

A Smooth $\text{CH}_3\text{NH}_3\text{PbI}_3$ Film via a New Approach for Forming the PbI_2 Nanostructure Together with Strategically High $\text{CH}_3\text{NH}_3\text{I}$ Concentration for High Efficient Planar-Heterojunction Solar Cells

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The photovoltaic performance of perovskite solar cells (PVSCs) is extremely dependent on the morphology and crystallization of the perovskite film, which is affected by the deposition method. In this work, a new approach is demonstrated for forming the PbI_2 nanostructure and the use of high $\text{CH}_3\text{NH}_3\text{I}$ concentration which are adopted to form high-quality (smooth and PbI_2 residue-free) perovskite film with better photovoltaic performances. On the one hand, self-assembled porous PbI_2 is formed by incorporating small amount of rationally chosen additives into the PbI_2 precursor solutions, which significantly facilitate the conversion of perovskite without any PbI_2 residue. On the other hand, by employing a relatively high $\text{CH}_3\text{NH}_3\text{I}$ concentration, a firmly crystallized and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is formed. As a result, a promising power conversion efficiency of 16.21% is achieved in planar-heterojunction PVSCs. Furthermore, it is experimentally demonstrated that the PbI_2 residue in perovskite film has a negative effect on the long-term stability of devices.

to 20.1%^[2,3] within five years. The theoretical limit of the PVSC efficiency has been estimated to be 31%, which is very close to the Shockley–Queisser limit (33%).^[4] Perovskite deposition is crucial to produce high-efficiency PVSCs. Generally, there are mainly three methods, including one-step solution spin-coating, vacuum vapor deposition, and two-step sequential deposition to prepare the hybrid perovskite film.^[5–13] Two-step sequential deposition has recently been reported,^[7] which provides an efficient and low-cost route to high-performance PVSCs.

In a typical two-step sequential deposition of perovskites such as MAPbI_3 ($\text{MA} = \text{CH}_3\text{NH}_3^+$), PbI_2 is first deposited on the substrate (mesoporous or planar scaffold) by spin-coating or vacuum evaporation, subsequently transformed into the perovskite (MAPbI_3) by exposing it to an

anhydrous isopropanol (IPA) solution of MAI. For the two-step sequential deposition, the conversion and film morphology of the final perovskite film strongly depend on the initial PbI_2 film during the first step of the process.^[7,14,15] Conventionally, PbI_2 from dimethyl formamide (DMF) solution tends to form a layered and dense crystalline film on a flat substrate. However, the complete conversion of PbI_2 to perovskite on exposure to the MAI solution usually requires several hours.^[7] However, this long reaction time in MAI solution could lead to the dissolution of perovskite films. These drawbacks make it difficult to fabricate planar-structured PVSCs by sequential deposition method.

Several strategies have been developed to solve this problem, including using elevated reaction temperature,^[16,17] controlling the crystallization of PbI_2 by employing strong coordinative solvent of dimethyl sulfoxide^[14] or using MAI vapor instead of MAI solution.^[18] Recently, a cloudy PbI_2 film prepared by gas-quenching treatment has been reported by Vak and co-workers,^[19] which also enhances the conversion of PbI_2 to perovskites in the process of roll-to-roll fabrication. Zhao & Zhu^[14] developed a new three-step sequential deposition process, where a unstable $\text{PbI}_2 \cdot \text{CH}_3\text{NH}_3\text{Cl}$ precursor film is first deposited on the mesoporous TiO_2 substrate and followed by thermal decomposition to form PbI_2 film; the PbI_2 film

1. Introduction

Organometallic halide perovskite materials have become a promising class of photovoltaic light absorbers for high-efficiency, low-cost thin-film solar cells.^[1] The efficiency of perovskite solar cells (PVSCs) has increased from an initial 3.8%

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can be rapidly converted into MAPbI₃. Dai and co-workers^[20] developed a layer-by-layer approach to form CH₃NH₃PbI_{3-x}Cl_x perovskite, namely by depositing a thin PbCl₂ through vacuum evaporation, followed by exposure into MAI solution to form perovskite. To the best of our knowledge, a simple and effective method for fast conversion of PbI₂ film into perovskite on flat substrate via two-step sequential deposition process at room temperature has not been reported. Although many groups have demonstrated that the PbI₂ residue in perovskite film has a positive effect on the efficiency of PVSCs,^[21–23] the effect of PbI₂ residue on the long-term stability of PVSCs is unclear.

In this work, we develop a very simple and effective method to readily form high-quality perovskite without PbI₂ residue via two-step sequential deposition at room temperature. We demonstrate that a reasonable design of nanostructure of both PbI₂ and MAPbI₃ is an important route to fabricate high efficient PVSCs. On one hand, we facilitate the conversion rate of PbI₂ by incorporating additive (4-*tert*-butylpyridine, TBP) into its precursor solution via self-assembly method to form a porous PbI₂ film (SAP-PbI₂). On the other hand, properly increasing the concentrations of MAI in the second step, a smooth and continuous perovskite thin films can be obtained. Compare to the conventional PbI₂ film (C-PbI₂), the devices fabricated from SAP-PbI₂ film show a dramatic performance improvement from 1.51% to 16.21%. Furthermore, the devices based on the high-quality CH₃NH₃PbI₃ film without PbI₂ residue show a better long-term stability.

2. Results and Discussion

Scheme 1 shows the process for fabricating perovskite films from (a) C-PbI₂ and (b) SAP-PbI₂ films. Traditionally, DMF is used to dissolve PbI₂, and then this precursor solution is spin-coated on a substrate to fabricate the PbI₂ film. However, owing to the high volatility of DMF, a fast crystallized, layered and dense PbI₂ film will be obtained, which cannot completely

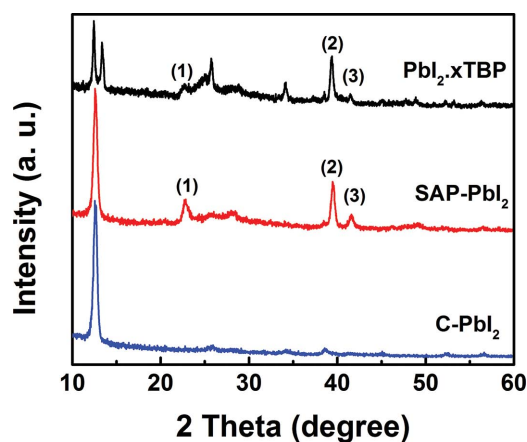
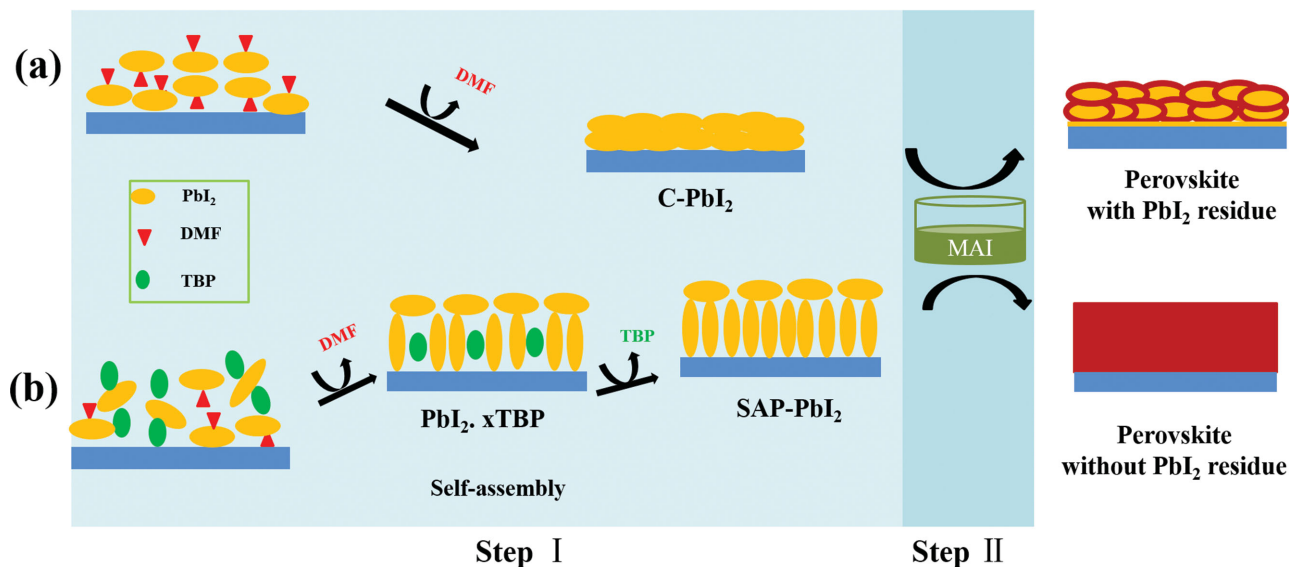


Figure 1. XRD pattern of the C-PbI₂, SAP-PbI₂, and PbI₂·xTBP films.

transform into perovskite in a short time.^[7,15] While introducing TBP into the PbI₂ precursor solution, PbI₂ will coordinate with TBP molecule which is a nitrogen-donor ligand to form coordination complexes (PbI₂·xTBP)^[24] after volatilization of DMF at room temperature. Through annealing at 70 °C for several minutes, PbI₂·xTBP complexes will decompose to PbI₂ and release TBP. It should be noted that the sites where TBP resided will become small holes. Meanwhile, the size and amount of the hole can be easily controlled by changing the concentration of TBP (see Figure S1, Supporting Information). The optimized amount of TBP for fabricating devices is 120 μL in 1 mL PbI₂ precursor solution.

Figure 1 shows the X-ray powder diffraction (XRD) pattern of PbI₂·xTBP, SAP-PbI₂, and C-PbI₂ film on glass. It has been reported that the PbI₂ deposited on flat substrate by spin-coating from DMF solution crystallizes in the form of the 2H polytype, and crystals grow in a preferential orientation along the *c* axis (blue curve).^[7] For SAP-PbI₂, we find that three additional diffraction peaks appeared, suggesting that the ligand TBP



Scheme 1. Schematics of the processes of fabricating PbI₂ and perovskite films: a) C-PbI₂ and b) SAP-PbI₂.

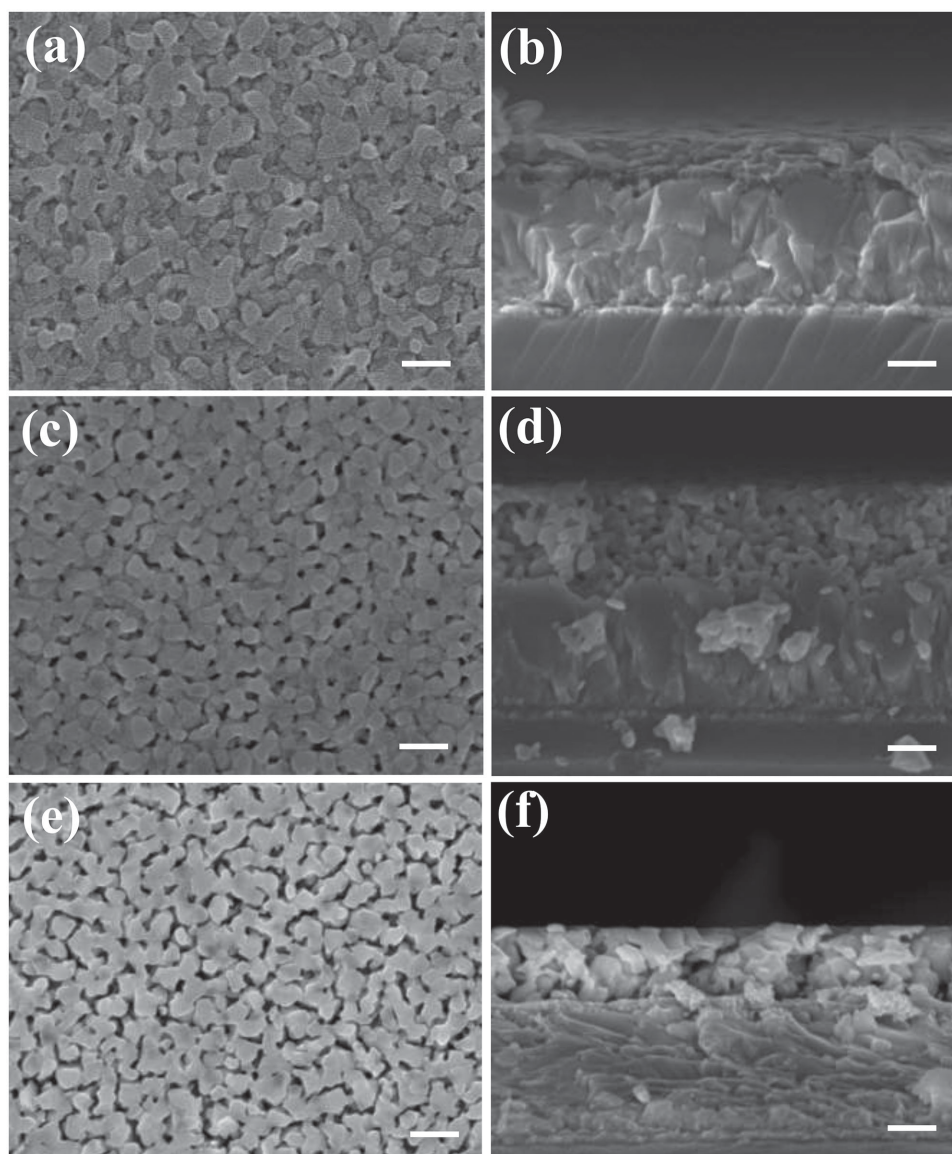


Figure 2. SEM images of a,b) C-PbI₂, c,d) SAP-PbI₂, and e,f) PbI₂·xTBP films formed on compact TiO₂/FTO glass substrate. The scale bars are 200 nm.

molecule induces a different orientation for PbI₂ crystal growth, which has been attributed to the formation of PbI₂·xTBP intermediate complex. The peaks labelled (2) and (3) in Figure 1 (red line) can be attributed to the (110) and (111) lattice planes of the 2H polytype, respectively. Peak (1) is assigned to a different PbI₂ variant, whose identification is beyond the scope of this report in view of the large number of polytypes that have been reported for PbI₂.^[7,25]

We then study the surface and cross-sectional morphology of C-PbI₂ and SAP-PbI₂ films. As shown in Figure 2, the conventional PbI₂ forms layered, dense, and non-uniform crystals. In contrast, SAP-PbI₂ film has a porous and much uniform surface due to the formation of self-assembled porous PbI₂·xTBP intermediate. The AFM image in Figure S2 (Supporting Information) reveals the formation of a smooth SAP-PbI₂ film with self-assembled PbI₂·xTBP intermediate that has a fairly smooth morphology with few big aggregates resulting

in a root-mean-square roughness (R_{rms}) of 8.6 nm, whereas the C-PbI₂ film shows a higher R_{rms} of 9.5 nm.

Due to the ordered crystal structure, the crystallized PbI₂ can react with CH₃NH₃I efficiently, only requiring the intercalation of CH₃NH₃I into the lattice to form perovskite CH₃NH₃PbI₃.^[26] In MAI solution, PbI₂ rapidly reacts and forms a thin layer of the perovskite at the solution–film interface, as indicated by the color change from the film. However, this surface layer does not aid in the diffusion of MAI further into the interior of the film, since the 3D structure lacks a van der Waals gap. Meanwhile, the morphology of PbI₂ also affects the permeation of MAI molecules. Bearing this in mind, we compared the dynamics of perovskite formation from these two different PbI₂ films.

Figure 3a,b shows the absorbance of perovskite from C-PbI₂ and SAP-PbI₂ films at different dipping times, respectively. Figure 3c shows the evaluation of the absorbance at 750 nm versus dipping time. Note that the MAI concentration here is

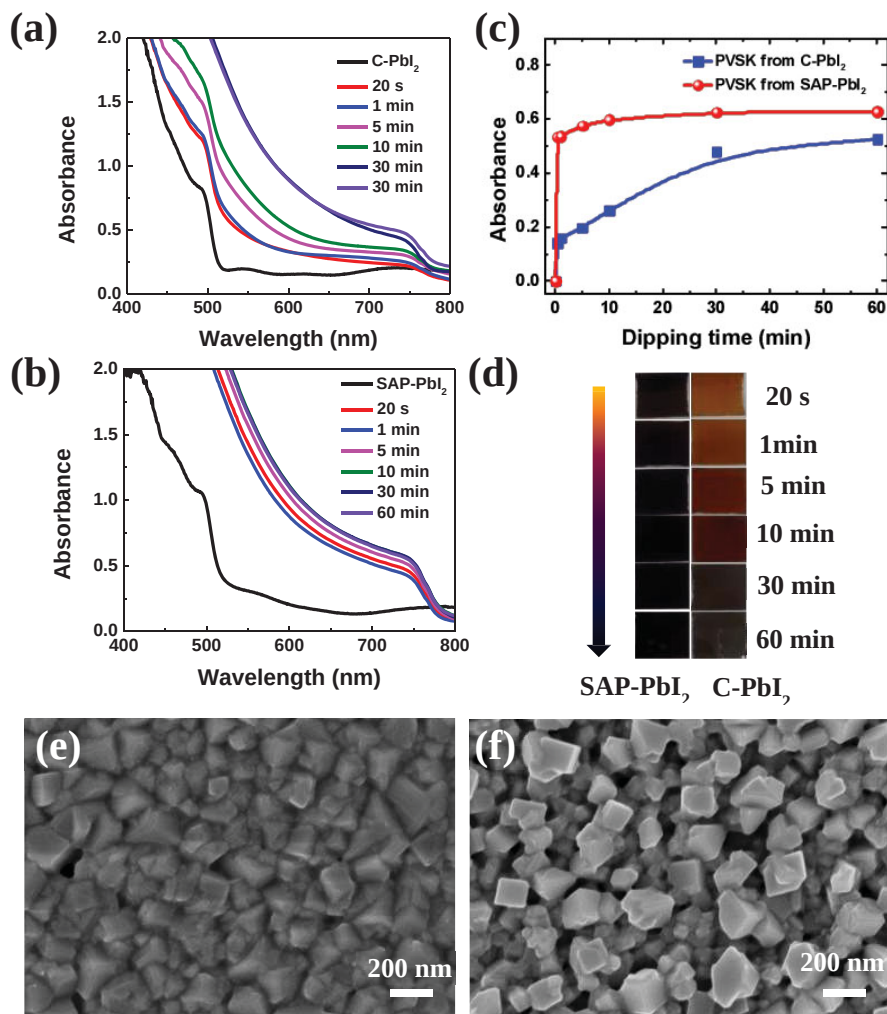


Figure 3. Effect of dipping time in 10 mg MAI per mL IPA solution on evolution of UV-vis absorption spectra of perovskite films deposited from a) C-PbI₂ and b) SAP-PbI₂ films; c) evolution of absorbance at 750 nm as function of dipping time; d) the real images of perovskite from different dipping time; top-view SEM images perovskite prepared from e) C-PbI₂ and f) SAP-PbI₂ films.

10 mg mL⁻¹ in isopropanol. We can see that the C-PbI₂ films show a very slow reaction rate with MAI and the absorbance increases quite slowly even prolonging the dipping time to 1 h. This agrees with the observation that the MAI will be prevented from diffusion into the PbI₂ layer by the thin compact perovskite films (see Figure 3e) formed on the PbI₂ surface. The peeling-off of perovskite occurs after dipping time of 30 min (see Figure S3, Supporting Information), which is detrimental to the morphology of the perovskite films. In striking contrast to the behavior of C-PbI₂, SAP-PbI₂ films react rapidly with MAI (see Figure 3d) and absorbance quickly increases from 0 to 0.53 upon dipping for 20 s, much higher than the absorbance of perovskite made from C-PbI₂ at 60 min. Prolonging the dipping time only slightly increases absorbance for the case of SAP-PbI₂. **Figure 4** shows the evolution of the XRD pattern versus dipping time. The SAP-PbI₂ sample converted into perovskites completely in 20 s, while the PbI₂ residue XRD peak is still detected after 30 min in perovskite from C-PbI₂ sample. Thus, we can see that a high-quality perovskite

film can be rapidly prepared in seconds by using SAP-PbI₂ at room temperature.

We fabricated planar PVSCs with the structure of FTO/compact TiO₂/CH₃NH₃PbI₃/spiro-MeOTAD/Ag. The detailed fabrication processes are described in the Experimental Section. Photovoltaic performance of the PVSCs based on C-PbI₂ and SAP-PbI₂ are measured under AM 1.5 (100 mW cm⁻²) light illumination. The *J*-*V* curves of these two types of PVSCs are illustrated in **Figure 5a** and the detailed parameters have been summarized in **Table 1**. It should be noted that more than 15 devices have been fabricated for each condition of PVSCs. The devices fabricated from C-PbI₂ showed poor performance with power conversion efficiency (PCE) of 1.51% (PCE_{avg} = 1.44 ± 0.04%). It should be noted that the PVSCs with similar structures and fabrication condition reported by other also have similar PCE.^[14a,27] The devices fabricated from SAP-PbI₂ showed a dramatically improved performance with *V*_{oc} = 1.04, *J*_{sc} = 16.07 mA cm⁻², FF = 0.64, and PCE = 10.67% (PCE_{avg} = 8.62 ± 1.79%). **Figure 5b** showed the

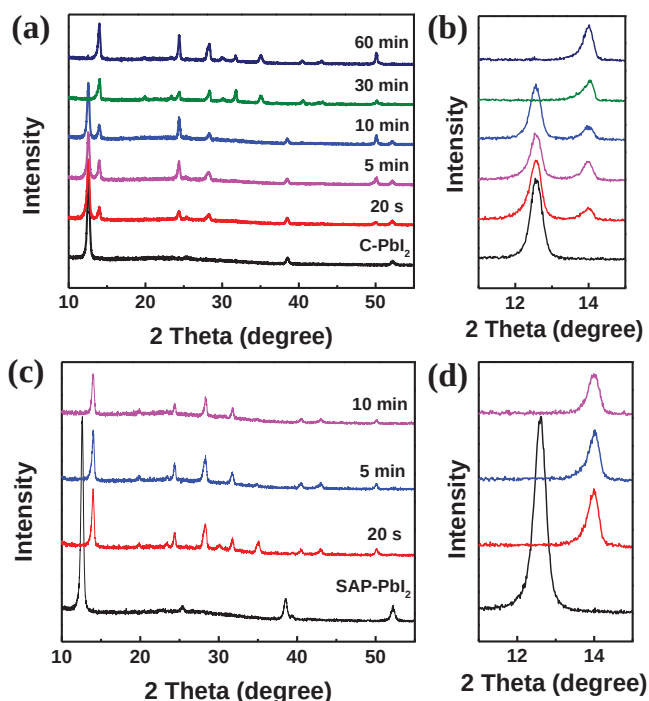


Figure 4. Effect of dipping time in 10 mg MAI in per mL IPA solution on evolution of XRD patterns of perovskite films deposited from a,b) C-PbI₂ and c,d) SAP-PbI₂ films, respectively.

incident photon-to-current conversion efficiencies (IPCEs) of our PVSCs. It is found that, for the SAP-PbI₂-based PVSCs have good IPCE, the spectrum covers from 300 to 800 nm and with the maximum being located at ca. 520 nm which is much better than that of C-PbI₂-based PVSCs, particularly from 400 to 800 nm. This result well agrees with *J*-*V* characteristics. The improved photovoltaic performance may be attributed to the fully converted of perovskite layer.

In order to further investigate the reasons for the improvement, we study the SEM cross-section of PVSCs without Ag (see Figure 6a,b). The devices made from SAP-PbI₂ show a pristine polycrystalline perovskite layer between compact TiO₂ and spiro-MeOTAD. However, the devices made from C-PbI₂ showing a large amount of PbI₂ still do not convert into perovskite and produce a PbI₂ layer upon the compact TiO₂ layer

Table 1. Photovoltaic performance parameters extracted from *J*-*V* measurement under standard AM 1.5 illumination (100 mW cm⁻²).

Sample ^{a)}	<i>V</i> _{oc} [V]	<i>J</i> _{sc} [mA cm ⁻²]	FF	PCE [%]
C-PbI ₂	1.03 ± 0.01	3.74 ± 0.14	0.37 ± 0.01	1.44 ± 0.04
Best	1.03	3.78	0.39	1.51
SAP-PbI ₂	1.00 ± 0.06	15.03 ± 0.68	0.57 ± 0.07	8.62 ± 1.79
Best	1.04	16.07	0.64	10.67

^{a)}The statistics is determined from 15 devices.

(see Figure 6b). It is generally reported that the conduction band minimum (CB_{min}) and valence band maximum (VB_{max}) for CH₃NH₃PbI₃ are to be -3.93 and -5.43 eV, respectively. According to previous study,^[21] the CB_{min} and VB_{max} for PbI₂ have values -3.45 and -5.75 eV, respectively. Although PbI₂ has been reported to exert a passivating function on the perovskite,^[21–23] excess PbI₂ in the interface of TiO₂/perovskite may to some extent block the electron transportation along the device because of its wide bandgap (see Figure 6c), which can be demonstrated from the results of impedance spectrum (IS) measurement.^[28] IS is a powerful tool to monitor the electrical properties of the interfaces within solar cells. Figure 6d shows the Nyquist plots of PVSCs under the light intensity of 100 mW cm⁻² at an applied voltage (1.0 V) close to *V*_{oc}. There are two semicircles in the Nyquist plots, namely, a small arc at high frequency and a large arc at low frequency, as shown in Figure 6d. According to previous studies,^[28] the low frequency (second arc) featured resistance (*R*₂) shall be assigned to the recombination resistance (*R*_{rec}) of solar cells. The high frequency (first arc) featured resistance, *R*₁, shall be assigned to the charge transport resistance (*R*_{ct}) within solar cells. From the plots, the charge-transfer resistance (*R*_{ct}) of 1.82 and 0.45 kΩ is obtained for the devices from C-PbI₂ and SAP-PbI₂, respectively. A higher *R*_{ct} of the C-PbI₂-based devices indicates that the unreacted PbI₂ inhibits the electron transfer from perovskite into TiO₂ layer.

It has been reported that the morphology of perovskite is a critical issue in planar-structured PVSCs.^[29] The pin-hole formation and incomplete coverage of the perovskites resulting in low-resistance shunting paths and weaken light absorption in the solar cell, which is attributed to the low photovoltaic

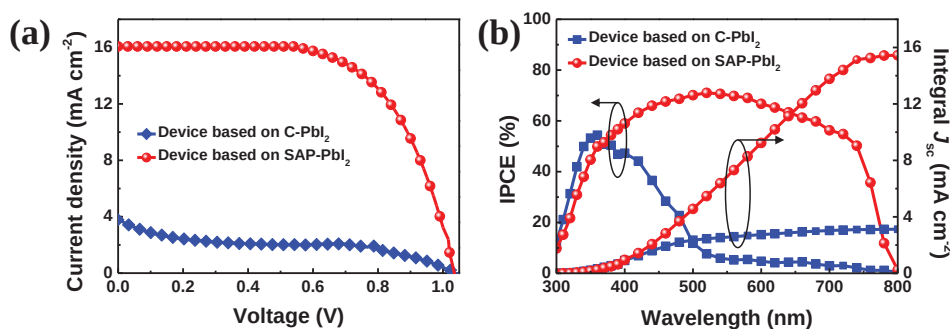


Figure 5. a) *J*-*V* curves; b) IPCEs and integral *J*_{sc} for the best PVSCs from C-PbI₂ and SAP-PbI₂.

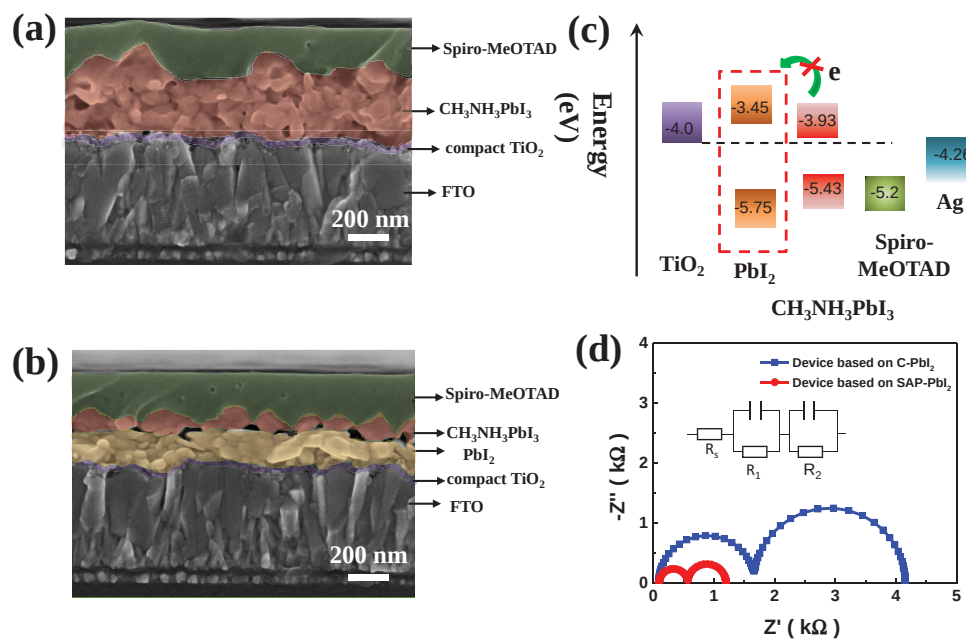


Figure 6. Cross-sectional SEM images of devices without Ag from a) SAP-PbI₂ and b) C-PbI₂ used 10 mg mL⁻¹ MAI solution. c) Energy-level diagram of the devices used in this report. d) Nyquist plots at $V = 1.0$ V for devices processed from C-PbI₂ and SAP-PbI₂.

performance of planar structures. According to previous report,^[30] porous perovskite film is detrimental to the performance of devices. Interestingly, in our work, it is found that the MAI concentration has a large impact on both the perovskite films formation and photovoltaic performances of devices. It is worth noting that C-PbI₂ film can hardly be converted into perovskite when a relatively high concentration of the MAI is used in the dipping process. Figures S4 and S5 (Supporting Information) show the photographs of the perovskite films and photovoltaic performance of devices based on C-PbI₂ film made from different MAI concentrations, respectively. The corresponding photovoltaic parameters were listed in Table S1 (Supporting Information). The C-PbI₂-based device performance is significantly dependent on the MAI concentrations. J_{sc} decreases when MAI concentration increases, which is in agreement with the previous report.^[31] However, owing to the porous characteristics, SAP-PbI₂ can still effectively convert into perovskite even at high concentration of MAI (≥ 15 mg mL⁻¹). **Figure 7** shows the surface morphology of SAP-PbI₂-based perovskite films from different MAI concentrations. When the MAI concentration is below 15 mg mL⁻¹, perovskite films present porous morphology and the lower the concentration, the larger the grain size, which is consistent with the previous report.^[31] Remarkably, with SAP-PbI₂, compact and uniform perovskite films with large grain size are formed by using a relatively high concentration of MAI (≥ 15 mg mL⁻¹) in dipping process (see Figure 7c–e). Figure 7f–h shows a uniform, finely crystalline, and pore-free perovskite film formed from 15 mg mL⁻¹ MAI solution. Figure 7i also reveals that increasing the MAI concentration can form a smooth perovskite film.

The photovoltaic parameters of devices incorporating perovskite films fabricated with a range of MAI concentrations in the immersion solution are summarized in **Table 2**. The $J-V$

curves are shown in Figure S6 (Supporting Information). We can clearly see that all device parameters depend on the MAI concentration, particularly J_{sc} and FF. The maximum performance was obtained for 15 mg mL⁻¹ MAI, which resulted in the best device exhibiting 14.20% PCE, 20.64 mA cm⁻² J_{sc} , and 1.08 V V_{oc} under 100 mW cm⁻² equivalent AM 1.5 sunlight. The average PCE for the optimum fabrication conditions is 12.76%, which is much more efficient than the 1.44% found for perovskite from conventional PbI₂ films.

Recently, chloride has been demonstrated to play a critical role in crystal growth of MAPbI₃.^[11,16] Interestingly, we can further improve the device performance via the addition of methylammonium chloride (MACl) in the immersion solution. The perovskite film fabricated from a mixture of MAI/MACl solution shows a more well-developed grain structure with larger grains than perovskite from pristine MAI solution (see Figure S7, Supporting Information). As shown in Figure S8 (Supporting Information), the resulting devices exhibited much higher J_{sc} compared with pristine MAI immersion solution. In order to understand this enhancement, we performed time-resolved photoluminescence (TR-PL) measurements, as shown in Figure S9 (Supporting Information), and fitted the resulting curves with a biexponential decay. The fitted parameters are summarized in Table S2 (Supporting Information). We can clearly see that the addition of chloride has a dramatic effect on the PL lifetimes. The average lifetime value of 8.0 ns for perovskite films immersed in a mixture of MAI/MACl solution is longer than that immersed in pristine MAI solution (3.75 ns). It has been reported that the slower decays can be correlated with longer diffusion lengths,^[11,16,32] allowing efficient charge collection in thicker films, thus a larger fraction of the solar spectrum can be harvested. As a result, J_{sc} can be improved via the addition of MACl in the immersion solution.

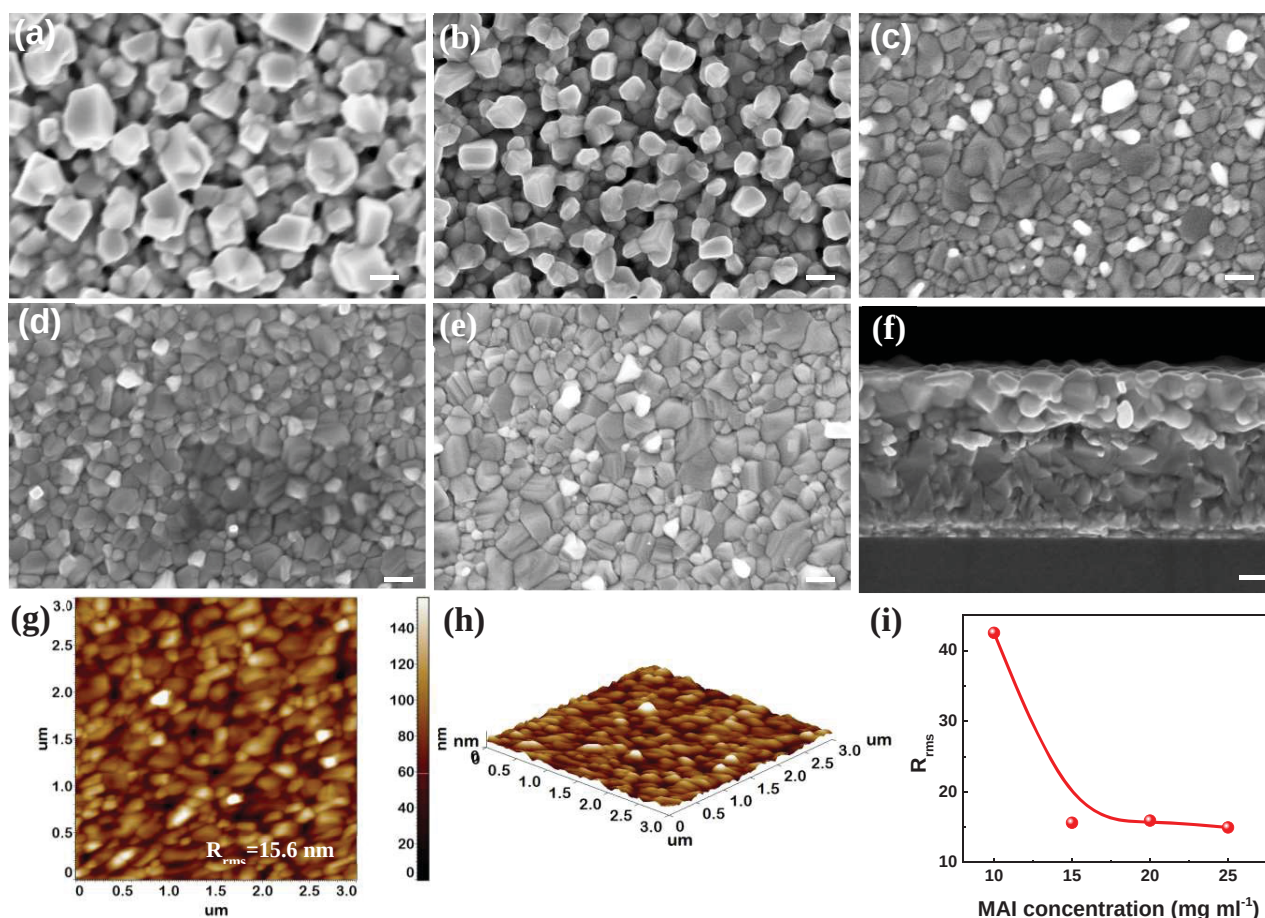


Figure 7. Surface SEM images of perovskite films from different MAI concentrations: a) 8, b) 10, c) 15, d) 20, and e) 25 mg mL⁻¹; f) cross-sectional SEM images of perovskite film from 15 mg mL⁻¹ MAI solution. The scale bars are 200 nm. g) AFM topography and h) 3D views of perovskite film from 15 mg mL⁻¹ MAI. The size of the AFM images is 3 × 3 μm². i) Dependence of R_{rms} of perovskite films on MAI concentrations.

As can be seen in **Figure 8a**, the best device exhibits 16.21% PCE, 22.49 mA cm⁻² J_{sc} , and 1.08 V V_{oc} under 100 mW cm⁻² equivalent AM 1.5 sunlight. The IPCE spectrum is shown in **Figure S10** (Supporting Information), which is consistent with the J_{sc} from J - V curves. Meanwhile, we also study the stabilized power output with time (**Figure 8b**). The photocurrent stabilizes within seconds to ≈19.4 mA cm⁻², yielding a stabilized PCE of 15.7%, measured after 200 s. In order to investigate the reproducibility of the PVSCs using SAP-PbI₂, 30 separate devices

Table 2. Characteristics of the PVSCs with different MAI concentrations used during dipping.

MAI in IPA [mg mL ⁻¹]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	Avg. PCE(best) [%] ^{a)}
8	0.98 ± 0.04	18.13 ± 0.70	0.42 ± 0.04	7.46 ± 0.98 (8.86)
10	1.05 ± 0.01	18.27 ± 0.52	0.54 ± 0.01	10.31 ± 0.36 (10.69)
15	1.07 ± 0.01	19.55 ± 1.15	0.61 ± 0.03	12.76 ± 1.14 (14.20)
20	1.05 ± 0.02	19.55 ± 0.55	0.58 ± 0.04	12.05 ± 0.96 (12.83)
25	1.06 ± 0.01	18.30 ± 1.35	0.50 ± 0.02	9.71 ± 0.75 (10.99)

^{a)}The statistics is determined from 15 devices.

were fabricated and tested. The histograms of the device photovoltaic parameters are presented in **Figure S11** (Supporting Information). Besides, we measured device efficiency with scan rates ranging from 0.10 to 0.30 V s⁻¹, as shown in **Figure S12** (Supporting Information). The results reveal a weak scan-rate dependence of the PCE. However, the SAP-PbI₂-based PVSC exhibits a little J - V hysteresis that the PCE of backward scanning is different to that of forward scanning as shown in **Figure S13** (Supporting Information), which is large for planar configurations.^[33] This needs to be taken into account when comparing PCEs of planar with mesoscopic architectures that do not show appreciable hysteresis. The appearance of hysteresis may be attributed to the ionic migration in the electric field generated by photoinduced charge migration in the compact perovskite film.^[34] As the aim of this work is to propose and demonstrate the new approach for forming the perovskite film with enhanced solar cell performances, the hysteresis will be discussed elsewhere.

Finally, we investigated the stability of devices incorporating the PbI₂-free perovskite. All cells are tested unsealed in ambient air (45%–65% humidity, 25 °C). As shown in **Figure 9**, devices prepared from SAP-PbI₂ exhibited a better stability than the C-PbI₂-based one. The devices based on SAP-PbI₂ remained

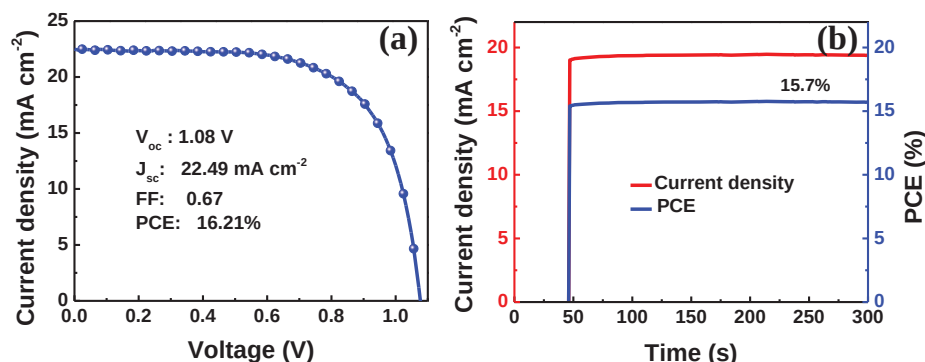


Figure 8. a) J - V curves for the best PVSCs from SAP-PbI₂; b) steady-state photocurrent output and PCE at the maximum power point (0.81 V).

over 60% of its initial PCE even after one month later. Obviously, PbI₂ residues in perovskite film have a negative influence on the long-term stability of devices. In order to find the possible reasons, we have done further studies. As shown in Figure S14 (Supporting Information), there are pinholes/voids formed at the C-PbI₂-based perovskite layer. Meanwhile, SAP-PbI₂-based perovskite film (without the PbI₂ residue) is well packed with no obvious pinholes/voids in the film. With the pinholes, the moisture in air will be easier to penetrate into and reach with the perovskite layer and thus degrade device stability.^[11a,35,36] As shown in Figure S15 (Supporting Information), the C-PbI₂-based perovskite device with PbI₂ residue will quickly react with water moisture and the color of the perovskite film change from deep

brown color to brownish yellow color. In contrast, we observed almost no color change for our perovskite films prepared from SAP-PbI₂ together with high MAI concentrations, even after they were exposed to air for more than one month. Therefore, it is important to prepare high-quality perovskite film without any PbI₂ residue for manufacturing PVSCs in the future.

3. Conclusion

In summary, we have developed a controllable strategy to readily fabricate high-quality perovskite via two-step sequential deposition at room temperature. A small amount of rationally chosen

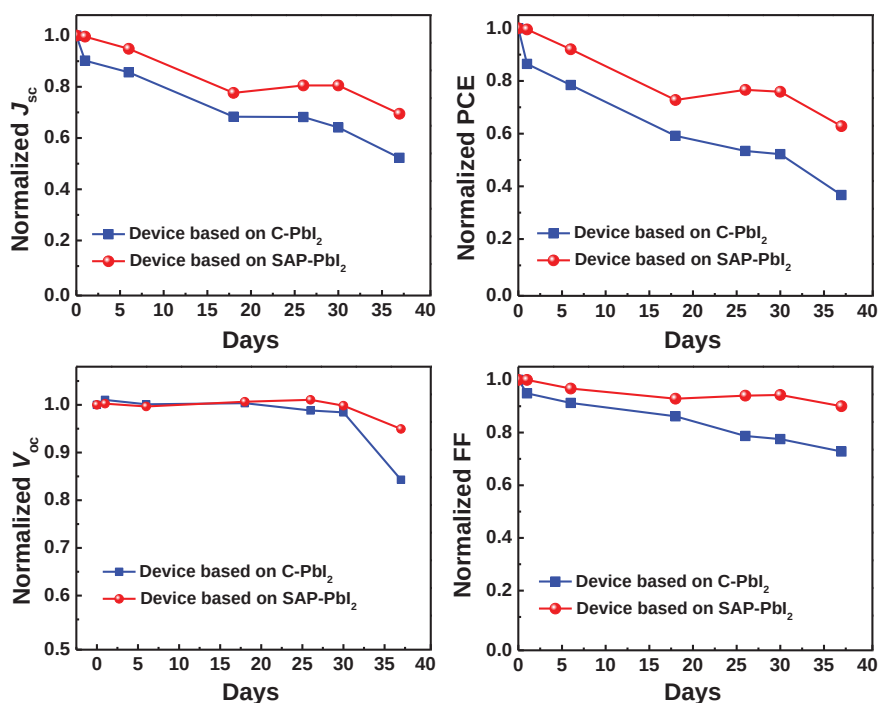


Figure 9. Device stability of PVSCs from C-PbI₂ and SAP-PbI₂ with time.

additive(s) was incorporated into the PbI_2 precursor solutions to form a self-assembled porous PbI_2 , which significantly facilitates the complete conversion of PbI_2 to perovskite. In addition, employing a relatively high MAI concentration, highly crystalline and uniform MAPbI_3 films have been prepared. As a result, a promising PCE (16.21%) is achieved in planar-heterojunction PVSCs. We demonstrate that our facile design of nanostructure for the synthesis of perovskite is a promising route to prepare high-performance solar cells. Furthermore, the PbI_2 residue in perovskite film has been proven to have a negative effect on the stability of devices in ambient air. A facile design of nanostructure also can pave the way toward industrial scalable roll-to-roll manufacturing of PVSCs.

4. Experimental Section

Materials and Reagents: Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. Spiro-MeOTAD was purchased from 1-materials. $\text{CH}_3\text{NH}_3\text{I}$ was synthesized according to a slightly modified reported procedure.

Device Fabrication: Laser-patterned, fluorine-doped tin oxide (F:SnO_2) coated glass ($15 \Omega \text{ sq}^{-1}$, Optrtech New Energy Co., Ltd., China) was cleaned with 2% hellmanex diluted in deionized water; rinsed with deionized water, acetone, and ethanol; and dried with clean dry N_2 . A thin layer of compact anatase TiO_2 was formed through spin-coating an acidic solution of titanium isopropoxide in ethanol on the clean substrates at 2000 rpm for 60 s, followed by a sintering process in a furnace at 500°C for 30 min. The PbI_2 precursor (without or with $120 \mu\text{L}$ TBP) was then spin-coated on the TiO_2 substrate at 4000 rpm for 30 s and dried at 70°C for 10 min. The films were then dipped in a solution of $15 \text{ mg CH}_3\text{NH}_3\text{I}$ in per mL 2-propanol for 20 s, rinsed with 2-propanol, and dried by N_2 gas. For the fabrication of the best-performing devices exhibiting a PCE of 16.2%, the immersion solution was modified with 1 mg MAI and 14 mg MAI in per mL 2-propanol. The hole transport layer was prepared by dissolving 72.3 mg spiro-MeOTAD and $28.8 \mu\text{L}$ TBP, $17.5 \mu\text{L}$ of a stock solution of 520 mg mL^{-1} lithium bis(trifluoromethylsulfonfyl)imide in acetonitrile in 1 mL chlorobenzene, and deposited by spin-coating at 2000 rpm for 30 s. Finally, 120 nm Ag was thermally evaporated on top of the device to form the back contact. For stability test, 50 nm Au was thermally deposited. The active area of this electrode was fixed at 0.06 cm^2 . All devices were fabricated in glove box.

Measurement and Characterization: Solar-simulated AM 1.5 sunlight was generated using a Newport AM 1.5G solar simulator (100 mW cm^{-2}), calibrated with an ISO 17025-certified KG3-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. The J - V curves were recorded from 1.2 to 0 V using a Keithley 2650 apparatus, scan rate was 0.15 V s^{-1} . SEM images were recorded using a LEO 1530 scanning electron microscope. The crystal phases were investigated by a Siemens D5005 X-ray diffraction system ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$). UV-vis absorption spectra were measured using a home-built goniometer. TR-PL spectra of the samples were measured according to our previous method.^[10] The IS were carried out under illumination, with an oscillating voltage of 10 mV and frequency of 1 Hz to 1 MHz. Devices were held at their respective open circuit potentials obtained from the J - V measurements, while the IS spectrum was being recorded. The IS spectra were fitted by Zview software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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