 4.4.** Tauc plot from absorption of n=1 and 2 samples.
the n=1 and n=2 samples and from the absorption peak we can know the bandgap should be 2.00 eV and 1.72 eV respectively.

The free energy ($\mu_{oc}$) of the perovskites are given by optical method with the external photoluminescence quantum yield (EQY).[159] The $\mu_{oc}$ is equal to the energy splitting of quasi-fermi level of electrons in conductive band and holes in valence band.[160, 161] According to the Kirchhoff’s law of radiation, which represents the detailed balance between emission and absorption, generalized by Würfel to account for non-equilibrium electron and hole populations[162]:

$$J_{PL} = \int \alpha(\omega) \frac{\Omega}{4\pi^2 \hbar^3 c_0^2} \frac{(\hbar \omega)^2}{\hbar \omega - \mu - \frac{\mu}{kT} - 1} d(\hbar \omega) \approx J_{0,rad} e^{\frac{\mu}{kT}}$$

(4.3)
where $J_{PL}$ is the emitted photon current density, which is proportional to the external photoluminescence intensity; $\alpha(\omega)$ is absorptivity depending on the absorption coefficient and thickness of the sample; $\Omega$ is the effective external emission angle; $c_0$ is the speed of light; $T$ is the temperature. The right side of the equation holds for excitation levels typical of solar illumination when Bose function can be substituted by Boltzmann distribution. For further calculation, $J_{PL}$ can be described by EQY, for $\text{EQY} = J_{PL}/J_{ex}$. Then equation (4.3) can be written by

$$\mu = kT\ln\frac{J_{PL}}{J_{0,rad}} = kT\left[\ln\frac{J_{ex}}{J_{0,rad}} + \ln(\text{EQY})\right] = \mu_{OC,rad} + kT\ln(\text{EQY}) \quad (4.4)$$

where $\mu_{OC,rad}$ is the maximum of the free energy when the EQY is 1, which means only radiative recombination happens under open circuit condition.
Table 5. Summary of bandgap, EQY and free energy of the two samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap (eV)</th>
<th>EQY (%)</th>
<th>$\mu_{oc,rad}$ (eV)</th>
<th>$\mu_{oc}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA$_2$SnI$_4$</td>
<td>2.00</td>
<td>0.32±0.08</td>
<td>1.701</td>
<td>1.552±0.006</td>
</tr>
<tr>
<td>BA$_2$MASn$_2$I$_7$</td>
<td>1.72</td>
<td>0.9±0.2</td>
<td>1.440</td>
<td>1.319±0.006</td>
</tr>
</tbody>
</table>

Table 5. Summary of bandgap, EQY and free energy of the two samples.

If all photons with energy higher than bandgap are absorbed, the $\frac{\mu_{oc,rad}}{e}$ will be the SQ limit of open circuit voltage. The non-radiative recombinations only affect the EQY, with 10 drop the free energy will lost 60 meV under the temperature of 300K. With the previous work in our group, the $\mu_{oc,rad}$ can be given by the equation below:

$$\mu_{oc,rad} = E_{\text{gap}} \frac{T_{\text{sun}} - T}{T} + kT \ln \frac{T_{\text{sun}}}{T} + kT \ln [f(T, T_{\text{sun}}, E_{\text{gap}}) \frac{\Omega_{\text{sun}} \bar{\alpha}_{\text{sun}}}{\Omega \bar{\alpha}_T}]$$ \hspace{1cm} (4.5)

In this equation, $k$ is Boltzmann constant, $T_{\text{sun}}$ is 5541 K, $T$ is 300 K, $\Omega_{\text{sun}}/\Omega = 6.8 \times 10^{-5}/\pi$. $\bar{\alpha}_{\text{sun}}$ and $\bar{\alpha}_T$ are the spectrally averaged film absorptivity, weighted by the black-body radiation spectra at $T_{\text{sun}} = 5541$ K and $T = 300$ K, respectively. $f(T, T_{\text{sun}}, E_{\text{gap}})$ is depicted as

$$f(T, T_{\text{sun}}, E_{\text{gap}}) = \frac{2 \left( \frac{kT_{\text{sun}}}{E_{\text{gap}}} \right)^2 + 2 \frac{kT_{\text{sun}}}{E_{\text{gap}}} + 1}{2 \left( \frac{kT}{E_{\text{gap}}} \right)^2 + 2 \frac{kT}{E_{\text{gap}}} + 1}$$ \hspace{1cm} (4.6)

Thus, with equation (4.5) and (4.6) we can calculate the $\mu_{oc,rad}$ under 1 sun irradiation which is 66 $\mu$W cm$^{-2}$, consequently we can get the $\mu_{oc,rad}$ of the whole light intensity series. Then with equation (4.4) we can calculate the free energy after measuring the EQY of the sample. Unless EQY is unit, the free energy is equal to $\mu_{oc,rad}$, or the free energy will be less than $\mu_{oc,rad}$.

Figure 4.5 is the EQY of the samples, measured by integrating sphere method. Under
1 sun condition (66 μW cm$^{-2}$), the EQY of the samples are 0.32% (n=1) and 0.9% (n=2), the results of free energy are shown in Figure 4.6, summarized in Table 5.

4.2.3. Ultrafast spectroscopy measurements

Figure 4.7 shows the log-log plot of PL$_0$ to injected carrier density $n_0$. PL$_0$ is the PL intensity at time 0, which means the initial intensity immediately after the laser pulse strike on the sample. This intensity is measured by TRPL measurement. The injected carriers are photo-generated carriers and the density can be given by the fluence of laser pulse $\Phi$, excitation photon energy $h\nu_{exc}$ and absorption coefficient of the excitation light $\alpha_{exc}$. The equation is $n_0=\Phi \alpha_{exc}/h\nu_{exc}$. $\Phi$ can be given by laser power divided by frequency and spot area; $h\nu_{exc}$ is the photon energy of 400 nm which is the excitation wavelength; $\alpha_{exc}$ can be given by the absorbance of 400 nm light and the thickness of the sample. Thus we get the plot of PL$_0$ to injected carrier density. As

![Figure 4.7](image-url)
seen in the figure, n=1 sample shows linear behavior while n=2 sample shows quadratic behavior. The light emission of samples are due to the radiative recombination including excitonic recombination and bimolecular recombination. The recombination rate can be described as \( R_{\text{rad}}=B_1n+B_2n^2 \). If in the sample excitons are main charge carriers, then \( R_{\text{rad}}=B_1n \) and PL\(_0\) is proportional to \( n \) and if free carriers are main charge carriers, then \( R_{\text{rad}}=B_2n^2 \) and PL\(_0\) is proportional to \( n^2 \). Thus, according to the results we can consider in n=1 sample excitons are main carriers and in n=2 sample there are more free carriers. As can be seen in Figure 4.8, the decays become shorter with the increasing of laser pulse, and lifetimes extracted from the

Figure 4.8. TRPL decay of different laser pulse fluence, upper is n=1 sample, fluence from 0.65 to 362.61 \( \mu \)J cm\(^{-2} \); down is n=2, fluence from 0.79 to 32.34 \( \mu \)J cm\(^{-2} \).
decays in Figure 4.8 are shown in Figure 4.9. The lifetime of n=2 sample is decreasing faster than n=1 sample.

To further confirm the photo-generated charge carriers in the two samples, pump-probe spectroscopy was carried out. Figure 4.10 is the plot of $\Delta T/T$ as a function of probe wavelength. For n=1 sample, photo-bleaching appears with two bleaching peaks at 522 nm and 603 nm. The 2 negative peaks at 560 nm and 627 nm are because of photoinduced absorption which leads to the excitation of electrons from one excited state to another. In n=2 sample, it is very different from n=1. Only one broadened positive peak at 685 nm. The result is corresponding to the TRPL measurement that is excitons in n=1 sample and free carrier in n=2 sample.
4.2.4. Conclusion

In this chapter, BA$_2$SnI$_4$ and BA$_2$MASn$_2$I$_7$ single phase thin films were fabricated. The absorption spectra determine the bandgaps of them are 2.00 eV and 1.72 eV, indicating higher $n$ number of BA$_2$MA$_{n-1}$Sn$_n$I$_{3n+1}$ perovskite possess smaller bandgap which will be more suitable for solar cell absorber materials. Besides, TRPL and pump-probe spectroscopy measurements were proceeded to get a good understanding of the photo-generated carriers in the samples.

Further studies need to be accomplished for higher $n$ number tin perovskite to understand the inner nature of this materials. Since the stability of tin perovskite is much worse than lead one, even 2D tin perovskite will degrade in 1h, how to solve the stability issue is another great challenge for tin perovskite solar cells.

Figure 4.10. Pump-probe spectroscopy of the $n=1$ and $n=2$ samples. Differential transmission of probe pulse as a function of probe wavelength.
5. Summary and outlook

Solar energy is the origin energy needed for life on earth, coming from the photosynthesis of plants. Solar cells is the most direct way to this inexhaustible energy resource. The first and second generation solar cells have been industrialized for several decades. Although the cost of these solar cells have decreased more than 90%, researchers are still contributing to new, simply operated, highly efficient solar cells. Under this circumstance, perovskite comes into everyone’s view.

Perovskite have already been studied for 10 year. Too many achievement are accomplished by researchers throughout the world. Despite the more than 25% power conversion efficiency, stability is always the biggest issue as the NREL statistics denoted “not stabilized” for perovskite solar cell every year. Hence, people tried to solve or avoid this problem. 2D perovskite is one of the ideas for improving stability. However, the confinement-well structure is not preferable for charge transport unless the growth orientation can be regulated. In this thesis, we also provided a film deposition method to improve the growth orientation and phase distribution for quasi-2D perovskite. Although result shows the film is mixture of different phases, the PCE is increased beyond 14% and the film is much more stable than those 3D films when exposed to ambient environment.

Another problem is toxicity of lead, which is almost eternal harm when released to the natural environment. Then tin perovskite solar cells have sprung out with highest PCE 9% to date. 3D tin perovskite possess lower bandgap than lead one, leading to high $J_{SC}$ but low $V_{OC}$. However, the photophysics of tin perovskite materials is still not very clear. Considering 2D tin perovskite should be more stable, we tried to fabricate different 2D tin perovskite thin films. The n=1 and n=2 films were successfully fabricated. Using time-resolved photoluminescence and pump-probe spectroscopy, the carrier behaviors were monitored and determined excitons for n=1 and free carriers for n=2. But the stability of 2D tin perovskite is much worse, they will degrade in 1h.
For the future, stability is still the one need to be improved especially for tin perovskite. Also, understanding the natural photophysics of tin perovskite material is another topic. After revealing the photophysics of tin perovskite, it might be possible to improve the PCE to higher level.
Supporting information to chapter 3

Device fabrication of (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$ 3D perovskite

The device structure is the same with quasi-2D perovskite solar cells, and the substrates were prepared in the same way when fabricating 2D perovskite solar cells. The only difference is the perovskite deposition process.

The precursor solution is prepared by mixing stochiometric of FAI, PbI$_2$, MABr, PbBr$_2$ that is the molar ratio of 0.83:0.83:0.17:0.17 in DMF/DMSO 4/1 mixed solvent. The concentration of Pb$^{2+}$ is 1.3M. ITO substrates are washed by deionized water, actone and isopropanol subsequently. Then the substrates are treat by UV-ozone for 10 min followed by deposition of PEDOT:PSS or PCP-Na. Then the coated substrates are dried at 140°C for 20 min. The perovskite film was deposited using the anti-solvent technique, and spin-coated, firstly at a speed of 2000 rpm for 2s, secondly at a speed of 4000 rpm for 30s and 0.2mL chlorobenzene was added as anti-solvent at 13s. Then the thin film was annealed at 100 °C for 10 min. Then PCBM solution in chlorobenzene of 20 mg mL$^{-1}$ was deposited at a speed of 1000 rpm for 60 s. 20 nm of C$_{60}$, 6 nm BCP and 100 nm aluminum were sequentially evaporated on top of PCBM layer under vacuum degree <10$^{-7}$ mbar.

Device characterization method, XRD, UV-vis absorption, SEM images and photoluminescence were all the same with 2D perovskite solar cells.
Figure A1. Semilogarithmic plots of steady state spectra of thin films grown on different substrates, glass, glass/PEDOT:PSS, glass/PCP-Na measured from perovskite side (up) and glass side (down).
Figure A2. XRD patterns and film images on different HTL of fresh sample and 80 days in the air; (a, c) film on PEDOT: PSS, (b, d) film on PCP-Na.

Figure A3. J-V curves of the 3D perovskite solar cells with device structure as: ITO/HTL/(FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$/PC61BM/C60/BCP/Al.
Figure A4. UV-vis absorption (a), XRD patterns (b) and SEM images (c) for PEDOT: PSS sample and (d) for PCP-Na sample. The scale-bar of SEM images is 2 μm.
Figure A5. Steady state photoluminescence (a) and TRPL spectra for different samples (b) excited from perovskite side, (c) excited from glass side.
Figure A6. Modification of solvent for vacuum assisted deposition method, the DMF/DMSO 1/2 shows the best device performance. The details are in the table below.

<table>
<thead>
<tr>
<th></th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in DMF</td>
<td>12.06</td>
<td>1.053</td>
<td>0.47</td>
<td>5.91</td>
</tr>
<tr>
<td>4/1</td>
<td>13.33</td>
<td>0.995</td>
<td>0.67</td>
<td>8.89</td>
</tr>
<tr>
<td>1/1</td>
<td>16.48</td>
<td>1.026</td>
<td>0.44</td>
<td>7.42</td>
</tr>
<tr>
<td>1/2</td>
<td>18.66</td>
<td>1.055</td>
<td>0.53</td>
<td>10.45</td>
</tr>
<tr>
<td>DMSO</td>
<td>19.35</td>
<td>0.998</td>
<td>0.49</td>
<td>9.39</td>
</tr>
</tbody>
</table>

Figure A7. Molecule structure of PCP-Na
Supporting information to chapter 4

Figure B1. AFM images of n=1 (left) and n=2 (right) samples, the image size is 50×50 μm.

Figure B2. PL spectra of the 2 samples under excitation of continuous-wave laser (405 nm). The orange curves (610.6 nm) belong to n=1 sample and red curves (710.8 nm) belong to n=2 sample.
Figure B3. Steady state spectra of n=1 and n=2 samples corresponding to Figure 4.8, under excitation of 400 nm.

Figure B4. The XRD pattern of n=3 thin film that deposited by vacuum-assisted method with some modifications at last. It is very unstable so that the XRD pattern was measured for several times each time with fresh sample.
References


References


