High-performance photovoltaic perovskite layers fabricated through intramolecular exchange

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The tremendous improvements in device architecture (1–3), high-quality film formation methodologies (4–6), and compositional engineering of perovskite materials (7–9) over the last 3 years have led to rapid improvements in the power conversion efficiency (PCE) of perovskite solar cells (PSCs). Although solar-to-electric PCE of up to 18% has been reported for PSCs (10), developing technologies further to achieve PCEs near theoretical values continues to be among the most important challenges in the solar cell industry to achieve economic feasibility.

Formamidinium lead iodide (FAPbI3) is a perovskite material that can potentially provide better performance than methylammonium lead iodide (MAPbI3) because of its broad absorption of the solar spectrum. In addition, FAPbI3 with the n-i-p architecture (the n-side is illuminated with solar radiation) exhibits negligible hysteresis with sweep direction during current-voltage measurements (8–13). However, compared to MAPbI3, it is more difficult to form stable perovskite phases and high-quality films of FAPbI3. Various methodologies such as sequential deposition (4), solvent-engineering (5), vapor-assisted deposition (14), additive-assisted deposition (15, 16), and vacuum evaporation (6) can now produce high-quality films of MAPbI3 with flat surfaces and complete surface coverage by controlling its rapid crystallization behavior and have led to substantial improvement in the PCE of MAPbI3-based PSCs.

Among these methodologies, two-step sequential deposition and solvent-engineering are representative wet processes that can yield perovskite films for high-performance PSCs. In the sequential deposition process, a thin layer of PbI2 is deposited on the substrate, methylammonium iodide (MAI) or formamidinium iodide (FAI) is then applied to the pre-deposited PbI2 to enable conversion to the perovskite phase. This process involves crystal nucleation and growth of the perovskite phase because of the reaction between PbI2 and an organic iodide such as MAI or FAI (4, 13, 17). However, the sequential reaction of organic iodides with PbI2 that occurs from the surface to the inner crystalline regions of PbI2 has been ineffective in producing high-performance perovskite films that are > 500 nm in thickness because of incomplete conversion of PbI2, peeling-off of the perovskite film in solution, and uncontrolled surface roughness. In contrast, the solvent-engineering process utilizes the formation of intermediate phases to retard the rapid reaction between PbI2 and organic iodide in the solution. While this process has been successfully used to form dense and uniform MAPbI3 layers, it has not been explored for FAPbI3 (5).

To deposit a uniform and dense FAPbI3 layer, Snaith et al. added a small amount of aqueous HI to a solution mixture containing PbI2, FAI, and dimethylformamide (DMF) (11). Very recently, Zhao et al. reported the deposition of highly uniform and fully covered FAPbI3 films using FAI and HPbI5, which is formed by the reaction of PbI2 and HI in DMF (18). The HI in the PbI2 layers retards the rapid reaction between FAI and PbI2. In addition, the release of HI from PbI2 at high temperatures allows the formation of a FAPbI3 layer by solid-state reaction with the neighboring FAI molecules. Stated differently, this process can be regarded as the transformation of PbI2-HI-FAI into FAPbI3, similar to the formation of MAPbI3 via the PbI2-dimethylsulfoxide (DMSO)-MAI phase in the solvent-engineering process (5).

However, we observed that the solvent-engineering process, which is effective for depositing dense and uniform MAPbI3 layers, yields FAPbI3 layers with pin-holes and a
rough surface. Although the FAPbI$_3$ film-quality including coverage and uniformity on the substrate have been improved, the performance of FAPbI$_3$-solar cells still lag behind those of MAPbI$_3$-based PSC (8), implying that more sophisticated deposition techniques are necessary for fabricating high-quality, thick FAPbI$_3$ films (> 500 nm), for achieving sufficient absorption up to a wavelength of 840 nm.

As expected from the conversion of PbI$_2$-DMSO-MAI to MAPbI$_3$ (5), the DMSO molecules intercalated in PbI$_2$ can be easily replaced by external FAIs because of its higher affinity toward PbI$_2$ compared to DMSO; the FAI molecules experience ionic interactions, whereas DMSO participates in van der Waals interactions (5, 19). Highly uniform and dense pre-deposited PbI$_2$-(DMSO) layers could be directly converted to FAPbI$_3$ because the inorganic PbI$_2$ framework would be retained. FAPbI$_3$ crystallization by the intramolecular exchange process (IEP) of DMSO intercalated in PbI$_2$ with FAI was schematically shown in Fig. 1A. The intramolecular exchange between DMSO and FAI can be described as

$$\text{PbI}_2\text{-DMSO} + \text{FAI} \rightarrow \text{PbI}_2\text{-FAI} + \text{DMSO} \rightarrow \text{removal}$$

and does not induce volume expansion, unlike the FAPbI$_3$ formed with FAI intercalating into pristine PbI$_2$ (discussed below) because the molecular sizes of DMSO and FAI are similar.

In this work, we report on the synthesis of a PbI$_2$-(DMSO) precursor with excellent capabilities for molecular exchange with FAI at low temperatures during the spinning process, as well as the fabrication of highly efficient FAPbI$_3$-based PSCs with certified PCEs exceeding 20%. To synthesize the PbI$_2$-(DMSO) precursors, precipitates were obtained by pouring toluene as a non-solvent into 1.0 M PbI$_2$ solution dissolved in isopropyl alcohol (IPA), on the pre-deposited PbI$_2$-(DMSO) layers (discussed below). It is evident from Fig. 1Da that well-crystallized FAPbI$_3$-based films were formed by IEP. The XRD pattern for the FAPbI$_3$ film derived from the PbI$_2$-(DMSO) complex film exhibits dominant (111) and (-222) diffraction peaks at 13.9° and 28.1°, respectively, corresponding to the FAPbI$_3$ trigonal perovskite phase (P3m1), in contrast with the XRD patterns of the FAPbI$_3$ powder (Fig. 1Db) (13). The intensity ratio of (-23) peak at 31.5° to the (-222) peak at 28.1° was 0.05. This value was much smaller than the corresponding intensity ratios (> 0.8) for the FAPbI$_3$ powder. Thus, IEP leads to high-quality pure FAPbI$_3$-based films with preferred orientation along the [111] axis.

Fig. S2 (21) presents the current density−voltage (J−V) curves measured under standard air-mass 1.5 global (AM 1.5G) illumination, and the external quantum efficiency (EQE) spectra of the fabricated cells with FAPbI$_3$-based layers fabricated with various amounts of MABr (0 to 20 mol%). The onset wavelength in the EQE spectra near 830 nm showed a non-linear blue shift with increasing amounts of MABr, indicating that there is unsymmetrical competition between FAI and MABr in forming the FAPbI$_3$-MABr$_x$ perovskite phase through an intramolecular exchange reaction. Nevertheless, the highest PCE of 19.2% was achieved for the film fabricated from a FAI solution containing 15 mol% MABr. To accurately determine the composition of the FAPbI$_3$-based layer, we investigated the lattice parameter using XRD and the band gap using the EQE for the film showing the best performance. Fig. S3 (21) shows the pseudocubic lattice parameter for (FAPbI$_3$)$_y$(MAPbBr$_x$)$_{1-y}$ as a function of $x$, in which the composition was controlled...
by a previously reported method (10). In this study, the pseudocubic lattice parameter of the FAPbI3/MAPbBr3 film fabricated by IEP with a FAI solution containing 15 mol% MABr is 6.348 Å. As indicated in Fig. S4 (21), the lattice parameter can be assigned as a = 5, corresponding to (FAPbI3)0.85(MAPbBr3)0.15. This result is in agreement with the value estimated using the band gap (1.49 eV) from EQE [Fig. S3 (21)], because pure FAPbI3 has a band gap of 1.47 eV and (FAPbI3)0.85(MAPbBr3)0.15, 1.55 eV (10). Fortunately, the simultaneous introduction of both MA+ cations and Br- anions in FAPbI3 even after incorporating 5 mol% of MAPbBr3 serves to stabilize the perovskite phase (10).

After comparing the absorption coefficients of FAPbI3 and MAPbI3 at wavelengths beyond 800 nm, we noted that the thickness of a FAPbI3 layer needed to be higher than the optimal thickness of a typical perovskite layer with a band gap of ~1.55 eV (300 to 400 nm) to guarantee fully light-harvesting around 800 nm (20, 22). We deposited FAPbI3-based layers with thickness of ~500 nm, and fabricated devices consisting of fluorine-doped tin oxide (FTO)-glass/barrier layer (bl)-TiO2/mesoporous (mp)-TiO2/perovskite/poly-triarylamine (PTAA)/Au (n-i-p architecture), as shown in the cross-sectional FESEM image of Fig. 2A. FESEM plane-view images of the device with film derived from PbI2(DMSO) complex and PbI2 films are shown in Fig. 2B. The FAPbI3 film derived from PbI2(DMSO) exhibited a dense and well-developed grain structure with larger grains than the FAPbI3 film derived from PbI2. Figure 2Ca shows the J-V curves measured via reverse and forward bias sweep for one of the best-performing solar cell. The devices based on PbI2 films, annealing at high temperature is required to achieve interdiffusion. Figure 3A compares XRD patterns for as-formed and annealed films by IEP and conventional process from PbI2(DMSO) complex film and PbI2 film, respectively; there is no appreciable difference in XRD patterns between as-formed and annealed film. This result confirms that the FAPbI3-based layer is formed by the IEP of DMSO and FAI (MABr) without additional annealing process. In addition, such an exchange can considerably favor crystallization into perovskite, compared to conventional interdiffusion from PbI2, and led to an increase in the XRD peaks intensity after annealing at 150°C for 20 min. However, the as-formed film with PbI2 showed XRD patterns assigned to PbI2, FAI, and FAPbI3, and a (002) peak at 12.5° corresponding to the PbI2 still remains after annealing at same temperature and time with IEP. In particular, the FAPbI3 film prepared by IEP is remarkably preferred (111)-oriented compared to FAPbI3 film annealed after preparing it by conventional process.

The advantages of IEP become further apparent upon comparing the J-V curves and PCEs of FAPbI3-based devices derived from PbI2(DMSO) complex films and conventional PbI2 films (Fig. 3, B and C). The devices based on FAPbI3 fabricated from PbI2(DMSO) showed superior PCEs with smaller deviations in the value, compared to those prepared from conventional PbI2 films. High-efficiency solar cells with average PCE of over 19% could be produced with a high degree of reproducibility by using the IEP. This study provides an effective protocol for fabricating efficient and cost-effective inorganic-organic hybrid heterojunction solar cells.

REFERENCES AND NOTES

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Fig. 1. PbI₂-complex formation and X-ray diffraction. (A) Schematics of FAPbI₃ perovskite crystallization involving the direct intramolecular exchange of dimethylsulfoxide (DMSO) molecules intercalated in PbI₂ with formamidinium iodide (FAI). The DMSO molecules are intercalated between edge-sharing [PbI₆] octahedral layers. (B) XRD patterns of (a) as-prepared PbI₂(DMSO)₂ powders, (b) vacuum-annealed PbI₂(DMSO) powders, and (c) as-deposited film on fused quartz substrate using PbI₂(DMSO) complex solution. (C) TGA of PbI₂(DMSO)₂ (red line) and PbI₂(DMSO) (dark blue line). (D) XRD patterns of (a) as-formed film of FAPbI₃ by IEP, and (b) FAPbI₃ powder.
Fig. 2. SEM observation, I-V and EQE measurements. (A) Cross-sectional FESEM image of the device consisting of FTO-Glass/bl-TiO2/mp-TiO2/perovskite/PTAA/Au. (B) The comparison of FESEM surface images of FAPbI₃-based layer formed on mp-TiO₂ by IEP and conventional method. (C) (a) J-V curves of best device measured with a 40 ms scanning delay in reverse (from 1.2 V to 0 V) and forward (from 0 V to 1.2 V) modes under standard AM 1.5G illumination, and (b) EQE spectra for best device and integrated JSC.
Fig. 3. Comparison of X-ray diffractions, performance, and reproducibility between IEP and conventional process. (A) XRD patterns of as-formed and annealed film for FAPbI$_3$-based layers formed by IEP (red line) and conventional (blue line) process. $\alpha$, $\#$, and $\ast$ denote the identified diffraction peaks corresponding to the FAPbI$_3$ perovskite phase, PbI$_2$, and FAI, respectively. (B) Representative $J$-$V$ curves for FAPbI$_3$-based cells fabricated by IEP and conventional process. (C) Histogram of solar cell efficiencies for each 66 FAPbI$_3$-based cells fabricated by IEP and conventional process.
Table 1. Comparison of layer thickness before and after FAPbI₃ phase is formed by conventional and intramolecular exchange process. The thin PbI₂ and PbI₂(DMSO) layers were deposited on a fused quartz glass, and their layer thickness was measured by alpha-step IQ surface profiler.

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<tr>
<th>Method</th>
<th>Before</th>
<th>After</th>
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<tr>
<td>Conventional process (PbI₂)</td>
<td>290 nm</td>
<td>570 nm</td>
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<td>IEP (PbI₂(DMSO))</td>
<td>510 nm</td>
<td>560 nm</td>
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