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Reproducible Planar Heterojunction Solar Cells Based on One-Step Solution-Processed Methylammonium Lead Halide Perovskites

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ABSTRACT:

Metal halide perovskites have been demonstrated as one of the most promising materials for low-cost and high-performance photovoltaic applications. However, due to the susceptible crystallization process of perovskite films on planar substrates and the high sensitivity of the physical and optoelectronic nature of the internal interfaces within the devices, researchers in different laboratories still experience poor reproducibility in fabricating efficient perovskite solar cells with planar heterojunction device structures. In this method paper, we present detailed information on the reagents, equipment, and procedures for the fabrication of planar perovskite solar cells in both “regular” n-i-p and “inverted” p-i-n architectures based on one-step solution-processed methylammonium lead triiodide (MAPbI₃) perovskite films. We discuss key parameters affecting the crystallization of perovskite and the device interfaces. This method paper will provide a guideline for the reproducible fabrication of planar heterojunction solar cells based on MAPbI₃ perovskite films. We believe that the shared experience on MA-based perovskite films and planar solar cells will be also useful for the optimization process of perovskites with varied compositions, and other emerging perovskite-based optoelectronic devices.

1. Introduction and Background

Metal halide perovskites have come under the spotlight due to their great success in photovoltaic and energy applications during the past few years.¹⁻⁶ As we show in Figure 1a, the perovskite materials have a general formula of AMX_3 , where A is an organic or alkali metal cation, M is a divalent metal cation, and X is a halogen anion that binds to both cations. Among these, methylammonium lead halide perovskites ($MAPbX_3$) are the most widely studied systems. Metal halide perovskites exhibit strong and easily tunable light absorption, excellent crystallinity, ambipolar charge transport, and long diffusion lengths for both electrons and holes.⁷⁻¹² Furthermore, they can be easily processed from solutions using low-cost raw materials. These unique features make perovskite solar cells promising as a new generation of photovoltaics. With the intense worldwide efforts on the materials, film deposition methods, device architectures and interface engineering, the power conversion efficiency of perovskite solar cells has rocketed from an initial value of 3.8% to the current record of 22.1% within few years, representing the fastest acceleration in efficiency in the history of photovoltaics.¹³⁻²⁰

Device structures of perovskite solar cells can be generally classified into two major categories: mesoporous and planar heterojunction structures. The initial studies on perovskite solar cells were based on the concept of dye-sensitized solar cells with perovskite nanocrystals as the sensitizers.^{13,21} By replacing the problematic liquid electrolyte with a solid-state p-type (2'-7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD) hole transporter, high-performance perovskite solar cells with increased

stability can be achieved.^{22,23} Most of the early studies on perovskite solar cells focused on devices with mesoporous titanium oxide (TiO_2) or aluminum oxide (Al_2O_3) scaffold. High-temperature derived compact TiO_2 layer and p-type spiro-OMeTAD were used as the electron-transporting layer (ETL) and hole-transporting layer (HTL), respectively (as shown in Figure 1b).^{19,22} Further investigation revealed that perovskite materials exhibit ambipolar charge transport and long charge diffusion lengths, justifying the observation of high charge collection efficiency and high efficiency in devices constructed with a simplified planar architecture.²⁴⁻²⁶

In a typical planar heterojunction solar cell, the perovskite light-harvesting layer is simply sandwiched between the ETL and HTL. Planar perovskite solar cells can be fabricated with the electron selective contact on the substrate side, or with the hole-selective contact on the substrate side. Throughout this manuscript, we will refer to cells with the electron-selective contact on the conducting oxide substrate side as n-i-p devices, and those inverted cells with the hole-selective contact on the substrate side as p-i-n cells. We give examples of such architectures in Figure 1c and 1d, respectively. Planar devices simplified the device architecture as well as the fabrication procedure of perovskite solar cells. In addition, extensive existing knowledge of hybrid interfaces in traditional thin film photovoltaics, such as copper indium gallium selenide (CIGS) and CdTe solar cells and especially in the research field of organic photovoltaics, can be utilized for interface optimization of these planar heterojunction perovskite solar cells. Moreover, the planar devices can be fabricated on large-area flexible substrates under low-temperature, which is desirable for the future

high-throughput industrial production process.^{27,28} The key feature of planar heterojunction, over its predecessor cell architectures incorporating a mesoporous scaffold, is that the light is absorbed and charge is generated in a solid non-porous perovskite thin film.

A key requirement in order to achieve efficient and reproducible planar heterojunction solar cell, is that the perovskite active layer should be uniform, continuous and “pin-hole free” to minimize “shunting” pathways. During the past few years, various deposition techniques including one-step coating, two-step deposition, vapor phase deposition and variations upon these methods have been developed to achieve a better control on the film quality of perovskites.^{14,15,22,25,29-33} Through optimizing composition of precursors and deposition processes, more and more groups are now able to deposit high-quality perovskite thin films on various planar substrates using simple one-step coating methods. However, due to the complex crystallization process, which is highly susceptible to environmental conditions, the film quality of perovskite on different planar substrates exhibits large difference under varied deposition conditions.³⁴⁻³⁶ In addition, the electronic and physical nature of the internal heterojunctions within the perovskite solar cells are also important and require careful control and optimization for efficient and reproducible devices. Presently, many researchers in different laboratories still experience poor reproducibility of devices when they follow the reported experimental procedural descriptions in the literature, which hinders and slows the global progress of perovskite solar cells research. Therefore, it is essential to have a detailed and high-reproducible methodology for the fabrication of efficient planar perovskite solar cells. If a standard and reproducible “control cell” existed, it would also make fair comparison

between different progress in different laboratories easier.

In this paper, we present detailed procedures for the fabrication of reproducible planar perovskite solar cells (n-i-p and p-i-n structures) based on one-step coating process. We use the benchmark $\text{MAPbI}_3(\text{Cl})$ perovskites fabricated from precursors composed of methylammonium iodide (MAI) and two different lead metal sources including lead chloride (PbCl_2) or lead acetate trihydrate ($\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$) as the example to discuss key parameters for the fabrication of high-quality perovskite films. In addition, we point out and discuss the key processes affecting the device performance of perovskite solar cells and our optimization strategy. We provide detailed information about the reagents, equipment and deposition parameters for PbCl_2 and $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ routes developed in our lab. We believe that this methods paper will be a useful guideline for the community to fabricate high-reproducible perovskite films and efficient planar solar cells based on one-step solution processed MAPbI_3 perovskites.

2. Conventional n-i-p perovskite solar cells fabricated from 3:1 MAI:PbCl₂ precursor

The first embodiments of perovskite employed as light harvester in solar cells were fabricated from a precursor composed of stoichiometric (1:1) molar ratio of lead iodide (PbI_2) and MAI in γ -butyrolactone (GBL) or *N,N*-dimethylformamide (DMF).¹³ We undertook a significant deviation from this, by processing the perovskite films from excess MAI in combination with PbCl_2 . This lead to a “mixed halide” perovskite, $\text{MAPbI}_{3-x}\text{Cl}_x$, with comparatively uniform surface morphology, and excellent crystallinity and electronic properties with long charge carrier lifetime and diffusion length.^{11,26,37} However, due to the slow crystallization with the

presence of excess hygroscopic MAI(Cl) component, the thin film growth is sensitive to the deposition conditions, especially the ambient humidity.³⁶ A certain amount of humidity actually appears to be beneficial. It has been reported that MAPbI_{3-x}Cl_x perovskite films deposited under controlled relative humidity (~30%) exhibited enhanced optoelectronic properties with significantly reduced carrier recombination as compared to the films grown in dry conditions.³⁸ Although the moisture can enhance the properties of perovskites, the relative humidity needs to be carefully controlled and high moisture results in poor surface morphology and fast decomposition of the perovskite films.³⁶ In order to achieve a better control of the film formation process, we carry out all the film deposition process for MAPbI_{3-x}Cl_x in a homemade dry-box (Figure S1 in the supporting information) with controlled humidity at ~15%.

2.1 Deposition of high-quality perovskite films from 3:1 MAI: PbCl₂ precursor

Even with spin-coating and curing in a controlled humidity atmosphere, we still observed incomplete coverage of perovskite films on planar substrates, which is non-ideal for planar devices. In this section, we will discuss two modified methods including “antisolvent-drenching” and “air-drying” assisted deposition for the fabrication of high-quality perovskites. The two modified deposition methods can significantly improve the surface coverage of perovskite films on planar substrates and result in improved device performance. The perovskite precursor solution was coated on a clean substrate by a consecutive two-step spin-coating process at 1200 and 2000 rounds per minute (r.p.m) for 25s and 12 s under low humidity (15–20%) condition. The acceleration is 500 and 1200 r.p.m/s

for the first and second step spin-coating program, respectively. For antisolvent-drenching, 350 μ l toluene (for a 2.8 $\times$ 2.8 cm substrate) was slowly (within $\sim$ 3 s) and continuously dispensed onto the pre-crystallized perovskite film, starting at 5 s after the spin program ramped to 2000 r.p.m. and proceeding for about 7s. The dispensing speed of the toluene needs to be carefully controlled and fast dispensing usually causes poor morphology of the obtained perovskite films.³⁹ It appears that the precise dispensing rate and time, and stage in spin-coating depends strongly on the perovskite precursor composition. For new compositions a broad trial of dispensing at different stages in spinning, and dispensing at different rates needs to be undertaken. For the air-drying method, the as-spun film (same speed and ramp rates as above) was immediately dried by holding the film in front of the dry air inlet to the dry-box with the air flow at 30-40 pound/ square inch (psi) for $\sim$ 30 s to accelerate the early stage nucleation process.³⁹ The drying time depends on the atmospheric condition in the dry-box and the distance between substrate and air outlet hole as well as the air flow rate. For our set-up, the optimized distance between the substrate and the dry air inlet hole of air blow is $\sim$ 10 cm. For best uniformity of drying, the substrate should be gently rocked by hand in small circles of $\sim$ 5 mm radius while being blown dry. After blowing, the color of film turns reddish brown while a dark brown color implies over-drying of the films. We give more detailed procedure on the modified deposition methods in the supporting information.

In Figure 2a-c, we show the scanning electron microscope (SEM) images of perovskite films on TiO₂ coated FTO substrates fabricated from three different deposition methods. The obtained perovskite films through antisolvent-drenching and air-drying assisted deposition

methods exhibit more uniform grains and almost no pinholes throughout the whole film. We systematically investigated the optical images at different stages of the crystallization (*i.e.* the as-spun films and films annealed at 60 °C for 5 min). Immediately after spin-coating, we observed the formation of yellow/transparent dendrites at room temperature for films deposited without any modification (Figure 2d). We assume that the yellow/clear dendrites are crystals of a chloride rich “precursor” phase.⁴⁰ The brown color region, which we infer to be iodide-rich perovskite crystals, appear surround the dendrites after thermally annealing at 60 °C for 5 min (Figure 2g).

For the films processed with antisolvent-drenching, both brown and transparent crystals appeared in the films just after spin-coating (Figure 2e). Interestingly, in this case, the crystal centers are surrounded by transparent domains. During the annealing at 60 °C for 5 min, the brown phase grows over the adjoining “chloride-rich” transparent phase giving rise to a large network of iodide rich perovskite crystals (Figure 2h). The air-drying method also produced both brown and transparent crystals just after spinning, but the density of brown crystals is lower than the toluene-assisted films (Figure 2f). During annealing (60 °C for 5 min), the behavior of crystal growth of both brown and transparent nucleation is similar to the toluene assisted film (Figure 2i). We conclude that the antisolvent-drenching and air-drying assisted methods are both helpful to produce more initial perovskite crystals, which could generate more continuous perovskite films after thermal annealing and polycrystalline film growth.

To demonstrate the degree to which the deposition methods influence the device performance, we fabricated conventional n-i-p planar heterojunction solar cells with the configuration of

glass/FTO/compact TiO₂/perovskite/spiro-OMeTAD/Ag. Without any modification for the deposition of perovskite films, the obtained solar cells in dry-box exhibit poor device performance with a maximum efficiency of 10.7%. Improved device performance with efficiencies of 15.9% and 17.6 % can be achieved for devices based on antisolvent-drenching and air-drying assisted deposition, respectively. We show the J-V curves for the champion devices with perovskite films deposited from three different deposition methods in Figure 3a, and more detailed device performance characteristics are shown in Figure S2 in the supporting information. We note that perovskite solar cells, especially those with conventional planar (n-i-p) structure comprising a compact TiO₂ electron selective contact, often exhibit anomalous hysteresis in the J-V curves. This results in a large difference between the power conversion efficiency estimated under different scan rates and in the forward and reverse scanning directions.⁴¹⁻⁴³ The hysteresis problem makes it difficult to obtain universal and unambiguous characterization and comparison of the obtained device performance. In our previous reports, we suggested that the steady-state power output (SPO) measured at the maximum power point under working conditions should be given as a critical indicator to fully evaluate the device performance.⁴¹ As we show in Figure 3b, our champion devices fabricated from antisolvent-drenching and air-drying assisted deposition also exhibit a higher SPO of ~14%. As a comparison, the SPO is ~7% for the champion device based on perovskite films derived from conventional deposition.

2.2 Interface modification with fullerene for n-i-p solar cells

The interfaces between perovskite films and n-type charge extraction layers have a significant

impact on the device hysteresis and long-term stability. As the most widely used ETL for perovskite solar cells, trap states and electronic defects in TiO_2 have been reported to be a major contributor to slow electron transfer from the perovskite to the TiO_2 at the interface, and poor ultraviolet light stability of devices.^{44,45} In addition, defects generated at the interface between the perovskite and the charge selective electrode could further contribute towards non-optimal operation. In previous reports from ourselves and others, we have shown that by modifying the n-type contact with a self-assembled fullerene monolayer, or thin films of fullerene (C_{60}) and fullerene derivatives,⁴⁶⁻⁵⁰ the electron extraction from perovskites to TiO_2 can be greatly improved, and the device hysteresis can be significantly reduced, in addition to improved device stability.^{46,48} However, to achieve reproducible devices comprising C_{60} electron extraction layer, several key parameters need to be carefully optimized.

A well-dissolved solution is critical for the deposition of uniform C_{60} films on the substrates. We prepare the C_{60} solution (~ 10 mg/ml) in the air with anhydrous 1,2-dichlorobenzene as the solvent. The solution is then kept under stirring at room temperature for over 6 hours in the glovebox to avoid the aggregation of C_{60} . Heating the solution at 60°C prior to use is helpful to the dissolving process but the solution needs to be cooled down to room temperature before spin-coating. As we just need a thin layer (several tens of nanometers) of the C_{60} film as the ETL, the surface roughness of substrate has a big influence on the morphology of final deposited film. We find that C_{60} layers deposited on rough FTO substrates (TEC 7, Pilkington) show non-uniform and discontinuous morphology. This can be simply identified by seeing

small aggregates on the surface directly after spin coating, and/or obvious discontinuous morphology after thermal annealing of perovskite films. By employing FTO substrates (TEC15, Pilkington) with a lower roughness and improving the surface wettability with oxygen plasma treatment right before perovskite film deposition, we can obtain uniform C_{60} layers with full coverage on the substrates.

In addition to uniformity, the thickness of the C_{60} film is closely associated with the electron-transporting properties and therefore needs to be carefully optimized. We show the J-V curves of champion devices with a range of C_{60} film thickness in Figure 3c, d. With a C_{60} film deposited at 1500 r.p.m (which gives an as deposited film thickness ~ 30 nm), we observe a significantly improved short-circuit current (J_{sc}) as well as fill factor (FF), in comparison to the devices with solely TiO_2 electron extraction layers. We were able to obtain a champion efficiency of 17.9% with the highest SPO of 16.4%. A higher spin-coating speed (above 2000 r.p.m) always generates a discontinuous C_{60} layer on the substrate, which results in exaggerated hysteresis in the J-V curves and lower overall efficiency.

3. Lead acetate trihydrate precursor for conventional planar solar cells

As shown in previous sections and many other reports, without additional treatment, it is still challenging to obtain pinhole-free perovskite thin films by one-step solution processing based on traditional lead halide precursor solutions ($PbCl_2$ or PbI_2 mixed with MAI in DMF). Over the last two years we have introduced a route to fabricate $MAPbI_3$ perovskite films with non-halide lead precursors, and specifically lead acetate trihydrate ($Pb(Ac)_2 \cdot 3H_2O$), as the starting material in the precursor.³³ We systematically investigated lead salts with varied

anions (PbCl_2 , PbI_2 , $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$) and found that the anions in the perovskite solution have an enormous influence upon perovskite crystallization kinetics and film formation.⁵¹ By using $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ as the starting material in the precursor, the crystal growth of perovskites was speeded up significantly, enabling formation of ultra-smooth and pinhole-free perovskite films through a simple one-step solution coating after ~ 5 min thermal annealing. In this section, we will discuss the effect of different lead precursors, mainly focusing on lead acetate trihydrate, on perovskite crystallization kinetics, thin film morphology and the obtained device performance.

3.1 High-quality perovskite films deposited from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor

The transition of perovskite precursors into thin films typically involves the evaporation of solvent, sublimation/evaporation of the by-products (e.g. $\text{CH}_3\text{NH}_3\text{X}$, $\text{X} = \text{Cl, I, Ac}$), crystal nucleation and growth, *etc.*, which can be described as follows:

We employed in-situ wide-angle X-ray scattering (WAXS) to probe the evolution of the perovskite crystal formation using precursors with different lead salts as the starting materials, as shown in Figure 4a-c. Crystallization kinetics of the systems are assessed by tracking key “precursor state” peaks (blue stick markers on the bottom-most) and defining t_{end} as the time when all “precursor state” peaks are gone, representing complete perovskite transformation. We clearly observed that the required annealing time, as indicated by the t_{end} , is much shorter for perovskites made from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ route than PbCl_2 and PbI_2 routes. We correlate this observation to the ease with which the by-product can be removed during perovskite film

formation. This was further confirmed by thermal gravimetric analysis (TGA) characterizations for the by-products of $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{I}, \text{Ac}$). The initial decomposition temperatures (defined by T at 95% weight) show a trend of $T_{\text{CH}_3\text{NH}_3\text{Ac}}$ (97.4 °C) $\ll$ $T_{\text{CH}_3\text{NH}_3\text{Cl}}$ (226.7 °C) $<$ $T_{\text{CH}_3\text{NH}_3\text{I}}$ (245.0 °C), clearly demonstrating that the $\text{CH}_3\text{NH}_3\text{Ac}$ is thermally unstable and much easier to be removed than $\text{CH}_3\text{NH}_3\text{Cl}$ and $\text{CH}_3\text{NH}_3\text{I}$.³³ Thus, at the same annealing temperature, the growth rate is much higher for the films processed from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, which tends to form a large amount of relatively smaller crystals on a short time scale. For more details of the effect of anions on perovskite crystallization kinetics, we refer the readers to a recent work done by Moore and co-workers.⁵¹

Here, we illustrate the surface property of perovskite films deposited from different lead precursors on compact TiO_2 coated FTO substrates. These films are made by simple spin-coating (without any air-drying and antisolvent drenching) in a nitrogen filled glove box. As can be seen from the top-view SEM images, the perovskite films made from PbCl_2 (Figure 4d) and PbI_2 (Figure 4e) routes are non-continuous with pinholes whereas thin films deposited from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ (Figure 4f) route exhibit a full coverage on the substrates without any pinhole. As shown in the insets of closer observations, the PbCl_2 precursor leads to crystalline platelets to be in tens of micrometer length scale whereas for the PbI_2 route and the $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ route, crystal grains are around a few hundred nm to one micrometer in size. In addition, from the cross-section SEM images, we observe that $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ route achieves much smoother perovskite thin films than that made from PbCl_2 and PbI_2 routes. Our previous atomic force microscopy (AFM) study of perovskite thin films confirmed a root mean squared

(RMS) roughness of 12.3 nm for $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ route on the scale of $15\ \mu\text{m} \times 15\ \mu\text{m}$, as opposed to 62.4 and 52.2 nm for PbCl_2 and PbI_2 routes, respectively.³³

3.2 Conventional planar solar cells fabricate from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor

We compare the devices with perovskite films deposited from different lead sources described above in conventional n-i-p planar heterojunction solar cells. To achieve the best device performance, we optimized the annealing temperature and annealing time for each particular route and all the deposition process of perovskite precursors were carried out in the glovebox. Note that, to keep the atmosphere clean and constant for each batch of devices, we purge the glovebox before we start a new spin-coating process. The total purging time depends on the spin-coating time used by the former user, which is usually 10 min purging after 20 min spin-coating. The optimized conditions (annealing temperature/time) are 100 °C/2h, 150 °C /40min, and 100 °C /5min for PbCl_2 , PbI_2 and $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor, respectively. The average power conversion efficiency with optimized conditions are 12.0, 9.3 and 14.0% based on perovskites deposited from PbCl_2 , PbI_2 and $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ routes, respectively. We also found that the SPO of the champion cell fabricated from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor was improved to ~13.4%, which is 88% of the highest scanned efficiency. As a comparison, the SPO is around 74 and 64% of the scanned efficiency for PbCl_2 and PbI_2 , respectively. Therefore, $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor enables not only much faster and more uniform crystallization but also improved device performance over the other two routes and good reproducibility of the results, as indicated by the smaller standard deviation of solar cell performance parameters. The major reason that leads to improved device efficiency via

Pb(Ac)₂·3H₂O route is due to the enhancement of open-circuit voltage (V_{oc}), and the trend of average V_{oc} as PbI₂ (0.85 V) ~ PbCl₂ (0.88V) < Pb(Ac)₂·3H₂O (0.99V). This can be attributed to a reduction in the contact area between p-type spiro-OMeTAD and n-type TiO₂ compact layer, originating from the non-continuous perovskite films made from PbCl₂ and PbI₂ routes. These pin-holes in the perovskite films lead to reduced shunt resistance in the devices, which we term “shunting”.

As a follow-up work, we further found that the film quality made from Pb(Ac)₂·3H₂O route can be significantly enhanced by adding an additive, hypophosphorous acid (HPA), in the precursor solution. HPA is commonly added as a stabilizer in commercial hydroiodic acid, which is one of the starting materials to synthesize MAI but is purified by recrystallization of the final product. During the optimization of Pb(Ac)₂·3H₂O routes, we noticed that our best solar cell results were always obtained when the MAI was dried but not purified via recrystallization following the synthesis. We realized that some ‘impurity’ left in the as-synthesized MAI should have a beneficial influence on the perovskite film formation. We found that the HPA additive in Pb(Ac)₂·3H₂O precursor has no effect on the pin-hole free nature but significantly improved the optoelectronic properties of the perovskite films via reducing the defect densities, estimated from 1.58×10^{16} to $3.25 \times 10^{15} \text{ cm}^{-3}$, by a factor of around 5. During the optimization process of our solar cell devices, we noticed that the film quality and device performance were significantly influenced by the precursor and processing conditions. The precursor with 30 wt% concentration (calculated based on the sum of chemicals in the solution) gave the best device performance. With higher precursor

concentration (~40 wt%), the obtained films became hazy and non-uniform, resulting in significantly decreased device performance.³² This may result from the drying process of precursor solution on substrates during the spincoating, which we will discuss in the next section. The HPA concentration in the precursor also need to be optimized and we found that the molar ratio of 7.5% for HPA/ $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ (3 μl in 1 ml 30 wt% precursor) gave the best device performance. Moreover, we need to mention that a drying process ~10 min (drying time depends on the atmosphere in the glovebox) after spin-coating is necessary to get reproducible mirror-like perovskite films and efficient devices on TiO_2 substrates. In addition, we found best device results when we use the solution immediately after adding the HPA in the precursor. By optimizing the composition of precursors and the film deposition process, we could obtain devices with an average efficiency over 15% with a small standard deviation of solar cell performance parameters, using the commercially available MAI.

4. Inverted planar solar cells fabricated from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ route

It has been demonstrated the hysteresis in the current-voltage characteristics of perovskite solar cells can be successfully suppressed or even eliminated with inverted p-i-n planar device structure by selecting proper fullerene-based electron transport materials on top of perovskite films.^{31,52} In a typical inverted device structure, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) are commonly used as p-type and n-type charge transport layers. Previous reports have pointed out that the PCBM layer can efficiently passivate the trap states in the perovskite films and reduce the charge recombination at grain

boundaries as well as the electrode interface, eliminating hysteresis and leading to improved device performance.⁵² Due to its low conductivity, the thickness of PCBM layer should be thin enough to act as efficient ETL and minimize the series resistance. However, a thin PCBM layer usually causes incomplete surface coverage on rough perovskite films, resulting in large leakage current and decreased device performance.⁵³ Perovskite films deposited from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor exhibit ultra-smooth and pin-hole free film properties, which makes this route ideal for the fabrication of efficient inverted planar perovskite solar cells. In this section, we will provide detailed recipe for the fabrication of reproducible inverted planar devices based on $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor, and then follow on to discuss the influence of hydration of $\text{Pb}(\text{Ac})_2$.

4.1 Key parameters for reproducible inverted planar solar cells

4.1.1 Deposition of high-quality perovskite films on PEDOT:PSS substrates

For inverted planar p-i-n solar cells, we carried out all the optimization on PEDOT:PSS coated indium tin oxide (ITO) substrates. Figure 5a shows the typical inverted planar device structure, in which solution processed bathocuproine (BCP) is used as an interface modifier, to improve the electronic contact between the fullerene and the metal electrode.⁵⁴ Except the deposition and thermal annealing (150 °C for 10 min) of PEDOT:PSS, all other processes were carried out in an N_2 -filled glovebox (~10 ppm O_2 , <1 ppm H_2O). As we clarified before, HPA with re-optimized concentration (~4.5 μl HPA in 1 ml precursor solution) is used as an additive in the precursor.

During the optimization of inverted solar cells, we noticed that the final device performance is

extremely sensitive to spin-coating conditions. The evaporation speed of organic solvent during the spin-coating process plays a critical role to obtain high-quality perovskite films and high-performance inverted planar solar cells based on $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ route. As we show in Figure 5b, we found that a lower acceleration of the spin-coating process is more favorable to get higher average device efficiency, and $\sim 8\text{s}$ is the most suitable ramp time for the spin-coating speed of 2000 r.p.m. In addition, due to the existence of a top hole in the lid of our spin-coater (as shown in Figure S3a in the supporting information), intense N_2 flow generated during the spin-coating process could speed up the solvent evaporation and affect the formation of perovskite films. A similar phenomenon has also been reported by Huang et al., who developed a gas assisted deposition method for the fabrication of smooth MAPbI_3 films employing precursor composed of MAI and PbI_2 with 1:1 molar ratio.⁵⁵ However, for the $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor, although the obtained perovskite film was dense and uniform with the N_2 flow from the top hole, the device performance is poor due to the fast drying of the precursor (Figure S3b in the supporting information). Based on this understanding, we have compared two kinds of different spin-coating processes with the lid open and totally closed (top hole blocked) to slow down the solvent evaporation. Inverted planar solar cells fabricated under these two spin-coating processes exhibited obviously improved device performance because of the slower solvent evaporation speed. We noted that under the lid-closed condition, the existed DMF vapor in the chamber of spin-coater is more helpful on improving the device reproducibility due to the further suppressed solvent evaporation. Interestingly, by properly controlling the solvent evaporation process, we were able to obtain

high-quality thin films on PEDOT:PSS using precursors with higher concentration and lower spin-coating speed (Figure 5c), which generates hazy films in our previous experiments with common spin-coating process. We also noticed that, for the processing of high-concentration precursors, slowing down the drying process after spin-coating was no longer helpful but detrimental to the obtained perovskite films. We need to put the samples on the preheated hot plate (100 °C) immediately after the spin-coating; otherwise the films become hazy even after ~1min drying. By using a precursor solution with 0.8 M $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ and 2.4 M MAI (solids in total ~42 wt%) in DMF under the optimized spin-coating, drying and annealing process, we can obtain highly reproducible p-i-n planar devices with efficiency over 15%. In addition, we observed negligible hysteresis of the devices (Figure 5d).

4.1.2 Interface engineering for inverted planar solar cells

The interfaces, especially the cathode interface is crucial to get efficient and reproducible p-i-n planar perovskite solar cells. As the most widely used ETL in inverted structure, it is convenient to deposit PCBM layer with optimal coverage and thickness through tuning the solution concentration and the spin-coating speed. In addition to the thickness and coverage, it has been demonstrated that post-treatment of PCBM layer is essential to get efficient inverted devices. It has been reported that, due to the thermal instability of MAPbI_3 perovskites, any post-annealing process at a temperature above 100 °C was possible to cause perovskite decomposition and result in a decrease of the charge carrier diffusion lengths.^{53,56} And hence, in most of the previous studies on inverted p-i-n perovskite solar cells, researchers tried to avoid thermal treatment after the deposition of perovskite films. However, Huang and

co-workers have proposed that the infiltration of the PCBM molecule into the perovskite layer under thermal annealing at 100 °C can significantly improve the device performance.⁵² The authors attributed the device improvement to more efficient passivation by PCBM upon the large density of traps in perovskite films during the thermal annealing. With enhanced crystallinity and reduced energetic disorder of PCBM by solvent annealing (during the thermal annealing) treatment, the device performance can be further improved.⁵⁷ These results indicate that the interface between the perovskite and the electron transport layer need to be carefully optimized.

During the optimization of inverted device structures based on $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor, we also noticed that mild thermal annealing process of PCBM is helpful to obtain a better electron transport interface. For our inverted devices, a post-annealing treatment at 100 °C after PCBM deposition significantly improved the device performance. Figure S4 shows the influence of thermal annealing treatment of PCBM layer on the device performance. We found that without post-annealing on PCBM, J-V curves of the obtained devices exhibit low device efficiency with low J_{sc} and FF, suggesting poor charge extraction interface. The highest average device efficiency could be obtained after 10 min thermal annealing treatment at 100 °C, while prolonged thermal annealing time resulted in decreased device performance, which can be attributed to the decomposition of the instable perovskite films.

The sensitive interface between PCBM and the metal electrode also needs to be further modified to obtain reproducible inverted planar devices and to avoid the quick degradation of devices after air exposure. It has been demonstrated that the oxygen and water in the air will

be adsorbed on the surface of PCBM and resulting in rapid degradation of the PCBM/metal contact. Introducing a thin protective layer such as BCP or n-type metal oxide (ZnO, TiO₂ and Cr₂O₃) on top of PCBM can greatly improve the device reproducibility and stability.^{28,35,53,58} In our devices, we employed a solution-processed BCP thin layer to achieve a better cathode interface. Isopropanol (IPA), which has negligible influence upon the perovskite films, was chosen as the solvent and the concentration of BCP solution was optimized and fixed at ~0.5 mg/ml.⁵⁴ Due to the poor solubility of BCP in IPA, heating (~ 100 °C for 1 h) is necessary to get a completely dissolved solution. We note that although BCP results in efficient and reproducible devices, it is likely to introduce long-term stability issues.

4.2 Controllable water content in Pb(Ac)₂ for reproducible devices

4.2.1 Dehydration of lead acetate trihydrate

Due to the easy-weathering property of Pb(Ac)₂·3H₂O, the varied hydration water over time makes it difficult to precisely control the water content and stoichiometric ratio of chemicals in the precursor. For example, we compared the as received Pb(Ac)₂·3H₂O materials in different bottles with the same product no. from Sigma-Aldrich and found obvious difference in the obtained devices even under the same recipe (Figure S5a in the supporting information). Even in the same bottle, the materials exhibit different crystals property with large crystals and small grain powders coexisting (Figure 5b in the supporting information). To achieve a better control of the precursors, totally dehydrated Pb(Ac)₂ synthesized from physical and chemical methods have been used in previous research works on Pb(Ac)₂ routes.⁵⁹⁻⁶² As reported, dehydrated Pb(Ac)₂ could be obtained by drying the Pb(Ac)₂·3H₂O under nitrogen

or vacuum at a temperature higher than its melting point (75 °C). The dehydration can also be carried out by dissolving the $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ in methoxyethanol or methoxyethanol-xylene mixture and distilling the water repeatedly at high temperature (above 90 °C).⁶³ However, the incomplete elimination of water and the by-products (e.g. oxoproducts) due to the decomposition of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ under high temperature will introduce more complicated and uncertain factors for the perovskite precursors. To date, the reaction of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ with acetic anhydride is the most efficient dehydration technique and has been used in several recent reports to synthesize dehydrated $\text{Pb}(\text{Ac})_2$. The reaction of the dehydration process can be described as follows:

We provide detailed processes for the dehydration of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ in the procedure section of supporting information. According to the characterization results from Fourier Transform Infrared Spectroscopy (FTIR) (Figure 6a), there is almost no obvious broad peak corresponding to the hydroxyl groups in the dehydrated samples, suggesting efficient elimination of the hydration water after the reaction. Moreover, there is no side reaction during the dehydration process based on acetic anhydride route and this can guarantee high purity of the final obtained dehydrated products.

4.2.2 Optimal water content in the precursor for reproducible inverted devices

We fabricated inverted p-i-n planar devices by employing the precursors composed of MAI and $\text{Pb}(\text{Ac})_2/\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$. However, we observed no major difference upon the device performance for devices fabricated from $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ and dehydrated $\text{Pb}(\text{Ac})_2$ starting

materials. We estimate that in 1 ml precursor composed of 0.8 M $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, the total water content in the solution is around 45.5 $\mu\text{l}/\text{ml}$ (2.25 μl from the HPA additive). We believe that the water molecule in the precursor has a significant influence on the crystallization process of perovskites, which has been also demonstrated by several other reports.⁶⁴⁻⁶⁷ To further quantify the optimal water content and achieve a better control of the devices fabricated from $\text{Pb}(\text{Ac})_2$ route, we systemically investigated the influence of water content on the device performance. In Figure 6b, we show the device performance parameters from the same batch solar cells based on perovskite films deposited from precursor with a range of water content. We observed a clear trend of enhancement on the device performance with the introduction of deionized water range from 0 to 20 μl in 1 ml perovskite precursor solution, while further increased water content resulted in decreased device efficiency. With the incorporation of water in the precursor, all device parameters including the J_{SC} , V_{OC} and FF increased and we achieved a champion efficiency of 17.1% and an average efficiency over 16% with optimal water content of 20 μl (Figure 6c). Note that there was almost no hysteresis in the J-V curves of the obtained inverted devices. As we show in Figure 6d, the SPO (16.9%) was almost the same as the highest scanned efficiency of our champion device.

5. Conclusion and outlook

In this methods paper, we have presented detailed recipes for the fabrication of high-efficiency and reproducible planar heterojunction (n-i-p and p-i-n structures) perovskite solar cells based on one-step solution-processed MAPbI_3 perovskites deposited from PbCl_2 and $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursors. Importantly, we have highlighted some of the peculiar

influencing factors, including processing methodology and solution compositions, which have to be considered and optimized when fabricating the solar cells. In addition, due to the excellent charge transport and light emission properties of metal halide perovskites, other optoelectronic applications, such as photodetectors, light-emitting diodes (LEDs), lasers, etc. also experienced fast development recently. We hope that our detailed methodology for perovskite films and planar solar cells provided in this paper is also helpful for these emerging applications.

ASSOCIATED CONTENT

Supporting information

Detailed information of all reagents we use for the perovskite precursor and solar cells, all procedure including the preparation of substrates, preparation and deposition of perovskite precursors, bottom and top charge transport layers, deposition of electrodes and solar cell characterization, key parameters optimized for perovskite film deposition, photograph of the drybox and spincoater in our lab, more detailed characterization results of devices fabricated from PbCl_2 and $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ precursor.

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Figure 1: (a) The crystal structure of typical AMX_3 metal halide perovskite. The schematic diagram of perovskite solar cells with mesoporous structure (b), conventional n-i-p (c) and inverted p-i-n planar structure (d).

Figure 2: SEM images of perovskite films deposited from different methods: conventional deposition (a), antisolvent-drenching (b) and air-drying assisted deposition (c); optical micrographs taken during the in situ thermal annealing of perovskite films from different deposition processes after spin-coating and anneal at 60 °C for 5 min: conventional deposition (d, g), antisolvent-drenching (e, h) and air-drying assisted deposition (f, i).

Figure 3: J-V curves (a) and stabilized power output (b) for perovskite solar cells in which the perovskite layer was deposited from conventional deposition, antisolvent-drenching and air-drying assisted deposition; J-V characteristics (c) and stabilized power output (d) of optimized perovskite solar cells with C_{60} layers deposited at different spin-coating speed.

Figure 4: Azimuthally integrated 1D plots at several key time points (t , in minutes) of annealing for films made from (a) PbCl_2 , (b) PbI_2 , and (c) $\text{Pb(Ac)}_2 \cdot 3\text{H}_2\text{O}$ routes; SEM images of perovskite films deposited compact TiO_2 coated FTO substrates from three different lead sources PbCl_2 (d), PbI_2 (e) and $\text{Pb(Ac)}_2 \cdot 3\text{H}_2\text{O}$ (f), (insets show images with higher resolution). (Reproduced with permission.³³ Copyright 2015, Nature Publishing Group.)

Figure 5. (a) Illustration of our inverted p-i-n planar device structure. Device efficiency fabricated from 40wt% precursor with different ramp time (b) and different spin-coating speed (c). (d) Device performance of optimized inverted planar solar cell based on perovskite film deposited from Pb(Ac)₂·3H₂O precursors. J-V curves measured from forward bias (FB) (black dash line) to short-circuit (SC) and back again (red solid line) exhibit no observable hysteresis.

Figure 6. (a) FTIR spectra of the lead acetate trihydrate and dehydrated lead acetate synthesized from the reaction with acetic anhydride; (b) Efficiency of devices derived from precursor composed of $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, dehydrated $\text{Pb}(\text{Ac})_2$ with different amount of water. J-V curves (FB-SC black dash line, SC-FB red solid line) (c) and stabilized power output efficiency and photocurrent (at 0.86V) for the champion device fabricated from dehydrated $\text{Pb}(\text{Ac})_2$ with optimized water content.

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