Impacts of MAPbBr$_3$ Additive on Crystallization Kinetics of FAPbI$_3$ Perovskite for High Performance Solar Cells

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Abstract: Blending perovskite with different cations has been successful in improving performance of perovskite solar cells, but the complex pathway of perovskite crystal formation remains a mystery, hindering its further development. In this paper, the detailed crystallization process of formamidinium lead iodide (FAPbI$_3$) perovskite films doped by methylammonium lead bromide (MAPbBr$_3$) additive was investigated by in situ grazing incident wide-angle X-ray scattering measurements during both spin coating and annealing. During spin-coating, it was found that the FAPbI$_3$ perovskite precursor easily formed a mixture of black perovskite phase ($\alpha$ phase) and non-perovskite yellow phase ($\delta$ phase) after the addition of MAPbBr$_3$, whereas only $\delta$ phase formed without MAPbBr$_3$. The $\delta$ phase gradually converted to $\alpha$ phase during annealing and there was only $\alpha$ phase left in both films with and without MAPbBr$_3$. However, the doped films presented high film quality without PbI$_2$ residue in contrast to the undoped films. These findings imply that the MAPbBr$_3$ additive can effectively suppress the formation of the unfavorable $\delta$ phase and trigger the formation of the optically active $\alpha$ phase even during spin-coating, which enhances the film quality possibly by removing the energy barriers from $\delta$ phase to $\alpha$ phase at room temperature. Finally, PSCs based on MAPbBr$_3$-doped FAPbI$_3$ were fabricated with a champion efficiency as high as 19.4% from 14.2% for the PSCs based on undoped FAPbI$_3$.

Keywords: perovskite solar cells; in situ GIWAXS; crystal structure

1. Introduction

Perovskite solar cells (PSCs) have attracted great attention in emerging photovoltaics, with current certified efficiency as high as 25.5% [1–4]. As one of their merits, the band gap of organic-inorganic halide perovskite materials can be continuously adjusted from 1.48 eV to 2.3 eV by alloying different halide ions. Formamidinium lead iodide (FAPbI$_3$) might be the most promising perovskite to approach the Shockley–Queisser limit due to its ideal bandgap of 1.48 eV [5]. As a matter of fact, most highly efficient PSCs were reported to use FA-based perovskites as light absorbing materials [6–9].

To achieve high absorption coefficient for maximized carrier generation as well as to enhance carrier life and mobility for efficient carrier diffusion and collection, lots of efforts have been dedicated to develop strategies improving film quality with minimized detrimental traps in bulk and at interfaces. Notably, the passivation strategies for bulk and interfaces are often decoupled as the type and concentration of defects are different [4]. It is well known that the lattice structure of pure FAPbI$_3$ is fragile and readily converts from $\alpha$ phase to non-perovskite $\delta$ phase at room temperature [10]. This is because the larger FA$^+$ ion leads to a larger tolerance factor of FAPbI$_3$, making the perovskite not a stable...
cubic structure at room temperature. Therefore, a small amount of MAPbBr₃ or MACI was usually introduced into FAPbI₃ to stabilize α phase FAPbI₃ with improved light and humidity stability [11–13]. For example, Kim et al. demonstrated how to stabilize pure FAPbI₃ using MACI to induce a stable intermediate prior to thermal annealing and finally obtained a certification efficiency of up to 24.6% [8,14]. Jeon et al. first revealed the effect of MABr in stabilizing the α-phase of FAPbI₃ [15]. A recent study by Yang et al. showed that they could maintain α phase of FAPbI₃ with the addition of MAPbBr₃ and without the assistance of MACI as stabilizer [16].

Despite these achievements in stabilizing FA-perovskite by using additives, the role of additives in the perovskite film formation process is not clear. There is already a report about the study of the crystallization mechanism of FAPbI₃ tuned by MACI [8]. However, the impact of MAPbBr₃ additive on crystallization mechanism of FAPbI₃ has not been well studied. Herein, in situ GIWAXS was used during spin coating and annealing of FAPbI₃ perovskite with different MAPbBr₃ concentrations to reveal the role of MAPbBr₃ affecting the perovskite crystallization kinetics. The results show that only optically inactive δ phase is formed during spin-coating without additives, whereas a mixture of δ and α phases appears during spin-coating after the addition of MAPbBr₃, and the subsequent annealing process will further promote the evolution of the δ phase to the α phase. Thus, it can be concluded that MAPbBr₃ additive can effectively inhibit the formation of δ phase and promote the formation of α phase even before annealing. Afterwards, combined with photoelectron spectroscopy analysis, we found that MAPbBr₃ in additives were involved in the mutual bonding between atoms or ions in the lattice after the post-annealing treatment, which led to the deduction of the process of perovskite crystallization. Afterwards, devices were fabricated based on FAPbI₃ doped with different MAPbBr₃ concentrations, and a champion PCE of 19.4% with negligible hysteresis was obtained with the help of MAPbBr₃. While the highest PCE of pure FAPbI₃ was only 14.2%, which is much lower than that of the target samples, our results indicate that the addition of MAPbBr₃ is sufficient to produce high-quality FA-based perovskite using the antisolvent method, resulting in the generation of high-performance PSCs.

2. Materials and Experimental

2.1. Materials

Tin (IV) oxide colloid solution (15 wt%) was purchased from Alfa-Aesar (Ward Hill, MA, USA). Lead iodide (PbI₂, 99.8%) was purchased from TCI (Shanghai, China). Formamidinium iodide (FAI), lead bromide (PbBr₂, 99.9%), methylammonium bromide (MABr), and 2,2’7,7’-tetrakis(N,N-di-p-methoxy-phenylamine)-9,9’-spirobifluorene (spiro-OMeTAD, 99%) was purchased from Xi’an Polymer Light Technology Corp. (Xi’an, China). Methy- lammonium chloride (MACI), bis (trifluoromethylsulfonyl)-imide lithium salt (Li-TFSI), 4-tert-butylpyridine(tBP), chlorobenzene (CB), acetonitrile, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and isopropyl alcohol (IPA) were purchased from Sigma-Aldrich (Munich, Germany).

2.2. Solution Preparation

Tin (IV) oxide colloid solution (15 wt%) was diluted within deionized (DI) water (1:4, v:v). The Spiro-OMeTAD solution was prepared by mixing 72.3 mg Spiro-OMeTAD, 35 µL Li-TFSI solution (260 mg Li-TFSI in 1 mL acetonitrile), and 30 µL tBP in 1 mL chlorobenzene. The perovskite precursor containing 241.6 mg FAI (1.4 M), 645.4 mg PbI₂ (1.4 M), 33.7 mg MACI (0.5 M) in 1 mL anhydrous DMF:DMSO 8:1 (v:v) was prepared as the undoped precursor. The 1.4 M MAPbBr₃ precursor was made by mixing stoichiometric MABr and PbBr₂ in the same process. Then, 50 mL MAPbBr₃ solution was added into the FAPbI₃ perovskite precursor to obtain the desired MAPbBr₃ concentration and stirred at 60 °C overnight.
2.3. Device Fabrication

PSCs were fabricated adopting a planar device architecture of ITO/SnO$_2$/Perovskite/Spiro-OMeTAD/MoO$_3$/Ag. ITO substrates were sequentially rinsed by sonication in detergent, DI water, acetone, and ethanol, and finally dried in air. Then, cleaned ITO substrates were treated in ultraviolet-ozone for 20 min. The SnO$_2$ colloid solution was spin coated on the ITO substrates at 3000 rpm for 40 s, followed by annealing at 150 $^\circ$C for 30 min. The perovskite precursor solution was spin coated on substrates following 2 steps: 1000 rpm for 10 s and 4000 rpm for 40 s. During the second step, 120 $\mu$L of chlorobenzene was drop-cast on substrates 10 s prior to the end of the program. The substrates then were immediately annealed at 110 $^\circ$C for 20 min. The spiro-OMeTAD solution was spin-coated on perovskite film at 4000 rpm for 30 s. Finally, a 10 nm MoO$_3$ and 100 nm Ag electrode was deposited by thermal evaporation.

2.4. In Situ GIWAXS Experiments

GIWAXS measurements were conducted at the BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray was 0.6887 Å (18 keV) and the scattering signals were collected by a MarCCD225 detector with a frame exposure time of 1 s. The sample to detector distance was 320 mm, calibrated by using a lanthanum hexaboride (LaB$_6$) sample. The X-ray incident angle was kept at 1$^\circ$ to enhance the surface sensitivity. The spin-coating process was conducted in an air-tight chamber under N$_2$ flow, which consists of a spin-coater and a motorized syringe for remote dropping of CB. After the perovskite precursor was dropped on the substrate, GIWAXS measurements and sample spinning could be triggered simultaneously, followed by a programmed CB antisolvent dropping on the film at a designated time within the 60 s for spinning at 4000 rpm. After spin coating, the sample was heated to 110 $^\circ$C by using remote control for 20 min. There was no visible sign of X-ray damage on the sample after measurements.

2.5. Device Characterization

The photocurrent density and voltage (J-V) of the fabricated PSCs were subsequently measured by using a Keithley 2400 sourcemeter under a standard AM 1.5 G illumination at 100 mW·cm$^{-2}$. The light intensity of solar simulator (Enli Tech, Kaohsiung City, Taiwan) was calibrated using a standard KG-5 filtered Si diode. Protocols of J-V measurements: all the devices related were tested at room temperature inside a glove box filled with nitrogen. The active area of devices is 0.075 cm$^2$. A typical scan was made with a dwell time of 0.1 s and a voltage scan step of 0.007035 V, and J-V tests method is referred to the reference [14]. The SEM images were acquired by using a field-emission scanning electron microscopy (ZeissG300 Microscope, Oberkochen, Germany). The AFM images of perovskite films were taken by a Bruker NanoScope 8 (Billerica, MA, USA) atomic force microscope in tapping mode. For photoemission experiments, as-prepared perovskite films were transferred into an ultrahigh vacuum (UHV) system with a base pressure better than 2 $\times$ 10$^{-9}$ mbar and kept in vacuum overnight for degassing. Photoemission measurements were performed in situ at room temperature after each deposition using a PHOIBOS 100 analyzer together with a monochromatic X-ray source (Al Ka: 1486.6 eV) for XPS and a helium light lamp (He I: 21.2 eV) for UPS, respectively. All UPS and XPS measurements are performed at room temperature. Using a gold reference sample, the instrumental energy resolution for XPS and UPS was estimated to be 0.45 eV and 15 meV, respectively. To extract the work function (WF) from the secondary electron cutoff (SECO) in the UPS spectra, a $-10$ V bias was applied to the samples. All photoemission spectra were collected at normal emission, and the binding energy was referred to the Fermi level of a sputter-cleaned gold foil electrically connected to the sample.

3. Results and Discussion

In situ GIWAXS measurements were carried out through the whole perovskite film fabrication process from spin-coating to annealing, as shown in Figure 1a. Figure 1b shows
a schematic drawing of the in situ GIWAXS experimental setup equipped with a spin coater, heating platform, and an antisolvent syringe under nitrogen environment. The GIWAXS patterns of perovskite films with and without MAPbBr$_3$ taken during spin-coating and annealing are present in Figures 2 and 3, respectively.

**Figure 1.** Schematics of the film fabrication procedure and the experimental setup for in situ GIWAXS measurement. (a) The steps of perovskite fabrication process and (b) The in situ GIWAXS experimental setup equipped with a spin coater, heating platform, and an antisolvent syringe under nitrogen environment.

**Figure 2.** The 2D GIWAXS patterns taken at different times during spin-coating for an undoped film in (a–c) and for a MAPbBr$_3$-doped perovskite film in (d–f), respectively. The derived 1D XRD spectra for the undoped film in (g) and for the MAPbBr$_3$-doped perovskite film in (h), respectively.
Figure 3. The 2D GIWAXS patterns taken at different time points during annealing for the undoped film in (a–c) and for the MAPbBr$_3$-doped perovskite film in (d–f), respectively. The derived 1D XRD spectra for the undoped film in (g) and for the MAPbBr$_3$-doped perovskite film in (h), respectively.

Figure 2a presents the GIWAXS pattern at the beginning of spin-coating of a undoped FAPbI$_3$ perovskite film, where no diffraction rings are visible. When chlorobenzene was dropped on the spinning films, diffraction rings instantly appeared near q = 8.3 nm$^{-1}$ (Figure 2b), which originated from the rapid crystallized non-perovskite yellow phase (δ phase) out of perovskite precursor due to saturation precipitation caused by the rapid volatilization of the polar solvent after the dropping of the antisolvent. After that, the intensity of the diffraction signal increased continuously till the end of spin-coating and Figure 2c reports the same GIWAXS pattern as Figure 2b with enhanced diffraction signals. To quantify the crystallization evolution, the q-dependent 1D-XRD spectra derived from GIWAXS patterns from 4 nm$^{-1}$ to 14 nm$^{-1}$ are present in Figure 2g. It is clear that there is only a peak at q = 8.3 nm$^{-1}$ present in the spectra after CB dropping, which indicates that only non-perovskite yellow phase (δ phase) forms during spin-coating in the film without MAPbBr$_3$, in line with previous reports [17,18].

Figure 2d reports GIWAXS pattern of a FAPbI$_3$ perovskite film doped by MAPbBr$_3$ at the beginning of spin-coating, where no diffraction rings are seen. When CB was dropped (Figure 2e), a diffraction ring attributed to δ phase instantly appeared at around q = 8.3 nm$^{-1}$ along with a new weak and broad diffraction ring around q = 9.9 nm$^{-1}$ attributed to α phase. The intensity of these two diffraction rings gradually became stronger till the end of spin-coating and the GIWAXS pattern is reported in Figure 2f with two diffraction rings at both q = 8.4 nm$^{-1}$ and q = 9.9 nm$^{-1}$. The evolution of the crystallization kinetics of the MAPbBr$_3$ doped perovskite films during spin coating can be seen well in the q-dependent 1D-XRD spectra in Figure 2h. It is obvious that the δ-phase peak shifts from 8.3 nm$^{-1}$ to 8.4 nm$^{-1}$ during spin-coating and is much weaker than the counterpart in Figure 2g for the film without MAPbBr$_3$, indicating that MAPbBr$_3$ can effectively suppress the formation of unfavorable δ phase during the spin-coating. Meanwhile, the appearance of the new α phase peak at near 9.9 nm$^{-1}$ implies that MAPbBr$_3$ can trigger the formation of black α phase perovskite even during spin-coating. All these GIWAXS results obtained during spin-coating prove that MAPbBr$_3$ can change the crystallization pathway of FAPbI$_3$ perovskite precursors possibly by reducing the phase transition barrier from δ phase to α phase at room temperature.

To study the crystallization kinetics during annealing, Figure 3a reports the GIWAXS pattern of the undoped FAPbI$_3$ perovskite film without MAPbBr$_3$ at the beginning of
annealing, where the diffraction ring at near $q = 8.3 \text{ nm}^{-1}$ is clear but with no visible features around $q = 10 \text{ nm}^{-1}$, consistent with the GIWAXS image at the end of spin-coating (Figure 2c). After 3 min of annealing in Figure 3b, the diffraction ring at near $q = 8.3 \text{ nm}^{-1}$ becomes weaker with a new diffraction ring appearing at $q = 9.9 \text{ nm}^{-1}$, indicating that the non-perovskite $\delta$ phase starts to transform to the black $\alpha$ phase during annealing. As can be seen from the corresponding $q$-dependent 1D-XRD spectra in Figure 3g, the peak intensity of the $\delta$ phase is still much higher than that of the $\alpha$ phase at this time, implying that the $\delta$ phase is still dominant at this time. After 20 min at the end of annealing, the diffraction ring at near $q = 8.3 \text{ nm}^{-1}$ completely disappears whereas the diffraction ring at near $q = 9.9 \text{ nm}^{-1}$ becomes much stronger in Figure 3c, indicating the completion of the FAPbI$_3$ perovskite film fabrication. Meanwhile, a very weak diffraction ring appears at near $q = 9.1 \text{ nm}^{-1}$, ascribed to the (001) crystal plane of PbI$_2$ [18–21]. This confirms the existence of a small amount of excess PbI$_2$ in the film, which indicates that PbI$_2$ was not completely converted to perovskite [8,22,23].

In contrast to the film without MAPbBr$_3$, two diffraction rings at both $q = 8.3 \text{ nm}^{-1}$ and $q = 9.9 \text{ nm}^{-1}$ are already present in the film doped by MAPbBr$_3$ at the beginning of annealing (Figure 3d), consistent with the results in Figure 2f at the end of spin-coating. After 3 min of annealing (Figure 3e), the $\delta$ phase diffraction ring at near $q = 8.3 \text{ nm}^{-1}$ becomes much weaker whereas the $\alpha$ phase diffraction ring at near $q = 9.9 \text{ nm}^{-1}$ becomes much stronger. The corresponding $q$-dependent 1D-XRD spectrum at this time in Figure 3h further indicates that the $\alpha$ phase already becomes dominant in the film. At the end of the annealing (Figure 3f), the $\alpha$ phase diffraction ring becomes even brighter without any sign of $\delta$ phase diffraction feature $q = 8.3 \text{ nm}^{-1}$. It is also noticed that no obvious excess PbI$_2$ formation is seen. The peak areas were calculated to determine the phase contents quantitatively. After annealing, the areas of $\alpha$-phase (001) peak are 18 (a.u.) in the undoped sample and 26.6 (a.u.) in the sample of perovskite with MAPbBr$_3$ respectively, and the undoped sample exhibited the obvious $\delta$ phase with the peak area of 0.02 (a.u.). All these GIWAXS results indicate that MAPbBr$_3$ can facilitate the full conversion of perovskite precursors into optically active $\alpha$ phase perovskite during annealing.

To better understand the influences of MAPbBr$_3$ on fabricated FAPbI$_3$ perovskite films, photoelectron spectroscopy characterization was performed for fabricated films with and without MAPbBr$_3$ as shown in Figure 4. For the undoped film, the Pb $4f_{7/2}$ (Figure 4a) and I $3d_{5/2}$ (Figure 4b) are located at 137.9 eV and 618.7 eV, respectively. After MAPbBr$_3$ doping, Pb $4f_{7/2}$ and I $3d_{5/2}$ shift to lower binding energy by $\sim$0.3 eV and $\sim$0.2 eV, respectively. In the meanwhile, N 1s (Figure 4c) and C 1s (Figure 4f) barely change their binding energies after MAPbBr$_3$ doping. Thus, the present XPS results suggest that MAPbBr$_3$ could interact with FAPbI$_3$ leading to electron transfer mainly from Pb-I octahedron, possibly due to higher electron affinity of Br anion from MAPbBr$_3$, which may lead to its increased structural stability.

To find out the film chemical composition, Table 1 reports the atomic ratio calculated from XPS of all the elements in the fabricated films with and without MAPbBr$_3$. It is noticed that the concentration of Cl is low with an atomic ratio of 0.02~0.01 for the two films in Table 1; however, the concentration of Cl in the precursor solution is about 0.5 mol/mL (equivalent to 35.7% of Pb ions), implying that Cl must escape from the film surface during the crystallization of perovskite in line with the previous reports [4,8]. It can be seen that the atomic ratio of Br in the film with MAPbBr$_3$ is only 0.06 in Table 1 in contrast to 0.21 mol Br ions in 1 mL precursor solution (equivalent to 15% of Pb ions), which is also probably due to partial escaping of Br ions from the surface. As Table 1 yields an estimated atomic ratio of I:Br to be 2.85:0.06 for the film doped by MAPbBr$_3$, its chemical structure is thus deduced as (FAPbI$_3$)$_{0.98}$(MAPbBr$_3$)$_{0.02}$. 


Figure 4. (a) Pb 4f7/2, (b) I 3d5/2, (c) N 1s, (d) C 1s, (e) Cl 2p, (f) Br 2p core-level spectra, and (h) SECO and (g) VB spectra for perovskite films with and without MAPbBr3.

Table 1. Proportions of elements on the film surface of the reference and target samples, where the proportions of each element are relative to the content of Pb atoms.

| Element | Content |
|---------|---------|
| Pb      | 1.00    |
| I       | 2.97    |
| Br      | 0       |
| C       | 1.88    |
| N       | 2.51    |
| Cl      | 0.02    |
| Reference | 1.00    |
| With MAPbBr3 | 0.98    |
|          | 2.85    |
|          | 0.06    |
|          | 1.72    |
|          | 2.30    |
|          | 0.01    |

To study the changes of electronic structure induced by MAPbBr3, the perovskite UPS spectra at the secondary electron cut-off (SECO) and valence band (VB) regions are shown in Figure 4g,h, respectively. As shown in Figure 4g, the work function (WF) of the undoped perovskite film derived from its SECO is ~4.5 eV, consistent with reported WK of FAPbI3 [24,25]. After doping with MAPbBr3, the WF is slightly deduced to 4.4 eV. As can be seen from Figure 4h, the valence band maximum (VBM) position before and after the doping of MAPbBr3 barely changes at 1.4 eV. Thus, the ionization energies (IE) of doped and undoped films are calculated to be 5.9 eV and 5.8 eV, respectively. Spiro-OMeTAD are widely used as hole transport layer (HTL) in PSCs and its IE is 5.2 eV [26,27]. Using Spiro-OMeTAD as HTL, the hole injection barriers $\Delta E_v$ for the doped and undoped FAPbI3 are deduced to be 0.7 eV and 0.6 eV, respectively. As a smaller $\Delta E_v$ will contribute to efficient injection of holes [21,24,25], MAPbBr3 additive in perovskite thus modifies the electronic structure of FAPbI3 with favorable interfacial energy alignment at the perovskite/spiro-OMeTAD interface.
Based on the synchrotron radiation based GIWAXS and photoemission results, we proposed a model depicting crystallization process of FAPbI₃ from the perovskite precursors with or without MAPbBr₃ as shown as Figure 5. It is worth mentioning that the role of Cl ions in precursor solution influencing the crystallization process is neglected in this model. The whole crystallization process can be divided into three processes in the proposed model: (1) after the anti-solvent dropping, δ phase preferentially forms in the undoped precursor solution, whereas a mixture of δ phase and α phase forms after the doping of MAPbBr₃ in the precursor solution; (2) at the initial stage of annealing, the δ phase in the undoped film starts to transfer to α phase perovskite, whereas the existing α phase perovskite in the doped film becomes dominant quickly at this stage with the presence of MAPbBr₃; and (3) finally, the δ phase in undoped films completely disappears and converts to α phase in both films. In the doped film, the large FA⁺ ions will be partially replaced by MA⁺ ions leading to formation of (FAPbI₃)₀.₉₈(MAPbBr₃)₀.₀₂.

![Schematic Diagram](image)

**Figure 5.** The schematic diagram depicting the crystallization process of FAPbI₃ perovskite films with and without MAPbBr₃ additive.

To check the morphology changes induced by MAPbBr₃ doping, scanning electron microscopy (SEM) and atomic force spectroscopy (AFM) measurements were carried out with data shown in Figure 6. As can be seen from the SEM image in Figure 6a, the undoped film presents large grains with an average size over a few microns as well as some pinholes near the grain boundaries, which normally is associated with the rapid nucleation process [28]. After the addition of MAPbBr₃ (Figure 6b), the doped film looks denser and more compact with smaller grain and almost no pinholes near the grain boundaries. As it is reported that MACl can promote the growth of perovskite crystal grains making the large grains [4,29,30], the Br⁻ anion from MAPbBr₃ could slowly diffuse during the perovskite film formation process, which slows down the rapid growth of perovskite grains, with defect density significantly reduced [4]. The improved morphology is also evidenced by AFM images in Figure 6c,d: the grains in the undoped film are more irregular whereas the grains in the doped film are more uniform and dense with fewer defects, in consistency with SEM results.

In order to study the effect of MAPbBr₃ on the optical properties of the perovskite layers, we conducted UV-visible absorption spectroscopy and photoluminescence spectrum (PL) of doped and undoped films. The absorption wavelength of the perovskite film doped with MAPbBr₃ is blue-shifted from 805.2 nm to 790.1 nm, as shown in Figure 7b, which corresponds to a band gap shift from 1.54 eV to 1.57 eV. The PL results (Figure 7c) followed a similar tendency to the UV-visible absorption: the emission peak showed a blue-shift from 825.0 nm to 814.2 nm with increased peak intensity, suggesting a lower carrier recombination due to the improved crystal quality.
Figure 6. Top-view scanning electron microscopy (SEM) images (upper panel) and atomic force spectroscopy (AFM) images (lower panel) of perovskite films with or without MAPbBr$_3$ additive: (a,c) the undoped perovskite film and (b,d) the MAPbBr$_3$-doped perovskite film.

Figure 7. (a) The energy level diagram for the SnO$_2$/perovskite/spiro-OMeTAD PSCs; (b) the absorption spectrum of perovskite on quartz; (c) the PL spectrum of perovskite on quartz; (d) the device architecture; (e) $J$-$V$ curves of PSCs based on films with and without MAPbBr$_3$ additive; (f) $J$-$V$ curves of perovskite with MAPbBr$_3$ devices prepared for both forward and reverse scans.
To investigate the impact of MAPbBr\(_3\) on FAPbI\(_3\) based photovoltaic device performances, PSCs using FAPbI\(_3\) perovskite with and without MAPbBr\(_3\) additive were fabricated and the device structure was ITO/SnO\(_2\)/perovskite/Spiro-OMeTAD/MoO\(_3\)/Ag, as shown in Figure 7d. The current density-voltage (J-V) curve of these PSCs and their corresponding J-V parameters are shown in Figure 7e. The champion power conversion efficiency (PCE) of the control devices based on undoped FAPbI\(_3\) is only 14.2%, with a short current density (J\(_{sc}\)) of 23.7 mA cm\(^{-2}\), an open circuit voltage (V\(_{oc}\)) of 0.99 V and a filling factor (FF) of 60.4%. The MAPbBr\(_3\) doped FAPbI\(_3\) based PSCs yielded a champion PCE up to 19.4%, which was mainly attributed to the significant enhancement of V\(_{oc}\) of 1.11 V and FF of 72%. The devices with MAPbBr\(_3\) exhibit negligible hysteresis, and the J-V curves of perovskite with MAPbBr\(_3\) devices prepared for both forward and reverse scans are shown in Figure 7f. The enhanced performance of PSCs should be attributed to the improved film quality with reduced defects density as well as the optimization of band alignment at the perovskite/spiro-OMeTAD interface by introducing MAPbBr\(_3\) additive into the FAPbI\(_3\) precursors.

4. Conclusions

In summary, we investigated the crystallization kinetic process of FAPbI\(_3\) perovskite precursor solutions with and without MAPbBr\(_3\) additive by using in situ synchrotron radiation based GIWAXS during both spin-coating and annealing. It was found that MAPbBr\(_3\) can effectively suppress \(\delta\)-phase formation while promoting \(\alpha\)-phase formation during spin-coating, resulting in a high-quality film without PbI\(_2\) residue. Combined with the photoelectron spectroscopy analysis, a model about the FAPbI\(_3\) crystallization kinetics was proposed. Furthermore, PL results also demonstrate the improved crystalline quality. Finally, performances of devices were analyzed together with other characterizations. Finally, PSCs based on MAPbBr\(_3\)-doped FAPbI\(_3\) were fabricated with a champion efficiency as high as 19.4% from 14.2% for the PSCs based on undoped FAPbI\(_3\).

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