Efficiency Enhancement of Perovskite Solar Cells by fabricating as-prepared film before sequential spin-coating procedure

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Abstract

Sequential spin-coating procedure is a widely adopted strategy to prepare $\text{CH}_3\text{NH}_3\text{PbI}_3$ on mesostructured TiO_2 electrode for organolead halide perovskite-based solar cells. However, this method suffers from the rough surface and excessively residual PbI_2 in the resulting perovskite film, deteriorating the device performance seriously. Herein, a facial modified sequential solution deposition method, by introducing an as-prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PbI_2 film before the traditional two-step process, was proposed to fabricate the perovskite-based solar cell with smooth morphology and trace amount of remaining PbI_2 . The optimal as-prepared film introduced improves the efficiency of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells from 9.11% to 11.16%. The enhancement of device performance can be attributed to the increased light absorption ability and decreased recombination rate of carriers in $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber.

Keywords: $\text{CH}_3\text{NH}_3\text{PbI}_3$; perovskite-based solar cells; residual PbI_2 ; modified sequential deposition method; smooth morphology

1. Introduction

Organometal halide perovskite-based solar cells have recently attracted much attention because of their excellent photoelectric properties, such as tuneable optical band gaps, high light absorption coefficients, ultrafast charge generation, high carrier mobility, long charge carrier diffusion length and so on.¹⁻³ In 2009, together with iodide liquid electrolyte, $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ were employed to fabricate sensitized solar cells by Miyasaka,⁴ and a power conversion efficiency (PCE) beyond 6% was obtained. But organometal halide perovskite is an ionic crystal, and it easily dissolves in ionic electrolyte.⁵ To solve the instability problem, Park first introduced spiro-OMeTAD as hole transport materials (HTM) to substitute the liquid iodide electrolyte,⁶ and PCE exceeding 9% was achieved. Since then, researches on perovskite solar cells have been triggered, including synthesizing new materials, discovering device mechanisms and developing different fabrication methods.⁷⁻¹⁰

There have been many technologies developed to prepare organolead halide perovskite MAPbX_3 ($\text{MA}=\text{CH}_3\text{NH}_3$, $\text{X}=\text{I}, \text{Cl}, \text{Br}$) thin films, such as chemical solution deposition methods,^{6,11-12} vapor-phase deposition¹³ and vapour-assisted solution processes.¹⁴ The most adopted process is solution deposition method which is clarified to one-step and two-step deposition procedure. In the one-step method, the precursors (e.g. MAI and PbI_2) are dissolved together in a polar solvent, such as dimethylformamide (DMF), and spin-coated on mesoporous TiO_2 -coated substrate. After then it is heated at 75-150 °C to evaporate the polar solvent.⁶ However, there is a serious drawback during this process. Poor film formation (incomplete surface coverage with pinholes) induced by extensive crystallization caused by solvent evaporation and strong ionic interaction between MAI and PbI_2 , limit the efficiency of devices.¹⁵ To get better perovskite morphology and higher PCE, two-step sequential deposition method was put forward by Grätzel.¹¹ PbI_2 crystal is first introduced from solution into a nanoporous TiO_2 film and subsequently transformed into the MAPbI_3 by exposing it to a solution of $\text{CH}_3\text{NH}_3\text{I}$. The perovskite morphology can be tuneable by control the morphology of PbI_2 crystal, and the highest PCE of 15% was achieved.

However, the average PCE was as low as 12% and the standard deviation was as large as ± 2.0 . Thus, a reproducible and efficient way is required. Park proposed a method called two-step sequential spin-coating procedure and MAI_3 solution spin-coated on PbI_2 film was the main difference from the former process.¹² The size of the MAPbI_3 crystal could be controlled by the $\text{CH}_3\text{NH}_3\text{I}$ solution concentration and an average PCE exceeding 16% with small standard deviation (less than 0.4) was achieved. Nevertheless, for the rapid reaction between PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$, the quick formation of the upper perovskite film retard the inner PbI_2 to react with $\text{CH}_3\text{NH}_3\text{I}$, leading to the remnant PbI_2 exists between TiO_2 and MAPbI_3 .¹⁵ It is generally acknowledged that the excess residual PbI_2 will block the electron injection from perovskite to TiO_2 .¹⁶ However, the trace amount of PbI_2 in perovskite film can retard the charge recombination and benefit to the device performance.¹⁷ Apparently, it is necessary to decrease the amounts of PbI_2 in perovskite film, so as to extend perovskite solar cell performance. Several modified strategies have been employed to meet this goal. Xu controlled the reaction temperature and $\text{CH}_3\text{NH}_3\text{I}$ solution concentration,¹⁸ Huang used $\text{CH}_3\text{NH}_3\text{I}$ as additive in PbI_2 solution¹⁹ and Kanatzidis increased the PbI_2 -coated film dipping time.¹⁷ Although they have tackled the PbI_2 issue, there is another problem existing in the two-step sequential spin-coating process, the fast crystallization tendency of the perovskite films leads to rough surface morphologies which could introduce shunts into the solar cells. It is necessary to develop a more reliable approach to acquire MAPbI_3 film with less remnant PbI_2 and smooth surface.

In this paper, a feasible pre-treatment was proposed to solve the problems. Before the two-step spin-coating procedure, we first dripped different concentration DMF solution including PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ on TiO_2 -coated layer to acquire the as-prepared film. The final crystallization and surface morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was very sensitive to the as-prepared film. All the samples with suitable as-prepared film had a decrease of remnant PbI_2 and smooth surface. Interestingly, light absorption capacity of these devices was improved. Compared with the untreated sample, PCE for optimal treated-device was enhanced from 9.11% to 11.06%. The improved device

performance can be owing to the increase of short-circuit current (J_{SC}), which is proved by light harvest efficiency (LHE) and photoluminescence (PL) spectra.

2. Experimental section

2.1 Materials

Lead iodide PbI_2 (99%), N,N-dimethylformide (DMF, 99%), 4-tert-butylpyridine(96%), lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI), acetonitrile (99.8%) and chlorobenzene (99.8%) were purchased from Sigma-Aldrich. Isopropanol (99.8%) and titanium isopropoxide were from Aladdin. $TiCl_4$ and hydrochloric acid were obtained from Shanghai Chemical Agent Ltd., China (Analysis purity grade) and 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene(spiro-MeOTA D) was from Luminescence Technology Corp., Taiwan. All the chemicals were directly used without further purification.

2.2 Synthesis of CH_3NH_3I crystal and TiO_2 block layer precursor solution

CH_3NH_3I was synthesized by reaction of 27.8 mL of CH_3NH_2 (40 wt% in methanol, TCI) with 30 mL of HI (57 wt% in water, Aldrich) in a round bottomed flask under vigorous stirring for 2 h in ice bath. The precipitated CH_3NH_3I was collected using rotary evaporator at 50°C for 1 h, washed with diethyl ether several times and finally dried at 60 °C in vacuum for 24 h.

The TiO_2 block layer precursor solution was synthesized by the available process as reported in literature. First, titanium isopropoxide (369 μ l) was diluted in isopropanol (2.53 ml) at 0.46 M. Meanwhile, a 2 M HCl solution (35 μ l) was diluted down with isopropanol (2.53 ml) to achieve a 0.026 M concentration. At last, the acid-containing solution was added dropwise to the titanium precursor solution under heavy stirring. The solution was filtered with a PTFE filter with 0.2 mm pore size before use²⁰.

2.3 Solar cell fabrication

Solar cells were fabricated in dry box with humidity inside being about 15%. The patterned FTO coated glass substrates (Nippon, thickness: 2.2 mm, sheet resistance 14 Ω^{-2}) were cleaned with deionized water, ethanol and acetone successively and then

subjected to an ozone-ultraviolet treatment for 15 min. Then the FTO substrates were coated with a compact TiO_2 layer deposited by spin coating the TiO_2 precursor solution at 2,000 r.p.m for 60 s and were subsequently under annealing at 500 °C for 30 min. The mesoporous TiO_2 layer composed of 25-nm-sized particles was obtained by spin coating a commercial TiO_2 paste (Dyesol 18NRT, Dyesol), which was diluted in ethanol (1:7, weight ratio), at 3,000 r.p.m for 30 s. Followed by heating at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and finally at 500 °C for 15 min respectively. The mesoporous TiO_2 film was then dipped into 20 mM TiCl_4 aqueous solution for 15 min at 70 °C and washed with deionized water and alcohol, with sintered at 500 °C for 30 min subsequently. Before the two-step spin-coating procedure, the TiO_2 -coated substrates were heated at 100 °C for 15 min and then spin-coated with different concentrations of DMF solution (30 μl) containing PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ at 3,000 r.p.m for 30 s. The molar ratio of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ was 1:1. The molar concentrations of PbI_2 in DMF were 0.1 M, 0.2 M, 0.3 M and 0.4 M, respectively. For the DMF solution of 0.1 M, 46 mg PbI_2 and 15.9 mg $\text{CH}_3\text{NH}_3\text{I}$ were resolved in 1 ml DMF under stirring at 70 °C. The corresponding films pre-treated by different concentrations of DMF solution could be defined as x-prefilm (x=0.1, 0.2, 0.3, and 0.4). After then, $\text{CH}_3\text{NH}_3\text{PbI}_3$ was formed by two-step spin-coating method. PbI_2 solution (1 M) was prepared by dissolving 462 mg PbI_2 in 1 ml DMF under stirring at 70 °C. PbI_2 solution (20 μl) was spin-coated on the pre-treated film at 6,000 r.p.m for 10 s (without loading time), the formed film can be named as PbI_2 -xprefilm. After spinning, the film was dried in air at 40 °C for 3 min and then at 100 °C for 5 min. After the substrate cooling down to room temperature, 200 μl of 0.038 M (6 mg ml^{-1}) $\text{CH}_3\text{NH}_3\text{I}$ solution in isopropanol was loaded on the PbI_2 -coated substrate for 20 s (loading time), which was spun at 6,000 r.p.m for 10 s and dried at 100 °C for 10 min. The formed perovskite film with pre-treatment was labelled as MAPbI_3 -xprefilm. After the substrate cooling down to room temperature, a hole transport layer solution was spin-coated at 2000 r.p.m for 30 s, in which 1 mL spiro-OMeTAD/chlorobenzene (72.3 mg/mL) solution was employed with addition of 18 mL Li-TFSI/acetonitrile (520 mg/mL), and 29 mL 4-tert-butylpyridine. Devices

were then placed overnight in dry air for the spiro-OMeTAD to oxidize completely. Finally, 80 nm gold electrodes were ion sputtered under vacuum of $\sim 10^{-6}$ Torr, at a rate of $\sim 0.07 \text{ nm}^{-1}$, to complete the devices. The active area of the cell was approximately 0.15 cm^2 .

2.4 Characterization and measurement

X-ray diffraction (XRD) was performed on a X-ray diffractometer (D8-Advance, Bruker, Germany) using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) at step size/time of $0.06^\circ/\text{s}$. The surface and cross-sectional morphology were observed using a field emission scanning electron microscope (FE-SEM, HITACHI SU-4800). Steady-state photoluminescence spectroscopy (PL) measurements were acquired using an Edinburgh Instruments FLS920 fluorescence spectrometer with an excitation wavelength of 460 nm. The absorption spectra of the perovskite coated films were measured by using a Cary 500 UV-vis-NIR Spectrophotometer. The current density-voltage (J-V) measurements were conducted under simulated AM 1.5 G sunlight of 100 mW/cm^2 using an AM 1.5 G type filter (Newport, USA). The light intensity was adjusted by using a standard Si cell. J-V curves were recorded with a Keithley model 2400 digital source meter at room temperature in the ambient air with humidity of 40-60%. A typical active area of 0.15 cm^2 was confined using a non-reflective mask for the J-V measurements.

3. Results and Discussions

The modified two-step procedure is depicted schematically in Fig. 1. Firstly, the mixed DMF solution containing PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was spin-coated on heated TiO_2 -coated film, and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI $_3$) and PbI_2 compound film was formed. Secondly, the MAPbI $_3$ was dissolved by dipping a PbI_2 solution on the pre-treated film above, in order to acquire the high crystalline of PbI_2 and keep tiny MAI preserved in the film. The tiny reserved MAI promote the inner PbI_2 converting to MAPbI $_3$. At last, MAPbI $_3$ with low remnant PbI_2 was obtained by loading MAI solution onto PbI_2 -xprefilm. The phenomenon of low remnant PbI_2 may be ascribed from the interaction between the initial MAI and PbI_2 in solution. The smooth morphology of MAPbI $_3$ film was achieved through adjusting the concentrations of

mixed DMF solution.

In our modified method, the mixed DMF solution containing PbI_2 and MAI is deposited on substrate to form the pre-film before the first step. Interestingly, there are more and more crystals covering on the surface of the substrate with the mixed DMF solution concentration increasing, as shown in Fig. S1. The crystals are indexed as the mixed structure of MAPbI_3 and PbI_2 , which can be confirmed by the XRD analysis later. The pre-film contributes to a non-pinhole PbI_2 film, whereas grate quantities of pin-holes are found in PbI_2 film which is prepared by tradition procedure. As shown in the Fig. S2, PbI_2 film gradually becomes compact from PbI_2 -0.1prefilm to PbI_2 -0.4prefilm sample.

Fig. 2 shows the surfaces and cross sections of the corresponding MAPbI_3 films, which is formed by spin-coating MAI on the PbI_2 -xprefilm, denoted as MAPbI_3 -xprefilm ($x=0, 0.1, 0.2, 0.3$ and 0.4). As seen in all the pre-treated samples, MAPbI_3 film is sensitive to the PbI_2 -xprefilm. For MAPbI_3 -0.2prefilm, it is apparently noticed that the roughness is decreased, and similar perovskite crystals spread uniformly on the TiO_2 substrate in Fig. 2b. However, perovskite grains of different sizes mix together and arrange disorderly for MAPbI_3 -0prefilm. And the cross-section view of Fig. 2c and Fig. 2d, directly indicates that the MAPbI_3 film without x-prefilm is rougher than MAPbI_3 -0.2prefilm. The reason may be ascribed to the MAI solution penetrating into the hole of PbI_2 film, leading to the simultaneous reaction on surface and inside of the PbI_2 film. And the perovskite crystal grows at random, as MAPbI_3 crystal corner and the gap between adjacent crystals can be seen in Fig. 2a clearly. In Seigo Ito's study, a smooth perovskite layer on mesoporous TiO_2 can enhance the shunt resistance of cell and would be able to block the short circuit between TiO_2 and spiro-OMeTAD.²¹⁻²² In addition to the difference of surface roughness, the perovskite layer thickness is varied. MAPbI_3 -0prefilm is about 460 nm, and MAPbI_3 -0.2prefilm is about 200 nm. According to Xing's research, the electron-hole diffusion length is about 100 nanometres in solution processed MAPbI_3 .²³ The perovskite layer with excess thickness may interfere with the electron injection into TiO_2 .²⁴

Nevertheless, the pin-holes are appearing on perovskite film for MAPbI_3 -0.4prefilm

sample. As shown in the high magnification in Fig. 2f, the TiO_2 substrate can be seen clearly. The light-generated electron and hole can recombine easily before collection, due to the direct contact between TiO_2 and spiro-OMeTAD.²⁵ It may be the main factor for worsening perovskite solar cell performance of MAPbI_3 -0.3prefilm and MAPbI_3 -0.4prefilm. Through controlling the roughness, thickness, and coverage of MAPbI_3 film, the best photovoltaic device based on MAPbI_3 -0.2prefilm is obtained.

XRD analysis was conducted to verify the phase composition of the x-prefilm, PbI_2 -xprefilm and the final MAPbI_3 layer on mesoporous TiO_2 films. As seen in Fig. 3a, MAPbI_3 and PbI_2 both exist in the x-prefilm. MAPbI_3 is polar tetragonal material at room temperature, and the MAPbI_3 films usually demonstrate the preferred orientation of (110) peak at 14.82° .²⁶ And the PbI_2 can be easily certified via the (001) at 12.56° .²⁷ Furthermore, the peak intensity of MAPbI_3 is stronger with the solution concentration increasing, and the 0.4-prefilm show the highest peak. It may be ascribed to the amount or the crystallinity of MAPbI_3 enhancement. After the formation of x-prepared film, the PbI_2 solution was spin-coated on it, and MAPbI_3 is resolved into PbI_2 and MAI.²⁸ In Fig 2b, there is no MAPbI_3 peak any more, leaving the PbI_2 peak exists, and PbI_2 -0.2prefilm has the highest peak intensity. But it is hard to detect the trace amount of MAI through XRD characterization. In Fig 2c, beside MAPbI_3 (110) peak mentioned above, other diffraction peaks at 20.48° , 23.46° , 24.47° , 28.40° , 31.86° , 40.49° and 43.19° can be assigned to (112), (211), (202), (220), (310), (224) and (314) diffractions respectively. All the samples show the same pattern positions, which is in agreement with previously reported MAPbI_3 in literature.²⁶ It is noteworthy that there is less PbI_2 exist in the pre-treated sample compared with the MAPbI_3 -0prefilm, which is observed in the XRD pattern, indicating that the residual MAI in PbI_2 -xprefilm facilitate the conversion of inner PbI_2 to MAPbI_3 . In addition, the high crystalline of MAPbI_3 in MAPbI_3 -0.2prefilm is beneficial to the photovoltaic performance in perovskite solar cell.

In order to figure out the function of tiny PbI_2 in perovskite solar cell, an illustration on the correlation between the morphology and the energy band gap diagram of the PbI_2 /perovskite film is demonstrated in Fig. 3d. In the path 1, the bottom PbI_2 block

the electron injection from perovskite to TiO_2 , as the conduction band of PbI_2 is located higher than that of the perovskite. But in the path 2 and 3, the remnant PbI_2 acts as a blocking layer between the TiO_2 semiconductor and the perovskite, reducing the probability of back electron transfer (charge recombination). Synthetically balance the double-edged effect of PbI_2 , it is necessary to control the trace amount PbI_2 in order to improve perovskite solar cell device performance.¹⁷

To avoid batch-to-batch variations in the photocurrent, cells were assembled in the same batch (8 devices), and the TiO_2 -coated films were selected at random before spin-coating by the solutions. Fig. 4 presents the typical J-V characteristics of perovskite solar cells based on different MAPbI_3 -xprefilm. The solar cell performance parameters extracted from the data are presented in Table 1. The MAPbI_3 -0prefilm-based cell exhibits a short-circuit photocurrent density (J_{SC}) of 17.65 mA cm^{-2} , open-circuit voltage (V_{OC}) of 0.94 V, and fill factor (FF) of 54.3%, yielding a power conversion efficiency of 9.11%. Through the addition of the 0.1-prefilm pre-treatment, the improved PCE of 10.08% is obtained. Surprisingly, the highest PCE of 11.06% is acquired based on the MAPbI_3 -0.2prefilm, by adjusting the amount of residual PbI_2 and the morphology of MAPbI_3 . Considering the similar FF and V_{OC} values in the samples of MAPbI_3 -0.2prefilm and MAPbI_3 -0prefilm, the efficiency enhancement was mainly contributed by the higher J_{SC} . The J_{SC} for MAPbI_3 -0.2prefilm increases to 20.08 mA cm^{-2} , which was due to the smooth morphology and trace amount of PbI_2 verified by above results. Furthermore, the stronger light absorption discussed below benefits the extension of J_{SC} . Nevertheless, with the pre-treated mixed solution beyond 0.2 M, the decrease of J_{SC} , V_{OC} , and FF lead to the device performance deterioration, and the main reason is due to the poor coverage of perovskite film. It is reported that photovoltaic performance was found to be strongly dependent on perovskite layer coverage.²⁹ As a result, the PCE drops to 6.46% for MAPbI_3 -0.3prefilm and 4.30% for MAPbI_3 -0.4prefilm. The averaged photovoltaic parameters extracted from J-V curves are collected in Figure S3, V_{OC} , J_{SC} , FF and efficiency exhibit the similar tendency on x value in the MAPbI_3 -xprefilm. From the J-V curves of various cells described above, the photocurrent is the most important

factor to the perovskite solar cell performance. To further understand the origin of this phenomenon, a series of optical absorption and photocurrent spectroscopic studies have been carried out. Fig. 5a shows the absorptance spectra measured with an integrating sphere for the five devices. All the films show absorption onsets at 800 nm with broad absorption ranging from the visible to near-IR region. In the whole visible region, the MAPbI₃-0.2prefilm exhibits the higher optical absorption ability, contributing to more light-generated electron and larger current density, compared with other devices. It may result from the better crystallinity of perovskite and smoother surface film, which has been discussed above. For the samples of MAPbI₃-xprefilm (x=0, 0.1, 0.2), the absorption curves display a similar trend. For example, as for MAPbI₃-0.2prefilm, the film harvests more than 93% of the incident photons between 420 and 650 nm. However, beyond 650 nm, the light-harvesting efficiency of the film decreases gradually and then drops sharply to zero near the band gap of the perovskite, which is consistent with Pellet's report.³⁰ For MAPbI₃-0.3prefilm, it is noteworthy that the absorbance above 650 nm was much higher than the previous three samples, which might be ascribed from low coverage and surface scattering of MAPbI₃ film.¹⁹ Moreover, the absorbance between 420 and 650 nm was lower than that of MAPbI₃-0.1prefilm and MAPbI₃-0.2prefilm, manifesting the smaller current density generated in MAPbI₃-0.3prefilm.

In addition, the steady-state photoluminescence (PL) measurement was conducted to investigate the recombination of the photo-generated electron. All the samples emission peaks are located at 770 nm (excitation wavelength: 460 nm) and consistent with previous reports of emission from MAPbI₃.³¹ However, the perovskite PL quantum yield of the MAPbI₃-0.2prefilm is largely reduced compared to that of the MAPbI₃-0prefilm, demonstrating an enhanced charge carrier extraction and reduced recombination.³² The thickness reduction of perovskite film and lower amount of residual PbI₂ before mentioned may lead to the decreased intensity of PL spectra. The poor performance of MAPbI₃-0.4prefilm is proved by the PL curve, where an intensively sharp peak appears at 770 nm. The high recombination is ascribed from the low coverage of perovskite film.

4. Conclusions

In summary, a facial and modified sequential spin-coating deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) absorber on mesoporous TiO_2 films was developed. The MAPbI_3 and PbI_2 compound pre-treated film was firstly formed by dipping different concentrations of DMF precursor solution containing PbI_2 and MAI before the two-step procedure. Then, the MAPbI_3 was dissolved to PbI_2 and tiny MAI through dipping a PbI_2 solution on the pre-treated film and the tiny reserved MAI facilitate the inner PbI_2 transforming to MAPbI_3 . Finally, the high-crystalline MAPbI_3 with trace remnant PbI_2 was obtained by loading MAI solution. In view of the surface roughness and coverage of the MAPbI_3 , the optimal concentration of precursor solution was obtained. Compared with MAPbI_3 -0prefilms, the efficiency boosted from 9.11% to 11.16% based on MAPbI_3 -0.2prefilms device. The improved device performance was mainly attributed to increasing J_{SC} , which should be the result of smoother surface morphology, less remained PbI_2 , higher light absorption, and lower recombination. This method opened up a new pathway for further improvement of device performance of perovskite solar cell fabricated by sequential spin-coating deposition.

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Tables

Table 1 Summary of MAPbI₃-xprefilm-based solar cell performance parameters with varying x values (x= 0-0.4).

Sample	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
MAPbI ₃ -0prefilm	0.94	17.65	54.3	9.11
MAPbI ₃ -0.1prefilm	0.94	18.68	56.9	10.08
MAPbI ₃ -0.2prefilm	0.97	20.08	56.8	11.16
MAPbI ₃ -0.3prefilm	0.87	15.06	49.5	6.46
MAPbI ₃ -0.4prefilm	0.83	14.21	36.4	4.30

Figures

Fig. 1 Schematic illustration of modified two-step spin-coating procedure for MAPbI₃ perovskite thin films.

Fig. 2 Top view FE-SEM images of (a) MAPbI₃-0prefilm, (b) MAPbI₃-0.2prefilm, (e) MAPbI₃-0.3prefilm, (f) MAPbI₃-0.4prefilm and cross-sectional FE-SEM image of (c) MAPbI₃-0prefilm, (d) MAPbI₃-0.2prefilm.

Fig. 3 (a-c) XRD spectra of x-prefilm, PbI₂-xprefilm, and MAPbI₃-xprefilm as a function of x value (x = 0-0.4); (d) model of the place of residual PbI₂ exists in the solar cell and the charge-injection/recombination retardation by the unconverted PbI₂.¹⁶⁻¹⁷

Fig .4 Current-voltage (J-V) curve of the MAPbI₃-xprefilm-based ($x = 0-0.4$) solar cell under a standard AM 1.5 solar illumination at an intensity of 100 mW cm².

Fig. 5 (a) Light-harvesting efficiency, (b) Steady-state PL spectra for MAPbI₃-xprefilm with varying x value (x = 0-0.4).