Exceptional Morphology-Preserving Evolution of Formamidinium Lead Triiodide Perovskite Thin Films via Organic-Cation Displacement

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ABSTRACT: Here we demonstrate a radically different chemical route for the creation of HC(NH$_2$)$_2$PbI$_3$ (FAPbI$_3$) perovskite thin films. This approach entails a simple exposure of as-synthesized CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite thin films to HC(NH)$_2$NH$_2$ (formamidine or FA) gas at 150 °C, which leads to rapid displacement of the MA$^+$ cations by FA$^+$ cations in the perovskite structure. The resultant FAPbI$_3$ perovskite thin films preserve the microstructural morphology of the original MAPbI$_3$ thin films exceptionally well. Importantly, the myriad processing innovations that have led to the creation of high-quality MAPbI$_3$ perovskite thin films are directly adaptable to FAPbI$_3$ through this simple, rapid chemical-conversion route. Accordingly, we show that efficiencies of perovskite solar cells fabricated with FAPbI$_3$ thin films created using this route can reach $\sim$18%.

Thin films of organic–inorganic halide perovskites have been studied extensively as light-absorbing materials, which are at the heart of perovskite solar cells (PSCs). The unique combination of low-cost processing and high power-conversion efficiencies (PCEs) rivaling those of conventional Si-based solar cells, holds out great promise for conventional Si-based solar cells, whereas the high performance of PSCs has been rather limited due to the rapid displacement of the MA$^+$ cations by FA$^+$ cations in the perovskite structure. The resultant FAPbI$_3$ perovskite thin films preserve the microstructural morphology of the original MAPbI$_3$ thin films exceptionally well. Importantly, the myriad processing innovations that have led to the creation of high-quality MAPbI$_3$ perovskite thin films are directly adaptable to FAPbI$_3$ through this simple, rapid chemical-conversion route. Accordingly, we show that efficiencies of perovskite solar cells fabricated with FAPbI$_3$ thin films created using this route can reach $\sim$18%.

During FAPbI$_3$ perovskite crystallization, which is undesirable. Therefore, manipulating the formation of FAPbI$_3$ perovskite thin film requires stricter control over the synthetic procedures, which is a major hurdle in the path of realizing its full potential in PSCs. Typically, hybrid perovskite thin films evolve from the reaction between their organic and inorganic halide precursor phases through "one-step" or "two-step" synthetic processes. Myriad innovations in this regard have been reported in the context of the formation of MAPbI$_3$ perovskite thin films with desirable morphologies and microstructural characteristics. Thus, there is an unprecedented opportunity to take advantage of these significant advances, where the MAPbI$_3$ perovskite phase in the thin film is converted directly to FAPbI$_3$ perovskite phase while preserving the desirable morphologies and microstructures of the original thin film. Ion-exchange reaction of MAPbI$_3$ + FA$^+$ $\leftrightarrow$ FAPbI$_3$ + MA$^+$ may be a possible strategy for the phase conversion. However, there are two intrinsic issues with this strategy: (i) ion-exchange reaction is highly reversible, which makes control of the forward reaction kinetically challenging, and (ii) in order to conduct this reaction at ambient pressure, the protonated formamidine (FA$^+$) generally requires to be dissolved in an alcohol solvent that also dissolves the perovskite phases, affecting the film morphologies. As a result, the conversion of a smooth MAPbI$_3$ perovskite thin film to FAPbI$_3$ using ion exchange leads to a dramatic change in the film morphology in the final film (see Figure S1 in Supporting Information (SI)). This is consistent with reports on ion-exchange-based perovskite interconversion.

These above issues have motivated us to discover a low-reversibility reaction route, without the use of detrimental solvents, for realizing morphology-preserving MAPbI$_3$ $\rightarrow$ FAPbI$_3$ perovskite conversion. Here, we show that the use of the following single-cation displacement reaction, which can be considered as a redox reaction, is a feasible strategy:

$$\text{MAPbI}_3(s) + \text{FA}(g) \rightarrow \text{FAPbI}_3(s) + \text{MA}(g)$$

Reaction 1 is also depicted in the top section of Figure 1, which involves the reduction of MA$^+$ into methylamine (CH$_3$NH$_2$ or MA) and the oxidation of formamidine (HC(NH)$_2$NH$_2$) as a byproduct during FAPbI$_3$ perovskite crystallization, which is undesirable.
(HC(═NH)NH$_2$ or FA) into FA'. (For the sake of brevity MA' (or FA') is considered as a single cation and MA (or FA) its elementary form.) As shown schematically in Figure 1 (bottom), simply exposing an as-deposited MAPbI$_3$, perovskite thin film to gaseous FA (150 °C, 4 min) completes the rapid MAPbI$_3$ → FAPbI$_3$ conversion while retaining the thin-film morphology. The detailed experimental procedures are included in SI. In the experimental setup (Figure S2), the gaseous FA (boiling point ~90 °C)$^{14}$ is produced by reacting formamidine acetate salt with sodium hydroxide at 150 °C and purified by passing through a CaO desiccant. The as-produced hot FA gas fills the experimental chamber and then reacts with the predeposited MAPbI$_3$, thin film. Partial or full conversion of MAPbI$_3$ to FAPbI$_3$ is achieved by performing the reaction for specific durations (up to 4 min). As expected, the backconversion of the as-converted FAPbI$_3$, thin films to MAPbI$_3$, is very sluggish in MA atmosphere using the similar experimental setup/condition (Figure S3), confirming the limited reversibility of reaction 1.

To validate the unique “morphology-preservation” feature of the MAPbI$_3$ → FAPbI$_3$, perovskite conversion process via organic-cation displacement, four different starting MAPbI$_3$, thin films were prepared using four different methods reported in the literature, viz. one-step spin-coating,$^{13}$ sequential deposition,$^{16}$ antisolvent treatment,$^{17}$ and MA-gas treatment.$^{18}$ These MAPbI$_3$, films exhibit rather distinct morphologies (Figure 2A,C,E,G) at micro/nanoscales. As reported in the literature, the MAPbI$_3$, perovskite films prepared using one-step spin-coating contains 1D branch-like structures$^{15}$, the two-step dipping method results in 3D cuboids,$^{16}$ and the antisolvent/MA-gas treatments$^{17,18}$ lead to smooth polycrystalline thin films. These morphological characteristics can meet different functional requirements in the devices, which has been demonstrated extensively in the literature. Remarkably, after the organic-cation displacement reaction (reaction 1), the morphologies of the resultant films (Figure 2B,D,F,H) simply mimic those of the original MAPbI$_3$, films in all the cases.

A closer look at the XRD patterns of these films before and after the conversion reveals that the XRD peaks at 2θ ~ 14.1° for MAPbI$_3$ have shifted to a lower angle of ~13.9° for FAPbI$_3$ (Figure 2C,F,I,L). Consistent with this observation, the characteristic XRD peaks also shift from ~28.4° to 28.1° (Figure S4A–D) in all cases. This confirms the conversion of MAPbI$_3$ to FAPbI$_3$ perovskite.$^7$ Note that the small variations in the peak positions between the four cases may be related to the variations in film crystallinity.$^{19}$ Also note that the XRD peak corresponding to the FTO substrate stays the same before and after the conversion (Figure S4), as expected. The success of this FA-gas-induced MAPbI$_3$ → FAPbI$_3$, phase conversion, while preserving the thin-film morphology, can be attributed to the following. First, MAPbI$_3$, exhibits cubic crystalline structure (space group $Pm\overline{3}m$)$^{20}$ at elevated temperature (150 °C) with a lattice parameter $a = 6.31$ nm, while FAPbI$_3$, also has a cubic, or pseudocubic, crystal structure (space group $Pm\overline{3}m$ or $Pm\overline{3}1$) with $a = 6.36$ nm. This inherent structural similarity favors MAPbI$_3$ → FAPbI$_3$, conversion. Second, there is a very small difference (~0.2%) between the densities of MAPbI$_3$ (4.092 g.cm$^{-3}$) and FAPbI$_3$ (4.101 g.cm$^{-3}$)$^{20}$ precluding any issues associated with volume change during the MAPbI$_3$ → FAPbI$_3$, conversion.

In order to understand the mechanism underlying the conversion process, X-ray diffraction (XRD) patterns are presented in Figure 3A,B showing the progression of reaction 1 at $t = 1–4$ min of FA-gas treatment at 150 °C. A shift of the peaks to lower 2θ with progressive conversion is observed in Figure 3A. Figure 3B shows the details of the XRD patterns in

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**Figure 1.** Cation displacement reaction between MAPbI$_3$, perovskite and HC(═NH)NH$_2$ (formamidine or FA) gas at 150 °C resulting in FAPbI$_3$, perovskite and CH$_3$NH$_2$ (methylamine or MA) gas, and schematic illustration depicting morphology-preserving MAPbI$_3$ → FAPbI$_3$, perovskite thin-film conversion.

**Figure 2.** SEM micrographs (top view) of the MAPbI$_3$, perovskite thin films deposited using (A) one-step spin-coating, (D) two-step dipping, (G) antisolvent treatment, and (J) MA-gas treatment. SEM micrographs of the corresponding converted FAPbI$_3$, perovskite thin films (FA gas, 150 °C, 5 min): (B), (E), (H), and (K). Corresponding XRD patterns (black: MAPbI$_3$, (before); red: FAPbI$_3$, (after)): (C), (F), (I), and (L).
the \(2\theta\) range 27.50–29.00°. The presence of phase-pure MAPbI\(_3\) perovskite at \(t = 0\) min is confirmed by the presence of the 220 reflection at \(2\theta = 28.42°\). With exposure to FA gas, the FAPbI\(_3\) perovskite 200 reflection starts to appear centered around \(2\theta = 28.10°\). With increasing FA-gas treatment duration, the intensity of the FAPbI\(_3\) perovskite 200 reflection increases, whereas the MAPbI\(_3\) 220 reflection decreases. At \(t = 4\) min, the MAPbI\(_3\) \(\rightarrow\) FAPbI\(_3\) conversion is nearly complete. It is encouraging that the formation of the undesirable “yellow” nonperovskite FAPbI\(_3\) phase and decomposition of perovskite into PbI\(_2\) phase are both suppressed during the conversion process, which could be related to the fact that FAPbI\(_3\) perovskite phase is thermodynamically more stable at the reaction temperature (150 °C). The overall phase-conversion kinetics are more than an order-of-magnitude faster than the ion-exchange process reported by Eperon et al.\(^\text{12}\) involving the use of solvents. In fact, such rapid conversion kinetics are responsible for the fundamentally different conversion mechanism in our cation-displacement process. In the ion-exchange process, the perovskite conversion progresses by gradual alloying of FA’ into MAPbI\(_3\), until an equilibrium in the solid–liquid system is reached, with a FA’-rich perovskite alloy (FAM\(_\text{A1-xPbI}_x\)) as the final product. The sluggish reaction kinetics allows sufficient time for the mixing of the FA’ and MA’ across the entire film. Correspondingly, the XRD patterns of the partially converted films show symmetric diffraction peaks, indicative of the formation of homogeneous single-phase FAM\(_{\text{A1-xPbI}_x}\) alloys.\(^\text{12}\) However, in our cation-displacement process, the reaction is much faster, and, thus, a heterogeneous two-phase mixture of MAPbI\(_3\) and FAPbI\(_3\) is observed in the partially converted perovskite film instead, and the reaction progresses until the MAPbI\(_3\) phase is depleted. Figure 3C,D show optical-absorption spectra for the films at \(t = 0–4\) min of FA-gas treatment at 150 °C, corresponding to the XRD patterns in Figure 3A,B. While the absorbance at low wavelengths in all the thin films is virtually indistinguishable, at longer wavelengths the extension of absorbance into near-infrared (NIR) region is clearly seen in Figure 3C. Figure 3D shows details of the absorption spectra in the NIR range, where the absorption is extended by \(\sim 30\) nm into the NIR after conversion. The partially converted films show mixed absorption feature of MAPbI\(_3\) and FAPbI\(_3\) perovskite thin films. This is consistent with the XRD results in Figure 3A,B.

This morphology-preserving MAPbI\(_3\) \(\rightarrow\) FAPbI\(_3\) conversion can find promising application in the fabrication of high-efficiency FAPbI\(_3\) PSCs. To demonstrate this, a dense, full-coverage MAPbI\(_3\) perovskite thin film was first deposited upon a 250 nm mesoporous TiO\(_2\)/compact-TiO\(_2\)/FTO anode using the MA-gas treatment method described elsewhere,\(^\text{18}\) where the uniform morphology of that thin film is clearly evident in Figure 4A (cross-section). After conversion, the morphology/microstructure of the mesostructured TiO\(_2\)/FAPbI\(_3\) perovskite and the FAPbI\(_3\) perovskite capping-layers appears indistinguishable from the original MAPbI\(_3\) thin film (Figure 4B). The morphology preservation is further confirmed by comparing the surface morphologies of the perovskite layers before and after conversion, as shown in Figure S5. The fabrication of the FAPbI\(_3\)-based PSCs was then completed by depositing Spiro-OMeTAD/Au cathode. Figure 4A shows the reverse-scan current density–voltage (\(J–V\)) response of the best FAPbI\(_3\)-based PSC (inset: stabilized \(J\) and PCE output at maximum power point) and (D) corresponding EQE spectrum.

Figure 3. XRD patterns of FA-gas-treated (150 °C) thin films for \(t = 0–4\) min. The dashed lines mark the peak positions of MAPbI\(_3\) perovskite. (B) Higher-resolution XRD patterns (overlaid) of thin films corresponding to those in (A). Dashed lines mark the MAPbI\(_3\), (220) and FAPbI\(_3\), (200) perovskite peak positions, respectively. (C) Optical absorption spectra of the FA-gas-treated (150 °C) thin films for \(t = 0\) to 4 min. (D) Details of the optical absorption spectra marked by the dashed rectangle in (C).

Figure 4. Cross-sectional micrographs: (A) MAPbI\(_3\) perovskite thin film and (B) converted FAPbI\(_3\) perovskite thin film. (C) \(J–V\) response of the best FAPbI\(_3\)-based PSC (inset: stabilized \(J\) and PCE output at maximum power point) and (D) corresponding EQE spectrum.
process yields a PCE of ~17% with a high $J_{SC}$ of 22.2 mA cm$^{-2}$ (Figure S7), which attests to the versatility of this method. These results show that the high quality of the starting MAPbI$_3$ perovskite thin films can be preserved in the resultant FAPbI$_3$ perovskite thin films during the FA-gas-induced conversion, which leads to the high performance in the FAPbI$_3$-perovskite-based PSCs.

In closing, the unprecedented organ-cation displacement approach presented here is very attractive for the processing of high-performance FAPbI$_3$-based PSCs and other types of devices, as it combines synergistically the clear advantage of high-quality MAPbI$_3$ perovskite thin-films deposition protocols and the desirable attributes of the FAPbI$_3$ perovskite. This approach has generic appeal, and it could be extended to the synthesis of other compounds (e.g., FASnI$_3$).

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02787.

* Experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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