

Electronic Supplementary Information

Long-term Stability of Organic-Inorganic Hybrid Perovskite Solar Cells with High Efficiency Under High Humidity Conditions[†]

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Materials:

Lead iodide (PbI_2 , 99%) was purchased from Sigma-Aldrich; The methylammonium iodide (MAI) (purity $\geq 99.5\%$), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spiro-bifluorene (spiro-OMeTAD) (purity $\geq 99.8\%$), Lithium-bis(trifluoromethanesulphonyl) imide (Li-TFSI) (purity $\geq 99.5\%$) and 4-tert-Butylpyridine (purity $\geq 96\%$) were purchased from Xi'an p-OLED Technology Corp; Polyvinyl alcohol (PVA) (molecular weight:20000 DA) was obtained from Shanghai YingJia Industrial Development Co.,Ltd; Dimethylformamide (DMF, anhydrous, 99.8%), Dimethyl sulfoxide (DMSO, anhydrous, 99.9%), Titanium tetrachloride (TiCl_4 , anhydrous, 99.5%) and Chlorobenzene (anhydrous, 99.9%) were purchased from Alfa Aesar; All the chemicals were used directly without further purification.

Device fabrication :

The fabrication of device was according to the previously reported procedure with some modification.^[1] Patterned FTO/glass substrates were ultrasonically cleaned with deionized water, acetone and ethanol respectively, and then followed by oxygen plasma cleaning for 10 min before use. FTO substrates were immersed into 200 mM TiCl_4 aqueous solution for 60 min at 70 °C and then washed with deionized water and ethanol. The spin-coating precursor solution was prepared by dissolving 0.191g of MAI and 0.553g of PbI_2 in 1 mL of anhydrous DMF and DMSO (with a volume ratio of 4:6) and pre-dissolved PVA (2 mg mL^{-1} , 3 mg mL^{-1} and 5 mg mL^{-1}) solutions, and then stirring continuously overnight at 60 °C in the glove box. The resulting solutions were filtered with 0.20 μm PTFE filters before use. After the clean FTO substrates with compacted TiO_2 were transferred into glove box, three solutions were spin coated on the FTO/c- TiO_2 substrates at 1000 rpm for 15 s, 6000 rpm for 55 s, after 25 s of spin-coating at 6000 rpm, 500 μL of chlorobenzene was quickly dropped onto the substrate and then the substrate were thermally annealed at 100 °C for 5 minutes. After substrate cooling to room temperature, hole transport material solution was spin coated onto perovskite films at 5000 rpm for 30s in glove box, where the solution of spiro-MeOTAD/chlorobenzene (72.3 mg mL^{-1}) was prepared by adding 28.8 μL 4-tert-butylpyridine and 17.5 μL Li-TFSI/acetonitrile (520 mg mL^{-1}). Finally, 80 nm thick gold electrodes were deposited on the top of HTL by thermal evaporation at 1.0×10^{-4} Pa. For each solar cell, the active area was determined to be 0.07 cm^2 .

Characterizations :

The UV-vis spectra are obtained on a UV2450 Spectrophotometer, A Fourier Transform Infrared Spectrometer (FT-IR, Nicolet IS10, Thermo Scientific) and Raman spectra (Raman Microscope, DXR, Thermo Scientific) are used to characterize the functional group of PVA. For FT-IR, the KBr pellet was used for the powder samples, and different perovskite power with and without PVA additive was performed in the range of 4000 - 500 cm^{-1} . Raman spectra were collected on a thermal dispersive spectrometer using a laser with an excitation wavelength of 532 nm at a laser power of 10 mW. Contact angle of different precursor solutions via dripping on the FTO glass with compact TiO_2 are conducted using a contact angle tester (JC2000D1, Powereach). The crystal structures and stability of the films are determined by X-ray diffraction (XRD) analysis with Cu K α radiation (D/max 2500 PC, Rigaku Corporation, Japan; 2 theta, $\lambda = 0.1542$ nm) at 40 kV. Field emission scanning electron microscope (FESEM, Philips XL30 FEG) is applied to analyze the surface and cross-sectional morphology. Atomic force microscope (AFM) was carried out using VEECO Nano Man VS Scanning Probe Microscope (SPM) in "tapping" mode. The photovoltaic characteristics are measured under 100 mW cm^{-2} (AM 1.5G) illumination using a Keithley Model 2400 multisource meter (Cleveland, OH, USA). A solar simulator (500 W Xe lamp) (ORIEL Solar 3A-94023A, America) is employed as the light source. For the stability of Pero-SCs, the unsealed cells were kept in a dark box in high humidity environment, and were tested every few days. All measurements mentioned above were conducted in ambient environment with humidity of 85 - 95% without any encapsulation.

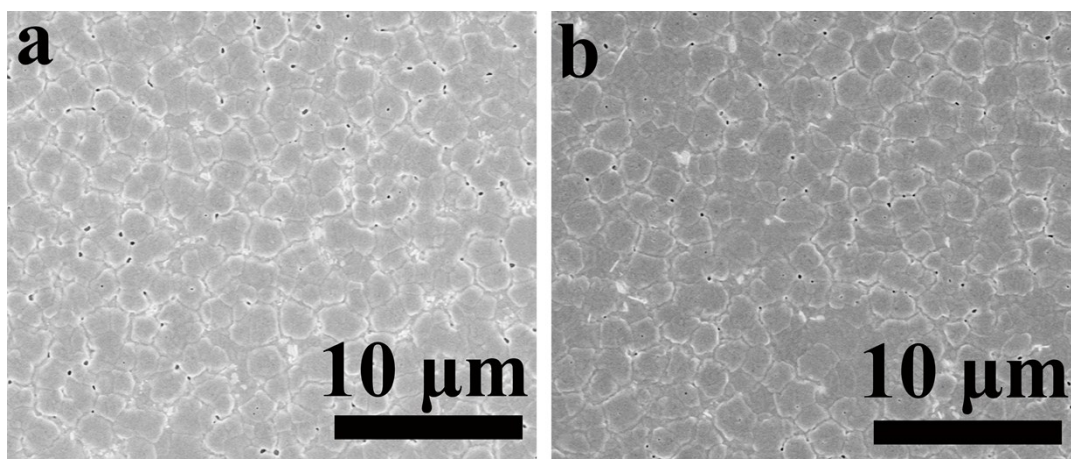


Fig. S1 SEM images (scan size = 20 $\mu\text{m} \times 20 \mu\text{m}$) of perovskite films with different concentrations of PVA. a) pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, b) perovskite film with PVA concentration of 2 mg mL^{-1} .

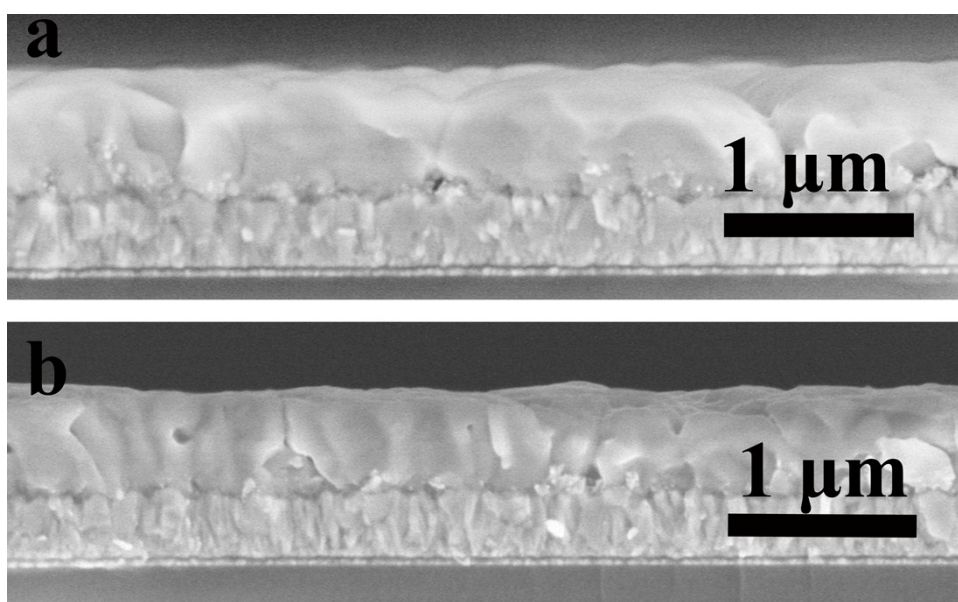


Fig. S2 Cross-sectional SEM images of the perovskite solar cells without (a) and with PVA (b).

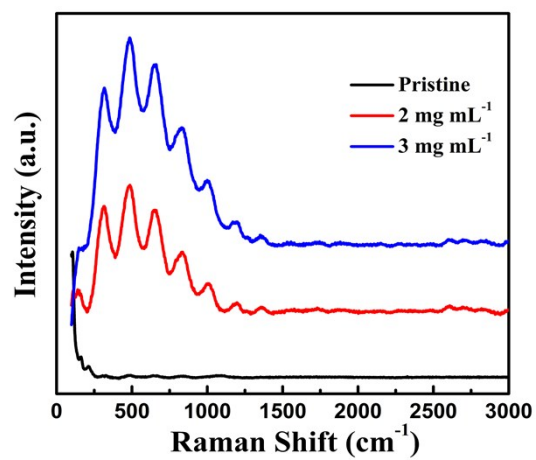


Fig. S3 Raman spectra of three types of sample on FTO substrates.

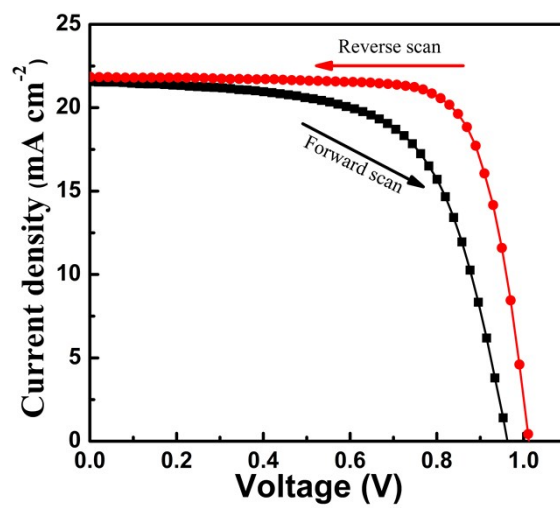


Fig. S4 J - V characteristics under both reverse and forward scan directions.

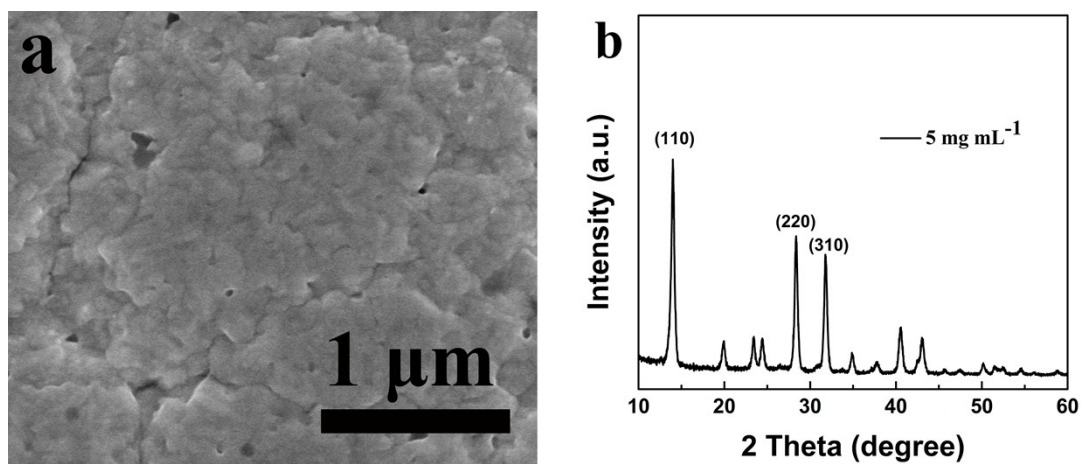


Fig. S5 (a) Top-view SEM images of the perovskite film with excess PVA (5 mg mL^{-1}) (b) X-ray diffraction patterns of the corresponding perovskite films.

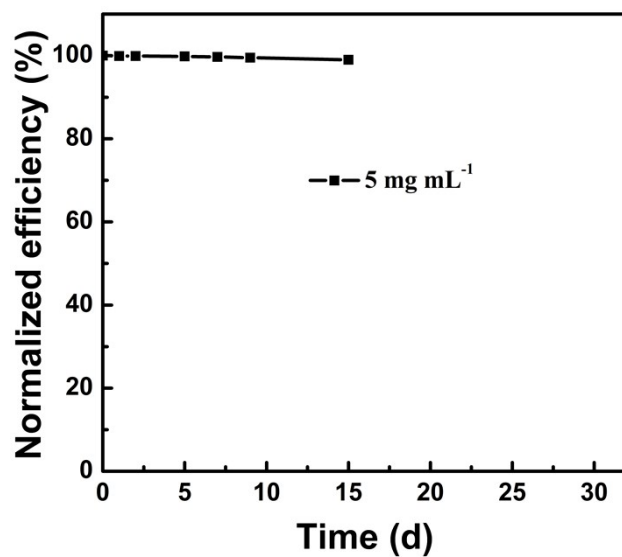


Fig. S6 Efficiency evolution of the perovskite solar cells with PVA 5 mg mL^{-1} in a high humidity (85%–95% RH) environment at room temperature without encapsulation for 15 days

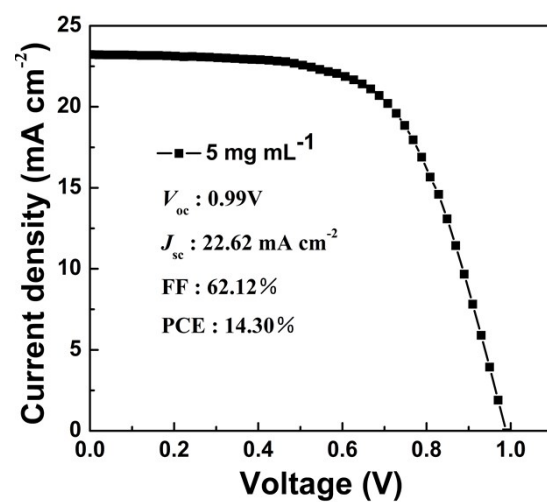


Fig. S7 J - V curves of devices doped with PVA concentration of 5 mg mL⁻¹

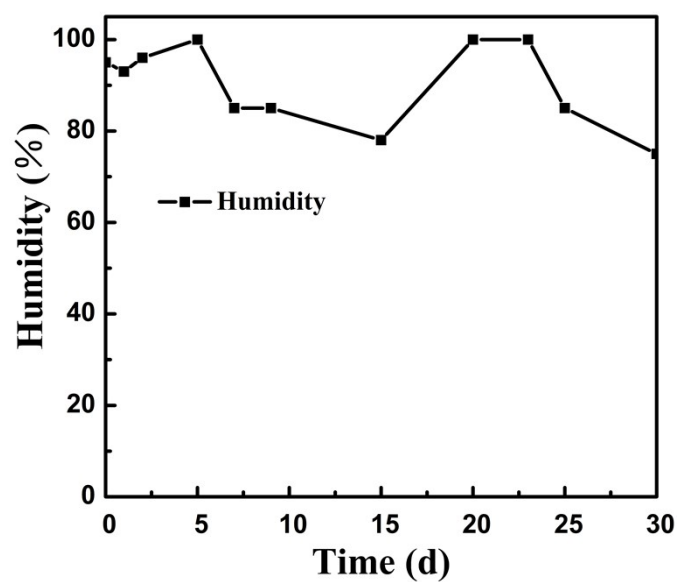


Fig. S8 The evolution of humidity in of test environment.

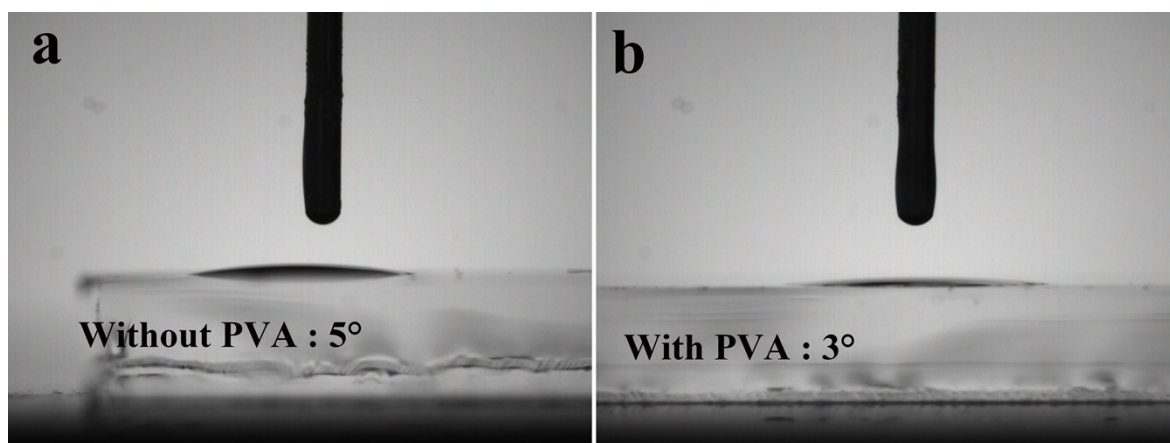


Fig. S9 Contact angle of different precursor solution with and without PVA. The smaller contact angle of the precursor solution containing PVA (3 mg mL^{-1}) dipped on the FTO glass suggests a better wettability. a) $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution without PVA, b) $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution with PVA concentration of 3 mg mL^{-1} .

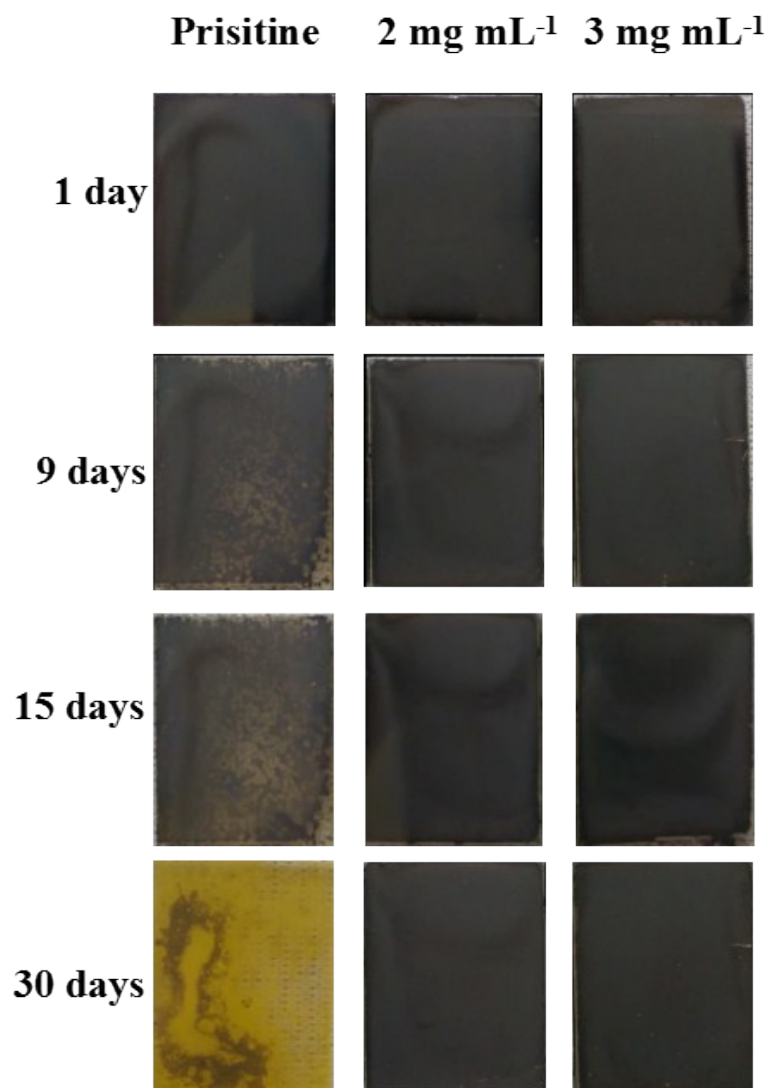


Fig. S10 Images of various perovskite films before and after exposed to atmosphere with 85-95% relative humidity.

[1] B. Cai, W.-H. Zhang, J. Qiu, *Chinese Journal of Catalysis* **2015**, 36, 1183-1190.