Microstructure variations induced by excessive PbX_2 or AX within perovskite thin films

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Experiment section

Materials.

The $HC(NH_2)_2I$ and CH_3NH_3Br were prepared according to procedure mentioned in previous work. All the commercial materials were used as received, including dimethyl sulfoxide (99.50%)

, Sigma-Aldrich), ethanol (AR Beijing Chemical Works), chlorobenzene (99.9%, Aladdin Industrial Corporation), hydrogen iodide (57%, Alfa Aesar), N,N-dimethylformamide (99.99%, Sigma-Aldrich), 4-tertbutylpyridine (99.90%, Sigma-Aldrich), spiro-OMeTAD (Xi'an Polymer Light Technology Corp.), lithium bis(trifluoromethylsulphonyl)imide (99.95%, Sigma-Aldrich), PbBr₂ (99.9%, Aladdin Industrial Corporation), PbI₂ (99.99%, Sigma-Aldrich) and CsI (99.90%, Aladdin Industrial Corporation).

Preparation of SnO₂ nanoparticle film. The SnO₂ colloid precursor (Alfa Aesar, tin (IV) oxide, 15.6% in H₂O colloidal dispersion) were diluted by H₂O to 2.67% before used. The final solution was spin coated onto glass/ITO substrates at 4000 r.p.m. for 30s, and sequently baked on a hot plate at 150 °C for 30 min in air.

Perovskite precursor solutions.

To be convenient, we marked different perovskite solutions without cesium introduction as FAMA. FAMA perovskite solutions were prepared by mixing different amount of FAI, PbI₂, MABr, PbBr₂ in anhydrous DMF: DMSO 4:1 (v:v). Furthermore, we defined the stoichiometric ratio of PbX2:AX (X: I or Br) as γ and summarized the detailed composition of the resulted precursor solutions in **Table S1**.

	PbI ₂ (M)	PbBr ₂ (M)	PbBr ₂ (M) FAI (M)	
γ=1.2	1*1.2	0.2*1.2	2*1.2 1 0.2	
γ=1.1	1*1.1	0.2*1.1	1	0.2
γ=1.05	1*1.05	0.2*1.05	1	0.2
γ=1.0	1*1.0	0.2*1.0	1	0.2
γ=0.91	1	0.2	1*1.1 0.2*1.1	
γ=0.83	1	0.2	1*1.2 0.2*1.2	

Table S1: summary of the detailed compositions for different PbX2:AX stoichiometric ratios.

CsI solution. CsI solution was deposited by dissolving CsI in pure DMSO with the concentration of 1.5 M;

 $(FAMA)_{95}Cs_5$ perovskite solution. $(FAMA)_{95}Cs_5$ perovskite solution was obtained by adding 15.8 μ L CsI into 300 μ L FAMA perovskite solution to achieve the desired cation composition.

Sample preparation and devices fabrication. The ITO substrate was sequentially washed with distilled water, acetone, ethanol and isopropanol. Then, diluted SnO₂ precursor was spin coated onto glass/ITO substrate at 4000 r.p.m. for 30s, and then annealed at 150 °C for 30 min in air. For the photo-active layer, one-step method used chlorobenzene as antisolvent was adopted. In detail, the perovskite solutions with different composition were spin-coated in a two-step program at 1000 and 5000 rpm for 10 and 30 s respectively. During the second step, 200 µL of chlorobenzene was poured on the spinning substrate 15 s prior to the end of the program. Straight after that, the as-fabricated films were baked at 100 °C for 1 h under a nitrogen atmosphere. After the perovskite annealing, 30 µL Spiro-OMeTAD solution doped with LiTFSI and tBP was deposited at 3000 rpm for 30 s. The hole transport material (HTM) solution was prepared by dissolving 80 mg spiro-OMeTAD, 30 µL 4-tert-butylpyridine and 35 µL Li-TFSI/acetonitrile (260 mg mL⁻¹) in 1 mL chlorobenzene. Finally, 100 nm Ag was thermally evaporated as counter electrode under a pressure of 5×10^{-5} Pa on top of the hole transport layer to form the back contact.

Characterization. One dimensional X-ray diffraction (XRD) spectra was obtained by using Rigaku D/MAX 2400 diffractometer with Cu K_c radiation. A cold field-emission scanning electron microscope equipment (SEM, Hitachi S-4800) was adopted to characterize top view morphology of perovskite thin films with varied stoichiometric ratios. Two-dimensional synchrotron radiation grazing incidence wide-angle X-ray scattering (GIWAXS) were performed at BL14B beamline, Shanghai synchrotron Radiation Facility with a wavelength of 0.6887 Å to analyze the crystallinity and orientation within the perovskite films. 2D GIWAXS data were acquired by using a MarCCD with a distance c.a. 450mm from the samples. J-V characteristics of photovoltaic devices were measured by using a Keithley 2400 source meter under simulated sunlight from an Oriel 300 solar simulator. The effective area of cells discussed in this work was 0.102 cm² defined by masks and the light intensity was calibrated by means of a KG-5 reference silicon solar cell.



Figure S1 a) XRD and b) UV-vis spectrum for perovskite films with corresponding stoichiometric ratios.



Figure S2 J-V curve for the champion devices with varied stoichiometric ratios as presented by γ .

Table	S2	Statistics	of	devices	performance	parameters	for	devices	based	on	different
compo	sitio	ns present	ed b	by:							

Sample	Voc (V)	Jsc (mA/cm ²)	PCE (%)	FF (%)
γ=1.2	1.054	21.59	15.35	67.43
γ=1.1	1.107	22.29	18.70	75.79
γ=1.05	1.114	22.68	19.68	77.9
γ=1.0	1.089	22.31	18.30	75.34
γ=0.91	1.078	21.90	16.84	71.32
γ=0.83	1.066	20.36	16.37	75.39



Figure S3 J-V curves with both reverse scan and forward scan directions for the typical devices with optimized excessive PbI_2

 Table S3 Summary of device performance parameters for both reverse scan and forward scan

 directions.

Scan direction	$V_{OC}(V)$	J _{SC} (mA cm ⁻²)	PCE (%)	FF (%)
Reverse scan	1.114	22.68	19.68	77.9
Forward scan	1.067	22.35	18.98	79.59



Figure S4 SCLC analysis for perovskite films with different stoichiometric ratios of PbI₂/AX.

	γ=1.2	γ=1.05	γ=1.0	γ <i>=</i> 0.83
Mobility (cm ² V ⁻¹ s ⁻¹)	2.07	2.61	2.39	0.89
Defect density (cm ⁻³)	3.65×10^{16}	3.08 × 10 ¹⁶	3.57×10^{16}	4.87×10^{16}

Table S4 Calculation results of carrier mobilities and defect densities derived from SCLC curves.



Figure S5 Time resolved photoluminescence decay for perovskite films with the four typical compositions.

	τ1 (ns)	τ2 (ns)
1.2	13.7	330.5
1.05	40.0	490.1
1.0	29.3	465.4
0.83	11.3	308.2

 Table S5 Statistics of the fitted data from TRPL spectra: