Reveal the growth mechanism in perovskite films via weakly coordinating solvent annealing

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ABSTRACT In this study, we investigated the nucleation mechanism of perovskite films by employing isopropanol (IPA), a weakly coordinating solvent, to anneal both PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the sequential deposition and CsPbI_3 in the one-step deposition. IPA solvent annealing (IPA SA) of PbI_2 films was carried out at different temperatures. The grain size, compactness, roughness and morphology of PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were seriously affected by annealing methods. Similarly, weakly coordinating solvent annealing process was also employed to anneal all inorganic CsPbI_3 perovskite in a one-step method. A continuous and dense CsPbI_3 film with uniform grain size was obtained. We recognized that weakly coordinating solvent annealing for perovskite could regulate the dissolution-recrystallization process via controlling the volume of residual solvent in perovskite intermediate films. The power conversion efficiency (PCE) of conventional $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells (PSCs) reached 17.4% and that of CsPbI_3 PSCs reached 2.5% based on this sequential IPA SA process.

Keywords: perovskite solar cells, solvent annealing, weak coordinating solvent, recrystallization

INTRODUCTION

Organic-inorganic hybrid perovskite solar cells (PSCs) have stimulated great interests in academia due to their ultrafast development of performance. The power conversion efficiency (PCE) of PSCs has reached 22.1% from 3.8% in the past few years [1,2]. Increasingly more attention is paid to reveal the growth kinetics of perovskite in deposition process to further improve the performance

of perovskite solar cells [3–20].

Sequential deposition method was firstly proposed by Grätzel's group in 2013 [18]. This method is an easy way to control the morphology of perovskite films because mesoporous TiO_2 limits the crystal size of PbI_2 which is the precursor in the fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_3$. A lot of publications study the properties (morphology, crystallinity, etc.) of PbI_2 which plays an important role in the nucleation of perovskite films. It was obvious that a good crystalline PbI_2 film with a rough surface could enlarge perovskite film grains. The better crystallization and greater specific surface area gradually become the desired characteristics of lead iodide precursor in two-step deposition method [21–27]. However, it is difficult to precisely control the growth time and growth rate of perovskite grains at mesoscopic domains. Also, for some other cases, such as application of perovskite for LED, controlled grain size is needed [28–32]. Meanwhile, some investigations focused on the direct treatment of perovskite films. Solvent annealing is an effective way to control the morphology and improve the surface performance of films. Huang *et al.* [33] firstly used DMF solvent annealing for perovskite films to reduce the grain boundaries in the year of 2014. Dai's group [34] investigated the intermediates of $\text{MAI-PbI}_2\text{-DMF}$ and $\text{MAI-PbI}_2\text{-DMSO}$ in a one-step method. In order to obtain better quality perovskite films, various solvents and methods were employed in the solvent annealing process [35–41]. These investigations improved grain growth, crystallization, and morphology of perovskite films. Unlike other solvent engineering processes, solvent anneal-

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Figure 1 The schematic diagram of fabrication methods for PSCs. (a) Sequential deposition; (b) one-step deposition.

ing is more suitable for surface morphology modification and investigation of nucleation. The vapor generally reacts strongly with nuclei on the surface of the film and affects the evaporation of residual solvent in films. However, very few researchers analyzed the densification and growth mechanism of perovskite films. Compared with those most commonly used strongly coordinating solvent (such as DMF, dimethyl sulfoxide (DMSO) and γ -butyrolactone (GBL)), very few researchers deeply studied weakly coordinating solvents (ethanol, acetonitrile, isopropanol, etc.) in fabrication of perovskite films [9,35,36,40]. But these weakly coordinating solvents could successfully mediate the nucleation and grain growth of perovskite films. Weakly coordinating solvents are more effective in modifying the morphology and affecting the initial nucleation during film formation instead of expanding nuclei from the original strongly coordinating solvent. The investigation of the influence of weak coordinating solvent for the perovskite nuclei growth is very important and useful.

Here we employed a weakly coordinating solvent annealing method using isopropanol (IPA) solvent annealing to study the growth kinetics of perovskite films (Fig. 1). IPA solvent annealing (IPA SA) was applied to anneal PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films in the sequential deposition method and also used for CsPbI_3 films in the one-step deposition process. For PbI_2 , IPA SA improved crystallization and increased the roughness of the films. Furthermore, the IPA vapor could slow down the

volatilization of methylammonium iodide (MAI) and increase the nucleation density of perovskite, which made the nucleation distribution more uniform in annealing of perovskite. The best $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cell with a pinhole free film exhibited a PCE of 17.1% and PSCs with a CsPbI_3 film showed a 30-fold improvement in PCE. Meanwhile, the stability and crystallinity of CsPbI_3 films were improved due to the formation of smaller clusters and better film compactness [28,29]. To the best of our knowledge, this is the first time that solvent annealing is used in the deposition of inorganic perovskite films. The investigation of IPA SA could be very useful for understanding the growth kinetics of both organic-inorganic hybrid and inorganic perovskites during deposition.

EXPERIMENTAL SECTION

Materials

PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$, CsI, titanium diisopropoxide bis(acetylacetonate) and spiro-OMeTAD were purchased from Sigma-Aldrich. Titanium dioxide nanoparticles (20 nm particle size) and solvents, 2-propanol (IPA, 99.5%) and DMF, DMSO, and acetone, were provided by Dyesol and Kelon respectively.

MAPbI₃ solar cells fabrication

Fluorine-doped tin oxide (FTO) glass substrates were cleaned sequentially in alkaline detergent, acetone, etha-

nol, and DI water for 15 min each, followed by drying with N₂ flow. A compact layer of TiO₂ (c-TiO₂) was deposited *via* spray pyrolysis at 450°C from a precursor solution of titanium diisopropoxide bis (acetylacetonate) in ethanol (volume ratio 1:39). The films were annealed at 500°C for 20 min and then cooled down to room temperature. The mesoporous TiO₂ (m-TiO₂) scaffold was spin-coated at 5,000 rpm for 30 s and annealed at 500°C for 30 min, in which the pristine paste was diluted in ethanol (weight ratio, 2:7). CH₃NH₃PbI₃ was synthesized using the two-step spin coating method and the following experiments except for gold deposition were carried out in a glove box in nitrogen. 60 µL of PbI₂ solutions in DMF (1 mol L⁻¹) were first spin-coated onto the substrates at 3,500 and 5,000 rpm for 3 and 5 s respectively. The films were annealed in nitrogen (called thermal annealing) or in IPA solvent ambiances at different temperature (45, 60, 60°C) for 5 min and then annealed at 100°C in N₂ for 5 min. The volume of the solvent dropped on the surface of the hot plate is 240 µL. During the second spin-coating process, 200 µL solution of CH₃NH₃I in IPA (8 mg mL⁻¹) was loaded on PbI₂ films for 50 s, which was spun at 4,000 rpm for 30 s and dried at 100°C in N₂ or IPA solvent ambience (IPA-SA-SA) for 5 min. The substrates were subsequently covered with 60 µL of a 72.3 mg mL⁻¹ solution of spiro-OMeTAD in 1 mL chlorobenzene with 28.8 µL of added 4-*tert*-butylpyridine, 17.5 µL of a stock solution of 520 mg mL⁻¹ lithium bis(trifluoromethylsulfonyl)imide in acetonitrile and 29 µL of 520 mg mL⁻¹ tris (2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine) cobalt(III) bis (trifluoromethylsulfonyl) imide in acetonitrile. This solution was spin-coated at 4,000 rpm for 30 s. Finally, 80 nm of a gold film was deposited using thermal evaporation.

CsPbI₃ films and solar cells fabrication

The methods and processes for preparing FTO and c-TiO₂ were the same as the above-mentioned preparation method. CsPbI₃ was synthesized using the one-step spin coating method. 124.8 mg of CsI and 221.76 mg of PbI₂ were mixed in 1 mL of DMF. 66 µL of HI solution (57% wt) was added in this solution. After stirring more than 1 h, 60 µL of CsPbI₃ solution was spin-coated on the FTO/c-TiO₂/m-TiO₂ substrate at 2,000 rpm for 30 s. Then this film was annealed in N₂ or IPA solvent at 100°C for 10 min. When fabricated CsPbI₃ solar cells, the substrates were covered with a solution of spiro-OMeTAD that is the same as mentioned in previous part. This solution was spin-coated at 4,000 rpm for 30s. Finally, 80 nm of a gold film was deposited using thermal evaporation.

Measurement and characterization

X-ray diffraction (XRD) diagrams were carried out using a Bede D1 system with Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained using field emission fitting SEM (FEI-Inspect F50, Holland). Atomic force microscopy (AFM) images were measured by an AFM 5500 (Agilent). The ultraviolet-visible (UV-vis) absorption spectrum were measured by a UV-vis spectrophotometer (Schimadzu UV-3101 PC). For previous measurements, perovskite films were deposited on FTO/c-TiO₂/m-TiO₂ substrates. And there were no spiro-OMeTAD and Au layers. Current-voltage measurements were carried out using Keithley 2400 under AM 1.5G illuminations (1,000 W m⁻²) from a solar simulator (Newport Oriel Solar 3A Class AAA, 64023A). The AM 1.5G sun light was calibrated using a standard Si-solar cell (Oriel, VLSI standards). The active area of devices is 0.04 cm². Electrochemical impedance spectroscopy (EIS) were measured with electrochemical workstation (CHI660d). The applied voltage perturbation had an AC amplitude of 35 mV with a frequency range from 1 MHz to 100 Hz. The impedance parameters were simulated by fitting of impedance spectrum through Z-view software.

RESULTS AND DISCUSSION

The fabrication schematics of CH₃NH₃PbI₃ prepared by the sequential solvent annealing method and CsPbI₃ prepared by the one-step deposition method are shown in Fig. 1a, b. The sequential deposition process is based on the two-step deposition method reported by Grätzel's group [18]. A weakly coordinating solvent, in this case, IPA, is chosen because it has a poor solubility of lead ions and weak interaction between solvent molecules and perovskite precursors [42]. In the first part, PbI₂ precursors were heated in the IPA solvent atmosphere at three different annealing temperatures (45, 60 and 80°C). After the subsequent annealing in a nitrogen atmosphere at 100°C, MAI was dropped and spin-coated on the PbI₂ film to form CH₃NH₃PbI₃ films. Perovskite films were then thermally annealed (TA) and dried in N₂ atmosphere. The three processes of CH₃NH₃PbI₃ films carried out at different solvent annealing temperatures are named as 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA, respectively. Control samples which were fabricated by conventional thermal annealing without any solvent named 45°C TA-TA.

Fig. 2a–d shows the AFM images of PbI₂ films based on different annealing processes and annealing temperatures to study the roughness and morphology of these PbI₂ films. Tapping mode was used in this measurement. In a

Figure 2 (a–d) AFM top views of PbI₂ films treated by 45°C TA, 45°C IPA-SA, 60°C IPA-SA and 80°C IPA-SA. (e–h) AFM top views of CH₃NH₃PbI₃ perovskite films treated by 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA, 80°C IPA-SA-TA.

previous study, we found the initial solvent annealing temperature greatly influenced the surface morphology of lead iodide films [25,26]. Here, in Fig. 2, the surface roughness of PbI₂ was hardly affected by IPA solvent atmosphere at low annealing temperature. When the PbI₂ was heated at 80°C, the roughness increased from 13 to 23 nm. Meanwhile, we found IPA SA could increase the average height of PbI₂ grains. The threshold heights of PbI₂ fabricated by the 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA were 93, 101, 114 and 116 nm, respectively. This result illustrated that the PbI₂ film had a higher roughness after the IPA SA process. Fig. 2e–h show the AFM images of CH₃NH₃PbI₃ using 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA. The roughness measurement of the surface (RMS) of the above-described perovskite is 50, 48, 35 and 46 nm, respectively. Compared with the film prepared with 45°C TA-TA process, the threshold height of CH₃NH₃PbI₃ films also decreased when PbI₂ was annealed in IPA solvent at 45 or 60°C. But the grain size of perovskite seemed increased through the IPA SA process.

Fig. 3a, b show the SEM images of CH₃NH₃PbI₃ films with 45°C TA-TA and 60°C IPA-SA-TA processes. The grain size of the CH₃NH₃PbI₃ film based on 60°C IPA-SA-TA is much larger than that based on 45°C TA-TA process. Fig. 3c shows the grain size statistics of perovskite films (calculated by Nano Measurement software). The mean grain size of the perovskite films prepared by 45°C TA-TA and 60°C IPA-SA-TA is 204 and 372 nm, respectively. This is because that the uneven and better crystalline PbI₂ film might led to larger grain size of perovskite films and better reaction between perovskite precursors. Note that, perovskite films treated

with 45°C TA-SA and 60°C IPA-SA-TA both have some pinholes or gaps on the surface. IPA SA significantly improved the optical absorption of PbI₂ as shown in Fig. 3d. The absorption at 500 nm of PbI₂ using IPA SA process was higher than that using TA process. For the UV-vis absorption of CH₃NH₃PbI₃ in Fig. 3d, the base line (the absorption at longer wave lengths than 800 nm) of UV-vis absorption of 60°C IPA-SA-TA or 80°C IPA-SA-TA becomes lower, which indicates a more homogenous surface of perovskite films with less diffuse reflection [43]. Each sample shows a good light absorption of CH₃NH₃PbI₃ in the range around 760 nm. We marked the absorptions (0.238, 0.234, 0.244 and 0.262) around 760 nm of CH₃NH₃PbI₃ perovskite films prepared from PbI₂ films using 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA processes. The 60°C IPA-SA-TA and 80°C IPA-SA-TA processes resulted in the better absorption of perovskite.

Fig. 3e shows the (001) peak of lead iodide at 12.6°. In comparison to 45°C TA-TA and 45°C IPA-SA-TA, the XRD peak corresponding to (001) plane of PbI₂ becomes higher after IPA SA. It is obviously that IPA SA enhanced the crystallization of lead iodide. Both annealing atmosphere and temperature affect crystallization of lead iodide. The formation of lead iodide films not only depends on temperature, but also the movement of IPA molecules and recrystallization of PbI₂. Meanwhile, this XRD peak becomes sharper and higher with the increase of annealing temperature when it was annealed in IPA solvent. This result confirmed that IPA could recrystallized PbI₂ films in the process of solvent annealing. Furthermore, such an improved crystallinity of PbI₂ has a double-sided effect. On one hand, it enhances the crystallization of

Figure 3 (a, b) SEM top views of perovskite films treated by 45°C TA-TA and 60°C IPA-SA-TA. (c) Grain size statistics of perovskite films based on 45°C TA-TA and 60°C IPA-SA-TA. (d, e) UV-vis absorption spectra and XRD patterns of PbI₂ and CH₃NH₃PbI₃ using 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA.

CH₃NH₃PbI₃, and on the other hand, it retards the conversion of lead iodide into perovskite. The XRD measurements of MAPbI₃ shown in Fig. 3e shows the denser and higher unreacted PbI₂ peak of (001) at 12.4° and the MAPbI₃ (110) peak at 14.6° were obtained from the improved crystalline PbI₂. 2Theta-Omega mode was used in our measurement. Residual lead iodide may bring about a passivation effect in perovskite solar cells which could improve the performance of devices [44,45].

In order to study and observe the direct influences of PbI₂ films based on different annealing processes on device performance, Fig. 4 shows the *J*-*V* curves, distribution of PSCs parameters, EIS and plots of $-dV/dJ$ versus $(J_{sc}-J)^{-1}$ of CH₃NH₃PbI₃ solar cells fabricated using different annealing processes for PbI₂. *J*_{sc} and *V*_{oc} mean the short circuit current density and open circuit voltage, respectively. Fig. 4a shows the *J*-*V* curves of perovskite solar cells fabricated from the PbI₂ films based on different annealing processes. In the case of PbI₂ with IPA SA, the PCE increases from 15.04% to 16.09% with the increased annealing temperature from 45°C to 60°C, which is followed by a decrease to 13.18% with the annealing temperature of 80°C. Meanwhile, the PCE of PSCs with the 45°C TA-TA process is 14.73% which is similar with the PCE of PSCs based on the 45°C IPA-SA-TA process. Fig. 4b shows the distribution of the efficiency, *V*_{oc}, FF (fill factor) and *J*_{sc} of the devices with 45°C TA-TA and IPA-SA-TA (45, 60 and 80°C) processes.

Compared with PSCs made from the 45°C TA-TA process, the statistical distributions of device performance is even more uniform and the value of *J*_{sc} and PCE become higher when the PSCs were treated by 45°C IPA-SA-TA or 60°C IPA-SA-TA. The solar cell with 80°C IPA-SA-TA got the worst performance. As reported in previous articles, several optoelectronic characteristics, such as film trap density, lifetime and EIS can be used to illustrate the improvement of morphology and ability of perovskite films [46–49]. In our study, SEM, EIS measurement and ideal factor characterization have been employed. To further investigate the photovoltaic performance, Fig. 4c shows the plots of $-dV/dJ$ versus $(J_{sc}-J)^{-1}$ and the linear fitting curves to calculate the ideal factor of the heterojunction [50]. The formula is expressed as: $-dV/dJ = (Nk_B T/e)(J_{sc}-J)^{-1} + R_s$, where *R*_s is the series resistance, *J*_{sc} is the short circuit current density, *J* is the current density flowing through the external load, *N* is the ideality factor of a heterojunction, *k*_B is the Boltzmann constant, *T* is the absolute temperature, *e* is the elementary charge, and *V* is the direct current (DC) bias voltage applied to the cell. For a general heterojunction solar cell, *N* is always between 1.3 and 2. The PSC based on 60°C IPA-SA-TA achieves the best *N* value of 2.7 which is the closest to 2. The fitting curve of this sample also shows the smallest slope. The solar cell agrees better with the ideal heterojunction solar cell. The 60°C IPA-SA-TA process effectively improved the junction ability of perovskite films.

Figure 4 (a), (c, d) J - V curves, plots of $-dV/dJ$ versus $(J_{sc}-J)^{-1}$ and the linear fitting curves of PSCs and EIS of the solar cell samples with 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA. (b) Distribution of the J_{sc} , V_{oc} , FF and efficiency of the devices with different annealing processes (45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA).

Table 1 By fitting with a simple equivalent circuit model, R_1 , R_2 and R_3 of PSCs using 45°C TA-TA, 45°C IPA-SA-TA, 60°C IPA-SA-TA and 80°C IPA-SA-TA processes

R/Device	Wo IPA SA	IPA 45°C	IPA 60°C	IPA 80°C
$R_1(\Omega)$	57	43	25	44
$R_2(\Omega)$	726	675	591	713
$R_3(\Omega)$	8331	17107	60925	11263

Fig. 4d exhibits EIS to study the charge transport ability in these PSCs [51,52]. Two semicircles were obtained in the Nyquist plots. By fitting with a simple equivalent circuit model, R_1 represents the electrolyte resistance, R_2 represents the transfer resistance which is obtained from the first semicircle in the high frequency range, and R_3 from second arc is related to the recombination resistance. Obviously, the curve of the transfer resistance for the sample treated by the 60°C IPA-SA-TA process shows a smaller value of 591 Ω than that for the sample treated by other annealing processes in Table 1. This should be due to a better charge-transfer ability. The recombination resistance of the PSC treated by 60°C IPA-SA-TA is the largest. A larger recombination resistance indicates a lower recombination loss that is also attributed to a suitable amount of residual lead iodide or better

crystallinity. The Abs, XRD, PCE, EIS and ideal factor analysis show that the annealing of PbI_2 significantly affects the crystallinity of perovskite films. Acetone, a kind of solvent with low solubility of Pb^{2+} and low boiling point, was used in a control experiment group. Fig. S8 shows Abs and XRD of PbI_2 and $CH_3NH_3PbI_3$ based on acetone solvent annealing processes. We found acetone showed the similar effect with IPA on the recrystallization of PbI_2 films. This result confirmed weak coordinating solvent could effectively rearrange PbI_2 crystals and affect quality of perovskite films.

For lead iodide, IPA atmosphere effectively modified the surface morphology and improved the crystallinity through poor solubility of lead iodide and weak coordination ability. Recrystallization process of lead iodide occurred under the solvent annealing conditions. Annealing temperature and solvent atmosphere function together to regulate this process. A dense but uneven PbI_2 film was achieved and led to larger grain sizes of the perovskite films and better reaction between perovskite precursors. However, if the perovskite grain growth could not be well controlled, gaps or pinholes are easy to form.

We employed the second IPA SA process for $CH_3NH_3PbI_3$ films fabricated from PbI_2 with 60°C IPA SA and the IPA SA process (100°C) for $CsPbI_3$ films in the

Figure 5 (a, b) AFM top view and SEM top view images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ treated by 60°C IPA-SA-SA process. (c, d) UV-vis absorption spectra and XRD patterns of perovskite using 60°C IPA-SA-SA process compared with that using 60°C IPA-SA-TA.

one-step deposition process, as shown in Fig. 1. The samples are referred as 60°C IPA-SA-SA and IPA-SA- CsPbI_3 , respectively. For our control samples, CsPbI_3 films were only annealed in N_2 at 100°C for 10 min (TA- CsPbI_3).

Fig. 5a shows the AFM image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films using the 60°C IPA-SA-SA processes. The RMS of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with 60°C IPA-SA-SA process is 36 nm. IPA SA process for $\text{CH}_3\text{NH}_3\text{PbI}_3$ resulted in a more homogeneous interface of perovskite compared with other annealing processes. Therefore, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film exhibited lower roughness and more uniform grain distribution. Fig. 5b shows the SEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with 60°C IPA-SA-SA process. When the 60°C IPA-SA-SA process was used, the grain size of the perovskite film became smaller but the perovskite grains became denser compared to that with 60°C IPA-SA-TA. This is an interesting phenomenon because solvent annealing was observed to enlarge perovskite domains and reduce the number of grain boundaries [33,37–39]. Here, the weakly coordinating solvent annealing for $\text{CH}_3\text{NH}_3\text{PbI}_3$ films leads to uniform grain size and a homogeneous surface with few pinholes. The grain size statistics of perovskite films shows the mean grain size of the perovskite films prepared by 60°C IPA-SA-SA is 218 nm. Additionally, the trend line of grain size sta-

tistic of perovskite based on 60°C IPA-SA-SA is sharper and higher than that of perovskites treated by 45°C TA-TA and 60°C IPA-SA-TA. This means that the grain size of this film is more concentrated. Thus, we found there is a more uniform distribution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nuclei in the formation process of 60°C IPA-SA-SA.

Fig. 5c, d show the UV-vis absorption and XRD analysis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films treated with the 60°C IPA-SA-SA process compared with that with 60°C IPA-SA-TA. The absorption slope around ~760 nm of perovskite films obtained via 60°C IPA-SA-SA is similar with that of the perovskite films prepared using 60°C IPA-SA-TA. Enlarging the image of absorption around 760 nm (from 700 to 800 nm), the perovskite film with 60°C IPA-SA-SA shows a better absorption. This is consistent with the above AFM and SEM measurements. Through the IPA SA for $\text{CH}_3\text{NH}_3\text{PbI}_3$, the (110) peak of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at 14.6° is sharper and higher, as shown in Fig. 5d. The (110) peak strength of perovskite based on 60°C IPA-SA-SA is 147.73, which is higher than that (113.64) based on 60°C IPA-SA-TA. Meanwhile, the (001) peak of PbI_2 at 12.4° is decreased because of the reduced amount of residual lead iodide. In our experiment, the detail interaction between IPA and the annealing materials was discussed. Firstly, IPA solvent vapor could provide a wet atmosphere so that the precursor ions and molecules could diffuse a longer

Figure 6 (a, b) SEM top views of CsPbI₃ films treated by TA-CsPbI₃ and IPA-SA-CsPbI₃. (c, d) UV-vis absorption spectra and XRD patterns of perovskite using TA-CsPbI₃ and IPA-SA-CsPbI₃.

distance than in thermal annealing. So the grain size and morphology were improved *via* IPA SA. Secondly, IPA vapor seriously affected the residual solvent in precursor crystal. Residual solvent is always strong Lewis additives, such as DMF, DMSO. These residual solvents have a very strong solubility of lead iodide or other perovskite precursors. In this process, IPA vapor modified the volume of residual solvent and affected the dissolution-recrystallization process for perovskite or perovskite precursor. Thirdly, IPA has a higher solubility for MAI than for lead iodide which could reduce the volatility of MAI and promote the growth of crystals. We also employed IPA SA to fabricate CsPbI₃ films. A planar structure was made in our experiment. With different annealing processes, CsPbI₃ films with different levels of compactness and grain sizes were obtained. In 2016, Luo *et al.* [46] used IPA dipping treatment for fabricating stable CsPbI₃ solar cells and achieved a PCE of 4.13%. IPA SA process carried out in this research was different from the dipping process. IPA solvent vapor reacted strongly with nuclei on the surface of CsPbI₃ films and modified the amount of residual solvent in films. We emphasized the research of the growth mechanism of perovskite in weak coordinating solvent environment and the effect of the annealing atmosphere on film crystallization. The re-

crystallization of CsPbI₃ was ascribed to a combination of annealing and IPA atmosphere. Meanwhile, based on Luo's article [46], we recognized IPA could stabilize α -phase of CsPbI₃ through affecting the transformation from Cs₄PbI₆ immediate to CsPbI₃. Fig. 6a, b show the SEM images of CsPbI₃ films fabricated by the TA-CsPbI₃ and IPA-SA-CsPbI₃. Note that, we tested these films after a period of time after films deposition. According to the report of Jin's group [53,54], there should be orthorhombic phase CsPbI₃ with large grain size shown in Fig. 6a. But according to our XRD result shown in Fig. 6d, CsPbI₃ has not totally degraded. Through the IPA SA, the CsPbI₃ film became more compact with uniform grains. There are more nuclei in the CsPbI₃ film obtained using IPA SA process. The grain size statistics of CsPbI₃ films fabricated *via* TA-CsPbI₃ or IPA-SA-CsPbI₃ processes shows the mean grain size of CsPbI₃ films is 340 nm and 150 nm, respectively. The orthorhombic phase also influence the grain size of CsPbI₃. The mean grain size of the CsPbI₃ film with TA-CsPbI₃ is more than twice the size of the CsPbI₃ film with IPA-SA-CsPbI₃. Meanwhile, the CsPbI₃ film with IPA-SA-CsPbI₃ shows a more concentrated distribution of grains. The differences of grain size and film coverage between CsPbI₃ films based on the thermal annealing process and IPA SA process are very

Figure 7 Photos of CsPbI₃ films using TA and IPA-SA processes changed with time.

obvious.

Fig. 6c shows the UV–vis absorption of CsPbI₃ films. It is obvious that the absorption of the CsPbI₃ film with IPA-SA-CsPbI₃ around 720 nm (the band gap of α -CsPbI₃ is 1.73 eV, corresponding to the optical absorption of 717 nm) is much higher than that with TA-CsPbI₃. This UV–vis absorption result is in good agreement with the SEM images. Better absorption of the CsPbI₃ film with IPA-SA-CsPbI₃ should be owing to the compacter morphology of CsPbI₃ films. Note that, the baseline of the CsPbI₃ sample with IPA-SA-CsPbI₃ is higher than that with the TA-CsPbI₃ process. This is caused by stronger light scattering due to the rough surface of the CsPbI₃ film. Therefore, the IPA SA process can also be used to effectively modify the surface morphology and roughness of CsPbI₃ films. Furthermore, as shown in Fig. 6d, the main XRD peak (100) of cubic CsPbI₃ (α -CsPbI₃) is sharper in the case of IPA SA. This suggests that the IPA SA results in better crystallization of CsPbI₃ films with a small grain size and good compactness.

We found this weakly coordinating solvent annealing process is a favorable way to control the grain size and enhance the compactness and the quality of both CH₃NH₃PbI₃ and CsPbI₃ films. The IPA SA process for both CH₃NH₃PbI₃ and CsPbI₃ films creates more nucleation centers and these centers were more evenly distributed. We recognized the IPA vapor could slow down the volatilization of MAI and residual original solvent, which made the nucleation distribution more uniform in annealing of perovskite. The dissolution-recrystallization process could be well regulated. Different from strongly coordinating solvent (DMF, DMSO, GBL, etc.), weakly

coordinating solvent annealing for perovskite could more effectively modify the morphology and affect the initial nucleation during film formation instead of expanding nuclei from the original strongly coordinating solvent. This may be attributed to the abilities of weakly coordinating solvent which has a poor solubility of lead ions, weak donating electron ability, good volatility and so on.

Interestingly, the IPA SA process is also helpful in improving the stability of the CsPbI₃ films. We put CsPbI₃ samples with the TA-CsPbI₃ or IPA-SA-CsPbI₃ process in an atmospheric environment at room temperature. The humidity was in the range from 40% to 80%. The photographs of CsPbI₃ films over time (from 0 to 280 min) are shown in Fig. 7. At the beginning, the color of CsPbI₃ based on the IPA-SA-CsPbI₃ process was blacker than that based on the TA-CsPbI₃ process. After being exposed to air for only 10 min, the TA-CsPbI₃ perovskite film had a significant degradation or phase change. The color of CsPbI₃ changed from brown to light yellow. However, the IPA-SA TA-CsPbI₃ perovskite film was very stable and remains black. The phase change of the samples with the TA-CsPbI₃ process was more severe with time, and the CsPbI₃ film became more transparent. After 220 min, the CsPbI₃ film with TA-CsPbI₃ underwent completely phase change, but there was still some residual α -CsPbI₃ left in the CsPbI₃ film with the IPA-SA-CsPbI₃ process. Therefore, the IPA-SA-CsPbI₃ process could effectively improve the stability and control the grain size of the CsPbI₃ film. Note that we found DMF solvent annealing could dissolve the films because of its strong coordinating ability and polarity. So strong coordinating solvent were

Figure 8 (a, b) J - V curves and distribution of the J_{SC} , V_{OC} , FF and efficiency of PSCs ($\text{CH}_3\text{NH}_3\text{PbI}_3$) with 60°C IPA-SA-SA process and 60°C IPA-SA-TA process. (c, d) J - V curves and distribution of the J_{SC} , V_{OC} , FF and efficiency of CsPbI_3 solar cells with IPA-SA- CsPbI_3 and TA- CsPbI_3 process.

not suitable for the solvent annealing for CsPbI_3 films.

Fig. 8a shows the J - V curves of the PSCs fabricated by the 60°C IPA-SA-TA process and the 60°C IPA-SA-SA process. The performance of the device was improved by this second solvent annealing process. PSCs using the 60°C IPA-SA-SA process exhibited the best PCE of 17.4%. In our measurements, reverse scan was carried out, where the number of sweep points is 100 and the dwell time is 30 ms. The integrated photocurrent estimated from the EQE curve (Fig. S5) is in good agreement with that measured from the IV characteristics shown in Fig. 8a. The IPA SA process for the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film greatly improved the performance of the PSCs. Fig. 8b shows the distribution of the PCE, V_{OC} , FF and J_{SC} of the devices treated by 60°C IPA-SA-TA and 60°C IPA-SA-SA. It is clear that 60°C IPA-SA-SA results in better V_{OC} and PCE. The theoretical (maximum) V_{OC} of a solar cell is the energy gap between the Fermi level of the electron transporter materials and the HOMO of the donor. But the energy loss at interfaces and in perovskite films also influence V_{OC} . Through IPA SA process, morphology, light absorption and crystallization of perovskite films were successfully improved. The reduced energy loss and improved carriers transport ability should be the reason for the increased PCE and V_{OC} . As shown in Fig. S3, a slight hysteresis was observed from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs with 60°C IPA-SA-SA. However, a strong hysteresis behavior

was shown from CsPbI_3 solar cells. This is due to the different device structures and film quality of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and CsPbI_3 in our research. But the aim of this work is to study the growth mechanism of perovskite films treated by IPA SA process. The previous SEM, XRD, UV-vis and other characterizations consistently confirmed that IPA SA was conducive to the crystallization and the growth of perovskite films.

Fig. 8c shows the J - V curves of CsPbI_3 PSCs using the IPA-SA- CsPbI_3 process and TA- CsPbI_3 process. Under illumination intensity of 100 mW cm^{-2} , the best CsPbI_3 device based on the IPA SA exhibits a J_{SC} of 5.48 mA cm^{-2} , a V_{OC} of 808 mV, and a FF of 0.554, resulting in a PCE of 2.5% (reverse scan, the dwell time is 10 ms). However, the best CsPbI_3 solar cells based on the TA process exhibits a J_{SC} of 0.24 mA cm^{-2} , a V_{OC} of 598 mV, and a FF of 0.563, resulting in a PCE as low as 0.08%. Fig. 8d shows the distribution of the PCE, V_{OC} , FF and J_{SC} of the CsPbI_3 devices treated by TA- CsPbI_3 and IPA-SA- CsPbI_3 . We found V_{OC} , J_{SC} and PCE were significantly increased for the IPA-SA- CsPbI_3 process. The effective improvement of the crystallinity and compactness of CsPbI_3 films is the reason for the enhancement of photoelectric performance. In addition to the properties of the perovskite itself, the additives of hole transport material (HTM), preservation environment, etc., all affected the stability of the device. To study the stability, the J - V

curves of CsPbI₃ based solar cells prepared by IPA-SA process within 100 h in dark are shown in Fig. S7 [55,56]. Although the stability of CsPbI₃ films were improved by IPA-SA process, the PCE of CsPbI₃ PSC decreased very quickly.

CONCLUSIONS

We studied the effect of the IPA SA process on the properties and performances of PbI₂ and CH₃NH₃PbI₃ films in the sequential deposition method. By using the IPA SA process, the interface morphology, crystallinity and grain size of the PbI₂ and CH₃NH₃PbI₃ films were successfully modified. We proposed that the IPA SA process could improve the performance and morphology of CH₃NH₃PbI₃ films *via* weak modification ability and the effect on initial nucleation during film formation. CH₃NH₃PbI₃ solar cells fabricated using the 60°C IPA-SA-SA process exhibited a best photoelectric conversion efficiency of 17.4%. At the same time, this IPA SA process was also effective in the fabrication of CsPbI₃. This weakly coordinating solvent process greatly enhanced the stability and photoelectric conversion performance of CsPbI₃ solar cells at room temperature. The stable CsPbI₃ solar cell with a PCE of 2.48% was attained. The weakly coordinating solvent annealing process presented here reveals the perovskite growth mechanism and nucleation kinetics. We believe this study is meaningful for the better preparation and application of perovskites.

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通过弱配位溶剂退火揭示钙钛矿薄膜生长机制

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摘要 本研究在两步法沉积 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 和一步法沉积 CsPbI_3 薄膜过程中使用弱配位溶剂异丙醇(IPA)对钙钛矿及钙钛矿前驱体进行溶剂退火处理,从而揭示了钙钛矿薄膜的成核机理。同时研究了退火温度对两步法中 PbI_2 前驱体进行溶剂退火处理时的作用。发现IPA溶剂退火工艺严重影响了 PbI_2 和 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜的晶粒尺寸、致密度、粗糙度和薄膜形貌。相同的弱配位溶剂退火工艺也被应用于制备全无机 CsPbI_3 钙钛矿。通过溶剂退火可以得到具有均匀晶粒尺寸、连续致密的全无机 CsPbI_3 薄膜。我们认为弱配位溶剂退火工艺可以通过有效地调控钙钛矿中间相中的残留溶剂量来影响钙钛矿成膜中的再结晶过程。通过IPA溶剂退火工艺, $\text{CH}_3\text{NH}_3\text{PbI}_3$ 钙钛矿太阳能电池光电转换效率达到17.4%,而 CsPbI_3 的光电转换效率达到了2.5%。