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Supporting Information

Temperature Gradient Induced Directional Growth of Perovskite Film

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Experimental section

Materials Synthesis

Zn power (AR), HCl (AR), KOH (AR) and Methylamine alcohol solution (AR) were purchased from Sinopharm. Dimethyl sulfoxide (DMSO, 99.9%), N,N-Dimethylformamide (DMF, 99.8%), Chlorobenzene (CB, 99.8%) were purchased from Sigma-Aldrich without further purification. Methylammonium iodide (MAI), Super Lead iodide (PbI_2), TiO_2(Dyesol, 18 NR-T) and Spiro-OMeTAD (99.8%) were purchased from Xi'an Polymer Light Technology Corp. (PLT).

Device Fabrication

Fluorine doped tin oxide (FTO)-coated glass was patterned by etching with Zn powder and 1 M HCl diluted in distilled water. The etched substrate was then cleaned with ethanol, saturated KOH solution in isopropanol, and water and then dried with clean dry air. Firstly, a 20-nm thick compact TiO_2 hole-blocking layer (The precursor are Titanium(IV) isopropoxide, 99.995% (metals basis) and Deionized water.) was deposited on the FTO-glass by atomic layer deposition (ALD). Subsequently, 300-nm thick TiO_2 mesoporous layer was deposited on the TiO_2 dense layer by spin-coating at a speed of 4000 rpm for 30 s from a diluted commercial TiO_2 paste (1:6 with ethanol by weight), followed by a sintering heat-treatment of 500 °C for 30 min in air. Then FTO glasses with spin-coated electron transport layer were transferred to glove box. The perovskite solution was prepared by mixing PbI_2: MAI (1:1 molar ratio) in DMF (1.33 M). After complete dissolution, 40 μL of perovskite solution was spin-coated on the mesoporous TiO_2 substrates in a two-step at a rotation speed of 1000 rpm for 10 seconds and 4000 rpm for another 30 seconds. 300 μL Chlorobenzene was drop-casted quickly 10 seconds before the 4000 rpm spin-coating finished. The perovskite films were then heated at 100 ℃ for 20 min.

For the constant temperature (CT-MA) and temperature gradient (TG-MA) methods, the as-prepared films were transferred to a home-made chamber to perform the gas healing. Details are as follows: For the CT-MA methods, we take 10 mL of methylamine alcohol solution in a weighing bottle and cap the bottle. Then take out the above-prepared perovskite film and clamp it with tweezers. Then open the bottle cap and place the perovskite film horizontally about 1cm above the liquid surface for about 2 seconds. And then the film is quickly removed from the CH_3NH_2 gas atmosphere and transferred to the glove box and annealed at 100 °C for 30 minutes. For the TG-MA methods, it is similar to the above process, except that the perovskite film prepared is placed on a 60 °C platform for pre-heat treatment, followed by methylamine gas healing. After removing the films from the CH_3NH_2 gas atmosphere, the films were quickly transferred to the glove box and annealed at 100 ℃ for 30 minutes. The Spiro-OMeTAD hole-transporting layer was prepared by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-tert-butylpyridine (96%, Sigma-Aldrich) and 17.5 μL of lithium bis(trifluoro-methanesulfonyl) imide (Li-TSFI, Sigma-Aldrich) solution (520 mg Li-TSFI (98%) in 1 mL acetonitrile (99.8%, Sigma-Aldrich) were added. After complete dissolution, 30 μL of Spiro-OMeTAD solution was deposited by spin-coating (3000 rpm, 30 s). Finally, 100 nm thick Au electrodes were thermally evaporated under vacuum to complete the PSCs fabrication.

Materials and Device Characterization

XRD spectra were measured by Ultima IV of Rigaku with Cu Kα radiation (1.5406Å). The UV-vis absorbance spectra were measured by Ocean Optics. Top view, cross-section SEM images were obtained with a field-emission scanning electron microscope (S-4800, Hitachi). Steady photoluminescence (PL) spectra were recorded on Ocean Optics excited at 460 nm. Transient photovoltage decay (TPV) measurements were done on a homemade system. The optical photos of the droplet were obtained through Contact angle measuring instrument CA100A. Electrochemical impedance spectroscopy (EIS) were measured by electrochemical workstation (ZAHNER-Elektrik GmbH & Co. KG, Germany). AFM measurements were performed in contact mode using AFM microscope (5400, Agilent, USA). I-V curves of the as-fabricated PSCs with different scanning directions 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). The typical active area of PSCs is 0.09 cm^2 defined by a 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.

Supplementary Figures:


primary 2 min 10 min 30 min 60 min

Figure S1. The optical photos of the droplet after degassing for different time.

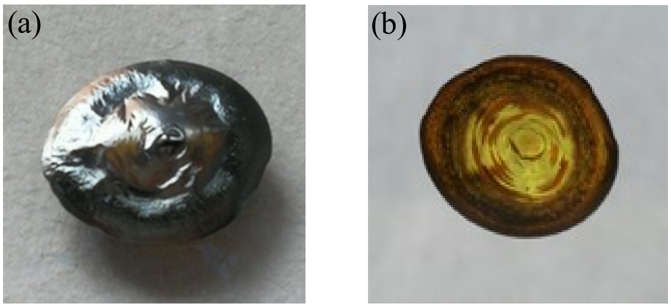

Figure S2. The optical photos of the droplet taken from the top and (b) bottom.

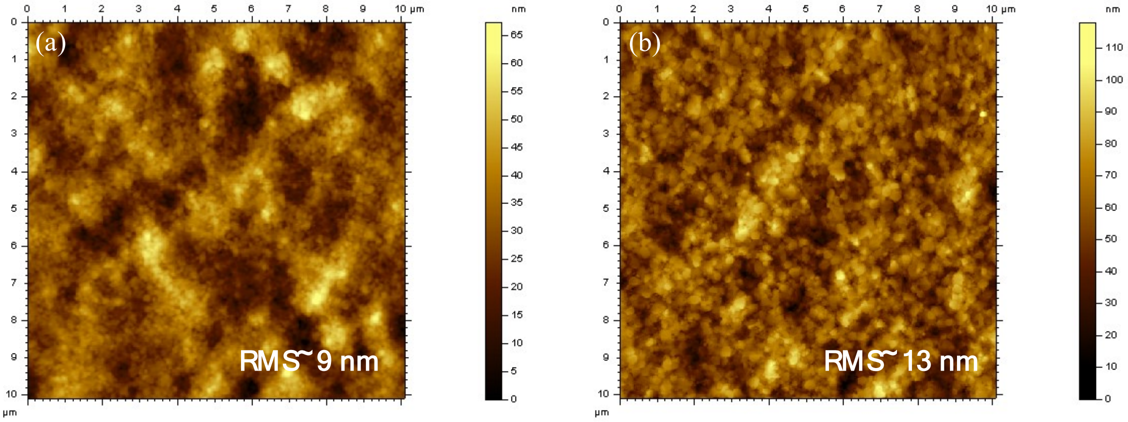

Figure S3. AFM images of top surfaces of MAPbI$_3$ perovskite thin films: (a) CT-MA film and (b) TG-MA film.

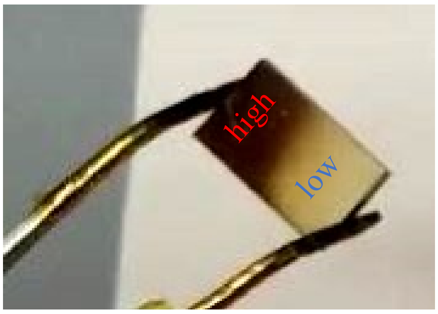

Figure S4. The color recovery behavior of the perovskite film at different temperature regions after removing the MA gas atmosphere.

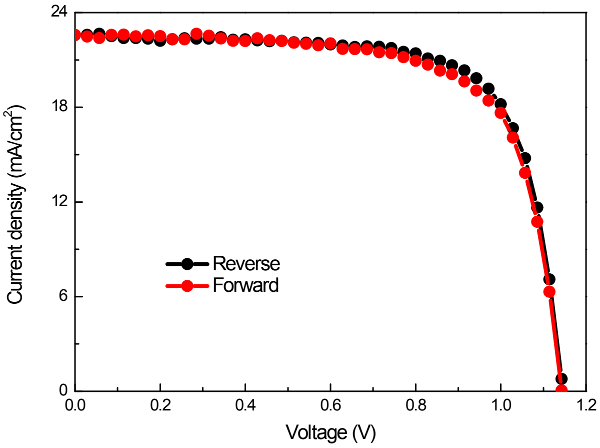

Figure S5. Forward- and Reverse J-V curves of the devices prepared by the TG-MA method.

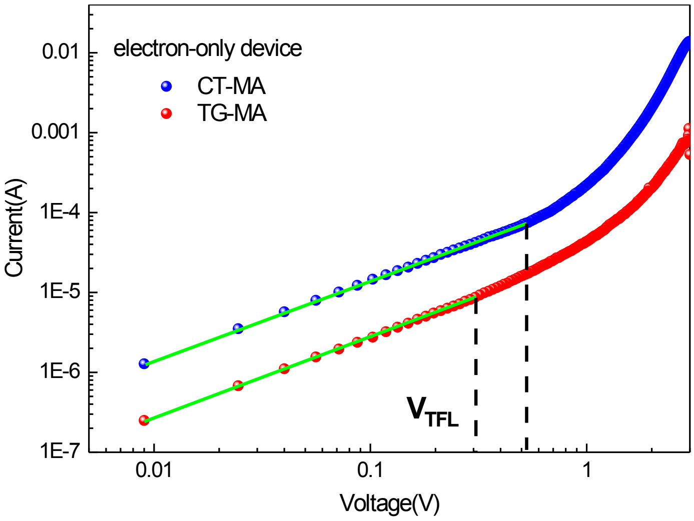

Figure S6. SCLC curves of electron-only device FTO/c-TiO_2/m-TiO_2/perovskite/PCBM/Au.

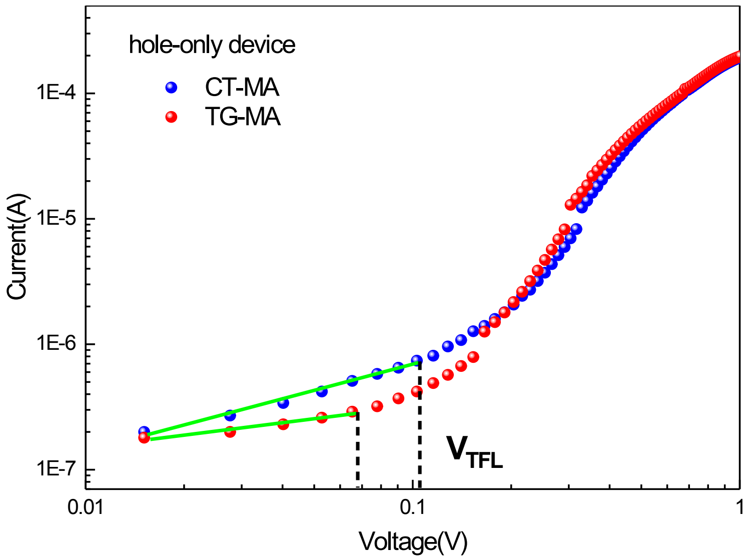

Figure S7. SCLC curves of hole-only device FTO/NiO/perovskite/Spiro-OMeTAD/Au.

Table S1 Device parameters of the PSCs prepared by the CT-MA and TG-MA methods.

Device condition	**V_{OC} (V)**	**J_{SC}(mA/cm^2)**	**FF(%)**	**PCE(%)**
CT-MA	1.09	20.52	72.18	16.14
TG-MA	1.15	22.53	77.60	20.16

Table S2 Detailed device parameters based on 15 devices.

Numbering	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
CT-MA-1	1.093	20.51	65.45	14.63
CT-MA-2	1.094	20.48	68.04	15.19
CT-MA-3	1.083	20.47	67.05	14.82
CT-MA-4	1.090	20.54	72.84	16.31
CT-MA-5	1.090	20.51	74.10	16.57
CT-MA-6	1.084	20.5	73.99	16.38
CT-MA-7	1.079	20.52	74.25	16.45
CT-MA-8	1.075	20.49	73.60	16.29
CT-MA-9	1.091	20.46	74.29	16.57
CT-MA-10	1.090	20.55	75.33	16.87
CT-MA-11	1.089	20.54	75.05	16.80
CT-MA-12	1.089	20.48	72.24	16.13
CT-MA-13	1.091	20.49	72.49	16.19
CT-MA-14	1.085	20.52	73.46	16.43
CT-MA-15	1.078	20.54	72.17	16.01
TG-MA-1	1.139	22.54	75.00	19.26
TG-MA-2	1.142	22.56	77.65	20.01
TG-MA-3	1.148	22.58	76.34	19.79
TG-MA-4	1.153	22.53	77.60	20.16
TG-MA-5	1.142	22.47	74.44	19.10
TG-MA-6	1.144	22.55	75.77	19.55
TG-MA-7	1.151	22.55	71.71	18.61
TG-MA-8	1.150	22.51	72.28	18.71
TG-MA-9	1.154	22.54	74.65	19.42
TG-MA-10	1.153	22.47	73.56	19.06
TG-MA-11	1.150	22.49	74.35	19.23
TG-MA-12	1.152	22.53	73.25	19.01
TG-MA-13	1.152	22.52	73.34	19.03
TG-MA-14	1.149	22.49	74.13	19.16
TG-MA-15	1.146	22.54	74.02	19.12