Electronic Supplementary Material

FA cation replenishment-Induced second growth of printed MA-free perovskites for efficient solar cells and modules

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Experimental Section

Materials： Lead iodide (PbI_2, Purity＞99.99%) was purchased from Xi'an eLight Co., Ltd., Cesium iodide (CsI, Purity＞99.9%), Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA, Purity≥99.5%), C_{60} (Purity≥99.5%), 2-phenylethanamine iodide (PEAI, Purity≥99.5%), were purchased from Xi'an Polymer Light Co., Ltd. Formamidinium iodide (FAI, Purity≥99.99%) was purchased from Greatcell. N,N-Dimethylformamide (DMF, Purity≥99.8%), Chlorobenzene (Purity≥99%) , isopropanol (IPA, Purity≥99.5%) and 1-Methyl-2-pyrrolidinone (NMP, Purity≥99.0%) were purchased from aladdin. Aluminum oxide nanoparticles (Al_2O_3, <50 nm particle size, 20 wt% in isopropanol) and Lead(II) chlonde ($PbCl_2$, Purity≥99.5%) were purchased from Sigma-Aldrich.

Thin film deposition and device fabrication: The ITO glass was cleaned through

ultrasonic cleaning by detergent, deionized water, and ethyl alcohol for 10 min each, respectively. After drying under N_2 flow, the substrate was subsequently treated in ultraviolet ozone for 10 min to raise the hydrophilicity and further clean the substrate surface. Hole transporting layer of PTAA was prepared by coating the solution in chlorobenzene (1.5 mg/mL) at 5000 rpm for 30 s and then heated at 120 °C for 10 min. The Al_2O_3 nanoparticle layer was deposited to modify the surface energy of PTAA layer with the original solution was diluted 1:50 in IPA and spin coating at 3500 rpm for 30 s and annealed at 120 °C for 10 min in ambient air. The substrate was transferred to a dry-air-filled glovebox after it cooled down to room temperature. For the perovskite thin film with small size substrate (2.5 × 2.5 cm^2) or large size substrate (10 × 10 cm^2), the perovskite absorber layer was subsequently deposited using the air-knife assisted slot-die coating method. PEAI dissolved in IPA with concentration of 2 mg/mL was spin coated onto the perovskite thin film surface at 5000 rpm for 30 s, followed by annealing at 100 °C for 10 min. The C_{60} film was evaporated to a thickness of 40 nm. The SnO_2 film was deposited by atomic layer deposition with Tin(IV) dimethylamide as Sn source and H_2O as O source at 110 °C for 200 cycles. All the devices for performance and stability evaluation were tested without encapsulation. Finally, the Ag electrode was thermally evaporated to a thickness of 120 nm.

Slot-die coating of perovskite films: The 1.1 M $FA_{0.83}Cs_{0.17}PbI_3$ 7.5% $PbCl_2$ precursor solution was prepared by dissolving FAI 342.6 mg, CsI 106 mg, PbI_2 1106 mg and $PbCl_2$ 50.1 mg in mixed 2.18 mL solvent of DMF and NMP (volume ratio is 6: 1) . The specific slot-die coating instrument parameters for printing 10 × 10 cm^2 films are as follows: The distance between the substrate and slot-die lip was 250 μm (Z =250 μm). The coating speed was 3 mm/s, and the solution supply rate was 4 uL/s. The angle between the air knife and substrate is about 45°, and the gas pressure was controlled at ~0.2 MPa. The prepared perovskite film was annealed in a glove box filled with dry air at 120°C for 10 minutes, and then annealed in the air at 150°C for another 10 minutes (Environmental conditions: 25 ± 2 °C, < 45 % relative humidity). For the FA cation

replenishment process, FAI solution with different concentrations was spin coated onto the perovskite thin film at 5000 rpm for 30s, followed by annealing at 100°C for 5 min.

Laser scribing procedure: The P1 isolation lines are scribed onto the ITO film by Helios fiber laser processing system at a wavelength of 1064 nm and minimal pulse duration of 30 ns. The Helios VIS laser with a wavelength of 532 nm and minimal pulse duration of 0.4 ns was applied for P2 and P3 scribing by means of induced ablation model. The P2 scribing procedure was carried out after the deposition of ALD-SnO_2 film and the P3 was after the deposition of metal electrode.

Characterization: XRD patterns were performed by Bruker D8 Advance using Cu Kα radiation at 40 kV and 40 mA. The morphologies of the films and solar cells were measured by SEM (FEI Apreo LoVac). The J–V curves were recorded using a digital source meter (Keithley 2400) and a Newport solar simulator (ORIEL-SOI3A) with an AM1.5G spectrum. The light intensity was adjusted to 100 mW/cm^2 using a standard Si detector. For the PSCs, both forward and reverse scans were measured with the scanning speed of 0.15 V/s. The EQE spectra were measured in DC mode on a spectrum corresponding system (Enlitech QE-R), calibrated by Si reference solar cell. The absorption properties, and chemical and electron states of perovskite films were analyzed with UV-vis (DektakXT). The Ultraviolet photoelectron spectroscopy (UPS) characterizations were obtained with a Thermo Fisher Scientific K-ALPHA+, using the HeI (21.22 eV) emission line and Al Kα radiation (1486.6 eV). TRPL lifetime was measured by the time-correlated single photon counting method with an Edinburgh Instruments FLS980 fluorescence spectrometer. The excitation source was used a picosecond pulsed diode laser at 405 nm.

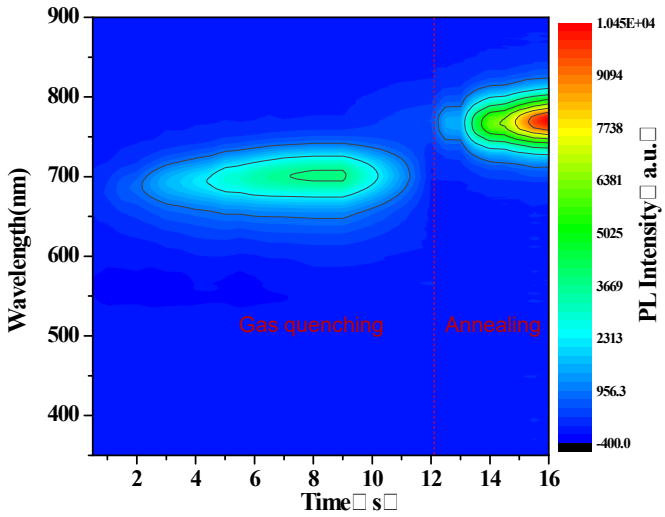

Fig. S1 The in-situ PL measurement that monitoring the formation kinetics of perovskite films.

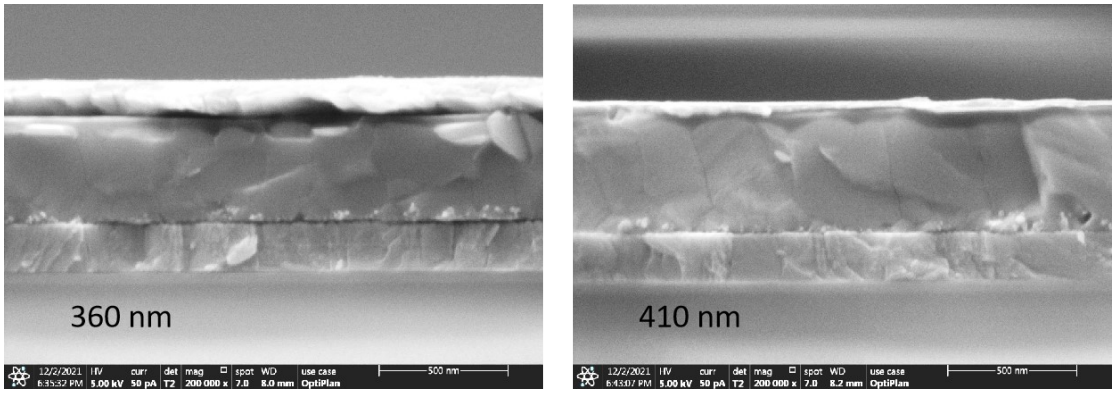

Fig. S2 Cross-section view SEM image of the FA0 and FAI4 based perovskite thin film.

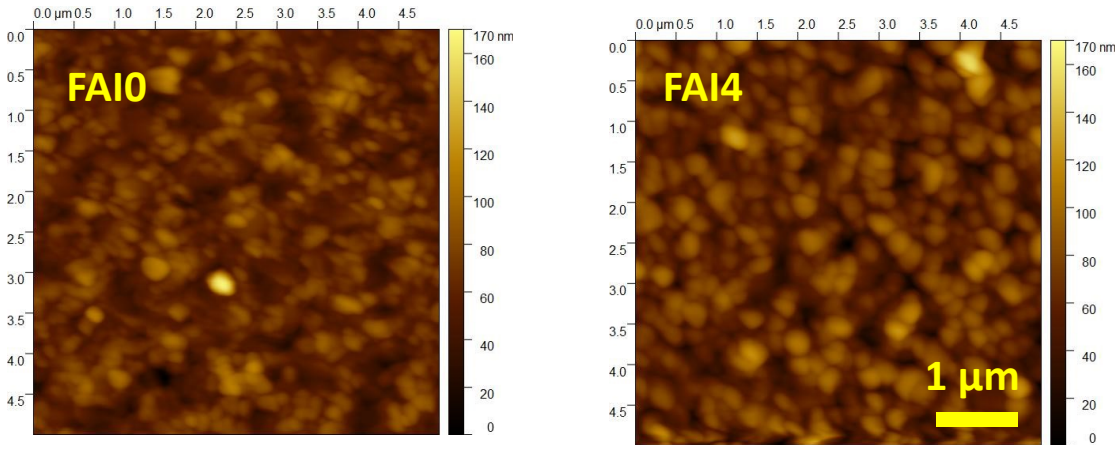

Fig. S3 AFM images of the perovskite thin film surface with different FA treatment concentration.

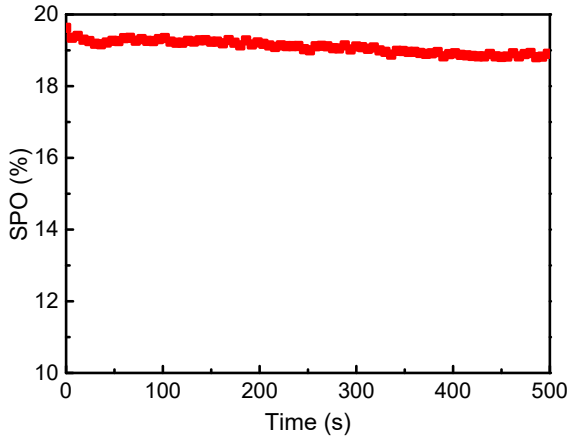

Fig. S4 The stabilized power output PCE of the perovskite solar cells.

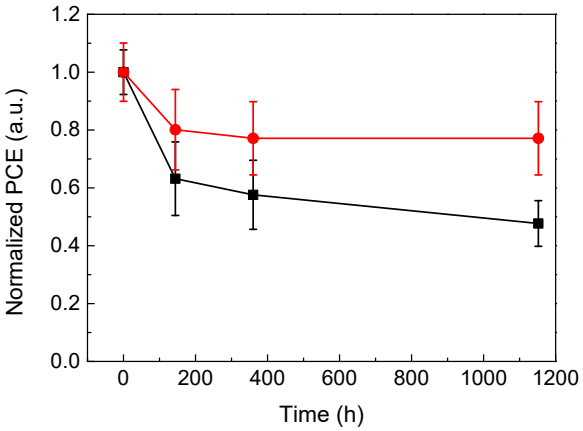

Fig. S5 Thermal stability test of the unencapsulated PSCs heated at 85°C.

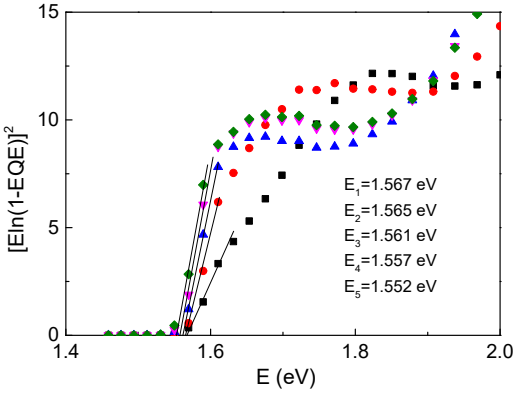

Fig. S6 The bandgap of perovskite materials with different FA treatment concentrations that calculated from the EQE results.

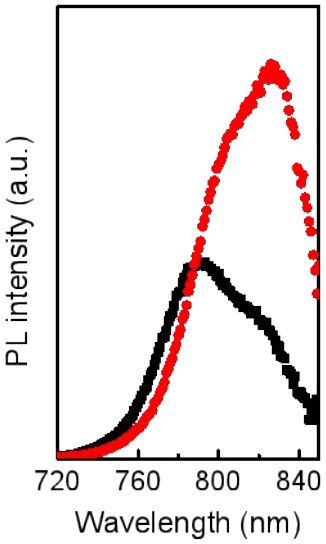

Fig. S7 PL of the FAI4-based perovskite thin film and initial film.

Fig. S8 The photograph of solt-die coated perovskite thin film with size of 10 cm × 10 cm.

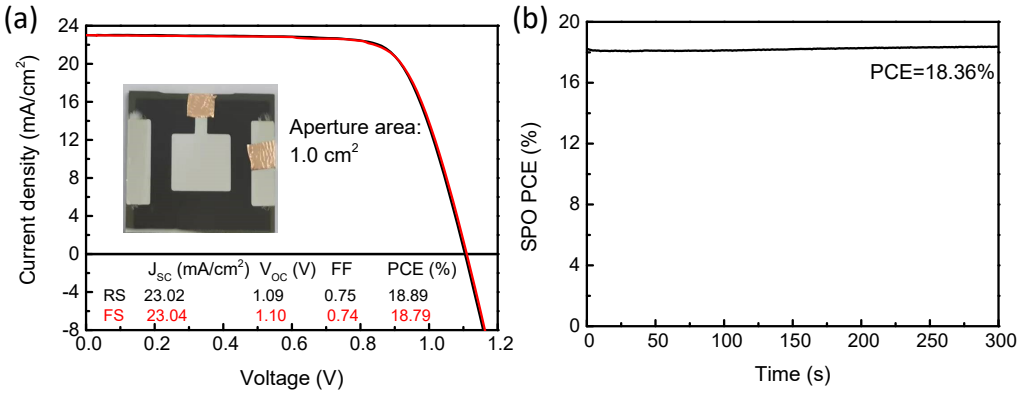

Fig. S9 (a) J-V curves of the large area (1 cm^2) perovskite solar cells, inset shows the photo of the device. (b) the steady-state of the large area (1 cm^2) PCE perovskite solar cells.

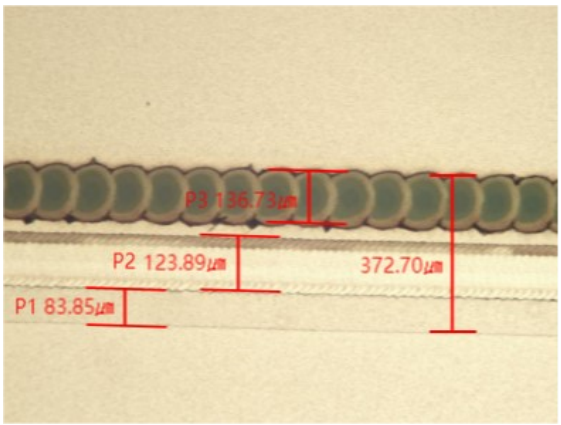

Fig. S10 Confocal microscope image of a module's P1 – P2 – P3 interconnection lines, and the geometric filling factor (GFF) is 0.938.

Table. S1 Device efficiency with an aperture area of more than 50 cm^2 .

PCE [%]	V_{oc} [V]	FF [%]	I_{sc} [mA]	Area [cm^2]	Sub-cell numbers	Method	Reference
18.6	20.74	78.4	198.9	Active 174	20	slot-die	1
19.54	15.35	76.1	108.55	Active 65	14	slot-die	2
15.3	20.89	72.0	207.05	Aperture 205	21	Blade	3
19.7	16.1	79.8	76.94	Aperture 50.1	14	Blade	4
11.80	13.16	64.8	126.684	Aperture 91.8	14	Blade	5
19.90	15.51	71.65	96.66	Active 54	14	Blade	6
17.56% This work	14.08	72.0	105.37	Aperture 60.84	13	slot-die	

Notes and references

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