

Additive-Modulated Evolution of HC(NH₂)₂Pbl₃ Black Polymorph for Mesoscopic Perovskite Solar Cells

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Supporting Information

ABSTRACT: Formamidinium lead triiodide (HC(NH₂)₂PbI₃ or FAPbI₃) is gaining increasing interest in the field of mesoscopic perovskite solar cells (PSCs) for its broader light absorption compared with the more widely studied $CH_3NH_3PbI_3$ (MAPbI₃). Because FAPbI₃ has two polymorphs ("black" α -FAPbI₃ and "yellow" δ -FAPbI₃) at ambient temperature, where α -FAPbI₃ is the desirable photoactive perovskite phase, it becomes particularly important to suppress the formation of the nonperovskite δ -FAPbI₃ for achieving high efficiency in FAPbI3-based mesoscopic PSCs. In this study, we demonstrate that the judicious use of low-volatility additives in the precursor solution assists in the evolution of α -FAPbI₃ through the formation of non- δ -FAPbI₃ intermediate phases, which then convert to α -FAPbI₃ during thermal annealing. The underlying mechanism involved in the additive-modulated evolution of α -FAPbI₃ upon mesoporous TiO₂ substrates is elucidated, which suggests guidelines for developing protocols for the fabrication efficient FAPbI₃-based mesoscopic PSCs.



1. INTRODUCTION

Organolead halide perovskites with the general formula APbX₃ $(A = CH_3NH_3 \text{ or } HC(NH_2)_2; X = I, Br, \text{ or } Cl)$ have been recently introduced as light absorber materials in mesoscopic perovskite solar cells (PSCs).¹⁻⁵ Although methylammonium lead triiodide (CH₃NH₃PbI₃ or MAPbI₃) with a bandgap of ~1.55 eV has been the most widely studied, $^{1-4}$ formamidinium lead triiodide $(HC(NH_2)_2PbI_3 \text{ or } FAPbI_3)$ perovskite is gaining increasing interest for its boarder light absorption.⁶⁻¹⁴ Because these polycrystalline perovskites in thin-film form are typically grown from a precursor solution for PSCs application, the understanding of their crystallization behavior is considered critical, and as such, extensive research has been pursued in the context of the MAPbI₃ perovskite.^{15,16} However, due to the polymorphism in $FAPbI_3$ at ambient temperature, ^{7,9,11,17} the understanding of the crystallization behavior of the monomorphic MAPbI₃ perovskite (space group I4/mcm)¹⁸ cannot be simply generalized to FAPbI₃. FAPbI₃ has two possible polymorphs at ambient temperature:^{7,9,11,17} (i) Trigonal perovskite phase (α -FAPbI₃, space group P3m1), which appears "black" with a direct bandgap of \sim 1.45 eV. (Note that singlecrystal X-ray diffraction has confirmed trigonal crystal structure of α -FAPbI₃,¹⁷ but a recent neutron diffraction study of powder samples suggests that α -FAPbI₃ phase may possibly exhibit a simpler cubic perovskite structure.¹⁹) (ii) Nonperovskite phase (δ -FAPbI₃, space group P6₃mc), which is "yellow" with an

indirect bandgap of 2.48 eV. Because the former phase is the desirable photoactive phase with promising optoelectronic properties, suppression of the formation of the latter δ -FAPbI₃ phase is an additional critical requirement for the fabrication of FAPbI₃-based mesoscopic perovskite solar cells (PSCs).^{17,20} Experimental studies have shown that although the "black" α -FAPbI₃ perovskite phase forms readily on planar substrates via the "one-step" method involving thermal-annealing of a spincoated stoichiometric FAPbI₃ precursor solution at relatively high temperatures (>140 °C),^{7,10,21,22} it rarely forms in the same way upon mesoporous TiO₂ scaffolds, regardless of the heat-treatment temperature (see Figure S1 in Supporting Information (SI)). This is presumably associated with the altered crystallization behavior when in contact with highsurface-area mesoporous TiO2 scaffold.23,24 However, in our early reports, it was revealed that phase-pure α -FAPbI₃ can form upon mesoporous TiO₂ scaffolds from a nonstoichiometric FAI-PbI₂ (FAI:PbI₂ = 1.5:1 molar ratio)⁷ or FAI-PbCl₂ $(FAI:PbCl_2 = 3:1 \text{ molar ratio})$ precursor solutions using the "one-step" method.²⁵ This implies that the use of additives (excess compositions beyond the stoichiometric FAPbI₃ precursors) in the precursor solution enables the formation

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Figure 1. (A) Schematic illustration of the FAPbI₃ phase formation upon mesoporous TiO_2 scaffolds by thermal-annealing of stoichiometric precursor solution with or without additives. XRD patterns showing the phase evolution starting from spin-coated precursor films: (B) without additive; (C) with NH₄Cl additive; (D) with MACl additive; and (E) with FACl additive. The molar amount of the additive is equal to that of FAI or PbI₂. (F) Cl content (Cl/Pb atomic ratio) in the films at different annealing durations (140 °C) measured using EDS.

of phase-pure "black" α -FAPbI₃ perovskite phase upon mesoporous TiO₂ scaffolds for mesoscopic PSCs.

Herein, we provide insights into the mechanisms involved in the crystallization of the photoactive "black" α -FAPbI₃ polymorph from solution via comparative use of various additives (NH₄Cl, MACl, FACl) with different volatilities in the "one-step" deposition upon mesoporous TiO₂ scaffolds. It is demonstrated that the lower-volatility additives that can form intermediate phases from FAPbI₃ precursor components suppress the formation of "yellow" δ -FAPbI₃ upon precursorsolvent removal at the spin-coating stage. This ultimately enables the gradual evolution of phase-pure α -FAPbI₃ during the subsequent annealing stage. The overall photovoltaic performance of the as-fabricated FAPbI₃-based mesoscopic PSCs shows strong dependence on the purity of the α -FAPbI₃ perovskite phase.

2. EXPERIMENTAL SECTION

2.1. Materials and Thin-Film Preparation. For the synthesis of $CH(NH_2)_2I$ (or FAI), 5 g of formamidine acetate (98%, Sinopharm, China) and 10 mL of HI solution (45 wt % in water, Sinopharm, China) were mixed and reacted at 0 °C for 2 h while stirring under N₂ atmosphere. However, for the synthesis of CH_3NH_3CI (MACl), 10 mL of methylamine (27 wt % in ethanol, Sinopharm, China) and 5 mL of HCl (36 wt % in water, Sinopharm, China) were mixed and reacted at 0 °C for 2 h. Finally, $CH(NH_2)_2CI$ (or FACl) was synthesized by mixing and reacting 12 g of formamidine acetate and 10 mL of HCl

(36 wt % in water) for 2 h. In each of the above cases, after rotary evaporation, the resulting powders were collected, recrystallized, and washed with a mixture of ethanol and diethyl ether by air-pump filtration. The solids were finally dried at 60 $^\circ$ C under vacuum.

A TiO₂ sol was prepared by mixing 10 mL of titanium(IV) isopropoxide (99%, Aldrich-Sigma, U.S.A.) with 50 mL of 2-methoxyethanol (98%) and 5 mL of ethanolamine (99%, Sinopharm, China) in a three-necked flask, each connected with a condenser, thermometer, and argon gas inlet/outlet. The mixed solution was heated to 80 °C for 2 h under magnetic stirring, followed by heating to 120 °C for 1 h. This two-step heating was then repeated two times to result in a viscous solution.

Powder of δ -FAPbI₃ and α -FAPbI₃ were synthesized as follows. PbI₂ (99%, Aldrich-Sigma, U.S.A.) and FAI in molar ratio 1:1 were dissolved in dimethylformamide (DMF, Aldrich-Sigma, U.S.A.) solution (40 wt %), and then drop-cast on glass slides and heated at 60 °C in air to produce "yellow" δ -FAPbI₃ crystals. These crystals are scratched from the glass slides and collected. For the synthesis of α -FAPbI₃ powders, the same procedure was followed except for the use of 140 °C annealing temperature and N₂ atmosphere.

2.2. Material and Film Characterization. X-ray diffraction (XRD) patterns were obtained on a diffractometer (D8 Advance, Bruker, Germany) using Cu K α radiation, with 0.02° step. UV–vis absorption spectra of the perovskite films were recorded using a spectrometer (U-4100, Hitachi, Japan). A field-emission SEM (S-4800, Hitachi, Japan) was used to observe the top surfaces and cross sections. All films for XRD, SEM, and UV–vis were deposited on FTO/glass substrates with a 30 nm layer of dense TiO₂ and a 300 nm layer of mesoporous TiO₂. The precursor solutions with or without

additives were spin-coated on these substrates at 4000 rpm for 40 s. Differential scanning calorimetry (DSC) measurements (PerkinElmer, Waltham, MA) were performed at a heating rate of 10 °C/min under N_2 atmosphere.

2.3. Solar Cells Fabrication and Testing. Fluorine-doped tin oxide (FTO) coated glass was patterned by etching with Zn powder and 1 M HCl diluted in distilled water. The etched substrate was then cleaned with ethanol, saturated KOH solution in isopropanol, and water, and then dried with clean dry air. Subsequently, 30 nm thick dense TiO_2 layer was deposited on the FTO glass by spin-coating (4000 rpm, 45 s) the TiO_2 sol from above, followed by a heat-treatment of 500 °C for 30 min in air. Subsequently, 300 nm thick TiO_2 mesoporous layer was deposited on the TiO_2 dense layer by spin-coating (4000 rpm, 30 s) a diluted commercial TiO_2 paste, followed by a sintering heat-treatment of 550 °C for 30 min in air.

The FAPbI₃ films were then deposited using the conventional "onestep" method. Here, a 35 wt % PbI₂:FAI (molar ratio of 1:1) solution in DMF was spin-coated (4000 rpm, 45 s), followed by a heattreatment at 140 °C. In case of additives, NH₄Cl or MACl or FACl with equal molar amount were added to the precursor solution. A solution of spiro-MeOTAD hole-transporting material (HTM) was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 mL of chlorobenzene (99.8%, Aldrich-Sigma, U.S.A.), to which 28.8 μ L of 4*tert*-butylpyridine (96%, Aldrich-Sigma, U.S.A.) and 17.5 μ L of lithium bis(trifluoro-methanesulfonyl)imide (LITSFI, Aldrich-Sigma, U.S.A.) solution (520 mg LITSFI (98%) in 1 mL acetonitrile (99.8%, Aldrich-Sigma, U.S.A.) were added. The HTM layer was deposited by spincoating (3000 rpm, 30 s). Finally, a Ag contact was thermally evaporated to complete the PSCs fabrication.

Current density (*J*)–voltage (*V*) characteristics of the as-fabricated PSCs were measured using a 2400 Sourcemeter (Keithley, U.S.A.) under simulated one-sun AM 1.5G 100 mW cm⁻² intensity (Oriel Sol3A Class AAA, Newport, U.S.A.), under both reverse (from $V_{\rm OC}$ to $J_{\rm SC}$) and forward (from $J_{\rm SC}$ to $V_{\rm OC}$) scans. The step voltage was 50 mV with a 10 ms delay time per step. The maximum-power output stability of the PSCs was measured by monitoring the *J* output at the maximum-power *V* bias (deduced from the reverse-scan *J*–*V* curves). The *J* output is converted to PCE output using the following relation: PCE = {*J* (mA cm⁻²) × *V* (V))/(100 (mW cm⁻²)}. A shutter was used to switch on and off the one-sun illumination on the PSC. Typical, active area of the PSCs is 0.09 cm² defined using a nonreflective metal mask.

3. RESULTS AND DISCUSSION

Figure 1A is a schematic diagram showing the FAPbI₃ phase formation upon mesoporous TiO₂ scaffolds by thermal annealing (140 °C) of spin-coated stoichiometric precursor films with and without the various additives (NH₄Cl, MACl, FACl). As shown in the Figure 1 and the UV–vis absorption spectra of the films (Figure S2 in SI), without additive and with NH₄Cl additive, annealing the precursor solution results in the formation of significant amount of "yellow" δ -FAPbI₃ phase (Reaction 1). When MACl and FACl additives are used, highpurity "black" α -FAPbI₃ phase evolves (Reaction 2)

$$PbI_2(l) + FAI(l) \rightarrow \delta - FAPbI_3(s)$$
 (1)

$$PbI_2(l) + FAI(l) \rightarrow \alpha - FAPbI_3(s)$$
 (2)

$$\delta$$
-FAPbI₃(s) $\rightarrow \alpha$ -FAPbI₃(s) (3)

In order to understand the above phase evolution behavior, X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) studies were conducted. Figure 1B–E show XRD patterns from freshly spin-coated films, and thermally annealed (140 $^{\circ}$ C) films (5 and 30 min) for each additive case, and Figure 1F shows the change of the Cl content in the films with increasing annealing duration. Four sets of samples are

measured: (Figure 1B) stoichiometric FAPbI₃ precursor solution without additive; (Figure 1C) with NH₄Cl additive; (Figure 1D) MACl additive; and (Figure 1E) with FACl additive. Note that the molar ratio of the additive to FAI or PbI₂ precursor is 1:1. See complete indexing of the XRD peaks of the as-formed α -FAPbI₃ in Figure S3 in SI.

In Figure 1B (no additive), right after spin-coating, the XRD pattern shows that significant amount of the δ -FAPbI₃ phase has formed. The full XRD pattern of the film is fitted using the Pawley method as shown in Figure S4 in SI, confirming the δ -FAPbI₃ crystalline phase with (010) texture. After 5 min of annealing, no other compounds except δ -FAPbI₃ is observed, and thus, the completion of the precursor-to-solid transformation is confirmed. Although the subsequent annealing influences the characteristics of the as-formed δ -FAPbI₃ phase, no trace of α -FAPbI₃ phase is observed, indicating the dominance of Reaction 1.

In Figure 1C, the effect of NH₄Cl additive on the overall phase evolution is found to be minor, as evinced by the trend in the XRD patterns, which is similar to that in Figure 1B, but with the exception of the formation of a small amount of α -FAPbI₃ in the film after 5 min annealing. EDS results in Figure 1F show that only half the amount of Cl (Cl/Pb = 0.5 atomic ratio) remains in the freshly spin-coated film, which indicates that most of the NH₄Cl has sublimed or evaporated during spin-coating. The highly volatile nature of NH4Cl in the solution state has also been reported by Chen et al.²⁶ The XRD pattern (Figure 1C) of the freshly spin-coated film does not show additional peaks except δ -FAPbI₃, which implies that the residual NH₄Cl additive possibly exists as $FAI \cdot PbI_2 \cdot NH_4Cl$ intermediate phases with low crystallinity. The Cl content in the film drops sharply to zero within 5 min of annealing (Figure 1F), and produces a small amount of α -FAPbI₃ via thermal decomposition of this intermediate phase. It is believed that the α -FAPbI₃ formed during the annealing stage was converted from the initially crystallized δ -FAPbI₃ after spin-coating because there is negligible change in the intensity of the δ -FAPbI₃ characteristic peak in the XRD patterns after prolonged (30 min) annealing (Figure 1C). This is further demonstrated later in Figure 2.



Figure 2. XRD patterns from "yellow" δ -FAPbI₃ powders (A) before and (B) after thermal annealing (140 °C for 30 min); XRD patterns from "yellow" δ -FAPbI₃ thin films upon mesoporous TiO₂ scaffolds (C) before and (D) after thermal annealing (140 °C for 30 min). The molar amount of the additive is equal to that of FAI or PbI₂.

In the case of MACl additive, right after the spin-coating step a "black" film is visible to the naked eye, instead of a "yellow" film as in the no-additive and NH4Cl additive cases. The corresponding XRD patterns (Figure 1D) are strikingly different as well. In Figure 1D, the XRD pattern for the freshly spin-coated sample shows a strong, well-resolved peak. At first glance, there appears to be no obvious difference in that peak as compared with the annealed films (5 and 30 min). However, a closer look at the peak positions (Figure S5 in SI) shows that there is a measurable shift to lower 2θ . The peaks at 14.02° and 28.18° in the XRD pattern for the freshly spin-coated sample are shifted to 13.90° and 28.06°, respectively, in the final film (30 min). To investigate this interesting change in the XRD patterns before and after annealing, UV-vis absorption spectra from both the films were collected. The absorption edge shift from 780 nm for the freshly spin-coated film to 830 nm for the 30 min-annealed film observed in Figure S6 in SI matches the absorption features of MAPbI₃^{27,28} and α -FAPbI₃ perovskites,^{7,25} respectively. Thus, it is reasonable to deduce that the perovskite that forms initially during the spin-coating of the film is MAPbI₃, gradually converts to α -FAPbI₃ in the final film, as proposed in Reaction 4. First, an anion-exchange reaction between FAI precursor and MACl additive is likely to occur, which results in the formation of the MAPbI₃ (solid) and FACl right after spin-coating. To demonstrate the feasibility of such anion-change reaction, a solution of PbI_2 :FACl:MAI = 1:1:1 (molar ratio) in DMF was spin-coated, where the film evolution was observed to be identical. With the formation of the intermediate mixture of MAPbI3 and FACl, the subsequent thermal annealing produces α -FAPbI₃ and MACl via cationexchange reaction between MAPbI₃ and FACl. Because α -FAPbI₃ is thermally more stable than MAPbI₃, the MACl additive tends to sublime during high-temperature annealing step. In that case, Reaction 4 moves forward, resulting in the formation of a phase-pure α -FAPbI₃ film. The chlorine amount is also monitored using EDS. The results in Figure 1F show a large initial amount of Cl (Cl/Pb = 1 atomic ratio) in the spincoated films, but after 5 min annealing the Cl amount is reduced (Cl/Pb = 0.1 atomic ratio), and finally no EDSdetectable Cl is found in the final film (30 min annealing). This further supports the Cl-modulated chemical process given in Reaction 4

$$FAI(l) + PbI_{2}(l) + MACl(l) \rightarrow MAPbI_{3}(s) + FACl(s)$$
$$\rightarrow \alpha - FAPbI_{3}(s) + MACl(g) \quad (4)$$

$$FAI(l) + PbI_{2}(l) + FACl(l) \rightarrow FAI \cdot PbI_{2} \cdot FACl(s)$$

$$\rightarrow \alpha \cdot FAPbI_{3}(s) + FACl(g) \qquad (5)$$

In the case of FACl additive, XRD pattern (Figure 1E) from the freshly spin-coated film does not show the presence of δ -FAPbI₃ either, but rather an unknown intermediate phase appears to be present. The intermediate phase is likely to be FAI·PbI₂·FACl adduct formed by interaction of Lewis base halide (I⁻ or Cl⁻) and the Lewis acid PbI₂.²⁹ In order to confirm the FAI·PbI₂·FACl adduct formation, Figure S7 in SI shows Fourier-transform infrared (FTIR) spectra of solid samples prepared by spin-coating using DMF solutions of FAI, FAI:PbI₂ (= 1:1), FAI:PbI₂:FACl (= 1:1:1), FACl:PbI₂ (= 1:1), and FACl, in which the stretching vibration of C=N (ν (C= N)) appears at 1697.6 cm⁻¹, 1709.6 cm⁻¹, 1711.1 cm⁻¹, 1713.0 cm⁻¹, and 1720.3 cm⁻¹, respectively. The ν (C=N) (1697.6 cm⁻¹) in FAI shows lower wavenumber than that (1720.3 cm⁻¹) in FACl, which is due to the stronger electron affinity of chlorine compared to iodine. With presence of Lewis acid PbI₂, the ν (C=N) are both lowered to 1709.6 and 1713.0 cm⁻¹ in the cases of FAI and FACl, which is related to the coordination of Lewis base halide (I⁻ or Cl⁻) with PbI₂. In the case of FAI:PbI₂:FACl (= 1:1:1), the ν (C=N) shows a medium value of 1711.1 cm⁻¹, which suggests the formation of the FAI·PbI₂· FACl adduct with mixed coordination behavior of the halide $(I^- \text{ and } Cl^-)$ with PbI₂. With subsequent annealing, there is a gradual reduction of the intermediate mixture, accompanied by the formation of crystalline "black" α -FAPbI₃ perovskite phase. The EDS results (Figure 1F) show that the rate at which the Cl content in the films decreases is relatively small compared to that in the MACl case. Still, considerable Cl amount (Cl/Pb = 0.6 atomic ratio) remains in the 5 min annealed film compared with Cl/Pb = 0.1 in the MACl case. After 30 min of annealing, the Cl has completely sublimed/evaporated. The increase in the amount of the α -FAPbI₃ phase and the corresponding decrease of the Cl content suggests that sublimation of Cl is one of the major driving forces for Reaction 5, which is similar to the MACl case (Reaction 4). The XRD and EDS results are also consistent with the evolution of the optical-absorption feature of phase-pure α -FAPbI₃ with annealing duration, as shown in Figure S8 in SI.

In order to support the phase-evolution argument discussed above, studies were conducted on free-standing powders. Figure 2A–B show the conversion of the "yellow" δ -FAPbI₃ phase to the "black" α -FAPbI₃ phase after annealing at 140 °C for 30 min. Also, DSC measurements shows that the "yellow" δ -FAPbI₃ powder starts to absorb heat at ~140 °C, whereas the "black" α -FAPbI₃ powder does not (Figure S9 in SI), confirming the occurrence of a phase transformation. Note that although the heat-treatments experiments are conducted isothermally, the DSC heating rate is 10 °C/min, which could be responsible for the heat-absorption peak occurring at a higher temperature of ~155 °C. This is consistent with the DSC results reported by Seok et al.⁸ In contrast, this beneficial phase transformation is suppressed in FAPbI3 thin films upon mesoporous TiO_2 scaffolds, as shown in Figure 2C–D. Because the area of the interface between FAPbI₃ and the substrate has increased significantly with introduction of the mesoporous TiO₂ scaffold, it is possible that the attendant increase in the relative interfacial energy may suppress the δ -to- α phase transformation in FAPbI₃. Although the exact reason behind this distinct phase transition behavior with or without the mesoporous TiO2 scaffold is the subject of follow-up studies, the results presented here highlight the importance of suppressing δ -FAPbI₃ formation during all reaction stages in the deposition of FAPbI₃ upon mesoporous TiO₂ scaffolds.

On the basis of the experimental observations above, the underlying mechanisms of the evolution of the "black" α -FAPbI₃ phase are shown schematically in Figure 3. We emphasize here that the "one-step" deposition method entails spin-coating of precursor solution followed by thermal annealing, where the DMF solvent, which is volatile despite its high boiling point, is typically used.¹ Therefore, the high-speed spin-coating of precursor solutions on the substrate is coupled with rapid evaporation of precursor solvent, which induces supersaturation, resulting in the precipitation of solids.³⁰ Note that the FTIR spectrum in Figure S10 in SI does not show obvious presence of DMF in the freshly spin-coated films, which suggests that most of the solvent-state DMF



Figure 3. Schematic illustration of the mechanisms for the evolution of $FAPbI_3$ phases upon mesoporous TiO_2 scaffolds. The blue hemispheres in (B) indicate that these sites are half-occupied by FA groups.

molecules have evaporated during spin-coating. Because the supersaturation driven by centrifugal force occurs upon a mesoporous TiO₂ scaffold at room temperature, substantial amount of the "yellow" δ -FAPbI₃ phase is formed via Reaction 2 immediately after spin-coating in the absence of any additives (Figure 1B). In the case of NH₄Cl additive, due to its high volatility, only a very small amount of the additive remains in the film and the formation of the "yellow" δ -FAPbI₃ phase at this stage is inevitable. Furthermore, the conversion of the "yellow" δ -FAPbI₃ phase to the "black" α -FAPbI₃ phase upon mesoporous TiO₂ scaffolds via Reaction 3 does not occur in the

subsequent annealing stage, and thus, the as-formed δ -FAPbI₃ remains in the resultant solid films. The formation of minor amount of α -FAPbI₃ is associated with a small amount of low-crystallinity intermediate phases. However, in the presence of MACl or FACl, the formation of the respective intermediate phases is favored over δ -FAPbI₃ during the initial spin-coating stage. In this situation, during the subsequent high-temperature annealing, the "black" α -FAPbI₃, which is the thermodynamically stable perovskite phase, gradually evolves along with the sublimation of Cl species.

Figure 4 shows surface morphology of as-prepared FAPbI₃ $(\delta$ -FAPbI₂ or α -FAPbI₂) layer on mesoporous TiO₂ substrates, without and with additives (NH₄Cl, MACl, FACl). Because the surface morphology of the FAPbI₃ solids is primarily affected by the reaction kinetics of its formation, the additives can exert great influence on the final morphology of these layers. And the nucleation and the growth stages in the formation of organicinorganic hybrid materials can occur simultaneously, which is responsible for the poor coverage in the one-step processed thin films.^{31,32} In this context, the poor morphology of the asformed FAPbI₃ in Figure 4A is typical. As discussed above, although NH₄Cl is used as an additive in the precursor solution, it evaporates or sublimes rapidly during spin-coating. Consequently, the morphology of the resulting FAPbI₃ thin film is not improved (Figure 4B). However, in the case of MACl (Figure 4C) or FACl (Figure 4D), the overall coverage of FAPbI₃ on the mesoporous TiO₂ is improved significantly. This is attributed to the slowing of the reaction kinetics due to the presence of the additives in the film. This is further supported by results from the study of the effect of the additive amount on the final morphology of the α -FAPbI₃ thin films. Similar to what is reported by Zhao et al.³³ in the case of MAPbI₃, the overall precursor-to-perovskite conversion rate is reduced with an increase in the additive amount, which produces films with different morphologies (Figure S11 in SI). With optimization, the use of equal-molar FACI:FAI or FACl:PbI₂ results in the near-complete coverage in the final



Figure 4. SEM images showing surface morphologies of the as-prepared $FAPbI_3$ layer upon mesoporous TiO_2 scaffolds (same magnification): (A) without additives; (C) with NH_4Cl additive; (D) with MACl additive; and (E) with FACl additive. The molar amount of the additive is equal to that of FAI or PbI₂.



Figure 5. (A) Cross-sectional SEM image of a typical FAPbI₃-based mesoscopic PSC showing its architecture. (B) J-V curves of FAPbI₃-based PSCs made from precursor solutions with and without additives.

perovskite film. These observed morphology changes due to the use of different additives, or the use of different amount of the same additive, are consistent with the proposed Clmodulated reaction routes in each situation.

Mesoscopic PSCs were fabricated to correlate the photovoltaic performance with the perovskite phase purity and the film coverage. The cross section of a typical mesoscopic PSC is shown in Figure 5A, where the mesoporous-TiO₂/FAPbI₃ layer, along with a thin capping FAPbI₃ layer, are sandwiched between a compact TiO₂/FTO electron-extraction layer and a spiro-OMeTAD/Ag hole-extraction layer. The J-V curves for the PSCs made without and with additives are shown in Figure 5B, and the efficiency statistics are shown in Figure S12 in SI. The importance of phase purity on the overall solar cell performance is readily reflected in the J-V curves. Because the major component in the no-additive and NH₄Cl additive cases is the undesirable nonperovskite "yellow" δ -FAPbI₃ phase, the overall power conversion efficiencies (PCEs) of those PSCs is 0.2-0.7%. In the case of MACl and FACl additives, the PCEs are significantly enhanced, further attesting the formation of phase-pure α -FAPbI₃ perovskite upon mesoporous TiO₂ scaffolds. Because the coverage of α -FAPbI₃ is another factor that influences the performance of FAPbI₃-based mesoscopic PSCs,²⁵ the best PSC with PCE of 13.7% is made from the use of equimolar FACl additive that results in near-full coverage. In contrast, in the case of MACl additive, the presence of more pinholes in the α -FAPbI₃ film are responsible for the relatively lower PCE of 7.0% of those PSCs. Because typical hysteresis is present in these PSCs (Figure S13 in SI), the stabilizing power output at maximum power point is monitored, showing a stable 12.7% at ~200 s duration (Figure S14 in SI). The effect of FACl additive amount on the J-V characteristics of the resultant mesoscopic PSCs are also studied, and the results are presented in Figure S15 in SI, which confirms that the overall performance is enhanced by optimal coverage of the thin perovskite capping layer (Figure S11 in SI). These results highlight the importance of the evolution of full-coverage photoactive "black" α -FAPbI₃ in achieving high efficiency in FAPbI₃-based mesoscopic PSCs.

CONCLUSIONS

We have demonstrated that suppressing the formation of the nonperovskite "yellow" δ -FAPbI₃ phase at all stages of the formation of FAPbI₃ on mesoporous TiO₂ scaffolds is essential for achieving high-purity "black" α -FAPbI₃ perovskite phase. This is because it is very difficult to convert any as-formed δ -FAPbI₃ phase to α -FAPbI₃ perovskite phase during subsequent thermal-annealing due to a barrier to the δ -to- α phase

transformation associated with the presence of the mesoporous TiO₂ scaffold. Low-volatility additives such as FACl and MACl are good candidates for assisting in the crystallization of phase-pure α -FAPbI₃ via the formation of intermediate mixtures, which prohibits the crystallization of the δ -FAPbI₃ phase. It is worth noting that additives, which are commonly regarded as agents for improving the film uniformity in the case of "one-step" solution-deposition of MAPbI₃, are of more importance in the case of FAPbI₃, especially in the context of the phase evolution of the desirable perovskite phase upon mesoporous TiO₂ scaffolds. This study provides an understanding of the crystallization behavior of FAPbI₃ from precursors with and without additives and suggests guidelines for the development of effective processing protocols of FAPbI₃ and other polymorphic materials (e.g., CsSnI₃, ³⁴ CsPbI₃, ³⁵) for meso-scopic photovoltaics.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.5b03169.

Additional results (XRD, SEM, UV-vis, FTIR, DSC, PVs performance data) are also included. (PDF)

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Notes

The authors declare no competing financial interest.

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