Restricting δ -phase transformation of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ via iodine-vacancy filling for efficient perovskite solar cells

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ABSTRACT Formamidinium lead halide (α -FAPbI₃) with a broad light absorption spectrum, has recently received considerable attention in optoelectronic applications. However, the FAI-PbI₂-DMSO (DMSO: dimethyl sulfoxide) intermediate anisotropic fibers readily form a non-perovskite phase (δ -FAPbI₃) and uncontrolled excess PbI₂, which hinders the further increase in the efficiencies of solar cells. Caculations indicate that iodine defects in polycrystalline films would enlarge the perovskite tolerance factor and result in the formation of iodide Frenkel defects. Herein, we introduce a post-treatment technique to heal the as-prepared FAPbI₃ thin layer and restrain the notorious δ -FAPbI₃ through vacancy filling. Furthermore, a new intermediate phase of FAI-PbI₂-DMSO-FACl led to a high-quality perovskite layer with an enlarged average grain size that exceeded 2 μm . Consequently, the power conversion efficiencies of FAPbI₃ solar cells were significantly enhanced due to the high crystallinity of the pure α -phase perovskite. Therefore, this method can be used to obtain high pure-black perovskite films and efficient solar cells.

Keywords: formamidinium perovskite solar cells, iodine vacancy, nonperovskite phase, post-treatment

INTRODUCTION

Organic-inorganic lead halide perovskite solar cells have attracted tremendous attention due to their power conversion efficiencies (PCEs), which have rapidly risen from 3.8% to 25.2% in a span of ten years [1–6]. Perovskite materials not only exhibit superior photoelectric properties but also can be easily fabricated through low-cost solution methods [7,8]. The most widely employed hybrid

perovskite materials in solar cells are methylammonium lead iodide (MAPbI₃) and formamidinium lead iodide (FAPbI₃). Compared with MAPbI₃, FAPbI₃ exhibits broader light absorption spectra, outstanding thermal stability and high efficiency, which are important properties for various applications, including solar cells, light-emitting diodes, memory applications, and optically pumped lasers [9–12]. However, the tolerance factor of FAPbI₃ is close to 1. A byproduct of δ -FAPbI₃, which has a wide bandgap of 2.43 eV forms easily, and thus, it is unsuitable for efficient solar cells [13–15]. Therefore, it is essential to develop an effective method for obtaining a pure α -FAPbI₃ perovskite layer.

In addition to the undesired δ -FAPbI₃ phase, the formation of crystal defects is another factor that decreases the quality of FAPbI₃ perovskite films. The larger FA⁺ cations can alter the lengths of Pb–I bonds, which results in the diffusion of the FA⁺ cations and the formation of iodine vacancies [16]. These iodine vacancies in FAPbI₃ can trigger ion migration and iodide Frenkel defects, which leads to the non-radiative recombination of perovskite crystals and hysteresis of the device performance [17]. Yao *et al.* [18] reported a facial method to hinder the formation of the δ -FAPbI₃ phase by introducing K⁺ in the perovskite. This suggests that K⁺ incorporation can affect the Pb–I bond energy and crystal structure. Furthermore, organic cations can easily escape from perovskite crystals when the temperature increases to 160°C, which is the transition temperature for the α -phase of FAPbI₃ [13,19]. Defects, including lead ions, ionic defects and clusters, will lead to the degradation of FAPbI₃ perovskite. Pre-

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vious studies showed that surface recombination plays an important role in the total carrier lifetime for perovskite layers [20,21]. Hence, it is crucial to explore a useful method for reducing the defect density in FAPbI₃ perovskite films. Furthermore, the mechanism of iodine defect formation in δ -FAPbI₃ is still unclear, and effective methods for preparing pure α -FAPbI₃ are limited.

In this work, the use of stoichiometric precursor ratios (FAI:PbI₂ = 1:1 (mol/mol)) resulted in iodine-anion-deficient ionic compounds, which was proven by the appearance of a peak of Pb⁰ in the X-ray photoelectron spectroscopy (XPS) spectrum. Hence, pure-phase α -FAPbI₃ was fabricated by a one-step solution deposition followed by post-treatment with a mixed FAX (FAI and FACl) solution, which was referred to as the vacancy filling (VF) method. The FAI could react with the excess PbI₂, and the FACl could enlarge the grain size of FAPbI₃ thin layer and restrict the δ -FAPbI₃ formation through iodine VF. Consequently, the improved FAPbI₃ perovskite solar cell exhibited a larger open-circuit voltage (V_{OC}) and short-circuit photocurrent density (J_{SC}). This VF method is critical for achieving further efficiency improvement of FAPbI₃ solar cells.

EXPERIMENTAL SECTION

Film fabrication (diethyl ether)

In an N₂ glove box, 461 mg of PbI₂, 172 mg of HC(NH₂)₂I, and 78 mg of dimethyl sulfoxide (DMSO, molar ratio 1:1:1) were added to 600 mg of dimethylformamide (DMF) at room temperature and stirred for 1 h. The completely dissolved solution was spin-coated on the substrates at 4000 rpm for 25 s and 0.5 mL of diethyl ether was slowly dripped on the rotating substrate for 10 s, during which the surface became turbid due to rapid vaporization of the DMF. Next, a 40 μ L of FAX solution (15 mg of FAI and 5 mg of FACl dissolved in 1 mL of isopropyl alcohol (IPA)), was dropped onto the as-prepared film. Similarly, a 40 μ L solution of either FAI (20 mg) or FACl (20 mg) dissolved in IPA (1 mL) was dropped onto an as-prepared FA film to prepare control samples. Subsequently, the as-prepared films were heated at 150°C for 30 min.

Solar cell fabrications

Fluorine-doped tin oxide (FTO) glasses (Pilkington, TEC15) were etched with 0.8 mol L⁻¹ HCl aqueous solution and Zn powder. The etched FTO glasses were cleaned with detergent, distilled water, ethanol and sonicated for 30 min. By means of spray pyrolysis, the

blocking TiO₂ layers (bl-TiO₂) were deposited onto the as-prepared FTO followed by heating at 510°C for 30 min. The mesoporous TiO₂ (mp-TiO₂) film was deposited onto the bl-TiO₂ layer by spin-coating of TiO₂ paste (Dyesol 30NR-T) followed by calcining at 510°C for 20 min.

The transparent perovskite film was heated at 100°C for 20 min in order to obtain a dense film. Then, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobi-fluorene) (spiro-OMeTAD) solution (25 μ L), which consisted of 73 mg of spiro-OMeTAD, 28 μ L of 4-*tert*-butyl pyridine and 17.5 μ L of lithium bis(trifluoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TFSI in 1 mL of acetonitrile) in 1 mL of chlorobenzene, was spin-coated on the perovskite film at 3000 rpm for 20 s. Finally, Au electrode with a thickness of 60 nm was deposited by using thermal evaporation under vacuum at a constant evaporation rate of 0.6 nm s⁻¹.

Characterizations

The morphology of the perovskite film was studied by field-emission scanning electron microscopy (FESEM, FEI Sirion 200, Netherlands). The crystal phases were obtained by X-ray diffraction (XRD, X'Pert Pro, Netherlands) using Cu K α radiation (λ = 1.54 Å). The photocurrent density-voltage (J - V) curves were measured under one sun illumination (AM 1.5G conditions, 100 mW cm⁻²) with a solar simulator (94043A, USA) equipped with Keithley 2400 source meter. During the measurements, a mask with a 0.09 cm² aperture area was used to prevent light scattering through the sides and to define the effective area of the device. Ultraviolet-visible (UV-vis) diffuse reflectance and absorption spectra were measured using a UV-vis spectrophotometer (SOLID3700, Shimadzu Co. Ltd, Kyoto, Japan). Incident photon conversion efficiency (IPCE) spectra were obtained with a spectral resolution of 5 nm, using a 300 W xenon lamp and a grating monochromator equipped with order sorting filters (Newport/Oriel). A Thermo Scientific ESCALAB 250Xi spectrometer from VG Scientific using 300 W Al K α radiation operating at a base pressure of 3 $\times$ 10⁻⁹ mbar was used to obtain X-ray photoelectron spectroscopy (XPS) data. The binding energies were referenced to adventitious carbon (C 1S line at 284.9 eV). The photoluminescence (PL) mapping signals were obtained with a laser confocal Raman spectrometer (Princeton Instruments, Acton Standard Series SP-2558), a digital charge-coupled device (CCD, PIXIS:100B_eXcelon) and a 485 nm laser (PicoQuant LDH-P-C-485, 0.4 mW with a 1% optical density filter), using a

homemade confocal microscope on a $5 \times 5 \mu\text{m}^2$ sample area. Atomic force microscopy (AFM) images were acquired in tapping mode with a 5500 AFM (Agilent Technologies, California, USA).

RESULTS AND DISCUSSION

The schematic diagram of the VF method for producing pure-phase FAPbI_3 films is illustrated in Fig. 1a. The equimolar FAI-PbI_2 solution was spin-coated on a mesoporous TiO_2 layer followed by washing with an anti-solvent of diethyl ether. Before the end of the spin-coating process, the transparent thin layer was post-treated by dripping FAX/IPA solution (15 mg of FAI mixed with 5 mg of FACl in 1 mL of IPA) onto it followed by annealing to remove the excess solvent. Unlike previous post-treatment techniques (annealed perovskite layers), this VF method treated the unannealed FAI-PbI_2 -DMSO, which was a colloidal film [22–24].

XPS was used to explore the influence of the VF method on the nature of the defects in the FA-based perovskite. Iodine vacancies and escaped FA^+ could result

in metallic Pb defects at the perovskite film surface. As shown in Fig. 1b, the $\text{Pb } 4f_{7/2}$ and $\text{Pb } 4f_{5/2}$ main peaks of the FAPbI_3 film with FAX treatment were located at binding energies of 138.3 and 143.2 eV, respectively. The FAPbI_3 film without FAX treatment had two additional peaks at 136.4 and 141.3 eV, which were attributed to metallic lead [25–27]. The metallic lead may have been present due to iodine vacancies. After FAX treatment, the intensity of the metallic lead in the FAPbI_3 film was reduced, implying that the FA^+ and I^- eliminated under-coordinated lead atoms through VF. Fig. 1c displays a schematic view of the perovskite crystal structure, where the organic cation and I anion occupy 1/4 and 3/4 of the face-centered cubic (FCC) lattice sites, while Pb resides at the center site. After the formation of iodine vacancies on the lattice sites, the structure of perovskite would collapse, resulting in iodide Frenkel defects. Theoretical studies suggest that the formation of iodide Frenkel defect leads to hysteresis of perovskite device performance [17]. Moreover, the tolerance of FAPbI_{3-x} with iodine vacancies was investigated. As shown in Fig. 1d, a tolerance

Figure 1 (a) Schematic illustration of the VF method for producing FAPbI_3 thin films. (b) XPS analyses involving the $4f_{7/2}$ and $4f_{5/2}$ spectra of Pb. (c) Crystal structure of FAPbI_3 perovskites with I vacancy. (d) Tolerance factor of FAPbI_{3-x} .

greater than 1 was caused by the increased iodine deficiency. This calculated result was discussed based on the XRD results below.

Fig. 2a and b show the SEM images of FAPbI₃ films without and with FAX treatment, respectively. As illustrated in Fig. 2a, the crystal grains of FAPbI₃ film without FAX treatment were smaller than 500 nm. After treatment with the FAX solution, the grain size of the perovskite layer became larger than 2 μm , demonstrating that the FAX treatment could effectively enhance the crystallinity of the perovskite film. In addition, the FAPbI₃ film without FAX treatment exhibited a rough surface and the presence of a white-colored phase, which was regarded as excess PbI₂ [23,28]. Although a moderate amount of PbI₂ could passivate the defects at the perovskite surface, uncontrolled PbI₂ reduced the reproducibility of devices [28,29]. After FAX solution treatment, the top view of the FAPbI₃ film became smooth, and the excess PbI₂ was removed by reacting with the FAX. To explore the effect of FAI and FACL on the FAPbI₃ morphology, the SEM images of FAPbI₃ films with different

weight ratios of FAI and FACL were investigated. As shown in Fig. S1, as the ratio of FACL increased, the grain size gradually increased. This implied that the FACL could increase the grain size of the FAPbI₃ thin layer. Based on previous reports, this phenomenon was ascribed to the reduced number of grain boundaries and the passivated perovskite surface due to post-treatment-assisted Ostwald ripening [30–33].

To further explore the influence of the FAX solution treatment on the phase of the final FAPbI₃ film, the XRD spectra were investigated. As shown in Fig. 2c, the XRD spectra of the FAPbI₃ films without FAX treatment exhibit peaks corresponding to PbI₂ (12.6°) and δ -phase FAPbI₃ (11.8°) [34]. This agrees with the calculated result shown in Fig. 1d. Interestingly, the intensity of the peaks of PbI₂ and δ -phase FAPbI₃ vanished after the FAX treatment of the FAPbI₃ films, suggesting that the VF method could effectively promote the transformation of the δ -phase to the black α -phase. To further elucidate the effect of FAI and FACL on the morphologies and crystallinities of perovskite films, FAI (20 mg mL⁻¹ in IPA)

Figure 2 Top-view SEM images of FAPbI₃ films (a) without and (b) with FAX treatment, where the scale bar is 2 μm . (c) The XRD results for FAPbI₃ films without and with FAX treatment.

and FAcI (20 mg mL⁻¹ in IPA) solutions were used to treat the precursor perovskite films. The SEM and XRD results shown in Fig. S2 indicate that FAI could react with excess PbI₂ in the FAPbI₃ film. However, the δ -phase FAPbI₃ was still present. On the contrary, FAcI could remove the δ -FAPbI₃ and enlarge the grain size (Fig. S1), but the excess PbI₂ remained. Thus, the mixed FAX not only removed the excess PbI₂ and the δ -phase, but also increased the perovskite grain sizes.

Based on previous reports, the intermediate phase could determine the morphologies and crystallinities of final films [35]. As shown in Fig. 3a and b, the XRD patterns of the FAI-PbI₂-DMSO, FAI-PbI₂-DMSO-FAI and FAI-PbI₂-DMSO-FAcI intermediate powders were investigated. After treatment with only the FAI solution, the main peak of the FAI-PbI₂-DMSO-FAI at around 8.1° was not different from that of the FAI-PbI₂-DMSO. However, the main peak of the FAI-PbI₂-DMSO-FAcI intermediate located at around 8.1° split into two peaks, which verified that the Cl anion was incorporated in the final intermediate phase. The new intermediate phase also suggests that the crystallization process of the perovskite was different [15].

XPS was used to study the chlorine content of the FAPbI₃ films before and after thermal annealing. As

shown in Fig. 3c, the two main peaks of Cl 2p in the FAI-PbI₂-DMSO-FAcI adducts appeared after post-treatment with the FAX solution. Interestingly, after being annealed at 150°C for 2 min, the Cl 2p peak in the FAI-PbI₂-DMSO-FAcI intermediate vanished. This revealed that the content of the Cl anions in the film after mild annealing decreased through the evaporation of FAcI, which is in good agreement with previous reports [15,36].

Based on the above analyses, Fig. 3d presents a plausible mechanism for the direct formation of black-phase FAPbI₃ films through iodine VF. The iodine-deficient FAPbI₃ δ -phase was generated through one-step solution deposition. After treatment with the FAX solution, the vacancies were filled with chlorine atoms. During the annealing process, the FAcI left the film as vapor through dual-ion exchange, and pure-phase FAPbI₃ films were obtained finally.

To elucidate the effect of the VF method on the photophysical properties of FAPbI₃ films, the confocal PL mapping test was conducted. Both samples were deposited on bare glass to avoid charge injection from the perovskite active layer to the FTO [37]. As shown in Fig. 4a and b, the perovskite thin film with FAX treatment had a much higher PL intensity, indicating that the film surface had fewer defects [38]. We attributed this to the

Figure 3 (a) XRD patterns of the FAI-PbI₂-DMSO, FAI-PbI₂-DMSO-FAI and FAI-PbI₂-DMSO-FAcI intermediate powders. (b) Expanded XRD region of 7.8°–8.5° for the corresponding intermediate powders. (c) XPS analyses of Cl 2p of FAI-PbI₂-DMSO-FAcI with and without annealing at 150°C for 2 min. (d) Schematic of FAPbI₃ formation *via* iodine VF.

Figure 4 PL mapping intensity images of FAPbI₃ films (a) with and (b) without FAX treatment. (c) PL spectra and (d) PL decay curves for FAPbI₃ films with and without FAX treatment on glass.

enlarged crystal grain size (SEM result in Fig. 2b) and the decreased number of iodine vacancies. Furthermore, the corresponding PL measurement in Fig. 4c showed the same result. The PL decay curves were used to further investigate the non-radiative recombination of the FAPbI₃ films with and without FAX treatment. By fitting the PL measurements with single exponential equations, the FAPbI₃ film with FAX treatment exhibited a much longer carrier lifetime (24.2 ns) than that without FAX treatment (8.6 ns), implying the beneficial influence of FAX treatment on the thin-film quality [39,40]. Therefore, the VF method could fill iodine vacancy defects, demonstrating great potential for obtaining highly efficient perovskite solar cells.

The vertical grain boundaries in the perovskite thin layer would increase the carrier recombination due to the presence of charge traps [26,41,42]. Thus, a perovskite thin layer with large grains would be expected to produce improved device performances. As illustrated in the cross-sectional SEM images in Fig. 5a and b, the FAPbI₃ film without FAX treatment contained many vertical grain boundaries, while the FAX treatment removed most of vertical grain boundaries. The estimated thicknesses of both perovskite layers were ~400 nm. To further in-

vestigate the FAPbI₃ film quality, AFM was utilized. The surface roughness of the FAPbI₃ film with FAX treatment in Fig. 5d was lower than that without FAX treatment in Fig. 5c. This result further demonstrated that the VF method was beneficial to reducing the number of point defects and glazing the perovskite layer.

As discussed above, the VF method could effectively decrease the number of defects in the FAPbI₃ films and eliminate the δ -phase FAPbI₃. Thus, we further explored the photovoltaic performance of devices prepared from FAPbI₃ films with and without FAX treatment. As shown in Fig. 6a, the device based on the FAX post-treatment showed an improved J_{SC} and V_{OC} . The FAPbI₃ device without the FAX treatment exhibited the best PCE of 10.4% with a J_{SC} of 17.1 mA cm⁻², a V_{OC} of 0.91 V and a fill factor (FF) of 66.8% under standard AM1.5 solar illumination. This efficiency level was consistent with those reported by other groups using solvent-engineering processing [8,43]. After post-treatment with FAX, the device achieved a best PCE of 17.2%, with a J_{SC} of 22.2 mA cm⁻², a V_{OC} of 1.03 V and an FF of 75.1%. The inferior device performances for FAPbI₃ devices with and without FAX treatment were attributed to the high number of Pb⁰ defects, as confirmed by the XPS results (Fig. 1b), the

Figure 5 Cross-sectional SEM images for FAPbI₃ films (a) with and (b) without FAX treatment, where the scale bar length is 1 μm . AFM topographies of FAPbI₃ films (c) with and (d) without FAX treatment.

Figure 6 (a) J - V curves for FAPbI₃ films with and without FAX treatment, and the (b) corresponding IPCE curves and (c) UV-vis spectra. (d) PCEs for the devices based on FAPbI₃ films with and without FAX treatment (40 samples for each condition).

different grain sizes, as confirmed by SEM (Fig. 2a and b), and the elimination of the δ -phase perovskite through VF, as indicated by XRD (Fig. 2c).

Fig. 6b compares the IPCE curves for devices based on FAPbI₃ films with and without FAX treatment, which

match well with the corresponding J_{SC} values from the J - V curves. In addition, the external quantum efficiency (EQE) of the control FA perovskite within the wavelength range of 600–800 nm were much lower than that of the sample with the FAX treatment. Compared with the

FAPbI₃ film without FAX treatment, the absorption spectra of the FAPbI₃ film with the FAX treatment exhibited a much higher intensity, which was consistent with the good crystallinity of the final film (Fig. 6c). The PCEs of the 40 devices with error bars are also displayed in Fig. 6d. For the FAPbI₃ solar cells based on the VF method, a higher-than-average PCE was achieved with outstanding device reproducibility.

CONCLUSIONS

We developed an efficient FAX post-treatment method for preparing high-quality FAPbI₃ layers of perovskite solar cells. The FAX post-treatment could remove the yellow δ -phase and reduce defects through iodine VF. A new intermediate phase was formed after the post-treatment, and the average grain size of the perovskite film exceeded 2 μm due to the introduction of FAcI. The resulting FAPbI₃ solar cells showed a remarkably improved V_{OC} and J_{SC} when compared with the control device without post-treatment. Thus, this VF method is critical for further improving the efficiencies of FAPbI₃ solar cells.

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填补碘空位抑制 $\delta\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ 相以制备高效太阳能电池

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摘要 $\alpha\text{-FAPbI}_3$ 钙钛矿材料因具有广泛的吸光范围, 近期在光电器件领域中得到了广泛关注. 然而, $\text{FAI-PbI}_2\text{-DMSO}$ 中间相会快速转变生成非钙钛矿相($\delta\text{-FAPbI}_3$), 并且带来不可控的过量 PbI_2 , 从而阻碍着光电转化效率的进一步提升. 本文通过计算发现碘空位缺陷会导致钙钛矿材料的容忍因子变大, 而且会引入弗仑克尔缺陷. 因此, 我们介绍了一种后处理的方法填补 FAPbI_3 中的碘缺陷, 来抑制 $\delta\text{-FAPbI}_3$ 的形成. 此外, 一种新的中间相 $\text{FAI-PbI}_2\text{-DMSO-FAI}$ 可以制备出大于 $2\ \mu\text{m}$ 的钙钛矿晶粒. 由于这个方法提高了 $\alpha\text{-FAPbI}_3$ 钙钛矿的结晶质量, 基于该材料的光伏器件效率也得到了提升. 本工作作为制备 $\alpha\text{-FAPbI}_3$ 钙钛矿材料和高效光伏器件提供了一个思路.