Controlled Crystallization of CH₃NH₃PbI₃ Films for Perovskite Solar Cells by Various PbI₂(X) Complexes

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Key Words

lead iodide complex, controlled crystallization, perovskite solar cell

Abstract

Lead halide complexes are efficient precursors to obtain high quality perovskite films and high performance solar cells. However, how the lead halide complex affects the crystallization kinetics and thus the film quality of perovskite has not been systematically studied. Herein, two PbI₂(X) complexes with different coordination strength of ligand X in complexation with PbI₂ (PbI₂(DMF) and PbI₂(DMSO)) are synthesized. The correlation between the morphology, evolution of the perovskite formation, defects state, carrier lifetime and the subsequent photovoltaic performance are investigated in details *via* a two-step coating method with various PbI₂(X) complexes. We find that PbI₂(DMSO) derived perovskite film shows larger grains and vertically oriented grain boundaries as well as enhanced photoluminescence intensity and longer carrier lifetime. As a result, highly efficient inverted planar perovskite solar cells with a power conversion efficiency up to 17.0% are achieved from PbI₂(DMSO) complex under 1 sun illumination. This research could open up a new pathway to further improve the performance of perovskite solar cells through the control of perovskite crystallization kinetics by choosing proper PbI₂(X) complex precursors.

1. Introduction

Perovskite solar cells (PVSCs) are a promising next-generation technology to produce lightweight, low-cost and flexible solar cell panels [1-12]. Currently, power conversion efficiencies (PCE) over 20% have been achieved for PVSCs, highlighting the exceptional photovoltaic properties of perovskite materials [13, 14]. The photovoltaic properties of the perovskite films are greatly dependent on the film quality (such as coverage, morphology, grain size, grain boundary and so on) and thus the crystallization process of perovskite [15-19]. Accordingly, efforts have been made to examine the crystallization kinetics. Firstly, the basic film processing parameters have been investigated by tuning the annealing temperature [20-23] and time [21], spin-coating rate [24], the atmospheric conditions [25, 26], or by employing different solvents [22, 27, 28] or additives [29-33]. Secondly, the starting materials including inorganic lead source and organic ammonia salt have been found to determine the perovskite crystal growth kinetics, which in turn affects the film morphology and device performance [34-40]. Recently, a stable complex of methyl ammonia iodide or bromide (MAI(Br)), lead iodide or bromide (PbI(Br)₂) and dimethyl sulfoxide (DMSO) was demonstrated to be a decisive factor in retarding the rapid reaction between MAI(Br) and PbI(Br)₂ in a solvent engineering method, which enabled the formation of a highly uniform and dense film [41-43]. Very recently, high quality formamidinium lead iodide (FAPbI₃) perovskite film was fabricated *via* the reaction between FAI and PbI₂(DMSO), providing an effective protocol for fabricating efficient PVSCs [13]. Later, the self-assembly of PbI₂(DMSO) complex was demonstrated to benefit the formation of ultraflat and dense perovskite film [44]. Complexes of PbI₂ and hydrogen halide are another type of efficient precursors. PbI₂(HI) was used to fabricate highly uniform FAPbI₃ films through a one-step spin-coating process [45]. Whereas PbI₂(HCl) complex was demonstrated to accelerate the formation of a pinhole free planar MAPbI₃ perovskite film in both one-step and sequential deposition methods [46]. These results indicate that lead halide complexes are efficient precursors to obtain high quality perovskite films and thus high performance solar cells.

Nevertheless, how can the lead halide precursor affect the perovskite formation which further governs its crystallization kinetics to determine the overall film quality has not been systematically studied yet. To elucidate a clear correlation of this transformation could contribute to develop efficient solar cells derived from high quality perovskite absorber layers, herein, we explore the ease fabrication of crystalline perovskite films from two synthesized PbI₂(X) precursors, PbI₂(DMF) and PbI₂(DMSO) *via* a simple two-step coating method. Through studying the perovskite formation over different precursors, crystallization kinetics and film qualities, carrier lifetimes, defects etc., we reveal that the presence of solvent molecule as ligands in lead halide precursors, like DMF and DMSO, is effective to promote the conversion of precursors to perovskite for high-quality crystalline film formation. For instance, PbI₂(DMF) with the weak coordinating ligand (DMF) allow being quickly converted into MAPbI₃ perovskite even at room temperature, whereas strong ligand DMSO constituted PbI₂(DMSO) requires a thermal annealing to facilitate the conversion process. These indeed provide means to further control the

crystallization kinetics of perovskite film. The resultant perovskite film made from $\text{PbI}_2(\text{DMSO})$ precursor showed densely packed large grains, of which the grain boundaries are vertically aligned, leading to a much reduced film defects and longer carrier lifetime than those from $\text{PbI}_2(\text{DMF})$ and pristine PbI_2 . As a result, highly efficient planar PVSCs with a PCE up to 17.0% have been achieved from $\text{PbI}_2(\text{DMSO})$ precursor.

2. Experimental

2.1 Materials

Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. PC_{71}BM was purchased from American Dyes Source, Inc. $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was purchased from Shanghai Materwin New Materials Co. Ltd. Poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) was purchased from Xi'an Polymer Light Technology Corporation. $\text{PbI}_2(\text{DMSO})$ was synthesized according to the reported procedure [13]. In a typical synthetic process, PbI_2 (50 g) was dissolved in dimethylsulfoxide (DMSO, 150 mL) at 60 °C and then toluene (350 mL) was slowly added into the PbI_2 solution. The produced white precipitation was filtered and dried for 3 h at room temperature and then annealed for 24 h in vacuum oven at 60 °C. $\text{PbI}_2(\text{DMF})$ was synthesized in a similar procedure. PbI_2 (50 g) was dissolved in *N,N*-dimethylformamide (DMF, 150 mL) at 60 °C and then toluene (350 mL) was slowly added into the PbI_2 solution. The produced light yellow precipitation was filtered and dried for 3 h at room temperature. ZnO nanoparticles were synthesized by a sol-gel process using Zn acetate and tetramethylammonium hydroxide (TMAH) [47]. A stoichiometric amount of TMAH dissolved in ethanol (0.55 M) was added dropwise to Zn acetate dihydrate (0.1 M, 30 mL) dissolved in DMSO followed by stirring for an hour at room temperature. After washing at least two times in ethanol, ZnO nanoparticles were dispersed in pure ethanol with a concentration of $\sim 20 \text{ mg mL}^{-1}$.

2.2 Device fabrication and testing

Prior to fabrication, the substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min of ultraviolet ozone (UV-Ozone) treatment. Then a layer of poly(3,4-ethylene dioxathiophene) : polystyrenesulfonic acid (PEDOT: PSS) (Baytron P AI4083) with a thickness of 30 nm was spin-coated onto the cleaned ITO and baked in air at 140 °C for 15 min. The substrates were transferred to a glovebox. For PTAA deposition, 5 mg mL^{-1} PTAA was prepared in toluene doped with 0.5 wt% F4-TCNQ. A layer of 10-15 nm PTAA can be formed after spin-coating at 6000 rpm for 45 s. The films were annealed at 110 °C for 10 min. The spin-coating was processed in the glove-box.

$\text{PbI}_2(\text{X})$ was dissolved in DMF at a concentration of 1M under stirring at 70 °C. The solution was kept at 70 °C during the whole procedure. The solution was then spin coated on the as-prepared PEDOT:PSS film at 6000 rpm for 60 s. The films were dropped with a solution of MAI in 2-propanol (IPA) (50 mg mL^{-1}) and spin-coated at 6000 rpm for 60 s. Afterwards, the as prepared films were heated at different temperatures for different times. The prepared perovskite films were 280 nm which were measured by scanning electron microscopy (SEM). An electron transporting layer (ETL) was then deposited *via* spin coating a layer of [6,6]-phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM , 20 mg mL^{-1}) in chlorobenzene at 2000 rpm for 45 s with a thickness of 40 nm. A 40 nm hole-blocking layer was deposited *via* spin-coating ZnO nanoparticles in ethanol at 4000 rpm for 30 s on the top of PC_{71}BM layer. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4}$ Pa) to deposit a 100 nm thick Al cathode with a shadow mask defining an active device area of 5.5 mm^2 .

The *J-V* characteristics were measured with Keithley 2400 measurement source units with the devices maintained at room temperature in air. The photovoltaic response was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm^{-2} , and the light intensity was calibrated with a standard photovoltaic reference cell. The devices were stored in glove-box in dark overnight before measurement. The forward *J-V* scans were measured from -0.1 V to 1.2 V with a scan rate of 0.1 V s^{-1} and a voltage step of 0.005 V while the reverse *J-V* scans were measured from 1.2 V to -0.1 V with a scan rate of 0.1 V s^{-1} and a voltage step of 0.005 V. For MPP measurement, the interval is 1 s with a constant applied bias. The EQE spectrum was measured using a Stanford Research System Model SR830 Lock-in Amplifier unit coupled with a monochromator and a 500W xenon lamp, and a calibrated Si photodiode with known spectral response was used as a reference.

2.3 Materials and Films characterization

The thermogravimetric analysis (TGA) was conducted on Pyris 1 thermo gravimetric analyzer (Perkin-Elmer). The X-ray diffraction (XRD) patterns were recorded at a scan rate of 5 deg/min on the Rigaku D/max-2550PC X-ray diffractometer with $\text{Cu K}\alpha$ radiation (1.5406 nm). The UV-visible absorption spectra were measured on a Varian CARY100 Bio spectrophotometer. The SEM data were scanned by S-4800 (Hitachi) field-emission scanning electron microscope (FESEM). The PL spectra (both of steady state and transient spectra) are measured using an FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer.

3. Results and discussion

The $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$ were characterized by thermogravimetric analysis (TGA). The results are shown in **Figure 1(a)**. Both powders exhibited a single-step decomposition process with weight loss of 13.7% and 14.5% for $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$, respectively, indicating the constitution of stoichiometric ligand with PbI_2 . Due to the different coordinating strength of ligand X in complexation with PbI_2 , $\text{PbI}_2(\text{X})$ showed varied decomposition processes. $\text{PbI}_2(\text{DMF})$ exhibits a low decomposition temperature below 50 °C and completely

convert into PbI_2 at 100°C , while $\text{PbI}_2(\text{DMSO})$ starts decomposition at $\sim 100^\circ\text{C}$ and complete decomposition at 150°C . The X-ray diffraction (XRD) patterns of the $\text{PbI}_2(\text{X})$ complexes (Figure 1(b)) were collected, which show different diffraction peaks to that of pristine PbI_2 as expected. Interestingly, as-prepared $\text{PbI}_2(\text{X})$ films (Figure 1(c)) showed lower crystallinity than that of PbI_2 film, and especially, the $\text{PbI}_2(\text{DMSO})$ film exhibited lowest crystallinity. The less crystalline characteristics contributed to the weaker absorption and blue shifted absorbance of the $\text{PbI}_2(\text{X})$ complexes films shown in Figure 1(d).

We then prepared perovskite films by two-step coating method in **Figure 2(a)**. Figure 2(b) showed the photographs of the PbI_2 and $\text{PbI}_2(\text{X})$ films as well as the perovskite films from PbI_2 and $\text{PbI}_2(\text{X})$ complexes with or without annealing at 90°C for 15 min. The corresponding UV-Vis absorption spectra of the prepared perovskite films before and after annealing are shown in Figure 2(c). PbI_2 and $\text{PbI}_2(\text{X})$ films were all smooth and $\text{PbI}_2(\text{X})$ films were light yellow while pure PbI_2 was yellow. This is consistent with the absorption spectra showed in Figure 1(d). After spin-coating of MAI, the initial smooth planar PbI_2 film turned to be very rough due to the volume expansion during MAI intercalation [13] and this process showed no apparent colour change. **Figure 3** provides the XRD patterns of the perovskite films annealed at various temperatures with a fixed annealing time of 15 min fabricated from PbI_2 , $\text{PbI}_2(\text{DMF})$, and $\text{PbI}_2(\text{DMSO})$. The XRD patterns shown in **Figure 3(a)** indicated the partial converted MAPbI_3 and residual PbI_2 without annealing. The residual PbI_2 cannot be completely converted to MAPbI_3 with the increased annealing temperature as detected by XRD. Interestingly, we find that the presence of ligands in precursors allow accelerating the reaction between PbI_2 and MAI to form perovskite. The kinetics seems to be dependent on the interaction strength between PbI_2 and ligand. For $\text{PbI}_2(\text{DMF})$ with a weak ligand of DMF, tens of seconds at room temperature is effective and sufficient to transform $\text{PbI}_2(\text{DMF})$ into dense, homogeneous and mirror-like dark brown MAPbI_3 films, which was confirmed by XRD patterns in Figure 3(b). Increasing the annealing temperature can enhance the crystallinity of the perovskite films. For $\text{PbI}_2(\text{DMSO})$ with a strong ligand of DMSO, the initial light yellow film only turned to light brown after spin-coating of MAI. XRD pattern in Figure 3(c) implied the formation of intermediate phases with diffraction peaks at 9° , 21.7° and 25.2° in addition of those of MAPbI_3 . There has no residual PbI_2 been detected. After annealing at 70°C for 15 min, the intermediate phase was completely converted to MAPbI_3 . With the increase of the annealing temperature, we can observe the improvement of perovskite crystallinity in the film. Thus, we concluded that the presence of ligands, DMF and DMSO to PbI_2 can be effective means to obtain a fully converted, uniform and dense perovskite films with mirror-like surface. $\text{PbI}_2(\text{DMF})$ can quickly convert into MAPbI_3 at room temperature, while $\text{PbI}_2(\text{DMSO})$ consisting with DMSO ligand requires thermal annealing to complete the conversion process.

It is well known that for two-step sequential deposition, the film quality and morphology strongly depend on the processing of the initial PbI_2 film.[44, 48-50] Thus we investigated the surface and cross-sectional morphology of the perovskite films fabricated from various $\text{PbI}_2(\text{X})$ complexes by scanning electron microscopy (SEM) as shown in **Figure 4**. Film fabricated from PbI_2 showed many disordered structures on the surface with height up to hundreds of nanometers while those fabricated from $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$ exhibited smooth and compact surfaces. The grain size and boundaries were quite different shown in the cross-sectional SEM images. PbI_2 and $\text{PbI}_2(\text{DMF})$ converted films show disordered grains and grain boundaries (Figure 4 (d) and (e)) while large oriented grains with vertically aligned grain boundaries were clearly identified for $\text{PbI}_2(\text{DMSO})$ converted film (Figure 4 (f)). The differences of grain size and grain boundaries among the three films were attributed to the various reaction characteristics between $\text{PbI}_2(\text{X})$ and MAI. The nucleation density is much higher for the film processed from $\text{PbI}_2(\text{DMF})$, which tends to form a large amount of relatively small crystals and disordered grain boundaries. In contrast, for $\text{PbI}_2(\text{DMSO})$ which reacts with MAI in a slower way, the low nucleation density at initial stage leads to large grains at later crystallization process. We speculate that the orientation of the crystal grains and vertically aligned grain boundaries are attributed to the slow decomplexation process between DMSO and PbI_2 during annealing. The vertically aligned grain boundaries were demonstrated to be beneficial for the infiltration of transporting layer materials on top, suppressing the recombination loss and enhancing carrier collection [25].

High-quality perovskite films are associated with slower PL decay and high PL efficiency with reduced non-radiative recombination [51-53]. To investigate the quality of the perovskite films fabricated from PbI_2 , $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$, steady-state PL and time-resolved PL decay were conducted and the spectra were shown in **Figure 5**. The films were spin-coated on glass slides under identical conditions for other measurements. Steady-state PL spectra were shown in Figure 5(a). $\text{PbI}_2(\text{DMSO})$ converted perovskite film showed the highest PL intensity, about 30 times higher than the other two films, indicating the reduced non-radiative recombination usually caused by defect states or shallow trapping levels in the film. The time-resolved PL decays measured at the peak emission at 765 nm were presented in Figure 5(b). Consistent with the results of the steady-state PL spectra, PbI_2 converted perovskite film showed the shortest carrier lifetime with a time-constant of $\tau_e = 47$ ns, while longer lifetime with τ_e of 130 ns and 523 ns for $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$ converted films. These results indicated that by controlling the reaction between PbI_2 and MAI, the quality of perovskite film can be optimized and film with reduced non-radiative recombination and long carrier lifetime was demonstrated.

To find the correlation between $\text{PbI}_2(\text{X})$ under layers and the photovoltaic performance, inverted PVSCs were fabricated with a configuration of ITO/hole transporting layer (HTL, including PEDOT:PSS and PTAA)/perovskite/ $\text{PC}_{71}\text{BM}/\text{ZnO}$ NPs/Al shown in **Figure 6(a)**. The perovskite films were fabricated under identical conditions for other measurements mentioned above. The devices were firstly optimized by tuning annealing temperature, annealing time and MAI concentration for the processing of the perovskite layer on PEDOT:PSS. Figure 6(b), (c), (d) showed the current density- voltage (J - V) curves of the three types of devices with different annealing temperatures. In the case of $\text{PbI}_2(\text{DMF})$ (Figure 6c), the increase of annealing temperature from 70°C to 90°C leads to a slight increase in short-circuit current density (J_{sc}) from 12.9 mA cm^{-2} to 16.8 mA cm^{-2} and a slight decrease in open-circuit voltage (V_{oc}) from 1.03 V to 0.97 V. And the overall PCE values slightly change from 9.9% to 12.0%. In sharp contrast, the effects of annealing temperature on the device performance are quite obvious in the cases of PbI_2 and $\text{PbI}_2(\text{DMSO})$ (see Figure 6(b) and 6(d)). Increasing the annealing temperature from

70°C to 90°C can significantly improve the J_{sc} for these two types of devices. Further increase of the annealing temperature to 100°C does not improve the performance due to a slight decrease in V_{oc} . **Figure 7** presents the dependence of the device performance on the annealing time from $PbI_2(DMF)$ and $PbI_2(DMSO)$. It was observed that the PVSCs with $PbI_2(DMF)$ converted perovskite layer annealed at 70°C for 15 min showed high performance with a PCE up to 10% and kept almost constant with different annealing time in the range of 15 min to 120 min, while those with $PbI_2(DMSO)$ converted perovskite layer showed very poor performance after annealing at 70°C for 15 min. Increasing the annealing time significantly improved the J_{sc} and PCE. The similar results were also observed when fabricating the perovskite layer with various MAI concentrations (**Figure 8**). The device performance fabricated from $PbI_2(DMF)$ was insensitive to the variation of the concentration of MAI spin-coated on top in the range of 40 to 50 mg mL⁻¹. In sharp contrast, the MAI concentration significantly affected the performance of $PbI_2(DMSO)$ based PVSCs. Obviously, it is the fast reaction characteristics between $PbI_2(DMF)$ and MAI which renders the performance of PVSCs within small variation, independent of the annealing temperature, annealing time and MAI concentration, comparing to the slower reaction between PbI_2 or $PbI_2(DMSO)$ and MAI.

The J - V and external quantum efficiency (EQE) curves of the best devices with PEDOT:PSS as HTL were shown in **Figure 9(a)** and **(b)** respectively. The corresponding parameters were also summarized in **Table 1**. The J_{sc} increased from 13.9 to 16.8 and to 17.4 mA cm⁻², V_{oc} increased from 0.94 to 0.97 and to 1.03 V, and fill factor (FF) increased from 0.71 to 0.74 and to 0.76 when PbI_2 was changed to $PbI_2(DMF)$ and to $PbI_2(DMSO)$. The increase in J_{sc} and V_{oc} is consistent with the reduced defect states and longer PL carrier lifetime in the $PbI_2(DMSO)$ converted perovskite film. The increase in PL lifetime of charge carriers in **Figure 5(b)** can lead to better charge collection at two electrodes and less bulk recombination, and therefore it leads to a higher J_{sc} . As shown in **Figure 5(a)**, the PL intensity of the film formed from $PbI_2(DMSO)$ is approximately 30 times greater than that from PbI_2 film, indicating the loss due to the non-radiative recombination is about 30 times larger in PbI_2 system than in $PbI_2(DMSO)$. This excessive non-radiative recombination between the two systems can lead to an open-circuit voltage difference ΔV , and the voltage difference ΔV can be quantified *via* the PL intensity [54-56] as (Supporting Information for details):

$$\Delta V = V_{oc} - V'_{oc} = kT / q \ln(\frac{\phi_{PL}}{\phi'_{PL}}) \quad (1)$$

Here, V_{oc} and V'_{oc} is the actual open-circuit voltage for the two systems, k is the Boltzmann constant, T is the temperature, q is the elemental charge, ϕ_{PL} and ϕ'_{PL} are the PL intensities measured from the two systems, respectively. Applying Equation (1) to PbI_2 and $PbI_2(DMSO)$ systems, the calculated voltage difference ΔV is 0.09 V. This result has a good agreement with the experimentally measured open-circuit voltage difference between PbI_2 of 0.94 V and $PbI_2(DMSO)$ of 1.03 V. The observed large oriented-crystalline grains and vertically aligned grain boundaries in $PbI_2(DMSO)$ converted perovskite film contribute to reduce the amount of non-radiative recombination and further contribute to an improved V_{oc} and J_{sc} in photovoltaic performance.

Except for PEDOT:PSS, PTAA has been demonstrated to be another type of efficient HTL for inverted planar PVSCs [57, 58]. We also optimized the PVSCs fabricated from $PbI_2(DMSO)$ with PTAA as HTL in this work. Compared to PEDOT:PSS, the PVSCs with PTAA showed a higher PCE of 17.0% with a higher J_{sc} of 19.4 mA cm⁻², a higher V_{oc} of 1.10V and a higher FF of 0.80 (**Figure 10(a)**). The improved performance was attributed to the further improved quality of the perovskite polycrystalline thin films on PTAA compared to those fabricated on PEDOT:PSS [58]. The calculated J_{sc} from EQE in **Figure 10(b)** reached 18 mA cm⁻², which is close to the measured photocurrent. No apparent hysteresis was detected with forward and reverse scans. To further confirm the accuracy of our PCE, we performed the photocurrent density and PCE as a function of time at the maximum power point (0.92 V). As shown in **Figure 10(d)**, the photocurrent and PCE remained stable within 300 s, and a stable PCE over 16% was demonstrated. The efficiency histogram in **Figure 10(c)** showed >80% of the devices PCE higher than 14%.

4. Conclusions

In summary, the correlation between the morphology, evolution of the perovskite formation, carrier lifetimes and the subsequent photovoltaic performance with the reaction kinetics between $PbI_2(X)$ complex and MAI and thus the later crystallization kinetics were investigated in details. The ligands, DMF and DMSO, were demonstrated to be effective in promoting a completely converted uniform and dense perovskite films with smooth surface. $PbI_2(DMF)$ with DMF ligand can be converted to $MAPbI_3$ at room temperature within tens of seconds, leading to resultant $MAPbI_3$ film consisting of small grains and disordered grain boundaries with short carrier lifetime. While the strong bounded $PbI_2(DMSO)$ derived perovskite film showed dense film with large grains and vertically oriented grain boundaries as well as enhanced PL and longer carrier lifetime. As a result, highly efficient inverted planar PVSCs with PCE up to 17.0% were achieved from $PbI_2(DMSO)$ complex. This research could open up a new pathway to further improving the performance of PVSCs through the control of perovskite crystallization kinetics by choosing proper $PbI_2(X)$ complex precursors.

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Figure 1. (a) TGA curves of $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$. XRD patterns of PbI_2 and $\text{PbI}_2(\text{X})$ powders (b) and their as-prepared films (c). (d) Absorption spectra of PbI_2 and $\text{PbI}_2(\text{X})$ films.

Figure 2. (a) Schematic of the two-step coating method for perovskite film fabrication. (b) Reaction between PbI_2 or $PbI_2(X)$ complexes and MAI . (c) UV-vis absorption spectra of the as-cast and the annealed perovskite films.

Figure 3. XRD patterns of the perovskite films annealed at various temperatures with a fixed annealing time of 15 min fabricated from PbI₂ (a), PbI₂(DMF) (b), and PbI₂(DMSO) (c). The star marked peaks belong to ITO.

Figure 4. Top view (a, b, c) and cross-sectional (d, e, f) SEM images of the perovskite films fabricated from PbI_2 (a, d), $\text{PbI}_2(\text{DMF})$ (b, e), and $\text{PbI}_2(\text{DMSO})$ (c, f). Insets in (a, b, c) show the higher magnification images. All films were annealed at 90 °C for 15 min.

Figure 5. (a) UV-vis absorption and steady state photoluminescence (PL) spectra of the optimized perovskite films fabricated from PbI_2 , $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$, respectively. (b) Time-resolved PL measurements taken at the peak emission wavelength (765 nm) of the various perovskite films. A 5 mW picosecond pulsed diode laser at 638.8 nm excited on the surface side of films.

Figure 6. (a) Schematic of the inverted PVSCs. The dependence of the performance of PVSCs on the annealing temperature fabricated from PbI_2 (b), $\text{PbI}_2(\text{DMF})$ (c) and $\text{PbI}_2(\text{DMSO})$ (d), respectively.

Figure 7. The dependence of the performance of PVSCs on the annealing time fabricated from PbI₂(DMF) (a) and PbI₂(DMSO) (b).

Figure 8. The dependence of the performance of PVSCs on the MAI concentration fabricated from PbI₂(DMF) (a) and PbI₂(DMSO) (b).

Figure 9. $J-V$ (a) and EQE (b) curves of the optimized PVSCs fabricated from PbI_2 , $\text{PbI}_2(\text{DMF})$ and $\text{PbI}_2(\text{DMSO})$ respectively.

Table 1. Summary of the best device performance for the PVSCs fabricated from various $\text{PbI}_2(\text{X})$ with different HTLs.

$\text{PbI}_2(\text{X})$	HTL	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
PbI_2	PEDOT:PSS	0.94	13.9	0.71	9.3
$\text{PbI}_2(\text{DMF})$	PEDOT:PSS	0.97	16.8	0.74	12.0
$\text{PbI}_2(\text{DMSO})$	PEDOT:PSS	1.03	17.4	0.76	13.6
$\text{PbI}_2(\text{DMSO})$	PTAA	1.10	19.4	0.80	17.0

Figure 10. (a) J - V curves for the best PVSCs measured by forward and reverse scans, fabricated using PTAA as HTL. (b) EQE curve for the best PVSC device. (c) Efficiency histogram of the 48 devices. (d) Stabilized photocurrent measurement of the PVSCs with PTAA HTL under 1 sun illumination.