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Growth Control of Compact CH$_3$NH$_3$PbI$_3$ Thin Films via Enhanced Solid-State Precursor Reaction for Efficient Planar Perovskite Solar Cells†

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Abstract

Abstract

\( \text{CH}_3\text{NH}_3\text{PbI}_3 \) (MAPbI\(_3\)) perovskite thin films that are solution-processed using the one-step or the two-step conventional method typically contain significant amount of defects (voids, pinholes) or Pbl\(_2\) impurities, which have a detrimental effect on the performance of planar perovskite solar cells (PSCs) fabricated using those films. To overcome this issue, we demonstrate that the enhancement of the solid-state reaction between inorganic-organic precursors is an effective route for the growth of compact, phase-pure MAPbI\(_3\) perovskite thin films with no voids or pinholes. To ensure uniform solid-state conversion (MAI + PbI\(_2\) → MAPbI\(_3\)) across the entire film thickness, a new successive spincoating/annealing (SSCA) process is used, where MAI is repeatedly infiltrated into a nanoporous PbI\(_2\) film, followed by thermal annealing. The mechanisms involved in the SSCA process are elucidated by monitoring the evolution of the phases during the reaction. Owing to these desirable characteristics (high-purity, full-coverage, enhanced smoothness and compactness) of the SSCA MAPbI\(_3\) films, planar PSCs based on these perovskite thin films deliver a maximum power conversion efficiency (PCE) close to 15%. Furthermore, PSCs fabricated using partially converted nanoporous PbI\(_2\) thin films deliver a surprising PCE approaching 10%, suggesting continuous MAPbI\(_3\) phase formation throughout the entire film at each spincoating/annealing process. The advantages gained from enhancing the solid-state precursor reactions allow better control over the growth of the perovskite, making the SSCA process more robust.

Graphical Abstract

A new solution-processing method is demonstrated for the deposition of compact CH\(_3\)NH\(_3\)PbI\(_3\) perovskite thin films for high-efficiency planar solar cells.
Introduction

The recent introduction of methylammonium lead triiodide (CH₂NH₃PbI₃ or MAPbI₃) perovskite as a strong light absorber has injected great excitement in the field of thin-film photovoltaics. MAPbI₃ possesses a combination of desirable properties, including favourable direct band gap, large absorption coefficient in the visible spectrum, high carrier mobilities, and long carrier-diffusion lengths for both electrons and holes. Over a short period of five years since perovskite solar cells (PSCs) were first introduced, their power conversion efficiency (PCE) shot up to 20.1%. While numerous PSCs studies have shown that the morphology of the MAPbI₃ thin film plays a central role in the PSCs performance, effective control of that morphology through processing still remains a challenge. Typically, deposition of MAPbI₃ perovskite thin films is accomplished using the one-step or the two-step solution-processing method. The conventional one-step method entails direct spin-coating of MAPbI₃ solution, followed by annealing at 70-150 °C. However, it is generally difficult to control perovskite crystallization and film uniformity at the elevated temperature in this method. In this context, the sequential (two-step) solution-processing method (see Fig. S1A), where spin-coated PbI₂ thin films are reacted with CH₂NH₃I (MAI) solution by dipping, followed by annealing, is gaining popularity over the one-step method. In general, the two-step method offers better control over the perovskite morphology compared with the one-step method. This is particularly true in the case of mesoscopic-oxide scaffold films, where complete PbI₂+MAI→MAPbI₃ reaction can take place rapidly due to the nanoscale nature of the PbI₂ within the nanoporous scaffolds. However, in the case of planar thin films, prolonged MAI-solution dipping is needed for the completion of the reaction with solution-deposited PbI₂ (typically dense) across the entire thin film that can be few hundred nanometers in thickness. The prolonged contact of the liquid MAI solution with the as-formed MAPbI₃ perovskite thin film appears to degrade its morphology making it somewhat porous with voids and pinholes (Fig. S1B), which is attributed to partial dissolution of perovskite (MAPbI₃→MAPbI₂+I) and the nature of the reaction between solid PbI₂ and liquid MAI solution. Such defects may cause reduced optical absorption, and the detrimental contact of the subsequently deposited hole-transporting material (HTM) with the TiO₂ blocking layer below the perovskite thin film. Thus, a dense perovskite thin film is generally desired.

In this context, uniform reaction between solid PbI₂ and solid MAI, instead of liquid MAI solution, is expected to provide better control over the planar MAPbI₃ perovskite thin-film morphology and reduce the occurrence of pinholes and voids. This can be achieved by replacing the dense PbI₂ thin film by a nanoporous solid PbI₂ thin film, and replacing the conventional second step of MAI solution dipping with repeated infiltration of MAI via spin-coating and then annealing -- a process we call successive spin-coating/annealing (SSCA). The mechanisms by which dense MAPbI₃ perovskite thin films are formed in the SSCA process are elucidated here. In contrast to the conventional two-step process, the promotion of the solid-state reaction between PbI₂ and MAI in the SSCA process results in high quality, compact MAPbI₃ perovskite thin films, precluding any adverse effect of the liquid MAI solution on the films. Here, the SSCA MAPbI₃ perovskite thin films and the planar PSCs made from these films are also characterized extensively. We show that these PSCs deliver a maximum PCE of 14.6%, with an open circuit voltage (Vₜₙ) of 1.05 V, which is attributed to the compact nature of the SSCA MAPbI₃ perovskite thin films.
Experimental

Raw chemicals and precursors preparation

All reagent grade chemicals were obtained commercially from Sigma-Aldrich, St. Louis, MO, unless noted otherwise. MAI was prepared in-house. In a typical procedure, 24 ml of 33 wt% methylamine (CH$_3$NH$_2$) solution in anhydrous ethanol was reacted with 10 ml of 57 wt% hydroiodic acid (HI) in water, in 100 ml of ethanol (excess CH$_3$NH$_2$) in a dry Ar atmosphere at room temperature. The solvent and the excess CH$_3$NH$_2$ were removed using a rotary evaporator, and the resulting MAI powder was harvested.

Successive spin-coating/annealing (SSCA) processing of MAPbI$_3$ perovskite thin films

First, 0.8 M PbI$_2$ (Alfa-Aesar, Ward Hill, MA) solution in N,N'-dimethylformamide (DMF) was spin-coated onto different substrates: plain glass, quartz, previously patterned fluorine-doped tin oxide (FTO) coated glass (TEC15, Hartford Glass Co., Hartford City, IN), or the patterned FTO-coated glass with a TiO$_2$ blocking layer (~15 nm). A smooth, nanoporous PbI$_2$ thin film was formed, which was then dried at room temperature under blowing air. Second, fresh MAI solution of 10 mg.ml$^{-1}$ in anhydrous isopropanol was spin-coated onto the as-prepared PbI$_2$ layer immediately, and it was then annealed at 150 °C for 1 min, which constitutes the first SSCA cycle. This SSCA cycle was then repeated 3-4 times. The excess MAI was washed using isopropanol, and the final thin films were annealed at 150 °C for 2 min to obtain a dark-colored perovskite film. The film thickness can be controlled via spinning conditions. The spin-coating condition of 4000 rpm, 15 s was used for all thin film deposition, which resulted in 250-300 nm MAPbI$_3$ perovskite thin films. The nature of the substrate (plain glass, quartz, FTO-coated glass, FTO-coated glass with TiO$_2$ blocking layer) did not have any obvious effects on the SSCA-processed MAPbI$_3$ perovskite films.

Fabrication of perovskite solar cells

For the fabrication of the PSCs, FTO-coated glass was patterned by 25% hydrochloric acid etching with zinc powder, and cleaned by soaking in a base bath (5 wt % NaOH in ethanol) overnight. After washing using deionized water and ethanol, a compact TiO$_2$ blocking layer was deposited on top of patterned FTO by spray pyrolysis at 450 °C. The perovskite layer was then deposited using the SSCA process (one, two or three SSCA cycles) as described above. This was followed by spin-coating a solution of a HTM, which consisted of 80 mg 2,2',7,7'-tetrakis(N,N-dip-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD; Merck, Germany), 30 μl bis(trifluoromethane) sulfonimide lithium salt stock solution (500 mg Li-TFSI in 1 ml acetonitrile), and 30 μl 4-tert-butylpyridine (TBP), and 1 ml chlorobenzene solvent. The HTM spin-coating process was performed in a dry-air atmosphere with humidity below 10%. Finally a 150 nm Ag layer was deposited using thermal evaporator and a shadow mask. The PSCs were stored in a dry-air atmosphere with humidity below 5%, and typically the performance of the PSC was measured one day after their fabrication.

Film and device structure characterization

X-ray diffraction (XRD) was performed on a X-ray diffractometer (D8-Advance, Bruker, Germany) using Cu Kα$_1$ radiation (λ=1.5406 Å) at step size/time 0.02°/1 s conditions. Surface morphology of the films were observed in a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Germany). The local roughness of the MAPbI$_3$ thin films were characterized using an atomic force microscope (AFM; 5500, Agilent, Santa Clara, CA) operated in contact mode.
Optical spectroscopy (transmission, reflection, absorption) of the films on quartz at each formation stage was conducted on a spectral response measurement system (QEXL, PV Measurements, Boulder, CO). Transmission electron microscopy (TEM) was used to characterize cross-sections of the whole PSCs. Note that this particular PSC has a thinner HTM layer compared to most of the other PSCs fabricated in this study. Samples from specific locations on the cross-sections were prepared by focused ion beam (FIB; Helios 600, FEI, Hillsboro, OR) and in situ lift-out. The TEM specimens were examined using TEM (2100F, JEOL, Tokyo, Japan) operated at 200 kV accelerating voltage.

Performance characterization of perovskite solar cells

The incident external quantum efficiency (EQE) spectra of the PSCs were recorded at a chopping frequency of 5 Hz in AC mode on a solar cell quantum efficiency measurement system (QEX10, PV Measurements, Boulder, CO). The current density ($J$) - voltage ($V$) characteristics of the PSCs were obtained using a 2400 SourceMeter (Keithley, Cleveland, OH) under simulated one-sun AM 1.5G illumination (100 mW·cm$^{-2}$) (Oriel Sol3A Class AAA Solar Simulator, Newport Corporation, Irvine, CA). A typical $J$-$V$ scan starts from forward-bias to short-circuit at the rate of 20 mV·s$^{-1}$. A typical active area of 0.12 cm$^2$ was defined using a non-reflective mask for the $J$-$V$ measurements. The steady-state maximum power output of the solar cells was measured by monitoring the current density ($J$) output at the maximum power voltage ($V$) bias for up to 300 s using a VersaSTAT MC potentiostat (Princeton Applied Research, Acton, MA). The current output can be converted to power conversion efficiency (PCE) output using the following relation: $\text{PCE} = (J \times V) / (100 \times \text{PCE})$. A shutter was used to switch on and off the one-sun illumination on the cell. The solar-cell testing was conducted in ambient atmosphere with humidity of 20-40%. Impedance spectroscopy (IS) on the PSCs was performed using a PARSTAT 2273 workstation (Princeton Applied Research, Acton, MA) with the frequency range of 0.1 Hz–100 kHz and the modulation amplitude of 10 mV. The IS spectra were analyzed using ZView 2.9c software (Scribner Associates, Southern Pines, NC).

Results and Discussion

SSCA process description and deposition mechanisms

The SSCA process is depicted schematically in Fig. 1. Briefly, a nanoporous PbI$_2$ thin film is first solution-deposited on a substrate, and MAI is then infiltrated via spin-coating. This is followed by thermal annealing, resulting in the rapid formation of the MAPbI$_3$ perovskite. The MAI infiltration/annealing process is repeated 3-4 times (cycles), which results in the full conversion of the entire PbI$_2$ thin film into a compact MAPbI$_3$ perovskite thin film. Note that it is critical to have a nanoporous PbI$_2$ thin film that allows effective capillary infiltration of the MAI solution. Such nanoporous PbI$_2$ is produced via room-temperature drying (under blowing air) of spin-coated PbI$_2$ (solution in DMF) films, whereas conventional drying at higher temperatures (70 to 150 °C) results in dense PbI$_2$ films (see Fig. S2). Figures 2A-2D show a series of XRD patterns following the phase evolution during the SSCA process. The indexed XRD pattern in Fig. 2A from the solution-deposited PbI$_2$ thin film shows strong <100> texture, which is consistent with what has been observed by others in PbI$_2$ thin films derived from solutions in DMF solvent. The XRD patterns in Figs. 2B, 2C, and 2D from the thin films after one, two, and three SSCA cycles, respectively, show the evolution and completion of the PbI$_2$+MAI→MAPbI$_3$ reaction, with no PbI$_2$ observed in Fig. 2D. The indexed XRD pattern in
Fig. 2D confirms the presence of pure β-MAPbI$_3$ phase (space group I4/mcm$^{17,18}$). More SSCA cycles result in the undesirable deposition of excess solid MAI on the surface (not shown here).

Figures 3A-3D are SEM images of top surfaces of the thin films corresponding to those in Figs. 2A-2D. In Fig. 3A, the PbI$_2$ crystals appear “plate” like, which is consistent with the strong texture observed in the XRD pattern (Fig. 2A). The PbI$_2$ thin film also appears nanoporous, and it is presumed that the interconnected pore channels extend through the thickness of the film. As mentioned earlier, such a nanoporous structure in the PbI$_2$ thin film is necessary for the SSCA process to work. With increasing number of SSCA cycles, the porosity reduces (Figs. 3B to 3D), which is related to the volume expansion associated with the intercalation of MAI into the PbI$_2$ structure to form MAPbI$_3$ perovskite.$^{16}$ This volume expansion originates from the crystallographic reconstruction of edge-sharing octahedra in PbI$_2$ (density 6.16 g.cm$^{-3}$) to corner-sharing octahedra in MAPbI$_3$ perovskite (density 4.16 g.cm$^{-3}$).$^{17,18}$ Also, the crystal shapes become more equiaxed with increased SSCA cycles, indicating a loss of texture. The MAPbI$_3$ perovskite thin film in Fig. 3D shows complete uniform coverage and compact morphology. The atomic force microscope (AFM) scan in Fig. 3E shows a smooth MAPbI$_3$ perovskite thin film, with a root mean square (RMS) roughness of 19.5 nm.

Figure 4 presents the evolution of the optical absorption spectra, corresponding to Figs. 3A-3D, during the SSCA process. With increasing number of SSCA cycles, a transition from PbI$_2$, with its sharp edge at ~520 nm, to pure MAPbI$_3$ perovskite, with its weak optical bleaching at ~570 nm and strong optical bleaching at ~760 nm,$^{5,19}$ is observed. These optical absorption results are consistent with the XRD (Fig. 2A-2D) and SEM (Fig. 3A-3D) observations.

It is clear from Fig. 3A that the pure PbI$_2$ thin film is nanoporous. During the first SSCA cycle of spin-coating of MAI solution, but before annealing, MAI infiltrates the PbI$_2$ nanopores and the following reaction takes place immediately upon contact at room temperature producing some amount of MAPbI$_3$:

$$RT$$

$$\text{PbI}_2(\text{solid}) + \text{MAI}(\text{solution}) \rightarrow \text{MAPbI}_3(\text{solid}) \quad (1)$$

This is confirmed in the XRD pattern of such a thin film in Fig. 5A (without annealing) which shows the presence of MAPbI$_3$, in addition to PbI$_2$ and MAI. Also, the SEM image of the top surface of that thin film in Fig. 5B shows traces of unreacted solid MAI, which appears to have crystallized during spin-coating by evaporation of the low-boiling point isopropanol solvent. Subsequent annealing promotes the solid-state reaction:

$$\Delta$$

$$\text{PbI}_2(\text{solid}) + \text{MAI}(\text{solid}) \rightarrow \text{MAPbI}_3(\text{solid}) \quad (2)$$

where all the MAI is consumed (Fig. 3B) and significantly more MAPbI$_3$ is produced, as observed in the XRD pattern in Fig. 2B. This is also confirmed visually, where the pure PbI$_2$ thin film darkens as soon MAI is first spin-coated, and darkens further after the annealing step (see Fig. S3). It is likely that the MAPbI$_3$ forms as a continuous layer on the surfaces of the PbI$_2$ platelets throughout the film during the first SSCA cycle, and the subsequent SSCA cycles result in the complete transformation of the PbI$_2$ into MAPbI$_3$. In this context, a variation of sequential deposition has been reported recently,$^{20,21}$ where inter-diffusion between MAI-PbI$_2$ stacking layers is claimed as the mechanism for the formation of the perovskite. This mechanism is not likely to be operative in the SSCA method because no distinct MAI layer on top of the spin-coated PbI$_2$ layer is observed in Fig. 5B. This can be attributed to a more porous PbI$_2$ film and the relatively low concentration (10 mg.m$^{-1}$) of the MAI solution used here in the SSCA process,
Solar cells based on SSCA perovskite thin films

Figures 6A-6D are cross-sectional transmission electron microscopy (TEM) bright-field images of the whole PSC fabricated using SSCA (three cycles) MAPbI₃ perovskite thin film. The overall view in Fig. 6A shows the compact nature of the MAPbI₃ thin film (~300 nm) and a well-constructed PSC with all its layers clearly delineated. Note the lack of any infiltration of HTM into the perovskite layer. Figure 6B shows a detailed view of the dense TiO₂ blocking layer (~15 nm), and high crystallinity in the MAPbI₃ layer. In Fig. 6C, well-defined grains and grain boundaries of MAPbI₃ perovskite are observed, and no pores/voids are visible even at the nanoscale. Such highly crystalline, dense structure of the perovskite thin film contributes to efficient light absorption and charge transport. The inset in Fig. 6C shows a high-resolution TEM image with interplanar spacing of ~0.64 nm, corresponding to (110) or (002) planes, further confirming the β-MAPbI₃ phase (lattice parameters: a=b= 8.849 Å, c=12.642 Å)¹⁸. Figure 6D is a TEM image of the interface between the MAPbI₃ and the HTM layers showing crystallinity of the MAPbI₃ right up to the interface. Figure 6E is a scanning-TEM image of the whole PSC and energy dispersive spectroscopy (EDS) elemental maps defining the different layers.

The TEM results confirm the formation of fully dense perovskite thin film. Such dense absorber layer eliminates any direct contact between HTM and the TiO₂-blocking layer which can act as a parallel diode in the equivalent circuit of the planar PSCs and decreases the V_{oc} of the corresponding PSCs.⁹ Therefore, a high V_{oc} value of 1.05 V (Table 1) was achieved in these PSCs without the use of any interfacial engineering. For comparison, V_{oc} less than 1 V is generally reported in PSCs employing similar structures made by various other solution-processing methods.⁹,¹⁶,²²-²⁷ This high V_{oc} value is also comparable to that reported recently for PSCs based on “solvent engineering” of the MAPbI₃ perovskite thin films.²⁸,²⁹

Figure 7A presents typical J-V characteristics of PSCs made with MAPbI₃ perovskite thin films processed using one or three SSCA cycles, under simulated one-sun AM 1.5G (100 mW·cm⁻²) illumination. The solar cell performance parameters extracted from these data are presented in Table 1. The PSC using one SSCA cycle shows an overall PCE of 9.1%, with a short circuit current density (J_{sc}) of 15.8 mA·cm⁻², open circuit voltage (V_{oc}) of 1.04 V, and fill factor (FF) of 0.554. This performance level for a planar PSC is quite remarkable considering the significant amount of PbI₂ present in the perovskite thin film (Fig. 2B). In contrast, a planar PSC based on MAPbI₃ thin film deposited using the conventional two-step method, which also contains significant amount of PbI₂, shows a very low PCE of 0.62% (see Fig. S4). This is attributed to the low J_{sc} value of 1.82 mA·cm⁻². The residual PbI₂ in the conventional two-step process typically exists as a layer between the MAPbI₃ perovskite and the TiO₂ blocking layer. As pointed out in an earlier study, the PbI₂ layer can act as a barrier for electron transfer from perovskite into TiO₂.³⁰ In contrast, the residual PbI₂ in the SSCA approach (one cycle) most likely exists as a distributed second phase throughout the perovskite film, and it does not affect the charge extraction significantly, as indicated by the reasonably high J_{sc} value of 15.8 mA·cm⁻². This makes the SSCA a robust solution-processing method for depositing MAPbI₃ perovskite thin films. While the performance of the one-SSCA-cycle PSC is reasonable, a significant improvement in the J_{sc} by ~23% (19.5 mA·cm⁻²) is observed in a typical three-SSCA-cycles PSC, reaching a PCE of 12.8%. The improved J_{sc} value for these PSCs is consistent with the

compared to what has been used by Xiao et al.²⁰ (MAI concentration 17.5-50 mg·ml⁻¹). Thus, in the SSCA process, the perovskite most likely forms by the solid-solid reaction between the interspersed mixture of MAI and PbI₂ throughout the thickness of the thin film.
enhanced absorption (Fig. 4) associated with the complete conversion of PbI$_2$ to MAPbI$_3$ (Fig. 2). (Fifteen each of one- and three-SSCA-cycle PSCs were tested; the maximum, minimum, and average PCE values are reported in Fig. S5.)

According to a procedure suggested by Snaith et al.\textsuperscript{31}, the stability of the maximum-power-point PCE of both PSCs as a function of time is measured, as shown in Fig. 7B. The steady-state PCEs of the one-SSCA-cycle and the three-SSCA-cycles PSCs reach ~9% and ~12%, respectively, consistent with the PCE from the $J$-$V$ characteristics (Fig. 7A and Table 1). However, the steady-state PCE of the one-SSCA-cycle PSC degrades down to ~7%, which could be due to the defects present in the perovskite thin film, whereas the PCE of the three-SSCA-cycles PSC exhibits promising stability over time.

Recombination resistance values ($R_{\text{Recomb}}$) as a function of bias voltage ($V$) for one-SSCA and three-SSCA cycle PSCs are presented in Fig. 7C. These are calculated from the analysis of the impedance measurements (see Fig. S6) using a model described elsewhere.\textsuperscript{32,33} While the impedances of the two cells are similar, they diverge slightly at higher bias voltages. These results, and the reasonably high PCEs and $J_{sc}$ values observed in one-SSCA-cycle PSC in Fig. 7A, suggest that there are no significant changes in the junction properties at the TiO$_2$/perovskite and/or perovskite/HTM interfaces after the first SSCA cycle.\textsuperscript{33} This is consistent with the discussion above, where the MAPbI$_3$ forms as a continuous layer on the PbI$_2$ platelets by reactions (1) and (2) throughout the thin film.

Fig. 8A presents the $J$-$V$ characteristics of the best PSC based on SSCA MAPbI$_3$ perovskite thin film. The PCE is as high as 14.6%, and reaches a level obtained in PSCs based on MAPbI$_3$ perovskite thin films made by vapour deposition and solution-vapour hybrid deposition.\textsuperscript{16,34-37} For this PSC (Fig. 8A), the $J_{sc}$ is 20.1 mA cm$^{-2}$, $V_{oc}$ is 1.05 V, and $FF$ is 0.692. The integrated $J_{sc}$ value of 19.1 mA cm$^{-2}$ from the EQE-$\lambda$ spectrum in Fig. 8B is consistent with the corresponding values from the $J$-$V$ characteristics. These excellent photovoltaic parameters are attributed to the enhanced light-harvesting and charge-transporting properties in the SSCA MAPbI$_3$ perovskite films with superior phase purity, compactness, smoothness, and full-coverage.\textsuperscript{9,38} The SSCA method, and the idea of promoting solid-state precursor reaction, presented here have generic appeal, and the SSCA method could be extended to other hybrid-perovskite materials and/or other PSC configurations.

Conclusions

We have demonstrated the effectiveness of promoting solid-state reaction between organic-inorganic precursors via a new SSCA process in the controlled formation of MAPbI$_3$ perovskite thin films. Results from characterization studies indicate that multiple SSCA cycles result in complete solid-state reaction between PbI$_2$ and MAI, resulting in phase-pure, compact, and smooth perovskite thin films with full coverage. Properties of the planar PSCs fabricated using the SSCA-processed MAPbI$_3$ perovskite thin films lend further support for the proposed deposition mechanisms. While PSCs fabricated from fully-reacted SSCA MAPbI$_3$ perovskite thin films deliver a maximum PCE close to 15%, PSCs with partially-reacted thin films deliver a PCE approaching 10%, attesting to the robustness of the SSCA method. Thus, SSCA constitutes a new, robust solution-processing route for controlled-morphology deposition of high quality hybrid perovskites for next-generation solar cells.
Acknowledgements

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Notes and references

Table 1. Solar cell performance parameters extracted from the J-V characteristics in Figs. 7A and 8A.

<table>
<thead>
<tr>
<th>Number of SSCA Cycles</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$FF$</th>
<th>$V_{OC}$ (V)</th>
<th>PCE (%)</th>
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<td>One</td>
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<td>1.04</td>
<td>12.8</td>
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<td>Three*</td>
<td>20.1</td>
<td>0.692</td>
<td>1.05</td>
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</tr>
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</table>

* Best PSC
Figures Captions

Figure 1. Schematic illustration of the successive spin-coating/annealing (SSCA) solution-processing method for the deposition of MAPbI₃ perovskite thin films.

Figure 2. XRD patterns from thin film on plain glass substrate: (A) after PbI₂ deposition (indexed as cubic PbI₂), (B) after one SSCA cycle, (C) after two SSCA cycles, and (D) after three SSCA cycles (indexed as β-MAPbI₃). The dashed line denotes PbI₂ 001 reflection.

Figure 3. SEM micrographs of top surfaces of thin film on a TiO₂-blocking-layer coated FTO-glass substrate: (A) after PbI₂ deposition, (B) after one SSCA cycle, (C) after two SSCA cycles, and (D) after three SSCA cycles. (E) AFM image of the MAPbI₃ perovskite film corresponding to (D) showing RMS roughness of 19.5 nm.

Figure 4. Optical absorption spectra of thin film on a quartz substrate after PbI₂ deposition, and after one, two, and three SSCA cycles.

Figure 5. (A) XRD pattern of thin film (on plain glass substrate) after PbI₂ spin-coating followed by MAI spin-coating, but before annealing. The three present phases are marked. (B) SEM image of the top surface of the thin film from (A) showing unreacted MAI (arrows).

Figure 6. Bright field TEM images of a typical whole PSC, where the MAPbI₃ thin film (~300 nm thickness) is deposited using the SSCA process: (A) overall view, (B) detailed view of interfaces between the FTO, the TiO₂ blocking layer (~15 nm), and the MAPbI₃, (C) detailed view of the polycrystalline MAPbI₃ film (inset: high resolution TEM image showing lattice fringes with interplanar spacing of ~0.64 nm), and (D) detailed view of the interface between the MAPbI₃ and the HTM. (E) STEM image of the whole PSC and corresponding elemental EDS maps showing the distribution of Sn, Ti, Pb, and I.

Figure 7. (A) Typical J-V characteristics of PSCs based on MAPbI₃ perovskite thin films deposited by the SSCA process (one and three SSCA cycles), under simulated one-sun AM 1.5G (100 mW·cm⁻²) illumination. (B) Steady-state PCE at maximum power as a function of time for a PSC based on MAPbI₃ perovskite thin films deposited by the SSCA process (one and three SSCA cycles). (C) Plots of recombination resistance (R_recomb) as a function of forward bias voltage for PSCs based on MAPbI₃ perovskite thin films deposited by the SSCA process (one and three SSCA cycles).

Figure 8. (A) J-V characteristics of a 14.6%-efficiency PSC based on MAPbI₃ perovskite thin films deposited by the SSCA process (three SSCA cycles), under simulated one-sun AM 1.5G (100 mW·cm⁻²) illumination. (B) External quantum efficiency (EQE) as a function of wavelength for the PSC in (A).
Zhou et al., Figure 1

Nanoporous PbI$_2$ 

Substrate

Infiltrate MAI

Repeat

Anneal

MAPbI$_3$

Perovskite
Zhou et al., Figure 2

Intensity (arb. units)

100
002
003
004

110,002
112,020
121,022
114,222
113,330,134
116,332
404

10
20
30
40
50
60

2θ (deg.)
Zhou et al., Figure 3
Absorption

400 500 600 700 800
Wavelength (nm)

- $\text{PbI}_2$
- 1 SSCA Cycle
- 2 SSCA Cycles
- 3 SSCA Cycles

Zhou et al., Figure 4
Zhou et al., Figure 5

(A) X-ray diffraction pattern showing the intensity (arb. units) as a function of 2θ (deg.). Peaks are labeled for PbI$_2$, MAPbI$_3$, and MAI.

(B) Scanning electron microscopy image showing a detailed view of the sample surface with a scale bar of 1 µm.
Zhou et al., Figure 7

(A) Stabilizing Output PCE (%) vs. Voltage, V (V)

(B) Stabilizing Output PCE (%) vs. Time (s)

(C) Recombination Resistance, $R_{\text{Recomb}}$ (Ω) vs. Forward Bias (V)

- 1 SSA Cycle
- 3 SSA Cycles

Voltage, V (V):
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0

Current Density, J (mA.cm$^{-2}$):
- 15
- 20

Stabilizing Output PCE (%):
- ~9%
- ~12%

Time (s):
- 0
- 50
- 100
- 150
- 200
- 250
- 300
Zhou et al., Figure 8

(A) Current Density, $J$ (mA·cm$^{-2}$) vs. Voltage, $V$ (V)

(B) EQE (%) vs. Wavelength, $\lambda$ (nm)

<table>
<thead>
<tr>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>FF</th>
<th>$V_{oc}$ (V)</th>
<th>PCE (%)</th>
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<tr>
<td>20.1</td>
<td>0.692</td>
<td>1.05</td>
<td>14.6</td>
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Graphical Abstract

A new solution-processing method is demonstrated for the deposition of compact CH$_3$NH$_3$PbI$_3$ perovskite thin films for high-efficiency planar solar cells.