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A low temperature gradual annealing scheme for achieving high performance perovskite solar cells with no hysteresis†

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CH₃NH₃PbI₃ is commonly used in perovskite solar cells due to its long diffusion length and good crystallinity. In this paper, in the one-step approach using CH₃NH₃I and PbCl₂ for forming the perovskite, we present a new low temperature annealing approach of gradually increasing the temperature to fabricate perovskite films. Various temperatures and temperature ranges for the formation of perovskite films have been studied. Using the gradual annealing process, we can tune the amount of chlorine in the atomic ratio of chlorine/iodine from 1.2 to 4.0%. Meanwhile, the gradual annealing process influences the quality of the perovskite film and importantly the device performance. The results show that through the optimized process, the film quality is improved with high surface coverage and good photoluminescence and reproducibility. We find that a higher amount of chlorine in the perovskite film plays a positive role in the device performance in the approach for achieving a power conversion efficiency of 14.9% with no obvious hysteresis.

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1 Introduction

Energy consumption has largely increased over the last decade.^{1,2} In order to meet the increasing energy demands, solar energy has drawn great attention. Three-dimensional organic-inorganic hybrid perovskites in the field of thin film solar cells have been intensively investigated due to their low cost and high efficiency.^{3–6} By a one-step approach, CH₃NH₃PbI₃ solar cells have achieved power conversion efficiencies (PCEs) of over 15%.^{6–9} Conventionally, these perovskite films are annealed at 100 °C or higher.^{10,11} For planar device architectures using the one-step method, the perovskite film morphology of a solution-processed organic lead trihalide is not ideal when compared to the film deposited by two-step methods and vapor deposition techniques.^{12–14} High annealing temperatures can also limit the choice of interfacial layer materials and the annealing process of an interfacial layer spin-coated on the perovskite film will also affect the film properties.^{15,16} Meanwhile, the ways to

control the amount of chlorine and its influence on the perovskite film are still unclear.^{17–20}

In this paper, in the one-step method using CH₃NH₃I and PbCl₂, we have introduced a new annealing process for forming lead trihalide-based perovskite films, in which the temperature is increased gradually from a low temperature value. By optimizing the perovskite film annealing process with a temperature from 60 °C to 80 °C for a total annealing time of 1 h, PCEs with values of 13.3% (average) and 14.9% (best) were obtained. Meanwhile, the perovskite device showed good reproducibility with no obvious hysteresis. Through our approach, the amount of chlorine can be tuned from 1.2 to 4.0% in the atomic ratio of chlorine over iodine in the perovskite material. Our results show that, in our annealing approach, the perovskite film with the higher chlorine ratio exhibits better device performance.

2 Experimental section

2.1 Materials

24 mL of 0.20 mol methylamine (33 wt% in absolute ethanol) was reacted with 10 mL of 0.04 mol hydroiodic acid (57 wt% in water with 1.5% hypophosphorous acid) with stirring at 0 °C for 2 h to obtain methylammonium iodide (MAI). After the previous reaction, the white precipitate of MAI was recovered by rotary evaporation at 60 °C for 2 h and then dissolved in ethanol followed by sedimentation in diethyl ether three times. The MAI powder was finally dried at 50 °C in a vacuum oven for 6 h. Perovskite precursor solution was prepared by mixing the MAI and lead chlorine powder in anhydrous dimethylformamide

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with a molar ratio of 3 : 1. The solutions (35 wt%) were stirred overnight at room temperature and filtered with 0.45 μm PVDF filters before device fabrication.

2.2 Device fabrication

The devices were fabricated with the structure of indium tin oxide (ITO)/PEDOT:PSS/perovskite/PC₆₁BM/PFN/Ag. ITO (15 Ω per square) glass substrates, were cleaned sequentially with detergent, acetone, and ethanol under sonication for 15 min. After drying with nitrogen, the substrates were treated with ultraviolet-ozone. PEDOT:PSS was deposited by spin-coating at 4000 rpm for 40 s and annealed at 120 $^{\circ}\text{C}$ for 10 min in air. After cooling down, the substrates were transferred into a nitrogen filled glovebox to avoid oxygen, moisture and unexpected contamination in air. The homogeneous 35 wt% perovskite precursor solution was then spin-coated on the PEDOT:PSS at 3000 rpm for 40 s. The samples were left to dry at room temperature in the glovebox for 30 min. The samples were then baked on a hot plate for 1 h at different temperatures using a new annealing process. In the new annealing process, we started at a low temperature of $X^{\circ}\text{C}$ that the X value includes 50 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$, 70 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$ and then gradually increased to the maximum temperature of 80 $^{\circ}\text{C}$. The temperature step is $(80 - X)/6^{\circ}\text{C}$ and the time interval for each step of annealing is 10 min. Meanwhile, we also annealed samples at a constant temperature of 100 $^{\circ}\text{C}$ for comparison. Afterward, the PC₆₁BM (20 mg mL⁻¹ in chlorobenzene) and PFN (0.5 mg mL⁻¹ in ethanol) were then sequentially deposited by spin coating at 1000 rpm for 40 s and 3000 rpm for 30 s, respectively. Silver electrodes were finally evaporated under high vacuum ($<3 \times 10^{-4}$ bar) through a shadow mask with a thickness of 100 nm.

2.3 Measurements

Morphologies of the perovskite films were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM). Atomic force microscopy (AFM) measurements were obtained by using a Nano Scope III (Digital Instrument) in the tapping mode. A Keithley 2635 source meter and Newport AM 1.5 G solar simulator were used for the measurement of current density–voltage (J – V) characteristics under 100 mW cm⁻² illumination. The EQE measurement was performed by using a system combining a xenon lamp, a monochromator, a chopper and a lock-in amplifier together with a calibrated silicon photodetector. The UV-vis absorption measurement was performed under a dark ambient environment by using spectroscopic ellipsometry (Woollam). The crystalline structures of the perovskite films were identified by X-ray diffraction (XRD) (copper K-alpha-1 X-ray (1.5405980 angstrom)). A 400 nm laser source (~ 50 μW , 2 MHz repetition rate) was used in the time resolved PL measurement. Ultraviolet photoelectron spectroscopy (UPS) spectra were obtained using a He discharged lamp (He I 21.22 eV, Kratos Analytical) with an experimental resolution of 0.15 eV. The samples were biased at -10 V to favor the observation of the secondary-electron cut-off from the UPS spectra. X-Ray photoelectron spectroscopy (XPS) measurement was carried out using a Physical Electronic 5600 multi-

technique system (monochromatic Al K α X-ray source). All the spectra were adjusted according to the standard value of the C 1s peak at 284.5 eV.

3 Results and discussion

3.1 Control of the atomic ratio of chlorine over iodine in perovskites under different annealing conditions

In our study, the perovskite films are prepared under different annealing conditions. We started at a low temperature of $X^{\circ}\text{C}$ which includes 50 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$, 70 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$. The temperature is gradually increased to the maximum temperature of 80 $^{\circ}\text{C}$. The temperature step is $(80 - X)/6^{\circ}\text{C}$ and the time interval for each step of annealing is 10 min. The samples prepared by the gradual annealing process are hereafter named as $X^{\circ}\text{C}$ –80 $^{\circ}\text{C}$ (including 50–80 $^{\circ}\text{C}$, 60–80 $^{\circ}\text{C}$, 70–80 $^{\circ}\text{C}$ and 80–80 $^{\circ}\text{C}$ (*i.e.* 80 $^{\circ}\text{C}$)). Meanwhile, control samples are prepared by using a constant temperature of 100 $^{\circ}\text{C}$ (the typically used temperature)²¹ for comparison. It should be noted that the lowest annealing temperature we used here is 50 $^{\circ}\text{C}$ because the reaction of perovskite precursors is too slow when the temperature is below 50 $^{\circ}\text{C}$. On the other hand, when the temperature is over 100 $^{\circ}\text{C}$, the reaction is vigorous and the morphology of the film is very rough and thus will not be studied here. Details of perovskite film formation are described in the Experimental section.

In order to study the gradual annealing process and investigate the chlorine amount, XPS is used to analyze the elemental composition as shown in Fig. 1. It should be noted that since the content of chlorine is very low and chlorine will be lost during the test process,²² the signal of chlorine is difficult to be detected. Fresh samples are prepared and quickly placed into the XPS chamber. The vacuum process time is also short at about 30 min. Because of careful operation, the XPS signal of the very little chlorine content could be probed. From the atomic percentage which was calculated from the XPS spectra,

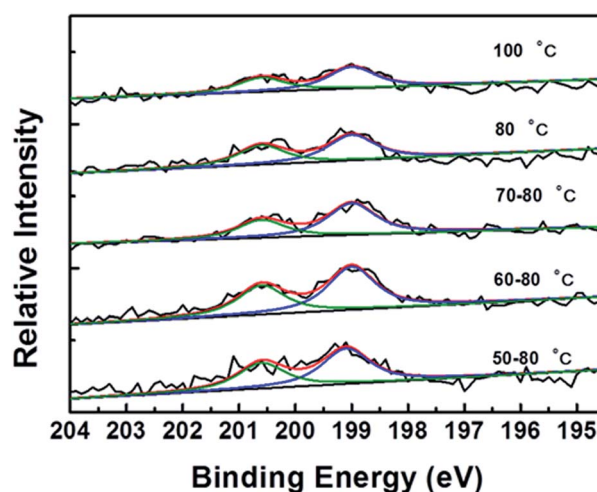
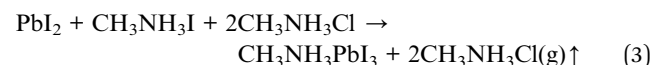
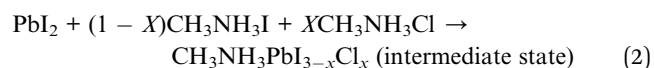
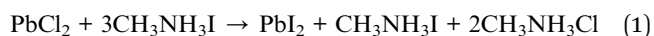


Fig. 1 Cl 2p core level XPS spectra of binding energies 198.9 eV and 200.5 eV (Cl 2p^{3/2} and Cl 2p^{1/2}) measured on the top surface of perovskite films purged with Ar gas during measurement.

the chlorine content of all the samples is below 1%. In this work, since the amount of chlorine is very little, we will use the atomic ratio of chlorine over iodine in perovskites to describe the amount of chlorine.

Generally, when the atomic percentage of the test chlorine exceeds 1%, it is usually regarded as $\text{CH}_3\text{NH}_3\text{Cl}$ or the unreacted PbCl_2 ,²² which can easily absorb water and then damage the lattice of perovskite. It is also one of the main reasons that perovskite solar cells are unstable. In our experiment, the devices are very stable, the PCE only decreases 25% for the unencapsulated device stored in a glove box for three months (which will be discussed later). Interestingly, when the starting temperature of the gradual annealing approach increases, the atomic ratio of chlorine/iodine increases first, then decreases as shown in Table 1, the atomic ratio falls further when annealed at a constant 100 °C. The perovskite film prepared by gradual annealing at 60–80 °C has the highest amount of chlorine ratio with a value of 4.0%. Consequently, through using different annealing processes, we can tune the amount of the chlorine ratio in chlorine/iodine from 1.2% (control) to 4.0%. In addition, the trend of the device performance follows that of the chlorine ratio (which will be discussed later).

With the gradual annealing processes (*i.e.* 50–80 °C, 60–80 °C, 70–80 °C), the amount of chlorine ratio is higher than 2.7%, which indicates the slow crystallization process in these samples. The amount of chlorine ratio is 1.2% with annealing at a constant temperature of 100 °C, which presents the rapid reaction of perovskite precursor materials as described below. We can adopt the reaction process of perovskite²³ as follows to understand the reaction and the change of chlorine ratio.



With the gradual annealing approach, the temperature increased step by step, thus the reaction and crystallization are slowed. The decelerated reaction and crystallization is critical to slow down the perovskite formation process and thus to improve crystal quality during annealing treatment, particularly at a relatively low annealing temperature.¹¹ At low annealing temperature, no $\text{CH}_3\text{NH}_3\text{Cl}$ is clearly sublimated, and reactions

(1) and (2) mainly occurred in the early stage of the process. The rate of sublimation of the organic species $\text{CH}_3\text{NH}_3\text{Cl}$ will increase with higher temperature.²¹ Thus, when the temperature is increased at a later stage, it favors the occurrence of reactions (3) and (4). As a result, more organic $\text{CH}_3\text{NH}_3\text{Cl}$ will be generated and the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ will convert to $\text{CH}_3\text{NH}_3\text{PbI}_3$ during the process.

For the high annealing temperature (80 °C or 100 °C case), eqn (4) will dominate in the reaction process and the intermediate state $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ is less produced. The high annealing temperature will accelerate the sublimation of $\text{CH}_3\text{NH}_3\text{Cl}$ which results in diminishing reactions (1) and (2), thus less $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ intermediate state yields, this result can be confirmed from the trace amount of chlorine detected in the XPS measurement. That is why the crystallization of the perovskite film annealed at 100 °C is inferior to that processed by gradual annealing. In summary, with gradual annealing at lower temperatures (*i.e.* 60–80 °C), eqn (1) and (2) have higher probability to react, leading to a higher concentration of chlorine detected in the perovskite film. Although the gradual annealing process would delay the overall reaction as compared to the case annealed at a constant temperature of 80 °C and 100 °C, the approach offers better conditions for the formation of perovskite films and thus give the best device performance (which will be described later).

3.2 Film morphology study

The morphologies of the perovskite films formed with gradual annealing at 50–80 °C, 60–80 °C and annealing at 100 °C are studied by AFM and SEM as shown in Fig. 2, the morphologies of films prepared under other conditions are shown in Fig. S1.† For samples with gradual annealing at 50–80 °C, homogeneous films are formed with a roughness of 11.2 nm, and the crystalline structure is observed. As the annealing temperature is increased to 60 °C–80 °C, the film has a drastic change in the appearance and the grain size increases, which is attributed to the volume expansion that commonly occurs in the process. The film roughness is relatively small with a value of 11.4 nm compared to the film roughness achieved by one-step perovskite fabrication, which is usually about 25 nm.^{24–26} The small roughness of the gradual annealing perovskite indicates that the layer has been fully covered and hence avoids short-circuit from the direct contact between the relatively conductive perovskite and the metal electrode.^{27,28} By increasing the annealing temperature further, the perovskite film forms lots of individual islands. They no longer form a densely interconnected network but individual islands with bigger gaps in

Table 1 Atomic ratios of chlorine/iodine were calculated from the high resolution XPS spectra and values for diffusion coefficients and diffusion lengths from fits to PL decays

Temperature (°C)	50–80	60–80	70–80	80	100
Cl/I percentage (%)	3.1	4.0	2.7	1.5	1.2
Diffusion length (nm)	911	1108	855	760	328
Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	0.04	0.06	0.04	0.03	0.02

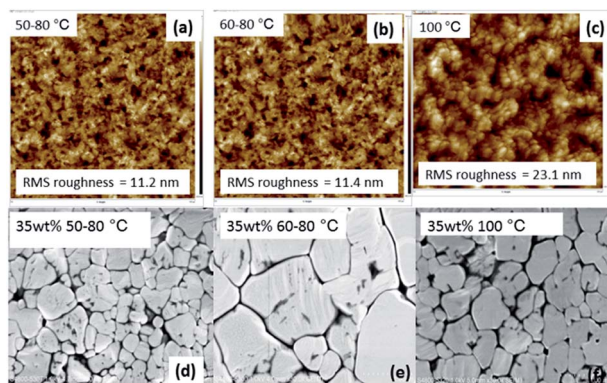


Fig. 2 AFM height images of perovskite films with gradual annealing at (a) 50–80 °C, (b) 60–80 °C and (c) directly annealing at 100 °C. SEM images of perovskite films formed on ITO/PEDOT:PSS substrates with a gradual annealing of (d) 50–80 °C, (e) 60–80 °C and annealing at (f) 100 °C as the reference. The thickness of perovskite films is about 300 nm.

between, resulting in larger uncovered areas.²¹ For instance, the film roughness increases to 23.1 nm for the case of 100 °C, which is also accompanied by a lower surface coverage.

XRD measurement is conducted to investigate the crystallinity of the material formed by different annealing processes as shown in Fig. 3, two characteristic lines can be identified (14.10° and 28.47°) which were assigned to the 110 and 220 diffraction peaks of a mixed-halide perovskite film with an orthorhombic crystal structure.²⁹ From the previous work, it is known that this perovskite material shows a tendency for preferential orientation with the *a*-axis.^{30,31} No clear impurity peaks are obtained in the spectrum analysis, indicating a complete conversion of the films. Here, we emphasize that full conversion is crucial to the reproducibility of the device performance, which will be discussed later.³² As the annealing temperature is changed from 50 °C–80 °C to 60 °C–80 °C, the intensity of the 110 and 220 peaks of the perovskite film increases then decreases largely with annealing temperatures of 70 °C–80 °C, 80 °C, and 100 °C. This

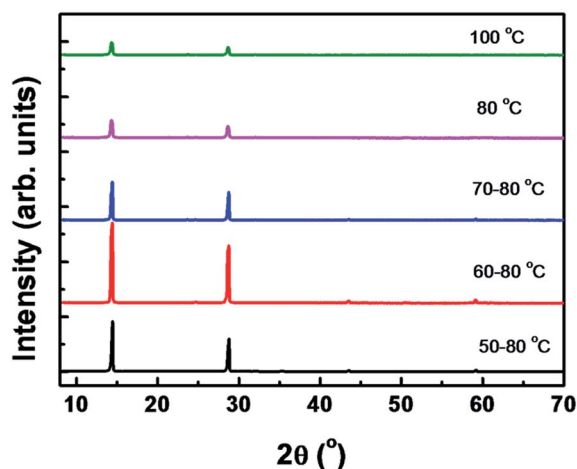


Fig. 3 The XRD spectrum of perovskite films on ITO/PEDOT:PSS substrates with different annealing processes.

phenomenon can be explained by the fact that less material is formed at high temperatures (70 °C–80 °C, 80 °C, and 100 °C), which indicates less crystalline areas and low perovskite formation, and it is supported by the results of SEM and XRD. The high annealing temperature especially 100 °C is undesirable since it can accelerate the formation of perovskite and would create lots of pinholes that are harmful for film crystallization.

3.3 Optical properties

Fig. 4 shows the steady-state photoluminescence (PL) spectra of perovskite films prepared under varying annealing conditions, the measured samples with a structure of ITO/PEDOT:PSS/perovskite. The enhanced PL of the gradual annealing process indicates that non-radiative decay is significantly suppressed through our gradual annealing method, especially for films gradually annealed at 60–80 °C with a 4.0% chlorine ratio that exhibit the strongest PL intensity. This implies that the non-radiative recombination channels are greatly suppressed, indicating that the defects are reduced through gradually annealing the precursor film particularly for the 60–80 °C case. We also investigate the time-resolved PL decays with a peak emission of 770 nm (± 10 nm) and a structure of ITO/PEDOT:PSS/perovskite/PC₆₁BM to emulate real device processing conditions. Values for diffusion constants and diffusion lengths conform to the PL decays using the diffusion model described by Samuel D. Stranks *et al.*³³ As shown in Table 1, the diffusion length for the gradually annealed precursor film at 60–80 °C with a 4.0% chlorine ratio in the mixed halide perovskite is greater than 1 μ m, which is much longer than the active layer of the device (300 nm) and corresponds with the reported results.³⁴ Besides, the perovskite film with a longer diffusion length shows higher photovoltaic performance (which will be discussed later), which can be explained by the face that the photogenerated charge in these perovskite films can be more efficiently extracted before recombination.

The absorption spectra of the gradually annealed perovskite films are also studied. Fig. 5(a) shows the absorption spectra of

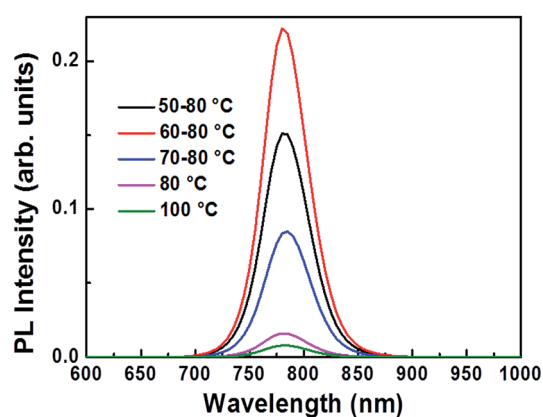


Fig. 4 Steady-state PL spectra of perovskite films with gradual annealing of 50–80 °C, 60–80 °C and 70–80 °C, annealing at 80 °C and 100 °C as reference with a structure of ITO/PEDOT:PSS/perovskite.

PEDOT:PSS/perovskite films under different annealing conditions. The perovskite absorption at a wavelength of around 740 nm significantly enhances when the thermal annealing process changes from 50–80 °C to 60–80 °C and then decreases as the annealing temperature increases further in the cases of 70–80 °C, 80 °C and 100 °C. The gradually annealed perovskite films exhibit improved absorption, especially when annealed at 60–80 °C. The changes in the absorption indicate the extent of precursor conversion. When annealed at 50–80 °C, the precursor conversion is low at the beginning, and the extent of conversion enlarges with increasing temperature. The sample annealed at 60–80 °C shows the highest absorbance indicating the largest extent of precursor conversion as confirmed by XRD. With further increasing the annealing temperature, larger islands with bigger gaps have been formed, and the larger uncovered areas result in the reduced absorption.

3.4 Photovoltaic performance

In Fig. 6(a), the current density (J)–voltage (V) characterization of solar cells with perovskite films formed from gradual annealing (60–80 °C) and direct annealing (100 °C) is measured, and other conditions are shown in Fig. S3(a).† Table 2 summarizes the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE of all the devices prepared by different annealing processes. When the gradual annealing temperature increases from 50–80 °C to 60–80 °C, J_{sc} increases

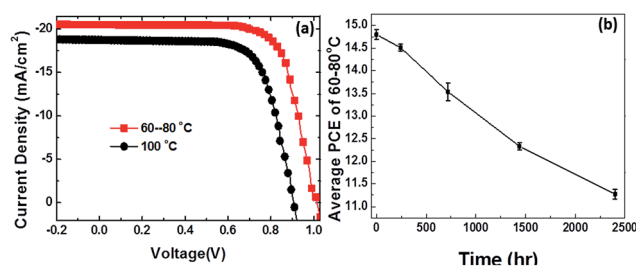


Fig. 6 (a) J – V curves under AM 1.5 illumination of devices made with different annealing processes. (b) The lifetime of PCE with gradual annealing at 60–80 °C of 4 devices in a glovebox without encapsulation.

Table 2 A comparison of the device performance^a

Annealing (1 h)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
50–80 °C	0.98	20.36	70	13.96
60–80 °C	1.00	20.71	72	14.91
70–80 °C	0.96	19.89	68	13.05
80 °C	0.94	19.67	67	12.39
100 °C	0.91	18.72	65	11.06

^a This table shows the V_{oc} , J_{sc} , FF and PCE of the reference device (annealing at 100 °C) and the device using the gradual annealing process of different temperatures under AM 1.5 G illumination with a light intensity of 100 mW cm⁻².

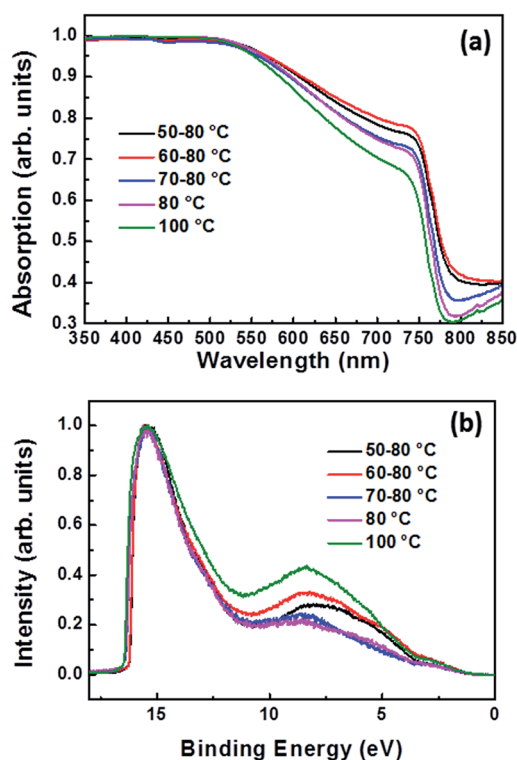


Fig. 5 (a) Absorption spectra of perovskite films with gradual annealing of 50–80 °C, 60–80 °C, 70–80 °C and 80 °C, annealing at 100 °C as reference. (b) Full scanning UPS spectra of the ITO substrate and PEDOT:PSS/perovskite films made from different annealing processes.

from 20.36 mA cm⁻² to 20.71 mA cm⁻². The further increase of the gradual annealing temperature to 70–80 °C will make J_{sc} decrease to 19.89 mA cm⁻². With a further increase of the annealing temperature, J_{sc} will drop to 18.72 mA cm⁻². The variation of J_{sc} corresponds to the absorption properties which indicates the extent of precursor conversion. Meanwhile, FF increases to 72% with increasing gradual annealing temperature from 50–80 °C to 60–80 °C and then decreases to 65% with higher annealing temperature. FF is partly influenced by the roughness of the films.³⁵ The change of V_{oc} can be described from the UPS measurement as shown in Fig. 5(b) that during the thermal annealing process the highest occupied molecular orbital (HOMO) value increases from 5.75 to 5.78 eV for temperatures from 50–80 °C to 60–80 °C and decreases to 5.54, 5.52 and 5.46 eV for temperatures at 70–80 °C, 80 °C, and 100 °C, respectively. HOMO is decreased by 0.32 eV when annealed at 100 °C compared to 60–80 °C. It shows that the annealing process significantly influences the open-circuit voltage (V_{oc}). As a result, PCE increases from 13.96% to 14.91% and then decreases to 11.06%. The hypothesis is that the poor device performance is associated with discrete islands and large pore sizes formed on the film. Besides, the effective free carrier generation will be limited by poor film coverage and hence causes unsatisfactory performance.³⁶ As a result, the highest PCE is achieved for the device prepared using the gradual annealing within 60–80 °C which obtains a PCE of 14.91%, a J_{sc} of 20.71 mA cm⁻², a V_{oc} of 1.00 V, and an FF of 72%. In order to confirm the accuracy of our PCE measurements, the external quantum efficiencies (EQEs) of the device is measured as shown

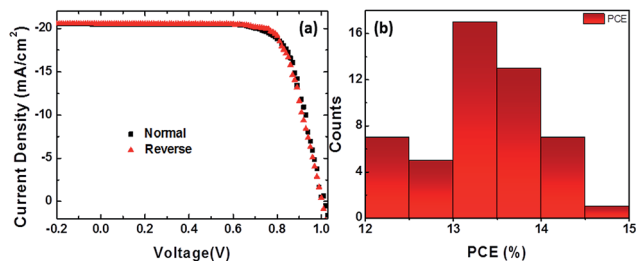


Fig. 7 (a) Photocurrents of perovskite solar cells prepared by the gradual annealing at 60–80 °C measured in different scanning directions. (b) PCE histograms of 50 devices prepared by gradual annealing at 60–80 °C.

in Fig. S3(b).† The calculated J_{sc} from the EQE spectra is similar with the measured J_{sc} .

The stability conditions for devices gradually annealed at 60–80 °C are shown in Fig. 6(b). After 3 months, the average PCE only decreases about 25% for several devices based on 60–80 °C gradual annealing which are stored in a glovebox without encapsulation. As shown in Fig. 7(a), no obvious hysteresis of photocurrents is observed by changing the sweep direction in the devices. In order to investigate the reproducibility of the solar cells using gradual annealing at 60–80 °C, 50 separate devices were fabricated and tested. The histograms of the device PCE is presented in Fig. 7(b). As can be seen, the average PCE is located at about 13.3%, while the highest PCE is observed at about 15% and 16% of the devices exhibit PCEs above 14%.

4 Conclusions

To summarize, we have demonstrated a new scheme of a gradual annealing process with relative low temperature to form the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite in a one-step approach using mixed halide precursors. The gradual annealing process can offer a favorable environment for the crystallization of perovskite; facilitate the formation of homogenous surface coverage and present micrometer-level diffusion lengths. The efficiency of a planar perovskite solar cell formed from the best gradual annealing process of 60–80 °C reaches about 15%. The devices also have good reproducibility with no obvious hysteresis. In addition, the atomic ratio of chlorine over iodine in the perovskite material has been discussed. The higher amount of the chlorine ratio of the gradual annealing process indicates a slower reaction process, which is important for perovskite formation. Our study reveals that the importance of controlling the formation reaction of perovskites is an alternative choice to achieve high performance perovskite solar cells. The method of using mixed halide precursors to tune the annealing process can be extended to other organometallic perovskite material systems. Our results may provide guidelines to develop stable and high-performance perovskite solar cells.

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