

Regulating crystalline phase of intermediate film enables FA_{1-x}

MA_xPbI₃ perovskite solar cells with efficiency over 22%

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Experimental Section

Materials: Lead iodide (PbI_2 , 99.99%), N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, $\geq 99.9\%$), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) (99.95%), 4-tert-butylpyridine (4-TBP, 96%) were purchased from Sigma-Aldrich. SnO_2 dispersion (15 wt% in H_2O) was purchased from Alfa Aesar. 2,2',7,7'-Tetrakis (N, N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) was purchased from Lumtec. Methylammonium chloride (MACl) was all purchased from Xi'an Polymer Light Technology in China. Formamidinium iodide (FAI) and methylammonium iodide (MAI) were purchased from Great cell Solar company. All salts and solvents were used without any further purification.

Solution Preparation: The 15 wt% SnO_2 colloid precursor was diluted with deionized water to 2.67wt% and then sonicated for 15 min to obtain SnO_2 precursor solution. For preparing PbI_2 precursor solution, 691.5 mg PbI_2 was added into 1 mL mixed solvent (DMF: DMSO = 9:1 in volume ratio) and stirred at 60 °C for 2 h. The FAI/MAI/MACl mixture solution was prepared by adding 360 mg FAI, 25.4 mg MAI, and 36 mg MACl into 4 mL IPA. For the preparation of Spiro-OMeTAD mixture solution, 72.3 mg Spiro-OMeTAD powder were dissolved in 1 mL CB with the addition of 17.5 μL Li-TFSI stock solution (520 mg/mL in ACN) and 28.8 μL 4-tertbutylpyridine (TBP).

Photovoltaic device fabrication: The patterned ITO glass substrate ($7 \Omega \text{ sq}^{-1}$) was sequentially washed by ultrasonic cleaner using water, ethanol, acetone, and isopropyl alcohol. Before use, the ITO glass was cleaned with ultraviolet ozone for 10 min. Then the SnO_2 precursor solution was spin-coated on ITO glass substrate at 4000 rpm. for 30 s, and annealed in ambient air at 150 °C for 30 min. It is better to clean the substrate with ultraviolet ozone for 10 min to improve the surface wetting. The two-step sequential deposition method was used to prepare the perovskite absorber in a N_2 glovebox or ambient air (relative humidity (R. H.) around 40%). In detail, firstly the PbI_2 precursor solution was spin-coated onto SnO_2 at 1500 rpm for 30 s and then annealed at 75 °C for 1 min to partially remove the solvent. After cooling to room temperature, the FAI/MAI/MAC mixture solution was dipped onto PbI_2 layer and held for 5 s before spin-coated at 2000 rpm for 30 s, followed by thermal annealing at 150 °C for 15 min in ambient air conditions (around 40% R.H.). Spiro-OMeTAD solution was spin-coated on the obtained perovskite film at 4000 rpm for 30 s. Finally, 80 nm of Au was thermally evaporated as a counter electrode using a shadow mask. The device size areas were 0.24 cm^2 . When measuring, a 0.1 cm^2 non-reflective mask was used to define the accurate active cell area.

Characterization

XRD patterns were collected with a Regaku D/Max-2500 diffractometer equipped using a $\text{Cu K}\alpha 1$

radiation ($\lambda = 1.54056 \text{ \AA}$). The XPS measurements were performed on an ESCALab220i-XL electron spectrometer (VG Scientific) using 300W Al K α radiation. Top-view SEM images were obtained using Hitachi S-4800. The surface roughness of perovskite film was measured by an AFM (Nanoscope V, Veeco) in tapping mode. The ultraviolet-visible (UV-vis) absorption was measured on a UV-vis spectrophotometer (UH4150, Hitachi). The steady-state PL and TRPL spectra were measured on an Edinburgh Instrument FLS 980. $J-V$ characteristics were measured with a solar simulator (450 W Model 94023A, Newport) with an AM 1.5 solar spectrum filter and a Keithley 2420 source meter. Light intensity was adjusted using an NREL certified Si solar cell. For the EQE measurement, the ORIEL IQE-200 measurement system was used.

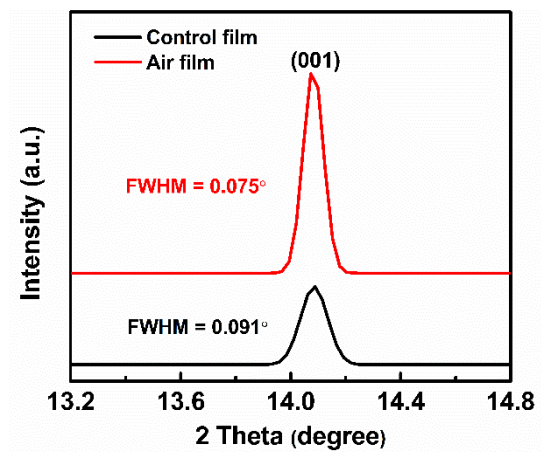


Fig. S1 Magnified (001) diffraction peaks of the control film and the air film in Fig. 2c.

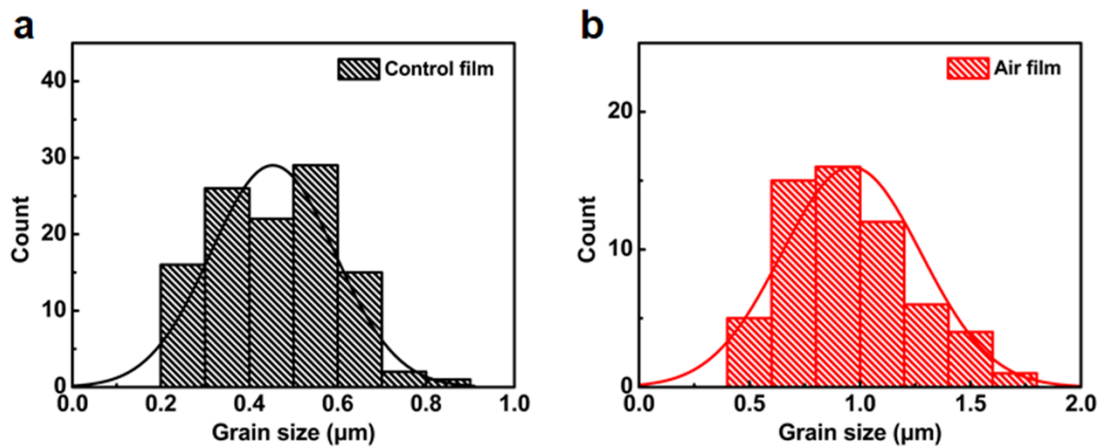


Fig. S2 The grain size histogram of perovskite films. Data were obtained from Fig. 2f and 2j.

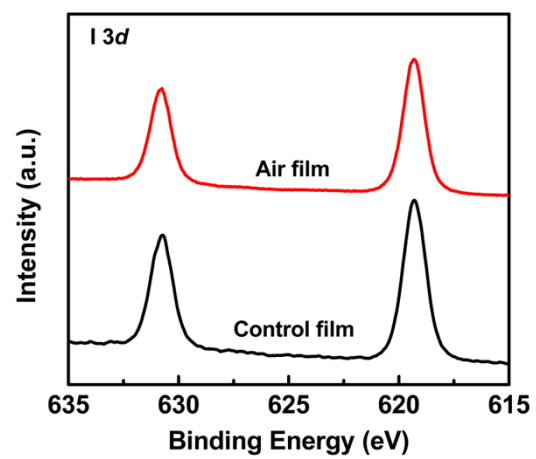


Fig. S3 XPS spectra for I 3d core-level energy.

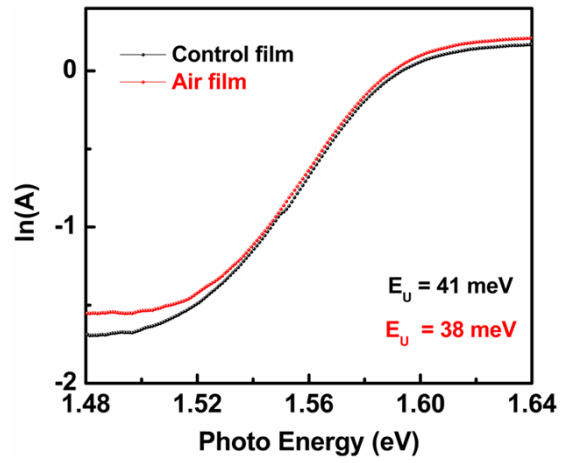


Fig. S4 The Urbach energy of the control film and the air film.

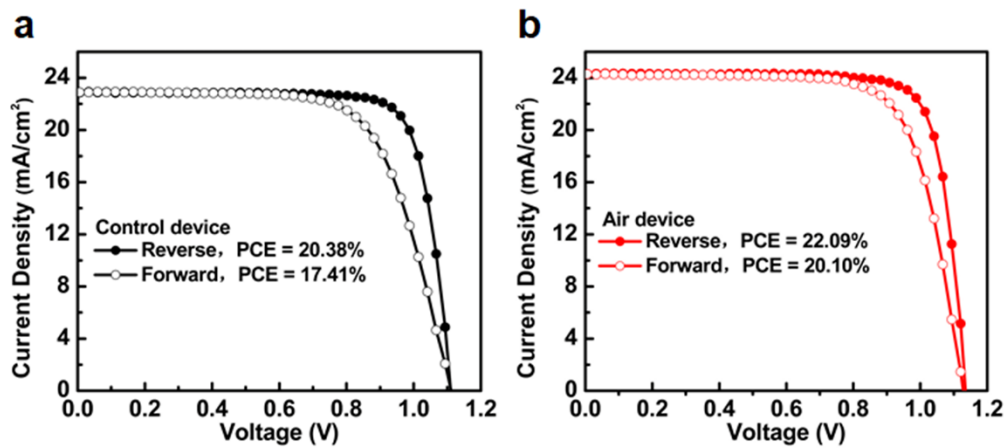


Fig. S5 Typical J - V curves of PSCs based on (a) the control film and (b) the air film.

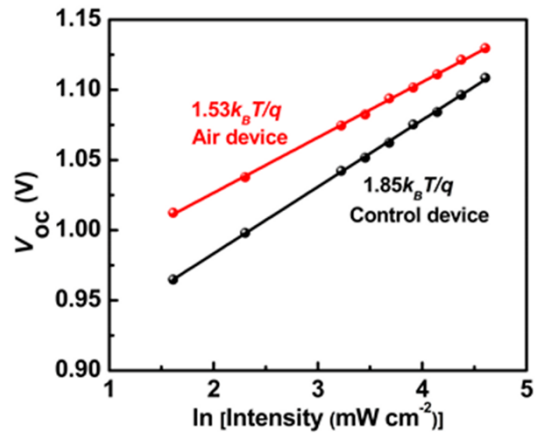


Fig. S6 V_{oc} versus illumination intensity of the two devices.

Table S1 the PL carrier lifetimes extracted from PL decay measurements.

	A_1	τ_1	A_2	τ_2	τ_{ave}
Control film	0.20	150.50	0.80	1408.53	1376.39
Air film	0.12	231.58	0.88	1670.09	1643.43

Note: $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$

Table S2. The hysteresis parameters derived from the $J-V$ curves of the control device and the air device.

Device	Scan direction	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	H-index (%)
Control	Reverse	1.109	22.92	80.10	20.38	14.6
	Forward	1.111	22.90	68.42	17.41	
Air	Reverse	1.130	24.35	80.30	22.09	9
	Forward	1.126	24.26	73.53	20.10	

Note: $H\text{-index} = (PCE_{\text{reverse}} - PCE_{\text{forward}})/PCE_{\text{reverse}}$

Table S3 Fitting results of Nyquist Plots.

Condition	Control device	Air device
R_s (Ω)	23.57	13.54
R_{rec} (Ω)	11368	17628

Table S4 Build-in potential (V_{bi}) analyzed from the Mott-Schottky Plots.

Condition	Control device	Air device
V_{bi} (V)	0.96	1.00