High-performance photovoltaic perovskite layers fabricated through intramolecular exchange

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The band gap of formamidinium lead iodide (FAPbI₃) perovskites allows broader absorption of the solar spectrum compared to conventional methylammonium lead iodide (MAPbI₃). The optoelectronic properties of perovskite films are closely related to the film-quality, so depositing dense and uniform films is crucial for fabricating high-performance perovskite solar cells (PSCs). We report an approach for depositing high-quality FAPbI₃ films, involving FAPbI₃ crystallization by the direct intramolecular exchange of dimethylsulfoxide (DMSO) molecules intercalated in PbI₂ with formamidinium iodide. This process produces FAPbI₃ films with (111)-preferred crystallographic orientation, large-grained dense microstructures, and flat surfaces without residual PbI₂. Using films prepared by this technique, FAPbI₃-based PSCs with maximum power conversion efficiency of over 20% were fabricated.

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 improve-

ments 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 solution-phase or solid-state 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 conver-

sion 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 HPbI₃, 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 FAPbI₃ film-quality including coverage and uniformity on the substrate have been improved, the performance of FAPbI₃-solar cells still lag behind those of MAPbI₃-based PSC (8), implying that more sophisticated deposition techniques are necessary for fabricating high-quality, thick FAPbI₃ films (> 500 nm), for achieving sufficient absorption up to a wavelength of 840 nm.

As expected from the conversion of PbI₂-DMSO-MAI to MAPbI₃ (5), the DMSO molecules intercalated in PbI₂ can be easily replaced by external FAIs because of its higher affinity toward PbI₂ 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 PbI₂-(DMSO) layers could be directly converted to FAPbI₃ because the inorganic PbI₂ framework would be retained. FAPbI₃ crystallization by the intramolecular exchange process (IEP) of DMSO intercalated in PbI₂ with FAI was schematically shown in Fig. 1A. The intramolecular exchange between DMSO and FAI can be described as

and does not induce volume expansion, unlike the FAPbI₃ formed with FAI intercalating into pristine PbI₂ (discussed below) because the molecular sizes of DMSO and FAI are similar.

In this work, we report on the synthesis of a PbI₂-(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 FAPbI₃-based PSCs with certified PCEs exceeding 20%. To synthesize the PbI₂-(DMSO) precursors, precipitates were obtained by pouring toluene as a non-solvent into 1.0 M PbI₂ solution dissolved in DMSO. The x-ray diffraction (XRD) pattern of the resulting complex (Fig. 1Ba) matched that of the PbI₂(DMSO)₂ phase (5, 19). The as-prepared PbI₂(DMSO)₂ was then annealed at 60°C for 24 hours in vacuum to obtain PbI₂(DMSO) by removal of 1 mol DMSO. The XRD pattern of the vacuum-annealed powder (Fig. 1Bb) did not match that of PbI₂(DMSO)₂, implying that the PbI₂(DMSO)₂ transformed into a different phase by releasing some DMSO molecules. The content of DMSO in the as-annealed powder was estimated by thermogravimetric analysis (TGA). TGA was suitable for this purpose because the only volatile species in the powder was DMSO. The TGA results of the PbI₂(DMSO)₂ and PbI₂(DMSO) complexes are shown in Fig. 1C. The PbI₂(DMSO)₂ complex exhibited a two-step decomposition process with weight-loss of 12.6% at each step, whereas the vacuum-annealed PbI₂(DMSO) complex showed a single-step decomposition. The decomposition of both the complexes was completed at the same temperature (138. 6°C). The powders obtained by vacuum-annealing PbI₂(DMSO)₂ complex at 60°C can be regarded as one of the most thermodynamically stable forms among the various crystalline PbI₂-(DMSO)-based complexes, which are similar with PbBr₂(DMSO) and PbCl₂(DMSO) (20). The DMSO content of

the vacuum-annealed PbI₂(DMSO) complex was also checked by elemental analysis (EA), which yielded H = 1.0% (1.1%); and C = 4.1% (4.4%), where the values expressed in parenthesis indicate the theoretical mass percent for a given element for C₂H₆SOPbI₂.

To fabricate FAPbI₃-based PSCs through IEP between DMSO and FAI (MABr) using pre-deposited PbI₂-DMSO layers and a FAI (MABr) solution, we first confirmed that the PbI₂(DMSO) phase was retained even after spin-coating with the PbI₂(DMSO) precursor dissolved in DMF. The XRD pattern for film coated on a fused silica substrate was compared with that of the initial precursor. As seen in Fig. 1Bc, the XRD pattern for the as-coated film was in consistent with that of the PbI₂(DMSO) complex powder, although its crystallinity is lowered. The as-coated PbI₂(DMSO) film also had a flat and dense surface, as shown in the field-emission scanning electron microscopy (FESEM) image in fig. S1 (21). Next, we investigated the formation of mixed FAPbI₃/MAPbBr₃ by IEP. We recently reported that the co-existence of MA/FA/I/Br in the PbI₂ skeleton improved the phase-stability of FAPbI₃ (10). The formation of mixed FAPbI₃/MAPbBr₃ layers via IEP was controlled by coating solution mixture with different mole ratios of MABr to FAI dissolved in isopropyl alcohol (IPA), on the pre-deposited PbI₂(DMSO) layers (discussed below). It is evident from Fig. 1Da that well-crystallized FAPbI₃-based films were formed by IEP. The XRD pattern for the FAPbI₃ film derived from the PbI₂(DMSO) complex film exhibits dominant (-111) and (-222) diffraction peaks at 13.9° and 28.1°, respectively, corresponding to the FAPbI₃ trigonal perovskite phase (P3m1), in contrast with the XRD patterns of the FAPbI₃ powder (Fig. 1Db) (13). The intensity ratio of (-123) 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 FAPbI₃ powder. Thus, IEP leads to high-quality pure FAPbI₃-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 FAPbI₃-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 FAPbI₃-MAPbBr₃ 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 FAPbI₃-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 (FAPbI₃)_{1-x}(MAPbBr₃)_x 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 $x \sim 5$, corresponding to (FAPbI₃)_{0.95}(MAPbBr₃)_{0.05}. 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 we fabricated also showed no hysteresis. Here, we believe that the hysteresis is highly dependent on the perovskite materials (FAPbI₃ or MAPbI₃) and cell architecture (n-i-p or p-i-n), although the ferroelectric properties of the perovskite itself are more likely to be the origin of the hysteresis in PSCs (23, 24). Thus, FAPbI₃-based PSCs with n-i-p architecture show negligible hysteresis between the reverse and the forward scan in the I-V characteristics. In contrast, FAPbI₃-based cells consisting of FTO/NIO/ perovskite/PCBM/LiF/Al (p-i-n architecture) showed very strong hysteresis [fig. S4 (21)]. *J*_{sc}, *V*_{oc}, and *FF* determined from the *J-V* curves were 24.7 mA cm⁻², 1.06 V, and 77.5%, respectively, and correspond to a PCE of 20.2% under standard AM 1.5G illumination. Figure 2Cb shows the EQE spectrum and integrated *J*_{sc} for one of the best-performing solar cell. The high *J*_{sc} is attributed to a very broad EQE plateau of >85% in the illumination wavelength range of 400 to 780 nm and broad light-harvesting up to a long wavelength of 840 nm, owing to the relatively low band gap (1.47 eV) of FAPbI₃. The *J*_{sc} value (24.4 mA cm⁻²) obtained by integrating EQE spectrum agreed well with that derived from the *J-V* measurement. The PCE of the best-performing cell (20.2%) was certified by the standardized method in the PV calibration laboratory, which confirmed a PCE of 20.1% under AM 1.5 G full-sun illuminations [fig. S5 (21)].

To gain more insight into the enhanced performance of the FAPbI₃-based PSCs, we compared the properties of the films fabricated by IEP with those obtained from a conventional sequential process. A sequential reaction such as inter-diffusion between FAI/MAI and PbI₂ through thermal annealing in organic iodide/PbI₂ multilayer films has been used to form perovskite FAPbI₃/MAPbI₃ films from inorganic PbI₂ films in the conventional process (17). Thus, considerable volume expansion occurs in the sequential deposition process based on PbI₂ because of the growth of perovskite crystals with the insertion of organic iodides into PbI₂ skeleton (14, 22). As expected, an initial PbI₂ film with thickness of ~ 290 nm was doubled to 570 nm for the film formed by the reaction of PbI₂ with FAI [Table 1 and fig. S6 (21)].

In contrast, the change in thickness observed by the application of the FAI (MABr) solution to the pre-deposited PbI₂-(DMSO) film was negligible. In fact, the reaction between FAI (MABr) and PbI₂(DMSO) was completed within 1 min during spin-coating and the FAPbI₃ perovskite phase was formed without sequential annealing. However, in a conventional process using 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 PCEs 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.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Figs. S1 to S6

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Fig. 1. PbI_2 -complex formation and X-ray diffraction. (A) Schematics of FAPbI_3 perovskite crystallization involving the direct intramolecular exchange of dimethylsulfoxide (DMSO) molecules intercalated in PbI_2 with formamidinium iodide (FAI). The DMSO molecules are intercalated between edge-sharing $[\text{PbI}_6]$ octahedral layers. (B) XRD patterns of (a) as-prepared $\text{PbI}_2(\text{DMSO})_2$ powders, (b) vacuum-annealed $\text{PbI}_2(\text{DMSO})$ powders, and (c) as-deposited film on fused quartz substrate using $\text{PbI}_2(\text{DMSO})$ complex solution. (C) TGA of $\text{PbI}_2(\text{DMSO})_2$ (red line) and $\text{PbI}_2(\text{DMSO})$ (dark blue line). (D) XRD patterns of (a) as-formed film of FAPbI_3 by IEP, and (b) FAPbI_3 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 *J*_{sc}.

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 FAPbI₃-based layers formed by IEP (red line) and conventional (blue line) process. α, #, and * denote the identified diffraction peaks corresponding to the FAPbI₃ perovskite phase, PbI₂, and FAI, respectively. (B) Representative J-V curves for FAPbI₃-based cells fabricated by IEP and conventional process. (C) Histogram of solar cell efficiencies for each 66 FAPbI₃-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.

Method	Before	After
Conventional process (PbI ₂)	290 nm	570 nm
IEP (PbI ₂ (DMSO))	510 nm	560 nm