

Electronic Supplementary Information

**Fabrication of formamidinium lead iodide perovskite thin films via
organic cation exchange**

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Materials Synthesis: Synthesis used chemicals and solvents that were reagent grade purchased from Sinopharm Chemical Reagent Co., Ltd, Sigma-Aldrich. Unless otherwise indicated, all starting materials were used without further purification.

PbI₂ powders were prepared by mixing KI and Pb(NO₃)₂ (molar ratio 2:1) in water with stirring for 0.5 h at room temperature. The PbI₂ precipitate were filtered and then dried at 200 °C under vacuum for 2 h.

NH₄PbI₃ powders were prepared by mixing equimolar NH₄I and PbI₂ in N,N-dimethylformamide (DMF, 99.8%). Then the mixture was heated at 80 °C for 2 h under vacuum to remove the solvent.

CH₃NH₃I (or MAI) was prepared using a reported method described in the literature S1. Briefly, 20 mL methylamine (30% in ethanol) and 24 mL of hydroiodic acid (47 wt% in water) were mixed and reacted at 0 °C for 2 h while stirring under N₂ atmosphere. After rotary evaporation, the MAI powders was collected and washed three times with ethyl ether and dried in a vacuum oven.

The starting NH₄PbI₃ films were deposited using one-step method. Here, a 40 wt% PbI₂:NH₄I (molar ratio 1:1) solution in DMF (99.8%) was spin-coated (4000 rpm, 30 s), followed by a heat-treatment at 100 °C for 2 min.

The starting MAPbI₃ films were deposited using the same one-step method. Here, a 40 wt% PbI₂:MAI (molar ratio 1:1) solution in DMF (99.8%) was spin-coated (4000 rpm, 30 s), followed by a heat-treatment at 100 °C for 5 min.

A TiO₂ sol was prepared by mixing 10 mL titanium (IV) isopropoxide (99%) with 50 mL 2-methoxyethanol (98%) and 5 mL ethanolamine (99%) 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. The sol was spin-coated (4000 rpm, 30 s) on fluorine-doped tin oxide (FTO)-coated glass substrates, followed by a heat-treatment of 550 °C for 30 min in air, to deposit a 30-nm thick compact-TiO₂ layer.

Solar Cell Fabrication: FTO/glass substrates were patterned by etching with Zn powder and 1 M HCl diluted in distilled water. The etched substrates were then cleaned with ethanol, saturated KOH solution in isopropanol, and water sequentially, and then they were dried in clean dry air. A 30-nm compact-TiO₂ layer was deposited on top of the etched FTO/glass substrates using the procedure described earlier. A 300-nm mesoporous-TiO₂ layer was then deposited by spin-coating a dilute commercial TiO₂ paste (1:3 with ethanol by weight) at 3500 rpm for 30 s, followed by a sintering heat-treatment of 550 °C for 30 min in air. The NH₄PbI₃ layer was then deposited using the one-step method, as described earlier. Then, these as-obtained films were put into the upper of the CVD tube furnace, while formamidine acetate (FA-Ac) was put on just below of the films. Then the tube was evacuated to under 10⁻² Pa, and at the same time heated up to 160 °C, and kept for 1h. A solution of spiro-MeOTAD (99%) hole-transporting material (HTM) coating was prepared by dissolving 72.3 mg spiro-MeOTAD in 1 mL chlorobenzene (99.8%), to which 28.8 μL 4-tert-butyl pyridine (96%) and 17.5 μL lithium bis(trifluoromethanesulfonyl)imide (LITSFI) solution (520 mg LITSFI (98%) in 1 mL acetonitrile

(99.8%) were added. The HTM was deposited by spin-coating (3000 rpm, 30 s). Finally, a 100 nm Ag electrode was thermally-evaporated to complete the solar cells. The cation exchange process based on MAPbI₃ and HPbI₃ was similar to that of the NH₄PbI₃. The HTM and the Ag layers were then deposited to complete the device assembly.

The preparation of MAPbI₃ by CVD method is as below: a 30 wt% PbI₂ solution in DMF (99.8%) was spin-coated (4000 rpm, 30 s) onto the mesoporous-TiO₂. Then the as-obtained PbI₂ films were put into the upper of the CVD tube furnace, while CH₃NH₃I was put on just below of the films. The tube was evacuated to under 10⁻² Pa, at the same time heated up to 120 °C, and kept for 90 min.

J-V characteristics of the as-fabricated solar cells were measured using a 2400 Sourcemeter (Keithley, USA) under simulated one-sun AM 1.5G 100 mW cm⁻² intensity (Oriel Sol3A Class AAA, Newport, USA), under both reverse (from V_{OC} to J_{SC}) and forward (from J_{SC} to V_{OC}) scans. The step voltage was 50 mV with a 10 ms delay time per step. 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 devices. Typical active area of the devices is 0.09 cm² defined using non-reflective metal mask. The intensity of the one-sun AM 1.5G illumination was calibrated using a Si-reference cell certified by the National Renewable Energy Laboratory. All device testing was conducted in the ambient with a relative humidity of ~30%.

Materials and Films Characterization. IR spectra were recorded on a FT-IR spectrometer (Nicolet iS10, Thermo Fisher, USA) and only major peaks are reported in cm⁻¹. XRD patterns were obtained using a X-ray diffractometer (D8 Advance, Bruker, Germany) using Cu K α radiation, with 0.02° step and 2 s/step dwell. UV-vis absorption spectra of the films were recorded using spectrometer (U-4100, Hitachi, Japan). A field-emission SEM (S-4800, Hitachi, Japan) was used to observe the top surfaces and cross-sections. AFM measurements were performed in contact mode using AFM microscope (5400, Agilent, USA). All films for FTIR, XRD, SEM, AFM and UV-vis measurements were deposited on FTO/compact-TiO₂/meso-TiO₂ for consistency.

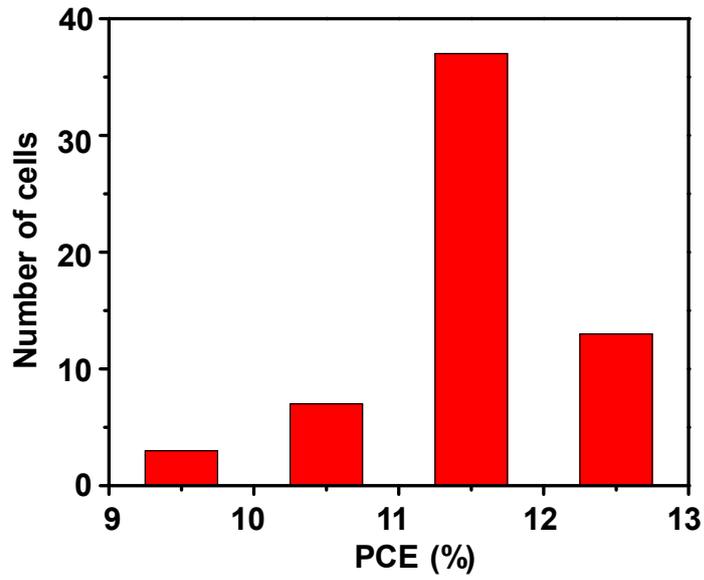


Fig. S1 The distribution of PCEs for 60 cells.

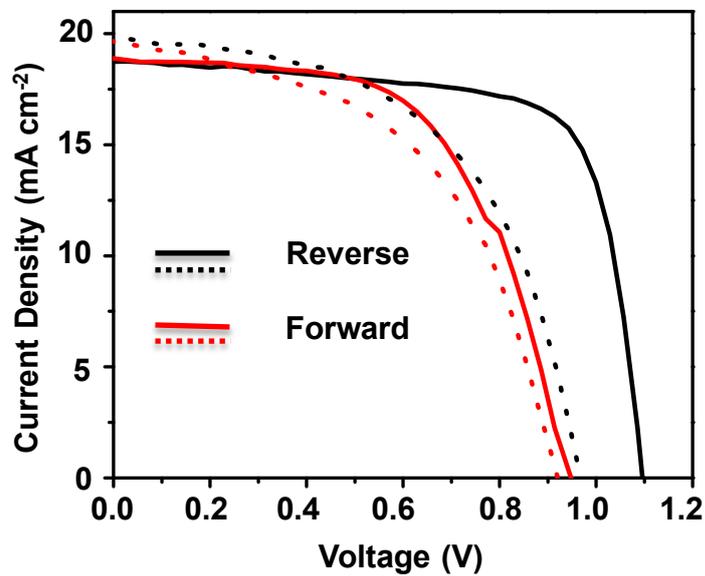


Fig. S2 J–V characteristics measured under AM 1.5G solar irradiance (100 mWcm⁻²) for champion devices. Solid: MAPbI₃ obtained from CVD method. Dot: FAPbI₃ obtained via one-step spin coating from PbI₂:PbCl₂:4FAI solution^{S2}.

Table S1 Performance parameters of the devices based on (1,2) FAPbI₃ and (3) MAPbI₃ films fabricated with different methods. 1. FAPbI₃ film obtained from cation exchange method. 2. FAPbI₃ film obtained via one-step spin coating from PbI₂:PbCl₂:4FAIS². 3. MAPbI₃ film obtained from traditional CVD method.

		J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η(%)
1	Rev.	22.2	0.94	0.59	12.4
1	For.	22.3	0.95	0.58	12.4
2	Rev.	19.7	0.97	54.4	10.4
2	For.	19.5	0.92	51.5	9.2
3	Rev.	18.7	1.10	72.4	14.8
3	For.	18.8	0.95	58.4	10.4

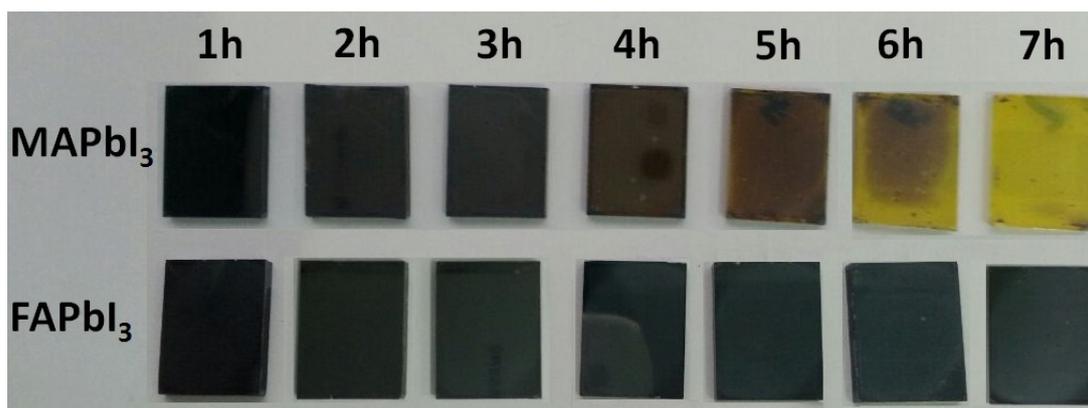


Fig. S3 The optical pictures of MAPbI₃ and FAPbI₃ films heated at 140 °C in nitrogen-filled glove box for 1-7 h, respectively.

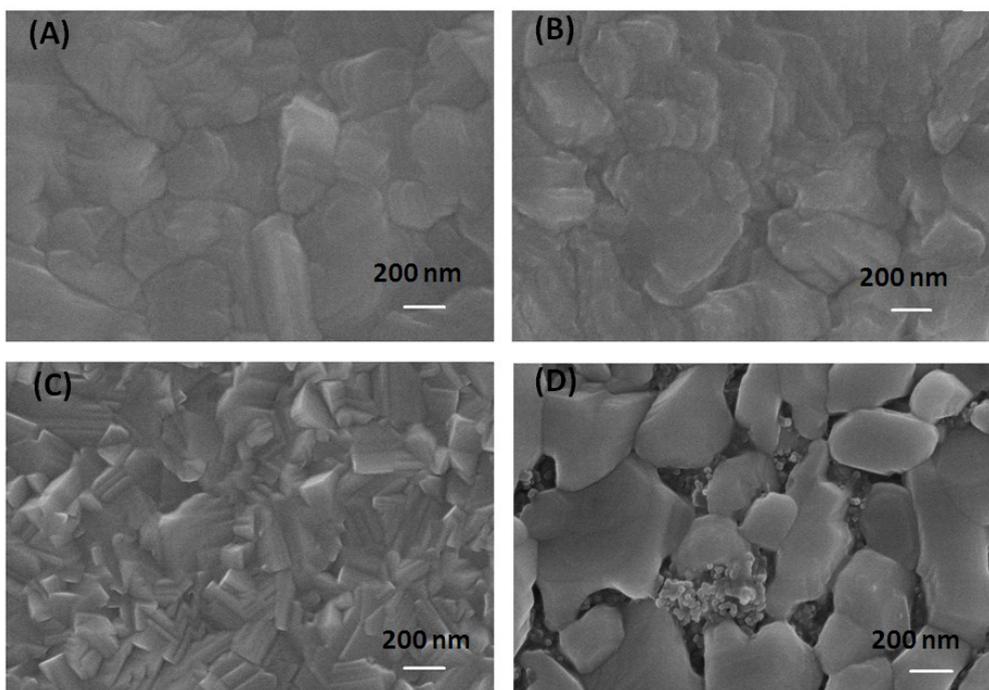


Fig. S4 SEM images of pristine FAPbI₃ (A) and MAPbI₃ (C) films, FAPbI₃ (B) and MAPbI₃ (D) films heated at 140 °C for 7 h, respectively.

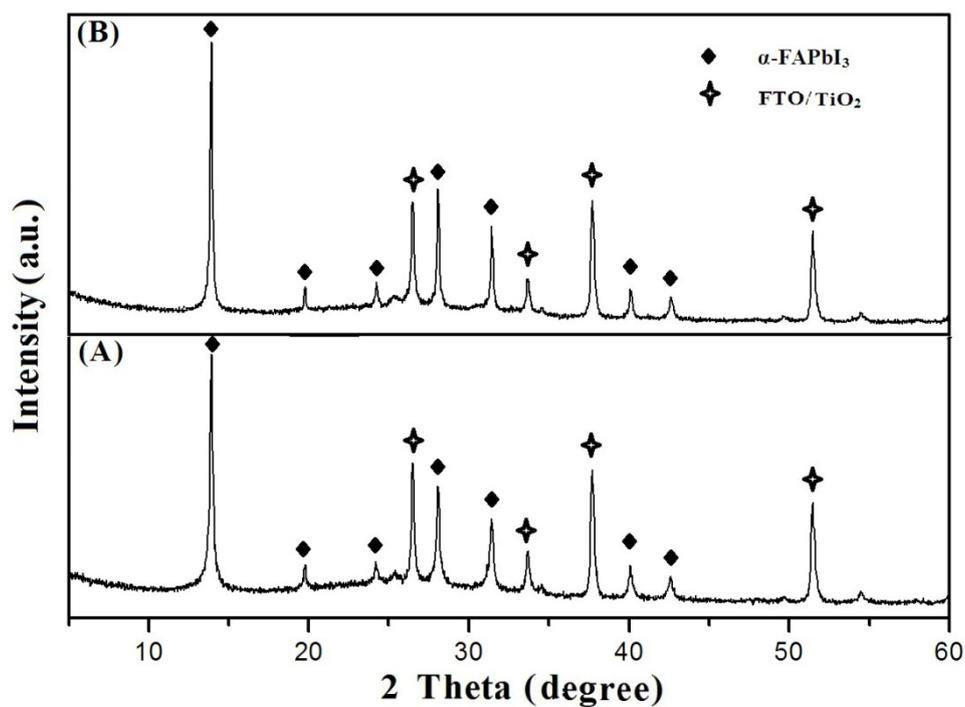


Fig. S5 XRD patterns of FAPbI₃ films fabricated from MAPbI₃ (A) and HPbI₃ (B) starting films, respectively.

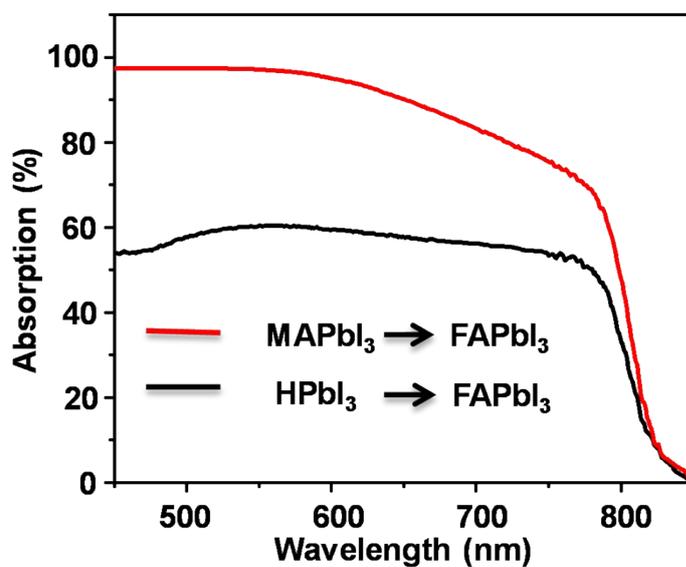


Fig. S6 The absorption spectra of FAPbI₃ films prepared from HPbI₃ and MAPbI₃, respectively, by the cation exchange method.

References

- S1. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643-647.
- S2. D. Wang, Z. Liu, Z. Zhou, H. Zhu, Y. Zhou, C. Huang, Z. Wang, H. Xu, Y. Jin, B. Fan, S. Pang and G. Cui, *Chem. Mater.*, 2014, **26**, 7145–7150.