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## Introduction

The recent introduction of methylammonium lead triiodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> or MAPbI<sub>3</sub>) perovskite, as a strong light absorber, has injected great excitement in the field of thin-film photovoltaics.<sup>1-4</sup> MAPbI<sub>3</sub> possesses a combination of desirable properties,<sup>3,4</sup> 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.<sup>5,6</sup> Over a short period of five years since perovskite solar cells (PSCs) were first introduced,<sup>7</sup> their power conversion efficiency (PCE) has increased to 20.1%.<sup>8</sup> While numerous PSCs studies

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## Growth control of compact CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> thin films *via* enhanced solid-state precursor reaction for efficient planar perovskite solar cells<sup>†</sup>

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CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPbI<sub>3</sub>) perovskite thin films that are solution-processed using either a one-step or two-step conventional method typically contain a significant number of defects (voids, pinholes) or Pbl2 impurities, which have a detrimental effect on the performance of planar perovskite solar cells (PSCs) fabricated using those films. To overcome this issue, we show that enhancement of the solid-state reaction between inorganic-organic precursors is an effective route for the growth of compact, phase-pure MAPbl<sub>3</sub> perovskite thin films with no voids or pinholes. To ensure uniform solid-state conversion (MAI +  $Pbl_2 \rightarrow MAPbl_3$  across the entire film thickness, a new successive spin coating/annealing (SSCA) process is used, where MAI is repeatedly infiltrated into a nanoporous Pbl<sub>2</sub> 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 MAPbl<sub>3</sub> films, planar PSCs based on these perovskite thin films delivered a maximum power conversion efficiency (PCE) close to 15%. Furthermore, PSCs fabricated using partially converted nanoporous Pbl2 thin films delivered a surprising PCE approaching 10%, suggesting continuous MAPbl<sub>3</sub> phase formation throughout the entire film at each spin coating/ annealing process. The advantages gained from enhancing the solid-state precursor reactions allow better control of the growth of the perovskite making the SSCA process more robust.

> have shown that the morphology of the MAPbI<sub>3</sub> thin film plays a central role in the PSCs performance,9 effective control of the morphology through processing still remains a challenge.<sup>10</sup> Typically, the deposition of MAPbI<sub>3</sub> perovskite thin films is accomplished using a one-step or two-step solution-processing method.<sup>1,3,4,10</sup> The conventional one-step method entails direct spin-coating of a MAPbI<sub>3</sub> solution, followed by annealing at 70-150 °C.9-11 However, it is generally difficult to control perovskite crystallization and film uniformity at the elevated temperature using this method. In this context, the sequential (two-step) solution-processing method (see Fig. S1A<sup>†</sup>), where spin-coated PbI<sub>2</sub> thin films are reacted with a CH<sub>3</sub>NH<sub>3</sub>I (MAI) solution by dipping, followed by annealing, is gaining popularity over the one-step method.4,10 In general, the two-step method offers better control of the perovskite morphology compared with the one-step method. This is particularly true in the case of mesoporous oxide scaffold films, where a complete  $PbI_2 + MAI \rightarrow MAPbI_3$  reaction can take place rapidly due to the nanoscale nature of the PbI2 within the nanoporous scaffolds.12 In the case of planar thin films, however, prolonged MAI-solution dipping is needed to complete the reaction with solutiondeposited PbI<sub>2</sub> (typically dense) across the entire thin film that can be few hundred nanometers in thickness.12 The prolonged contact of the liquid MAI solution with the as-formed MAPbI<sub>3</sub>

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perovskite thin film appears to degrade its morphology, making it somewhat porous with voids and pinholes (Fig. S1B<sup>†</sup>), which is attributed to the partial dissolution of perovskite (MAPbI<sub>3</sub>  $\rightarrow$ MA<sup>+</sup> + I<sup>-</sup> + PbI<sub>2</sub>) and the nature of the reaction between the solid PbI<sub>2</sub> and liquid MAI solution.<sup>13</sup> Such defects may cause reduced optical absorption, and the detrimental contact of the subsequently deposited hole-transporting material (HTM) with the TiO<sub>2</sub> blocking layer below the perovskite thin film.<sup>3,9</sup> Thus, a dense perovskite thin film is generally desired.

In this context, a uniform reaction between solid PbI2 and solid MAI, instead of a liquid MAI solution, is expected to provide better control over the planar MAPbI<sub>3</sub> perovskite thinfilm morphology and reduce the occurrence of pinholes and voids. This can be achieved by replacing the dense PbI<sub>2</sub> thin film with a nanoporous solid PbI2 thin film, and replacing the conventional second step of MAI solution dipping with the repeated infiltration of MAI via spin-coating and then annealing, a process called successive spin-coating/annealing (SSCA).14 The mechanisms by which dense MAPbI<sub>3</sub> 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 MAPbI<sub>3</sub> 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  $(V_{OC})$  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 a 33 wt% methylamine ( $CH_3NH_2$ ) solution in anhydrous ethanol was reacted with 10 ml of 57 wt% hydroiodic acid (HI) in water, in 100 ml of ethanol (excess  $CH_3NH_2$ ) in a dry Ar atmosphere at room temperature. The solvent and excess  $CH_3NH_2$  were removed using a rotary evaporator, and the resulting MAI powder was harvested.

# Successive spin-coating/annealing (SSCA) processing of MAPbI<sub>3</sub> perovskite thin films

First, a 0.8 M PbI<sub>2</sub> (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<sub>2</sub> blocking layer (~15 nm). A smooth, nanoporous PbI<sub>2</sub> thin film was formed, which was then dried at room temperature under blowing air. Second, a fresh MAI solution of 10 mg ml<sup>-1</sup> in anhydrous isopropanol was spin-coated onto the as-prepared PbI<sub>2</sub> layer immediately, and was

then annealed at 150 °C for 1 min, which constitutes the first SSCA cycle. This SSCA cycle was then repeated 3 to 4 times. The excess MAI was washed with 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 by the spinning conditions. The spin-coating conditions of 4000 rpm for 15 s was used for all thin film depositions, which resulted in 250–300 nm MAPbI<sub>3</sub> perovskite thin films. The nature of the substrate (plain glass, quartz, FTO-coated glass, and FTO-coated glass with a TiO<sub>2</sub> blocking layer) did not have any obvious effects on the SSCA-processed MAPbI<sub>3</sub> perovskite films.

#### Fabrication of perovskite solar cells

For the fabrication of the PSCs, the 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 with deionized water and ethanol, a compact TiO<sub>2</sub> blocking layer was deposited on top of the 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), 30 µl 4-tert-butylpyridine (TBP), and 1 ml chlorobenzene solvent. The HTM spin-coating process was performed in a dry-air atmosphere with less than 10% humidity. Finally a 150 nm Ag layer was deposited using a thermal evaporator and a shadow mask. The PSCs were stored in a dry-air atmosphere with a humidity below 5%, and the performance of the PSC was typically 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 Ka1 radiation  $(\lambda = 1.5406 \text{ Å})$  at step size/time of  $0.02^{\circ}/1$  s. The surface morphology of the films was observed by scanning electron microscopy (SEM; LEO 1530VP, Carl Zeiss, Germany). The local roughness of the MAPbI<sub>3</sub> thin films were characterized by atomic force microscopy (AFM; 5500, Agilent, Santa Clara, CA) operated in contact mode. Optical spectroscopy (transmission, refection, 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. The samples from specific locations on the cross-sections were prepared by focused ion beam (FIB; Helios 600, FEI, Hillisboro, OR) and in situ lift-out. The TEM specimens were examined by TEM (2100F, JEOL, Tokyo, Japan) operated at a 200 kV accelerating voltage.

#### Performance characterization of perovskite solar cells

The incident external quantum efficiency (EOE) 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 onesun AM 1.5G illumination (100 mW cm<sup>-2</sup>) (Oriel Sol3A Class AAA Solar Simulator, Newport Corporation, Irvine, CA). A typical J-V scan starts from a forward-bias to a short-circuit at a rate of 20 mV s<sup>-1</sup>. A typical active area of 0.12 cm<sup>2</sup> was defined using a non-reflective mask for the *I-V* measurements. The steady-state maximum power output of the solar cells was measured by monitoring the current density (1) 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 a power conversion efficiency (PCE) output using the following equation: PCE = (I (mA)) $cm^{-2}$  × V (V))/(100 (mW cm<sup>-2</sup>)). A shutter was used to switch on and off the one-sun illumination on the cell. Solar-cell testing was conducted in the ambient atmosphere with a 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 was first solution-deposited on a substrate, and MAI was then infiltrated *via* spin-coating. This was followed by thermal annealing, resulting in the rapid



Fig. 1 Schematic illustration of the successive spin-coating/annealing (SSCA) solution-processing method for the deposition of  $MAPbI_3$  perovskite thin films.

formation of MAPbI<sub>3</sub> perovskite. The MAI infiltration/annealing process was repeated 3 to 4 times (cycles), which resulted in full conversion of the entire PbI<sub>2</sub> thin film into a compact MAPbI<sub>3</sub> perovskite thin film. Note that it is critical to have a nanoporous PbI<sub>2</sub> thin film that allows effective capillary infiltration of the MAI solution.<sup>15</sup> Such nanoporous PbI<sub>2</sub> was produced by the room-temperature drying (under blowing air) of spin-coated PbI<sub>2</sub> (solution in DMF) films, whereas conventional drying at higher temperatures (70 to 150 °C) resulted in dense PbI<sub>2</sub> films (see Fig. S2<sup>†</sup>). Fig. 2A-D 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<sub>2</sub> thin film showed a strong  $\langle 100 \rangle$  texture, which is consistent with that observed by others in PbI2 thin films derived from solutions in DMF.<sup>16</sup> The XRD patterns in Fig. 2B-D from the thin films after one, two and three SSCA cycles, respectively, show the evolution and completion of the  $PbI_2 + MAI \rightarrow MAPbI_3$  reaction, with no PbI<sub>2</sub> observed in Fig. 2D. The indexed XRD pattern in Fig. 2D confirmed the presence of a pure  $\beta$ -MAPbI<sub>3</sub> phase (space group 14/mcm<sup>17,18</sup>). More SSCA cycles resulted in the undesirable deposition of excess solid MAI on the surface (not shown here).

Fig. 3A–D present SEM images of the top surfaces of the thin films corresponding to those in Fig. 2A–D. In Fig. 3A, the PbI<sub>2</sub> crystals appear "plate" like, which is consistent with the strong texture observed in the XRD pattern (Fig. 2A). The PbI<sub>2</sub> thin film also appears nanoporous, and it was presumed that the interconnected pore channels extend through the film thickness. As



Fig. 2 XRD patterns of a thin film on a plain glass substrate: (A) after Pbl<sub>2</sub> deposition (indexed as cubicPbl<sub>2</sub>), (B) after one SSCA cycle, (C) after two SSCA cycles, and (D) after three SSCA cycles (indexed as  $\beta$ -MAPbl<sub>3</sub>). The dashed line denotes the Pbl<sub>2</sub> 001 reflection.



Fig. 3 SEM images of the top surfaces of the thin film on a  $TiO_2$ blocking-layer coated FTO-glass substrate: (A) after PbI<sub>2</sub> deposition, (B) after one SSCA cycle, (C) after two SSCA cycles, and (D) after three SSCA cycles. (E) AFM image of the MAPbI<sub>3</sub> perovskite film corresponding to (D) showing a RMS roughness of 19.5 nm.

mentioned earlier, such a nanoporous structure in the PbI<sub>2</sub> thin film is essential for the SSCA process to work. With increasing number of SSCA cycles, the porosity decreases (Fig. 3B–D), which is related to the volume expansion associated with the intercalation of MAI into the PbI<sub>2</sub> structure to form MAPbI<sub>3</sub> perovskite.<sup>16</sup> This volume expansion originates from the crystallographic reconstruction of the edge-sharing octahedra in PbI<sub>2</sub> (density 6.16 g cm<sup>-3</sup>) to corner-sharing octahedra in MAPbI<sub>3</sub> perovskite (density 4.16 g cm<sup>-3</sup>).<sup>17,18</sup> In addition, the crystal shapes become more equiaxed with increased number of SSCA cycles, indicating a loss of texture. The MAPbI<sub>3</sub> perovskite thin film in Fig. 3D shows complete uniform coverage and a compact morphology. The atomic force microscopy (AFM) image in Fig. 3E shows a smooth MAPbI<sub>3</sub> perovskite thin film, with a root mean square (RMS) roughness of 19.5 nm.

Fig. 4 presents the evolution of the optical absorption spectra, corresponding to Fig. 3A–D, during the SSCA process. With increasing number of SSCA cycles, a transition from PbI<sub>2</sub>, with its sharp edge at ~520 nm, to pure MAPbI<sub>3</sub> perovskite, with its weak optical bleaching at ~570 nm and strong optical bleaching at ~760 nm,<sup>5,19</sup> was observed. These optical absorption results are consistent with the XRD (Fig. 2A–D) and SEM (Fig. 3A–D) observations.

Fig. 3A shows that the pure  $PbI_2$  thin film is nanoporous. During the first SSCA cycle of spin-coating of the MAI solution,



Fig. 4 Optical absorption spectra of the thin film on a quartz substrate after  $Pbl_2$  deposition, and after one, two and three SSCA cycles.

but before annealing, MAI infiltrates into the  $PbI_2$  nanopores and the following reaction takes place immediately upon contact at room temperature, producing a certain amount of MAPbI<sub>3</sub>:

$$PbI_{2}(solid) + MAI(solution) \xrightarrow{RT} MAPbI_{3}(solid)$$
(1)

This was confirmed in the XRD pattern in Fig. 5A (without annealing), which shows the presence of  $MAPbI_3$ , in addition to  $PbI_2$  and MAI. In addition, the SEM image of the top surface of



Fig. 5 (A) XRD pattern of the thin film (on plain glass substrate) after a  $Pbl_2$  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) shows the unreacted MAI (arrows).

the thin film shown in Fig. 5B revealed traces of unreacted solid MAI, which appears to have crystallized during spin-coating by evaporation of the low-boiling point isopropanol solvent. Subsequent annealing promoted the solid-state reaction:

$$PbI_2(solid) + MAI(solid) \xrightarrow{\Delta} MAPbI_3(solid)$$
 (2)

where all the MAI is consumed (Fig. 3B) and significantly more MAPbI<sub>3</sub> is produced, as observed in the XRD pattern in Fig. 2B. This was also confirmed visually, where the pure PbI<sub>2</sub> thin film darkens as soon as MAI is first spin-coated, and darkens further after the annealing step (see Fig. S3<sup>†</sup>). The MAPbI<sub>3</sub> forms as a continuous layer on the surfaces of the PbI<sub>2</sub> platelets throughout the film during the first SSCA cycle, and the subsequent SSCA cycles result in the complete transformation of PbI<sub>2</sub> into MAPbI<sub>3</sub>. In this context, a variation of sequential deposition was reported recently,20,21 where inter-diffusion between MAI-PbI<sub>2</sub> stacking layers is claimed as the mechanism for the formation of the perovskite. This mechanism is unlikely to be operative in the SSCA method because no distinct MAI layer on top of the spin-coated PbI2 layer was observed in Fig. 5B. This can be attributed to a more porous PbI<sub>2</sub> film and the relatively low concentration (10 mg ml $^{-1}$ ) of the MAI solution used here in the SSCA process, compared to that used by Xiao *et al.*<sup>20</sup> (MAI concentration 17.5–50 mg ml<sup>-1</sup>). Therefore, in the SSCA process, the perovskite most likely forms by a solidsolid reaction between the interspersed mixture of MAI and PbI<sub>2</sub> throughout the thickness of the thin film.

#### Solar cells based on SSCA perovskite thin films

Fig. 6A-D show cross-sectional transmission electron microscopy (TEM) bright-field images of the whole PSC fabricated using SSCA (three cycles) MAPbI<sub>3</sub> perovskite thin films. The overall view in Fig. 6A shows the compact nature of the MAPbI<sub>3</sub> 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. Fig. 6B shows a detailed view of the dense TiO<sub>2</sub> blocking layer ( $\sim$ 15 nm), and high crystallinity in the MAPbI<sub>3</sub> layer. In Fig. 6C, well-defined grains and grain boundaries of MAPbI3 perovskite were observed, and no pores/ voids were visible even on the nanoscale. Such a 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 an interplanar spacing of  $\sim 0.64$  nm, corresponding to the (110) or (002) planes, further confirming the β-MAPbI<sub>3</sub> phase (lattice parameters: a = b = 8.849 Å, c = 12.642 Å (ref. 18)). Fig. 6D presents a TEM image of the interface between the MAPbI<sub>3</sub> and HTM layers, showing the crystallinity of the MAPbI<sub>3</sub> right up to the interface. Fig. 6E shows a scanning-TEM image of the whole PSC and energy dispersive spectroscopy (EDS) elemental maps defining the different layers.

The TEM results confirmed the formation of a fully dense perovskite thin film. Such a dense absorber layer eliminates any direct contact between HTM and the TiO<sub>2</sub>-blocking layer, which can act as a parallel diode in the equivalent circuit of the planar PSCs and decreases the  $V_{\rm OC}$  of the corresponding PSCs.<sup>9</sup>



Fig. 6 Bright field TEM images of a typical whole PSC, where the MAPbI<sub>3</sub> thin film (~300 nm thickness) is deposited using the SSCA process: (A) overall view, (B) detailed view of the interfaces between the FTO, the TiO<sub>2</sub> blocking layer (~15 nm), and MAPbI<sub>3</sub>, (C) detailed view of the polycrystalline MAPbI<sub>3</sub> 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 MAPbI<sub>3</sub> and the HTM. (E) STEM image of the whole PSC and corresponding elemental EDS maps showing the distribution of Sn, Ti, Pb, and I.

Therefore, a high  $V_{\rm OC}$  value of 1.05 V (Table 1) was achieved in these PSCs without interfacial engineering. For comparison, a  $V_{\rm OC}$  less than 1 V is generally reported in PSCs employing similar structures made using various other solution-processing methods.<sup>9,16,22–27</sup> This high  $V_{\rm OC}$  is also comparable to that reported recently for PSCs based on "solvent engineering" of the MAPbI<sub>3</sub> perovskite thin films.<sup>28,29</sup>

Fig. 7A presents the typical J-V characteristics of PSCs made with MAPbI<sub>3</sub> perovskite thin films processed using one or three SSCA cycles, under simulated one-sun AM 1.5G (100 mW cm<sup>-2</sup>) illumination. The solar cell performance parameters extracted from the data are presented in Table 1. The PSC using one SSCA cycle showed an overall PCE of 9.1%, with a short circuit current

Table 1 Solar cell performance parameters extracted from the  $J\!-\!V$  characteristics in Fig. 7A and 8A

Number of SSCA cycles	$J_{\rm SC}  ({ m mA \ cm^{-2}})$	FF	$V_{\rm OC}$ (V)	PCE (%)
One	15.8	0.554	1.04	9.1
Three	19.5	0.629	1.04	12.8
Three <sup>a</sup>	20.1	0.692	1.05	14.6

<sup>a</sup> Best PSC.



Fig. 7 (A) Typical J-V characteristics of PSCs based on MAPbI<sub>3</sub> perovskite thin films deposited by the SSCA process (one and three SSCA cycles), under simulated one-sun AM 1.5G (100 mW cm<sup>-2</sup>) illumination. (B) Steady-state PCE at maximum power as a function of time for a PSC based on MAPbI<sub>3</sub> perovskite thin films deposited by the SSCA process (one and three SSCA cycles). (C) Plots of the recombination resistance ( $R_{\text{Recomb}}$ ) as a function of the forward bias voltage for PSCs based on MAPbI<sub>3</sub> perovskite thin films deposited by the SSCA process (one and three SSCA cycles). (C) Plots of the recombination resistance ( $R_{\text{Recomb}}$ ) as a function of the forward bias voltage for PSCs based on MAPbI<sub>3</sub> perovskite thin films deposited by the SSCA process (one and three SSCA cycles).

density  $(J_{SC})$  of 15.8 mA cm<sup>-2</sup>, 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 PbI<sub>2</sub> present in the perovskite thin film (Fig. 2B). In contrast, a planar PSC based on a MAPbI<sub>3</sub> thin film deposited using the conventional two-step method, which also contains a significant amount of PbI2, showed a very low PCE of 0.62% (see Fig. S4<sup>†</sup>). This was attributed to the low  $J_{\rm SC}$  value of 1.82 mA  $cm^{-2}$ . The residual PbI<sub>2</sub> in the conventional two-step process typically exists as a layer between the MAPbI<sub>3</sub> perovskite and the TiO<sub>2</sub> blocking layer. As pointed out in an earlier study, the PbI<sub>2</sub> layer can act as a barrier for electron transfer from perovskite to TiO<sub>2</sub>.<sup>30</sup> In contrast, the residual PbI<sub>2</sub> 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<sup>-2</sup>. This makes the SSCA a robust solutionprocessing method for depositing MAPbI<sub>3</sub> perovskite thin films.

While the performance of the one-SSCA-cycle PSC is reasonable, significant improvement in the  $J_{\rm SC}$  by ~23% (19.5 mA cm<sup>-2</sup>) was observed in a typical three-SSCA-cycles PSC, reaching a PCE of 12.8%. The improved  $J_{\rm SC}$  value for these PSCs is consistent with the enhanced absorption (Fig. 4) associated with the complete conversion of PbI<sub>2</sub> to MAPbI<sub>3</sub> (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 the procedure suggested by Snaith *et al.*,<sup>31</sup> the stability of the maximum-power-point PCE of both PSCs as a function of time was measured, as shown in Fig. 7B. The steady-state PCEs of the one-SSCA-cycle and the three-SSCA-cycles PSCs reached ~9% and ~12%, respectively, which is 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 degraded to ~7%, which could be due to the defects present in the perovskite thin film, whereas the PCE of the three-SSCA-cycles PSC cycles PSC exhibited promising stability over time.

The recombination resistance values ( $R_{\text{Recomb}}$ ) as a function of the bias voltage (V) for one-SSCA and three-SSCA cycle PSCs are presented in Fig. 7C. These were calculated from an analysis of the impedance measurements (see Fig. S6†) using a model described elsewhere.<sup>32,33</sup> While the impedances of the two cells were similar, they diverge slightly at higher bias voltages. These results, and the reasonably high PCEs and  $J_{\text{SC}}$  values observed in one-SSCA-cycle PSC in Fig. 7A, suggest that there are no significant changes in the junction properties at the TiO<sub>2</sub>/ perovskite and/or perovskite/HTM interfaces after the first SSCA cycle.<sup>33</sup> This is consistent with the discussion above, where the



**Fig. 8** (A) J-V characteristics of a 14.6%-efficiency PSC based on MAPbl<sub>3</sub> perovskite thin films deposited by the SSCA process (three SSCA cycles), under simulated one-sun AM 1.5G (100 mW cm<sup>-2</sup>) illumination. (B) External quantum efficiency (EQE) as a function of the wavelength for the PSC in (A).

 $MAPbI_3$  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 the SSCA MAPbI<sub>3</sub> perovskite thin film. The PCE was as high as 14.6%, and reached the level obtained in the PSCs based on MAPbI<sub>3</sub> perovskite thin films made by vapour deposition and solution-vapour hybrid deposition.<sup>16,34-37</sup> For this PSC (Fig. 8A), the  $J_{\rm SC}$  was 20.1 mA cm<sup>-2</sup>,  $V_{\rm OC}$  was 1.05 V, and FF was 0.692. The integrated  $J_{SC}$  value of 19.1 mA cm<sup>-2</sup> from the EQE- $\lambda$  spectrum in Fig. 8B is consistent with the corresponding values from the *I-V* characteristics. These excellent photovoltaic parameters were attributed to the enhanced light-harvesting and chargetransporting properties in the SSCA MAPbI<sub>3</sub> perovskite films with superior phase purity, compactness, smoothness, and fullcoverage.9,38 The SSCA method and the idea of promoting a solid-state precursor reaction have generic appeal, and the SSCA method can be extended to other hybrid-perovskite materials and/or other PSC configurations.

## Conclusions

We demonstrated the effectiveness of promoting a solid-state reaction between organic-inorganic precursors via a new SSCA process in the controlled formation of MAPbI<sub>3</sub> perovskite thin films. The results from characterization studies indicate that multiple SSCA cycles result in a complete solid-state reaction between PbI<sub>2</sub> and MAI, resulting in phase-pure, compact, and smooth perovskite thin films with full coverage. The properties of the planar PSCs fabricated using the SSCA-processed MAPbI<sub>3</sub> perovskite thin films lend further support for the proposed deposition mechanisms. While the PSCs fabricated from fullyreacted SSCA MAPbI3 perovskite thin films delivered a maximum PCE close to 15%, PSCs with partially-reacted thin films delivered a PCE approaching 10%, highlighting the robustness of the SSCA method. Therefore, SSCA constitutes a new, robust solution-processing route for the controlledmorphology deposition of high quality hybrid perovskites for the next-generation solar cells.

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