Stable tin perovskite solar cells enabled by widening the time window for crystallization

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ABSTRACT Tin perovskite solar cells (TPSCs) are the most promising candidates for lead-free perovskite solar cells (PSCs). However, the poor crystallization and chemical stability of Sn perovskites are the two challenging issues for further application of TPSCs. Here, we present a strategy to stabilize $\text{CH}(\text{NH}_2)_2\text{SnI}_3$ (FASnI_3) perovskite enabled by an amine complex, $\text{CH}_3\text{NH}_3\text{I} \cdot 3\text{CH}_3\text{NH}_2$, which can hinder the major degradation issue caused by the oxidation of Sn^{2+} to Sn^{4+} . The resulting Sn perovskite films exhibit enhanced crystallinity and stability in comparison with those made with conventional inorganic SnF_2 additives. Finally, the device achieved a higher external quantum efficiency for charge extraction and a power conversion efficiency (PCE) of 9.53%, which maintained more than 90% of the initial efficiency after 1000 h of light soaking under the standard AM 1.5 G solar illumination.

Keywords: lead-free perovskite, FASnI_3 , perovskite solar cells, crystallization, stability

INTRODUCTION

In recent years, lead halide perovskite solar cells (PSCs) have developed rapidly as a promising photovoltaic technology [1–7]. At present, the certified power conversion efficiency (PCE) of PSCs has exceeded 25%, which is close to that of the commercial monocrystalline silicon solar cells [8]. However, the toxicity of lead (Pb) inevitably arouses extensive attention to the promotion of PSCs [9,10]. In this regard, lead-free perovskites have attracted great attention [11,12]. One of the most feasible strategies is to replace Pb with less toxic tin (Sn) for their similar ns^2np^2 electronic configuration and coordination

geometry [13,14]. The Sn-based perovskite should have essentially similar semiconductor properties as the Pb-based counterpart [15,16]. In addition, full or partial replacement of Pb with Sn can adjust the band gap in the infrared region, which holds the potential for the application of tandem solar cells [17–21]. However, the poor crystallization and the chemical instability of Sn^{2+} due to the oxidation to Sn^{4+} hindered the development of efficient Sn-based PSCs [16,22].

The stability and crystallinity of the Sn-based perovskite have been successfully improved by various approaches [22–36]. Inorganic compounds like SnF_2 and SnCl_2 are the most popular additives for the compensation of oxidized Sn^{2+} [23–26]. Metallic tin has been reported for reducing the Sn^{4+} to Sn^{2+} via a comproportionation reaction [27,28]. Application of organic halide to form two-dimensional (2D)-3D hierarchy structure has also been widely reported to effectively protect Sn-based perovskites from oxidation and improve the crystallization [29–35]. Besides, it has been reported that the addition of a certain amount of small organic molecules or polymers, such as trimethylamine (TMA) [22], potassium salt of hydroquinone sulfonic acid (KHQSA) [36], 4-fluorobenzohydrazide (FBH) [37], liquid formic acid (LFA) [38], 8-hydroxyquinoline (8-HQ) [39], pentafluorophenoxyethylammonium iodide (FOEI) [40] and poly(vinyl alcohol) (PVA) [41], can enhance the stability by improving crystallization and reducing defects caused by oxidation. Among them, SnF_2 is the most commonly used additive in Sn PSCs. However, if SnF_2 is applied at a high molar ratio of over 10%, it will aggregate at the surface of Sn perovskites via phase segregation and might

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hinder the charge extraction of Sn-based PSCs. Therefore, it is still highly desired to explore new strategies to overcome the poor crystallization and instability issues of Sn-based PSCs.

In this work, we report a strategy to stabilize $\text{CH}(\text{NH}_2)_2\text{SnI}_3$ (FASnI_3) perovskite with an amine complex, $\text{CH}_3\text{NH}_3\text{I}\cdot 3\text{CH}_3\text{NH}_2$ (MAI·3MA). In comparison with the conventional $\text{FASnI}_3\cdot x\text{SnF}_2$ sample, the target Sn perovskite films exhibited improved crystallization and chemical stability owing to the time window widened up to 180 min for crystallization by the amine complex. Attributed to these benefits, the photovoltaic devices based on the Sn-target film achieved a higher efficiency for charge extraction and a PCE of 9.53%. Moreover, the device maintained over 90% of its initial PCE after light soaking under AM 1.5 G (100 mW cm^{-2}) for 1000 h. This work provides a new simple strategy for fabricating efficient and stable Sn-based PSCs.

EXPERIMENTAL SECTION

Materials

The following chemicals were used as obtained from commercial sources, including SnI_2 (99.99%, Sigma-Aldrich), $\text{CH}(\text{NH}_2)_2\text{I}$ (FAI; >98%, Tokyo Chemical Industry Co., Japan), $\text{CH}_3\text{NH}_3\text{I}$ (MAI, >98%, Tokyo Chemical Industry Co., Japan), SnF_2 (>99%, Sigma-Aldrich), C60 (99.5%, Sigma-Aldrich), bathocuproine (>99%, Wako), and methylamine (MA, 30%, water, Sinopharm Chemical Reagent Co., Ltd.). All solutions were filtered with a $0.2 \mu\text{m}$ polytetrafluoroethylene (PTFE) filter before use. The amine complex of MAI·3MA was synthesized according to our previous work [42].

Solar cell fabrication

Patterned indium tin oxide (ITO) glass substrates were cleaned in the order of detergent, deionized water, acetone and isopropanol for 20 min by ultra-sonicated. Then, the cleaned ITO substrates were treated by ultraviolet-ozone for 30 min before the deposition of the PEDOT:PSS layer. The perovskite precursor solution composed of 1 mol L^{-1} SnI_2 and 1 mol L^{-1} FAI in dimethyl sulfoxide (DMSO) was stirred at room temperature for 2 h. The PSCs were fabricated according to our previous work [43]. In short, the precursor solution was spin-coated on the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer at 1000 r min^{-1} for 12 s and 5000 r min^{-1} for 48 s in the glove box. Chlorobenzene ($150 \mu\text{L}$) was *in-situ* dripped onto the perovskite film after 30 s during the second step. Then the perovskite films were annealed at

60°C for 10 s and 100°C for 12 min. Three Sn perovskite films were fabricated and denoted as Sn-control-1 (FASnI_3 with 5% SnF_2 in molar ratio), Sn-control-2 (FASnI_3 with 5% SnF_2 and MAI in molar ratio), and Sn-target (FASnI_3 with 5% SnF_2 and 2% MAI·3MA in molar ratio), respectively. Finally, 50 nm C60, 8 nm bathocuproine (BCP) and 70 nm Ag electrode were evaporated under high vacuum ($<2 \times 10^{-7}$ Torr). The device areas were defined by a mask with an aperture area of 0.09 cm^2 .

Characterization

The light absorbance spectra were obtained by a Shimadzu ultraviolet-visible (UV-Vis) 3600 spectrophotometer. The X-ray diffraction (XRD) was measured by using a Rigaku Ultima IV diffractometer and Cu K α radiation. The scanning electron microscopy (SEM) images were measured by a Zeiss ultra plus field emission scanning electron microscope. The X-ray photoelectron spectroscopy (XPS) spectra were measured by a Kratos Axis UltraDLD with X-ray source of Al K α (mono), with the incident angle and take-off angle at 90° and 45° , respectively. The steady-state photoluminescence (PL) and time-resolution PL (TRPL) spectra were measured by using an FLS1000 photoluminescence spectrometer with excitation at a wavelength of 550 nm. The space charge limited current (SCLC) and Mott-Schottky analysis were performed by using a multifunctional electrochemical analysis instrument (Zahner, Germany) under dark at room temperature. The current-voltage (*I*-*V*) curves were measured under forward scan (-0.1 to 0.8 V) or reverse scan (0.8 to -0.1 V) by a fixed step voltage of 20 mV and delay time of 50 ms by a solar simulator with standard AM 1.5 G sunlight (100 mW cm^{-2} , WXS-155S-10, Wacom Denso). The aperture area was defined by a mask of 0.09 cm^2 . Monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra were measured by a monochromatic incident light of $1 \times 10^{16} \text{ photons cm}^{-2}$ in director current mode (CEP2000BX, Bunko-Keiki). The light intensity of the solar simulator was calibrated by a standard silicon solar cell. The solar cells were firstly encapsulated in a nitrogen-filled glovebox by cavity glass and UV-curable glue for the stability test.

RESULTS AND DISCUSSION

Fig. 1 shows the precursor solutions for Sn-control-1, Sn-control-2, and Sn-target films, which were exposed in the air as fresh, and for 60 and 180 min, respectively. Initially, all the precursor solutions exhibited the color of light yellow (Fig. 1a). After 60 min of exposure in the ambient air, the color of the surfaces of the Sn-control-1 and Sn-

Figure 1 Photographic images of Sn-control-1, Sn-control-2 and Sn-target precursor solutions exposed in air for (a) 0, (b) 60 and (c) 180 min, respectively. Top view SEM images of the (d) Sn-control-1, (e) Sn-control-2 and (f) Sn-target films. AFM surface morphology of the (g) Sn-control-1, (h) Sn-control-2 and (i) Sn-target films. The calculated RMS values are 35, 37 and 21 nm, respectively.

control-2 precursor solutions turned into dark red owing to the oxidation, which was not preferred to form Sn perovskite films (Fig. 1b). With exposure time increasing to 180 min, the colors of the Sn-control-1 and Sn-control-2 solutions turned into dark red completely, whereas the Sn-target solution still maintained light yellow as fresh ones (Fig. 1c). The unique characteristics of MAI-3MA were reported in our previous work on Pb-based perovskites, where the amine complex of MA^+ with multiple MA molecules had hydrogen bonding and fast proton exchange [42]. Therefore, the amine complex of MAI-3MA plays an important role in inhibition of the oxidation of Sn^{2+} [44], due to the extra donor electron groups in the amine complex.

To deeply understand the advantages of the additive, the UV, XRD and XPS of the Sn perovskite films made by aged target and control solutions were provided. As shown in Fig. S1, the aged target solution shows similar light absorbance as the fresh precursor. However, the

films prepared with aged control-1 and control-2 solutions show an obvious decrease of light absorbance. The XRD patterns in Fig. S2 show similar results, which indicates that the aged control-1 and control-2 precursors undergo a poor crystallization while the additive can solve this problem. The Sn^{4+} content of the films prepared by the aged solutions was measured by XPS and the results are shown in Fig. S3, which also demonstrate that the precursor was protected from oxidation by adding MAI-3MA.

We further observed the surface morphology of the films of the Sn-control-1, Sn-control-2 and Sn-target. It should be noted that the Sn-control-1 and Sn-control-2 solutions still tended to be oxidized in the glove box at ~ 100 ppm oxygen concentration. We spin-coated 24 films in about 2–3 h, during which we observed the formation of red liquid droplets on the walls of the bottles containing the control-1 and control-2 solutions. As mentioned earlier, this is a detrimental factor for film

morphology, which caused the formation of pinholes in the films, as shown in Fig. 1d–f (this oxidation problem has been avoided during the preparation of actual devices, which will be explained later). The Sn-target film is denser with a larger grain size than the Sn-control-1 and Sn-control-2 films. Moreover, the atomic force microscopy (AFM) images in Fig. 1g–i show a similar trend with SEM images. The root mean square (RMS) values were calculated to be 35 nm for the Sn-control-1 film, 37 nm for the Sn-control-2 film, and 21 nm for the Sn-target film, respectively. We compared the surface morphology of the films prepared with different ratios of the amine complex in the precursor solution (1%, 1.5%, 2% and 3% in molar ratio). As shown in Fig. S4, the films become denser with the increased molar ratio of the amine complex in the range of 1%–2%, and the film with a ratio of 2% shows the largest grains and densest morphology. We ascribe the improved film morphology to an improved quality of the precursor solutions with less oxidized impurities. During the film preparation process (generally 120–180 min), there is trace oxygen (1–100 ppm) in the glove box, where the control solutions and spin-coated films may undergo oxidation, making them less likely to produce good morphologies. Previous reports have demonstrated that electron donating additives (such as TMA [22]) tend to favor the formation of SnI_2 complexes. We suggest a similar role for the

MAI-3MA additive; therefore, the presence of this additive could slow down its consumption as a product in the global crystallization reaction. The slower film formation in turn leads to the observed improvement in crystallinity and grain size. However, if the molar ratio increases to 3%, the film becomes non-dense and discontinuous with large voids. Therefore, we choose the FASnI_3 film with 2% amine complex for the following investigations.

We then investigated the stability of these three films, which were exposed in the air with ~20% humidity and at ~25°C, respectively. The light absorbance spectra of the films oxidized in the air for 0, 45, 90, 135 and 180 min are shown in Fig. 2a–c. The decay of the spectra after oxidation in the air is significantly slower for the Sn-target film than the Sn-control-1 and Sn-control-2 films. For quantitative analysis, Fig. 2d shows that the light absorbance at 600 nm remained 69% after 180 min exposure in the air for the target film, almost 1.9 times of that from the Sn-control-1 and Sn-control-2 films, indicating an improved resistance to oxidation and higher stability in the air.

The stability of the Sn perovskite films was further investigated by XRD. As given in Fig. 2e, the XRD patterns show that the intensity of the target film is much higher than that of the other control films, in which three peaks near 14.0°, 28.2°, and 42.9° are indexed from the

Figure 2 The recorded UV curves of the (a) Sn-control-1, (b) Sn-control-2 and (c) Sn-target films oxidized in an air environment of ~20% humidity, ~25°C for 0, 45, 90, 135 and 180 min, respectively. (d) The plotted normalized decay of the UV absorption values at 600 nm from (a–c). (e) XRD patterns of the Sn-control-1, Sn-control-2 and Sn-target films deposited on ITO glass, the details of the position, intensity and the FWHM values of the films are listed in Table S1. Narrow sweep of XRD patterns between 13° and 15° of the (f) Sn-control-1, (g) Sn-control-2 and (h) Sn-target films after 0 and 3 h of oxidation in an air environment of ~20% humidity, ~25°C.

(100), (200) and (300) planes of FASnI_3 film, respectively [30]. The intensity and full width at half maximum (FWHM) of the (100) peaks are listed in Table S1, which indicate that the Sn-target film shows preferred crystalline orientation. Fig. 2f–h show the XRD patterns of the films in fresh and after oxidation for 180 min in the air (the XRD patterns of the Sn-control-1 and Sn-control-2 films in Fig. 2f, g were magnified about ~ 4 times in comparison with that for Sn-target in Fig. 2h). A new phase identified as the simultaneous existence of Sn^{4+} and Sn^{2+} appears around 14.5° for the Sn-control-1 and Sn-control-2 films, which is consistent with the previous studies [45,46]. It can be observed that the Sn-target film exposed in the air after 180 min only shows a decrease in (100) intensity with no obvious peak near 14.5° , which indicates the target film exhibiting enhanced stability in the air.

In addition, we further used XPS to test the state of Sn in the films. Fig. S5 shows the XPS results of the Sn element for the as-prepared samples. The Sn^{4+} contents in the Sn-control-1 and Sn-control-2 films were calculated to be 21.81% and 22.08%, respectively, while the Sn^{4+} content in the Sn-target film was calculated to be 10.98%. This result demonstrates that the amine complex slows

down the oxidation of Sn^{2+} during the film preparation process. After oxidation in the air for 180 min, the content of Sn^{2+} at the film surface nearly disappeared for the Sn-control-1 and Sn-control-2 films, as shown in Fig. S6a–c. In contrast, Sn^{2+} remained on the Sn-target film surface. We further explored the contents of Sn^{2+} at different depths in the oxidized films by etching. As shown in Fig. S7, the Sn^{2+} contents within the Sn-target film at different etching times (corresponding to the depth in the film) were well preserved in contrast to the Sn-control-1 and Sn-control-2 films, indicating that the Sn-target film is far better preserved from oxidation.

We investigated the dynamics of the charge carriers in the Sn-control-1, Sn-control-2 and Sn-target films and recorded their steady-state PL spectra. As given in Fig. 3a, the PL intensity of the Sn-target film is stronger than those of the Sn-control-1 and Sn-control-2 films, which implies that the non-radiative recombination was suppressed. The lifetime values of the PL are 0.59, 0.47 and 8.98 ns for the Sn-control-1, Sn-control-2 and Sn-target films, respectively, in Fig. 3b. This result indicates that non-radiative recombination was significantly reduced in the Sn-target film.

Figure 3 (a) Steady-state PL spectra of the Sn-control-1, Sn-control-2 and Sn-target films. The samples are deposited on glass. (b) TRPL spectra of the Sn-control-1, Sn-control-2 and Sn-target films. (c) Dark J - V curves of the devices with a structure of ITO/SnO₂/perovskite/C60/Ag (the inset shows the structure configuration) derived from the SCLC analysis. (d) Mott-Schottky analysis plots of the Sn-control-1 film, Sn-control-2 film and Sn-target film-based TPSCs.

We then fabricated solar cells based on the Sn-control-1, Sn-control-2 and Sn-target films with an active area of 0.09 cm^2 and a device structure of ITO/PEDOT:PSS/perovskite/C60/BCP/Ag. It should be mentioned that, while preparing the devices, we optimized the film spin coating process by limiting the exposure time to less than 60 min to reduce the oxidation effect in the oxygen-containing environment (100 ppm). We obtained the PCEs of 4.58%, 4.33% and 9.53% for the Sn-control-1, Sn-control-2 and Sn-target film-based devices, respectively. The I - V curves are depicted in Fig. 4a. The forward and reverse scan of I - V curves are demonstrated in Fig. S8, and the details of open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF) are listed in Table S2. It was demonstrated that the hysteresis effect was also suppressed in the target film-based PSCs, which could be attributed to the lower trap density [38]. Therefore, the enhancement of device performance could be attributed to the reduced carrier recombination in the perovskite layer [47,48]. Besides, 24 devices were fabricated for each condition and the histogram of PCE of the devices is given in Fig. 4c. The integrated current densities for the devices based on the Sn-control-1, Sn-control-2 and Sn-target films were calculated to be 13.79,

13.46 and 19.97 mA cm^{-2} from the external quantum efficiency (EQE) spectra in Fig. 4b, which are in agreement with the J_{SC} measured by I - V curves. The higher EQE spectrum indicates that the target film-based device can extract the charge carriers more efficiently than those with insulator SnF_2 at the surface of the controlled Sn perovskite films.

In order to gain further insight into the enhanced device performance, we used the SCLC method to find the defect density for our devices, *via* employing the electron-only device configuration: ITO/ SnO_2 /perovskite/C60/Ag. Fig. 3c demonstrates three different regions in the logarithmic I - V curves: a linear ohmic region (slope = 1), a nonlinear trap-filling region (slope > 2), and a trap-free space charge limit current region (slope = 2). According to the trap-filled limit voltage (V_{TFL}) in region 2, the defect density (N_t) can be calculated from Equation (1) [49,50]:

$$N_t = 2\varepsilon_0\varepsilon_r V_{\text{TFL}} / eL^2, \quad (1)$$

where ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$), ε_r is the relative permittivity of the perovskite material ($\varepsilon_r = 32$) [9], e is the electron charge, and L is the thickness of the perovskite film (here we test the thickness

Figure 4 (a) I - V curves of the devices based on the Sn-control-1, Sn-control-2 and Sn-target films (the inset shows the device configuration). (b) EQE spectra of the Sn-control-1 film, Sn-control-2 film and Sn-target film-based devices. (c) The statistical box chart for the distributions of PCEs measured from the devices of the Sn-control-1, Sn-control-2 and Sn-target films (24 devices for each). (d) The stability test of encapsulated TPSCs under light soaking (AM 1.5 G, 100 mW cm^{-2}) in air with a relative humidity of ~20%–25% and a temperature of 25°C .

of perovskite film by a step profiler, and the L values of Sn-control-1, Sn-control-2, and Sn-target films are all 200 nm) in the devices. The values of V_{TFL} of the Sn-control-1, Sn-control-2 and Sn-target films are 0.34, 0.49, and 0.18 V, respectively. As a result, the derived defect density of $2.63 \times 10^{16} \text{ cm}^{-3}$ for the Sn-target film-based device was lower than that of the Sn-control-1 film ($4.51 \times 10^{16} \text{ cm}^{-3}$) and the Sn-control-2 film ($6.50 \times 10^{16} \text{ cm}^{-3}$). These results suggest that the target film has a defect passivation effect and therefore lower trap density. As shown in Fig. S9 and Table S3, the cell based on the Sn-target film exhibited a relatively lower saturation current density ($2.471 \times 10^{-5} \text{ mA cm}^{-2}$) than the Sn-control-1 film-based cell ($9.299 \times 10^{-5} \text{ mA cm}^{-2}$) and the Sn-control-2 film-based cell ($1.173 \times 10^{-4} \text{ mA cm}^{-2}$), which implies less charge recombination in the Sn-target film [51]. We also conducted the Mott-Schottky analysis to characterize the built-in potential of our devices (Fig. 3d). The built-in potential was derived from the intercept of the x axis of the Mott-Schottky plot [50,52]. It was demonstrated that the built-in potential of the device based on the Sn-target film (0.39 V) was higher than those of the Sn-control-1 film-based cell (0.27 V) and the Sn-control-2 film-based cell (0.26 V) (Table S3), indicating reduced charge recombination and energy offset at the heterojunction in the device based on the Sn-target film [53], in agreement with the dark current measurement result.

Finally, we investigated the operational stability of the three sets of cells in the air (humidity ~20%–25%, temperature ~25°C). The encapsulated Sn-target film-based cells maintained over 90% of its initial efficiency under simulated illumination of AM 1.5 G (100 mW cm^{-2}) after 1000 h of light soaking (the normalized efficiency attenuation was depicted in Fig. 4d red line). In contrast, the Sn-control-1 and Sn-control-2 films-based devices both lost more than 60% of their initial efficiencies within 500 h (Fig. 4d, black and blue lines, respectively). The variations of V_{OC} , J_{SC} and FF are also presented in Fig. S10. The enhanced stability of the target-device may be explained by a lower defect concentration and an improved crystallinity [40]. The target solar cells with fewer defects demonstrated excellent operational stability under light soaking, which is consistent with previous findings [54–56].

CONCLUSIONS

In summary, we presented a strategy to stabilize FASnI_3 perovskite with an amine complex. This solution provides very encouraging results, alleviating several problematic

aspects of the Sn-based thin film perovskites. The additive allows for an enhanced crystallinity, hindered oxidation rate and lower defect concentration, thereby enhancing the efficiency and stability of tin perovskite solar cells (TPSCs). Despite those remarkable improvements, we still draw the reader's attention to the fact that the defect density in our optimal TPSC ($2.63 \times 10^{16} \text{ cm}^{-3}$) is still higher than that of lead-based PSCs (10^{13} – 10^{14} cm^{-3}) [57,58]. This is most likely one of the main reasons why the efficiency of TPSCs still lags behind that of their Pb-based counterpart to date. With promising results from the additive strategy to improve stability and morphology, we suggest that the next major step to project TPSCs forward is to further reduce the defect density within TPSCs. With that goal in mind, we should aim to enhance the efficiency up to 15% with high operational stability, in order to provide a viable alternative to lead-based PSCs.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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拓宽溶液到结晶的时间窗口以获得稳定的锡基钙钛矿太阳能电池

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摘要 锡基钙钛矿太阳能电池(TPSC)是最具有应用前景的一类无铅钙钛矿太阳能电池(PSC). 然而, 锡基钙钛矿结晶性差和化学不稳定性是制约其进一步应用的两个挑战性问题. 本文中, 我们提出了一种策略, 通过胺络合物 $\text{CH}_3\text{NH}_3\text{I} \cdot 3\text{CH}_3\text{NH}_2$ 有效抑制了由 Sn^{2+} 被氧化为 Sn^{4+} 引起的钙钛矿降解问题, 来获得更稳定的 $\text{CH}(\text{NH}_2)_2\text{SnI}_3$ (FASnI₃)钙钛矿薄膜. 与仅使用常规的 SnF_2 添加剂制备的锡基钙钛矿薄膜相比, 添加 $\text{CH}_3\text{NH}_3\text{I} \cdot 3\text{CH}_3\text{NH}_2$ 后制备的薄膜的结晶性和稳定性得到增强. 最终, 所制备的器件获得了更高的外量子效率和9.53%的光电转换效率, 在标准的AM 1.5G模拟太阳光下老化1000 h后, 其效率仍然保持了初始效率的90%以上.