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Smooth $\text{CH}_3\text{NH}_3\text{PbI}_3$ from controlled solid–gas reaction for photovoltaic applications†

Jian Mao,^a Hong Zhang,^a Hexiang He,^b Haifei Lu,^a Fengxian Xie,^a Di Zhang,^a
Kam Sing Wong^b and Wallace C. H. Choy^{*a}

The merits of high power conversion efficiency (PCE) and easy preparation make organic–inorganic perovskite solar cells one of the most promising solar devices. However, PCE is greatly dependent on the morphology of perovskite thin film. Here, we report a solid–gas reaction method to fabricate very smooth $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with high coverage. Through controlling the reaction rate between $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 by tuning the PbI_2 substrate temperature and the evaporation rate of $\text{CH}_3\text{NH}_3\text{I}$, we obtain a $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer with roughness of 7.37 nm. Besides, no post-treatment annealing is needed after film formation using our approach. With about 250 nm perovskite active layer, the solar cells exhibit a PCE of 10.0% with little hysteresis.

1. Introduction

As one of the emerging and globally investigated solar cells, three-dimensional organic–inorganic perovskite has attracted remarkable attention in recent years for its high absorption coefficient from 300 nm to 800 nm ($1.5 \times 10^4 \text{ cm}^{-1}$ at 550 nm),^{1,2} long exciton diffusion length (1 micrometer for polycrystal³ and 175 micrometers for single crystal⁴), easy solution process,^{5–7} and low cost.⁸ The general chemical formula of perovskite is ABX_3 ($\text{A} = \text{CH}_3\text{NH}_3$ or $\text{HC}(\text{NH}_2)_2$, $\text{B} = \text{Pb}$ or Sn , and $\text{X} = \text{Cl}$, Br , or I). Through simply varying the elements of A, B, and X, the band gap of perovskite can be easily tuned from 1.3 eV (ref. 9) to 2.3 eV (ref. 10) for wide band absorption of sunlight. With their considerably increasing power conversion efficiency (PCE),⁶ perovskite solar cells (PSCs) have great potential to approach the theoretical maximum efficiency of 33.7% for single p–n junction solar cells, which was predicted when the band gap of the absorber material was about 1.34 eV.¹¹

The study of three-dimensional organic–inorganic perovskite dates back to several decades ago;^{12,13} however, not until recently has it been applied in solar cells. In 2006, Kojima and co-workers¹⁴ utilized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite as sensitizer in solar cells and reported a PCE of 2.19%. After several years of research, the certified efficiency of perovskite solar cells has been improved to 20.1%.¹⁵ Despite the exciting progress, there are still some challenges to overcome in practical applications of PSCs. For example, repeatability and stability of perovskite solar cells are not very good. The anomalous hysteresis¹⁶

dependent on the scan direction and scan rate of the applied voltage to perovskite solar cells is also a concern. Besides, it is quite difficult to prepare perovskite thin film with full coverage.¹⁷ In the conventional one-step solution coating method, perovskite precursor is prepared from a mixture of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 (ref. 2) or $\text{CH}_3\text{NH}_3\text{I}$ and PbCl_2 (ref. 3) in dimethylformamide (DMF)^{6,18,19} or gamma-butyrolactone (GBL)^{20,21} solvent. The easily obtained morphology with incomplete coverage^{19,22–25} might be related to the solvent-induced intermediates²⁶ of $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{DMF}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ as well as the colloidal nature²⁷ of precursors in solvent, with size ranging from tens of nanometers to micrometers. On the other hand, dual-source vapor deposition^{22,28} without the use of solvent has been reported to offer quite smooth perovskite thin film with very good coverage. However, the device performance from this approach is very sensitive to the evaporation rates of the two sources. More recently, a vapor-assisted solution process (VASP)²⁹ has been developed; this approach needs a relatively high temperature (150 °C) to sublimate $\text{CH}_3\text{NH}_3\text{I}$ powder and anneal perovskite thin film. The fabrication of efficient perovskite solar cells at low temperature with smooth morphology and complete coverage is still desired.

Herein, we report a solid–gas reaction method to fabricate $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. The evaporated $\text{CH}_3\text{NH}_3\text{I}$ molecule interacts upon contact with solid PbI_2 spin-coated onto the substrate at 60 °C under vacuum and leads to a compact and smooth thin film with high coverage. No extra annealing is needed after formation of the film. Besides, we find that the solid–gas reaction of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ at room temperature is very slow and occurs only at the surface of PbI_2 . Nevertheless, the PbI_2 substrate heated to 60 °C can completely convert PbI_2 into $\text{CH}_3\text{NH}_3\text{PbI}_3$. This can be explained by the improved diffusion rate of $\text{CH}_3\text{NH}_3\text{I}$ molecules within the PbI_2 layer and the increased reaction rate between the solid PbI_2 and gaseous $\text{CH}_3\text{NH}_3\text{I}$ at higher temperature. By optimizing the substrate

^aDepartment of Electrical and Electronic Engineering, The University of Hong Kong, Pok Fu Lam Road, Hong Kong, China. E-mail: chchoy@eee.hku.hk

^bDepartment of Physics, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

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temperature, $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate, and PbI_2 thickness, we obtain a perovskite thin film of about 250 nm, which gives a PCE of 10.0% with little hysteresis.

2. Experimental

2.1. Materials

Lead(II) iodide (PbI_2 , 99.9%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), and chlorobenzene (CB, 99.8%) were purchased from Sigma-Aldrich. Isopropanol (IPA, anhydrous, 99.8%) was bought from Acros Organics. PEDOT:PSS (P VP Al 4083) was purchased from Clevios. PC_{61}BM was purchased from Solarmer Energy Inc. Poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) was purchased from 1-Material. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was synthesized by reacting 13.5 ml methylamine (CH_3NH_2 , 33 wt% in ethanol, Sigma-Aldrich) and 15 ml hydroiodic acid (HI, 57 wt% in water, Sigma-Aldrich) under ice bath for 2 hours. The white precipitate was obtained by removing the solvent using a rotary evaporator at 55 °C. The precipitate was purified by recrystallization, which started with dissolving the precipitate in ethanol followed by adding excess diethyl ether to obtain the precipitate again. The process was repeated for three times. After recrystallization, the precipitate was dried at 60 °C for 24 hours in vacuum.

2.2. Device preparation

The perovskite solar cells have a structure of ITO/PEDOT:PSS (40 nm)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (150–250 nm)/ PC_{61}BM (50 nm)/PFN (1–2 nm)/Ag (120 nm). ITO substrate was washed successively with deionized water, acetone, and ethanol. After UVO treatment, the ITO substrate was spin-coated with PEDOT:PSS at 4000 rpm for 40 s and annealed at 130 °C for 15 min. PbI_2 was dissolved in DMF with concentration of 300 mg ml^{-1} , 462 mg ml^{-1} , and 550 mg ml^{-1} and stirred at 60 °C for more than 10 hours before use. Yellow PbI_2 precursor was spin-coated on PEDOT:PSS at 5000 rpm for 10 s and immediately dried at 90 °C for 15 min (300 mg ml^{-1} leads to about 60 nm; 462 mg ml^{-1} leads to about 100 nm; and 550 mg ml^{-1} leads to about 130 nm). After drying, the samples were mounted on a sample holder and then placed in the vacuum chamber. The PbI_2 side of the sample was face down on the $\text{CH}_3\text{NH}_3\text{I}$ source. The distance between sample and $\text{CH}_3\text{NH}_3\text{I}$ source was fixed at approximately 30 cm. Besides, the volume of the vacuum chamber was about 58 000 cm^3 . The chamber pressure was controlled at 10^{-4} Pa, and the metal sample holder was heated to the desired temperatures of 50 °C, 60 °C, and 70 °C with stability of ± 1 °C. The density of $\text{CH}_3\text{NH}_3\text{I}$ was assumed as 1 g cm^{-3} , as reported by Snaith.²² The evaporation rate was controlled at 0.5 $\text{\AA s}^{-1}$, 0.9 $\text{\AA s}^{-1}$, and 1.3 $\text{\AA s}^{-1}$ *via* tuning the evaporation current, and it was recorded using Maxtek Model TM-400. After evaporation for 60–80 min, the excess $\text{CH}_3\text{NH}_3\text{I}$ was washed with IPA. PC_{61}BM (20 mg ml^{-1} in CB) was spin-coated atop at 1500 rpm, followed by PFN (0.2 mg ml^{-1} in ethanol) at coating rate of 3000 rpm. Finally, 120 nm Ag was evaporated on PFN at a vacuum pressure of 3×10^{-4} Pa.

2.3. Characterization

Simulated AM 1.5 sunlight (100 mW cm^{-2}) was generated by the ABET AM 1.5G solar simulator and calibrated using a Hamamatsu silicon reference cell. The current density–voltage curve of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells was recorded using the Keithley 2635 SourceMeter. Incident photon-to-current efficiency (IPCE) was measured with a home-built system combining a Newport xenon lamp, an Acton monochromator, and a chopper with a Stanford lock-in amplifier. High-resolution scanning electron microscope (SEM) images were obtained using the LEO 1530 FEG SEM. Before SEM measurement, 5 nm gold was evaporated on $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. X-ray diffraction (XRD) spectrum was measured with the Empyrean model from PANalytical equipped with Cu anode material (K-alpha, $\lambda = 1.540598 \text{ \AA}$). The generator voltage and current were 40 kV and 40 mA, respectively. Atomic force microscopy (AFM) was performed using a Bruker Veeco Multimode V in trapping mode.

3. Results and discussion

Fig. 1 shows the schematic image of the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film *via* solid–gas reaction at low temperature under vacuum. Details of the operation conditions can be found in the Experimental section. The evaporated $\text{CH}_3\text{NH}_3\text{I}$ molecules react with heated PbI_2 upon contact and result in the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$, which can be preliminarily judged by the color change of the thin film from yellow to dark brown.

When the substrate temperature is at room temperature, we observe that the PbI_2 substrate after evaporation of excess $\text{CH}_3\text{NH}_3\text{I}$ is not dark brown, but yellow. However, after heating the substrate to 60 °C during evaporation, the evaporated device becomes dark brown. XRD spectra show the crystalline properties of the PbI_2 on substrate and of perovskite from evaporation of $\text{CH}_3\text{NH}_3\text{I}$ at room temperature and 60 °C, as plotted in Fig. 2. The peaks at 30.27° and 35.08°, marked with blue asterisk, exist in all devices and are assigned to ITO (PDF # 39-1058). Peaks at 12.52°, 25.35°, 38.44°, and 52.12° are observed in the PbI_2 samples before $\text{CH}_3\text{NH}_3\text{I}$ evaporation, which are

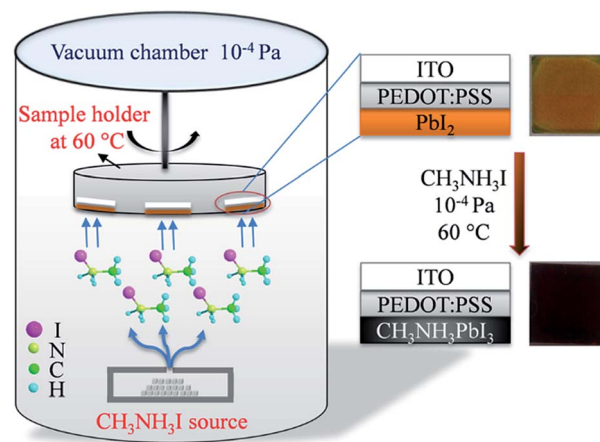


Fig. 1 Schematic image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ formation *via* solid–gas reaction at low temperature under vacuum.

attributed to the PbI_2 crystal (PDF # 07-0235), corresponding to (001), (002), (003), and (004) lattice phases, respectively. After the evaporation of excess $\text{CH}_3\text{NH}_3\text{I}$ at room temperature and the wash by isopropanol (IPA), peaks at 12.52° , 38.44° , and 52.12° still exist. In addition, new peaks at 14.03° , 28.27° , and 31.74° are observed and assigned to the characteristic peaks of $\text{CH}_3\text{NH}_3\text{PbI}_3$,³⁰ which means the evaporated samples at room temperature are a mixture of PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$. On the other hand, for the evaporated samples annealed at 60°C during evaporation, all peaks assigned to PbI_2 disappear, indicating complete conversion of PbI_2 into $\text{CH}_3\text{NH}_3\text{PbI}_3$. This phenomenon should be attributed to the increased diffusion rate of $\text{CH}_3\text{NH}_3\text{I}$ in the PbI_2 layer and the increased reaction rate between $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 at higher temperature. After getting energy from the heated substrate, $\text{CH}_3\text{NH}_3\text{I}$ molecules with increased kinetic energy can easily diffuse throughout the PbI_2 layer. On the other hand, in terms of chemical kinetics, the reaction rate between $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 (as described by eqn (1)) is a function of the rate constant and reactants' concentration, as shown in eqn (2),



$$\nu = \kappa[\text{CH}_3\text{NH}_3\text{I}]^a[\text{PbI}_2]^b \quad (2)$$

where ν is reaction rate, κ is rate constant, $[\text{CH}_3\text{NH}_3\text{I}]$ is mole concentration of $\text{CH}_3\text{NH}_3\text{I}$, a is order in $\text{CH}_3\text{NH}_3\text{I}$, $[\text{PbI}_2]$ is mole concentration of PbI_2 , and b is order in PbI_2 .

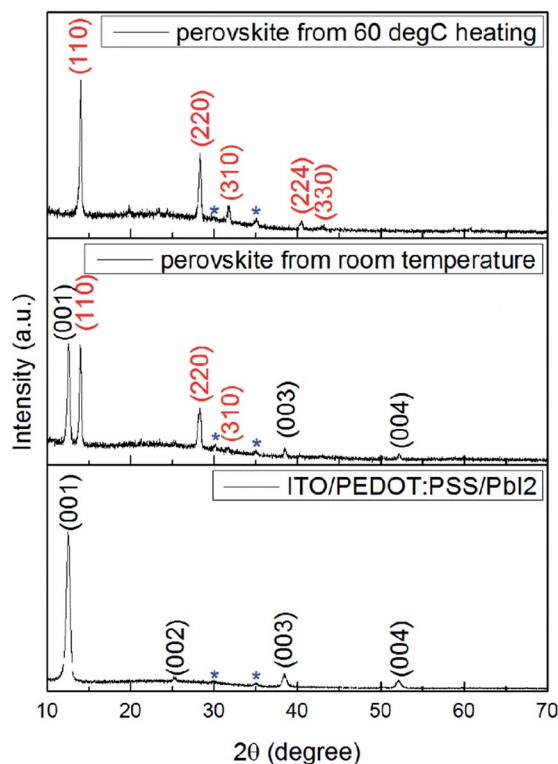


Fig. 2 XRD spectrum of PbI_2 on ITO/PEDOT:PSS, perovskite on ITO/PEDOT:PSS from room temperature, and perovskite on ITO/PEDOT:PSS from substrate at 60°C . The peaks marked with blue asterisk at 30.27° and 35.08° were assigned to ITO (PDF # 39-1058).

Following the Arrhenius equation, the rate constant κ is dependent on temperature:

$$\kappa = Ae^{-E_a/RT} \quad (3)$$

where A is constant, E_a is activation energy of reaction, R is the universal gas constant, and T is temperature.

Referring to eqn (2) and (3), when the temperature is raised, the rate constant κ increases, and thus the reaction rate ν increases. This result also indicates that the reaction between $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 is endothermic.

3.1. Effects of substrate temperature on perovskite thin film

Substrate temperatures of 50°C , 60°C , and 70°C during evaporation of $\text{CH}_3\text{NH}_3\text{I}$ were investigated. By studying the absorption spectra of the perovskite film as shown in Fig. 3a, we find that the absorption of perovskite increases with the substrate temperature from 50°C to 60°C , which means the crystallization quality of the formed perovskite is better at

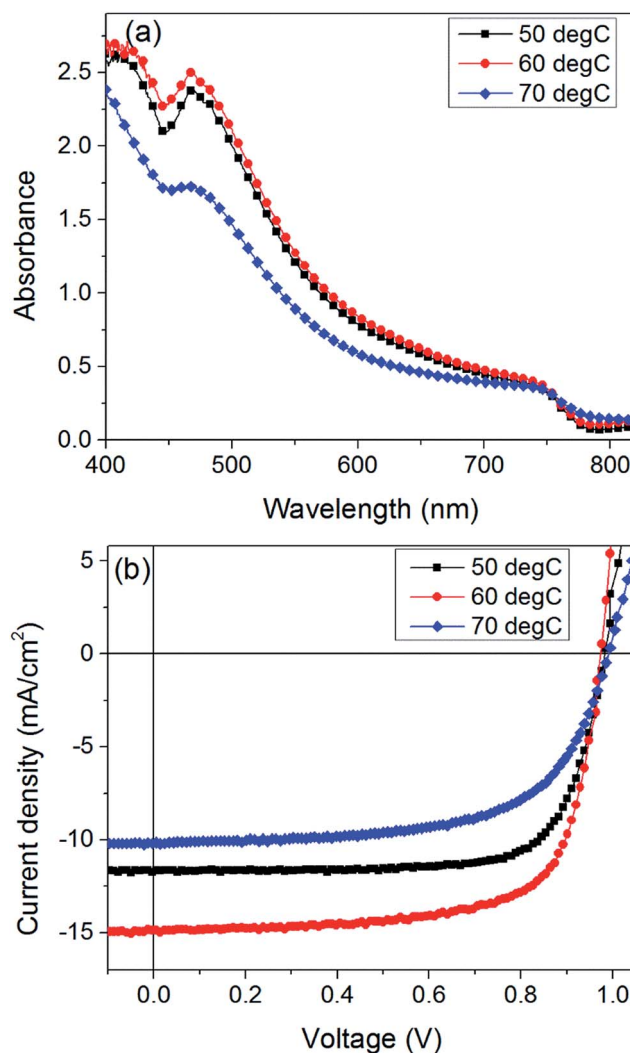


Fig. 3 (a) Absorbance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films and (b) J - V characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells prepared from substrate at 50°C , 60°C , and 70°C .

higher temperature. However, when the substrate temperature is further increased to 70 °C, the absorption decreases. In addition, the color of the perovskite film becomes lighter than perovskite prepared at the substrate temperatures of 50 °C and 60 °C. Two reasons might account for this result.

First, when the temperature is further increased to higher temperature and reaches 70 °C, it could favour the backward reaction in the reversible reaction^{31,32} (eqn (1)). In this case, the decomposition rate of $\text{CH}_3\text{NH}_3\text{PbI}_3$ might increase, and less perovskite will form (and thus the color will become lighter). Another possible reason is that it is thermodynamically unfavorable for $\text{CH}_3\text{NH}_3\text{I}$ molecules to deposit on hot PbI_2 substrate with a temperature of 70 °C. The majority of evaporated $\text{CH}_3\text{NH}_3\text{I}$ molecules are either evacuated away or deposit on the cold chamber wall. Thus, the formation of perovskite is hindered. A similar phenomenon of degraded perovskite film at a much higher temperature is also observed in the reaction between PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$.³³ The reduced absorbance of perovskite thin film prepared at a substrate temperature of 70 °C is accompanied by decreased PCE of the corresponding

solar cells, specifically, decreased short-circuit current density (J_{sc}). Fig. 3b shows the current density–voltage plot of perovskite solar cells from the substrate at 50 °C, 60 °C, and 70 °C. The PCE of device increases from 8.37% ($J_{\text{sc}} = 11.38 \text{ mA cm}^{-2}$) to 10.00% ($J_{\text{sc}} = 14.65 \text{ mA cm}^{-2}$) when increasing substrate temperature from 50 °C to 60 °C, then decreases to 6.33% ($J_{\text{sc}} = 10.18 \text{ mA cm}^{-2}$) when the temperature is further improved to 70 °C.

3.2. Effects of $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate on perovskite film

Based on eqn (2), the reaction rate between PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ depends on the concentration of $\text{CH}_3\text{NH}_3\text{I}$, so we changed the concentration of $\text{CH}_3\text{NH}_3\text{I}$ by controlling the evaporation rate of $\text{CH}_3\text{NH}_3\text{I}$, using the optimized substrate temperature of 60 °C. Evaporation rates of 0.5 Å s^{-1} , 0.9 Å s^{-1} , and 1.3 Å s^{-1} were investigated. Fig. 4 shows the scanning electron microscope (SEM) and atomic force microscopy (AFM) images of the perovskites prepared from different $\text{CH}_3\text{NH}_3\text{I}$ evaporation rates. SEM shows that the average diameter of perovskite crystal size increases slightly with increasing evaporation rate. This increased crystal size might be attributed to the improved

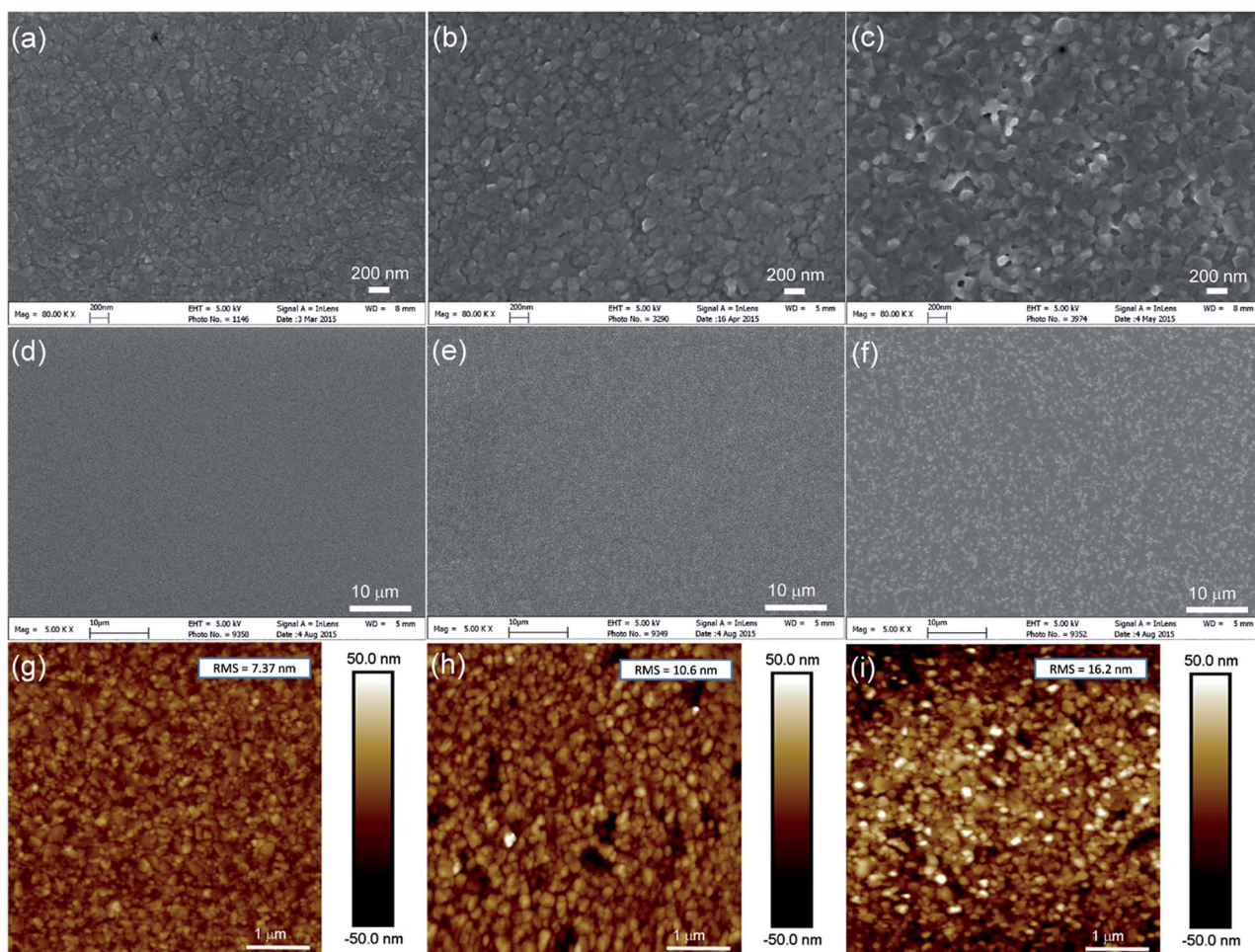


Fig. 4 (a) High-resolution SEM image, (d) low-resolution SEM image, and (g) AFM image of perovskite thin film from the $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate of 0.5 Å s^{-1} . (b) High-resolution SEM image, (e) low-resolution SEM image, and (h) AFM image of perovskite thin film from the $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate of 0.9 Å s^{-1} . (c) High-resolution SEM image, (f) low-resolution SEM image, and (i) AFM images of the perovskite films from the $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate of 1.3 Å s^{-1} . The size of the AFM image is $5 \mu\text{m} \times 5 \mu\text{m}$.

forward reaction rate of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$. Besides, the roughness (R_q) of perovskite films from $\text{CH}_3\text{NH}_3\text{I}$ evaporation rates of $0.5 \text{ \AA s}^{-1}$, $0.9 \text{ \AA s}^{-1}$, and $1.3 \text{ \AA s}^{-1}$ are 7.37 nm, 10.6 nm, and 16.2 nm, respectively. The increased roughness under higher evaporation rate might be due to uneven nucleation rate. Deposited $\text{CH}_3\text{NH}_3\text{I}$ reacts with surface PbI_2 and leads to primary nucleation of $\text{CH}_3\text{NH}_3\text{PbI}_3$. At a higher evaporation rate, more $\text{CH}_3\text{NH}_3\text{I}$ will present at the surface of PbI_2 , which favours the secondary nucleation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on the primary sites. The nucleic sites of big crystal size might grow at higher rates for their larger contact area. As a result, the big crystal will grow even larger, while the growth of small-crystal nucleic sites is diminished. Accordingly, the roughness is enhanced. Nevertheless, under low evaporation rate, the nucleation rate for formation of perovskite seeds is quite uniform over the substrate because no extra $\text{CH}_3\text{NH}_3\text{I}$ presents at the surface, and newly evaporated $\text{CH}_3\text{NH}_3\text{I}$ almost equally deposits at each nucleic site. Indeed, the roughness from the evaporation rate of $0.5 \text{ \AA s}^{-1}$ is even smaller than that (8.3 nm) of the one with the highest certified perovskite solar cells.³⁴ On the other hand, the lower $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate of $0.1\text{--}0.2 \text{ \AA s}^{-1}$ was investigated. However, we find that the color of the device after evaporation of $\text{CH}_3\text{NH}_3\text{I}$ for more than two hours is slightly brown, which means that a small amount of perovskite has formed. Perovskite solar cells with this thin film exhibit very poor performance (less than 1%). We attribute the result to a too-slow reaction rate between PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$. The lower $\text{CH}_3\text{NH}_3\text{I}$ evaporation rate leads to lower concentration of $\text{CH}_3\text{NH}_3\text{I}$. Too-low concentration of $\text{CH}_3\text{NH}_3\text{I}$ diminishes the chance of effective collision between gaseous $\text{CH}_3\text{NH}_3\text{I}$ molecules and PbI_2 . According to collision theory,³⁵ effective collision is the premise for two compounds to react with each other. As a result, the formation of perovskite under such condition is quite difficult.

3.3. Perovskite film from PbI_2 with different thicknesses

We have prepared 60 nm and 100 nm thick PbI_2 films *via* spin-coating their precursors with concentrations of 300 mg ml^{-1} and 462 mg ml^{-1} in DMF, respectively. After evaporation of excess $\text{CH}_3\text{NH}_3\text{I}$ with a rate of $0.5 \text{ \AA s}^{-1}$ and substrate temperature at 60°C , the formed perovskite thin films from 60 nm and

100 nm thick PbI_2 are measured to about 150 nm and 250 nm using Step Profiler. With these perovskite active layers, the corresponding solar cells exhibit PCEs of 6.49% and 10.0%, respectively (ESI†). However, we failed to prepare even thicker perovskite from 130 nm PbI_2 (from 550 mg ml^{-1} PbI_2 in DMF). Though we evaporated all of the $\text{CH}_3\text{NH}_3\text{I}$ (1.5 g) that can be stored in our source boat, the conversion of PbI_2 into perovskite is not complete, resulting in lower absorption of perovskite thin film and poor performance of the solar cell (less than 2%). We attribute the result to the too-large volume of our vacuum chamber (approximate $58\,000 \text{ cm}^3$). The utilization of evaporated $\text{CH}_3\text{NH}_3\text{I}$ in such a big chamber is very low. Most of the $\text{CH}_3\text{NH}_3\text{I}$ is deposited on the cold wall or evacuated away.

3.4. Photovoltaic performance after post-annealing

Photovoltaic characterization was performed after making 250 nm perovskite film into solar cells. The cross-section SEM image of the cell is shown in Fig. 5a. PEDOT:PSS and PC_{61}BM work as hole transporting layer and electron transporting layer, respectively. PFN³⁶ is used as dipole between PC_{61}BM , and silver cathode to facilitate electron transport. The corresponding energy diagram is shown in Fig. 5b. Post-annealing of deposited perovskite thin film at 100°C was investigated. Fig. 5c shows the J - V curve of perovskite solar cells from 100°C with annealing of perovskite thin film for 0 min, 10 min, and 20 min. The J_{sc} of perovskite solar cells increases with increasing annealing time, which can be explained by the improved crystallization of perovskite thin film. However, it should be noted that annealing at 100°C , even for 10 min, would reduce the V_{oc} and FF. This phenomenon has also been reported by Ziqi Liang and co-workers.³⁷ The drop of V_{oc} might be due to increased non-radiative recombination centres under annealing at 100°C .^{38,39}

3.5. Optimized device performances

The champion device without post-annealing has a PCE of 10.0%, J_{sc} of 14.65 mA cm^{-2} , V_{oc} of 0.93 V, and FF of 0.73 (as shown in Fig. 6a). The J_{sc} matches well with the value obtained (14.01 mA cm^{-2}) by integrating IPCE, as shown in Fig. 6b. The histograms of J_{sc} , V_{oc} , FF, and PCE of 20 samples are displayed in Fig. 6c–f. It can be seen that the average PCE is more than 8%. Compared with the reported high-performance

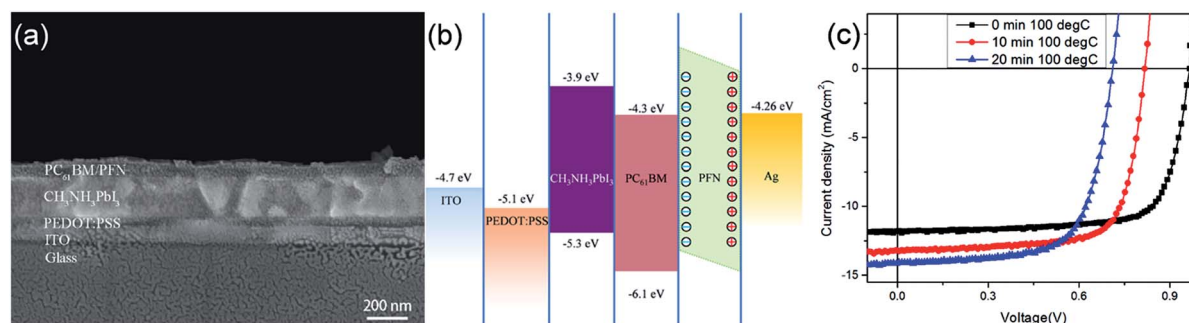


Fig. 5 (a) Cross-sectional SEM image of perovskite solar cell. (b) Energy level diagram of the solar cell with structure of ITO/PEDOT:PSS (40 nm)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (250 nm)/ PC_{61}BM (50 nm)/PFN (1–2 nm)/Ag (120 nm). (c) Current density–voltage curves of perovskite solar cell after 0 min, 10 min, and 20 min post-annealing of perovskite thin films at 100°C .

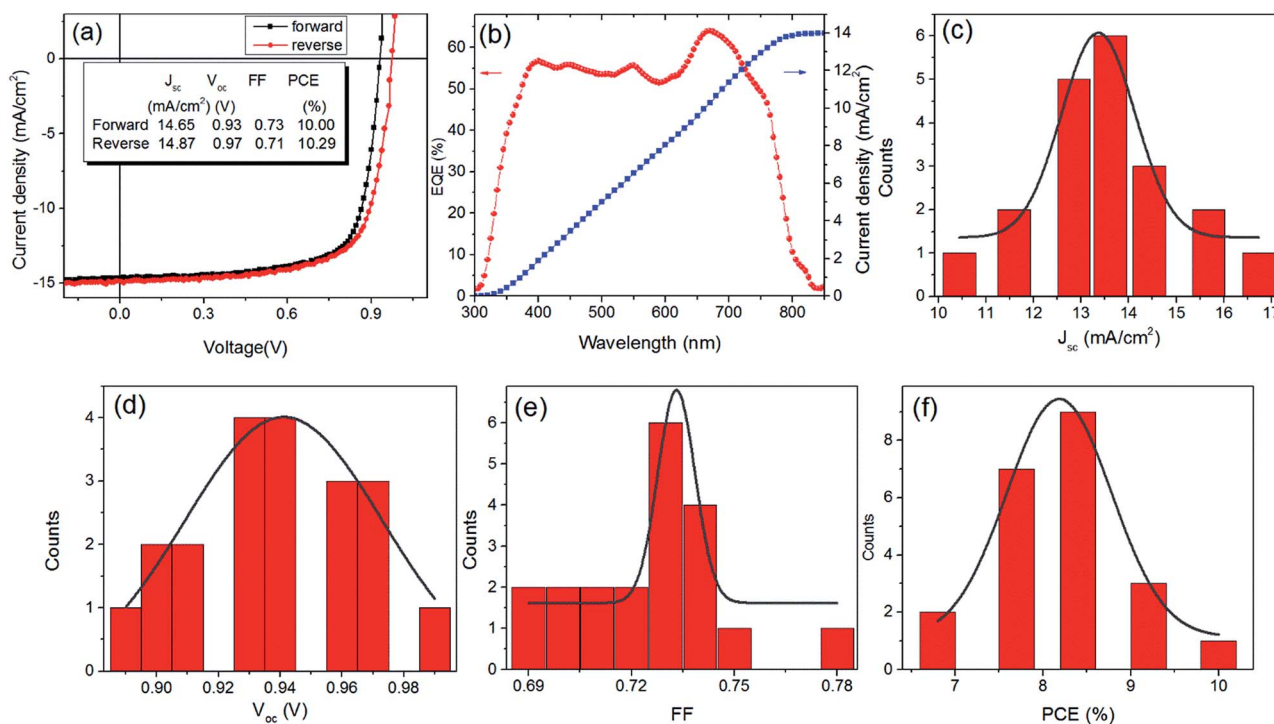


Fig. 6 (a) Current density–voltage curve and (b) incident photon-to-current efficiency (IPCE) of CH₃NH₃PbI₃ solar cells. (c) J_{sc} , (d) V_{oc} , (e) FF, and (f) PCE histograms of 20 samples.

CH₃NH₃Pb(I,Cl)₃ solar cell,^{7,40,41} which contains more than 400 nm active layer, the lower PCE and especially the lower short-circuit current of perovskite solar cells from our approach are mostly attributed to thinner perovskite layer. The large vacuum chamber (approximately 58 000 cm³) in our lab makes the utilization of evaporated CH₃NH₃I very low, leading to incomplete conversion of thick PbI₂ into perovskite even after evaporating all of the CH₃NH₃I that can be stored in the source boat. As a result, thick perovskite is hard to get under the current condition. However, this issue should not be a problem for vacuum chambers with small volume and large source boat. The hysteresis that occurs in most perovskite devices^{42–44} is also investigated in our device. The scan rate of our device is 0.13 V s^{−1}, which is slightly lower than the usually reported 0.15 V s^{−1}.⁴² It is generally accepted that hysteresis is more severe at a lower scan rate.⁴⁶ Our results are shown in Fig. 6a. It can be seen that the PCEs of our device are very close under forward (PCE = 10.0%) and reverse scan (PCE = 10.3%), which indicates that the hysteresis in our device is very small.

4. Conclusions

In summary, a solid-evaporated gas reaction method has been developed to fabricate CH₃NH₃PbI₃ perovskite solar cells with very smooth morphology and high coverage. No post-treatment annealing is needed after the film formation in our approach. The smooth morphology originates from the slow reaction of solid PbI₂ and diluted gas CH₃NH₃I molecule and the uniform nucleation rate. Compared with traditional one-step or two-step methods where solvent-induced intermediates might account

for the complete coverage, our approach avoids the use of solvent during film preparation and results in high coverage. A PCE of 10.0% and low hysteresis have been achieved using our device. Consequently, this work contributes to the development of low-temperature and simple approaches for fabricating perovskite solar cells.

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