

Supporting Information

Efficient and Stable Full-Printed Mesoscopic Perovskite Solar Cells with Potassium Hexafluorophosphate Additives

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EXPERIMENTAL SECTION

MATERIALS AND REAGENTS

All materials and reagents are used as is, without any purification, unless otherwise stated. Lead iodide (PbI₂, >99.99%), 5-aminopentanoic acid hydroiodide (5-AVAI), methylammonium iodide (MAI, ≥99.5%) and γ -butyrolactone (GBL) were purchased from Xi'an P-OLED Company. KPF₆ was purchased from Innochem. titanium dioxide, zirconium dioxide and carbon pastes were purchased from Wonder Solar, China. FTO was supplied by China Advanced Electronics Technology Co.

PRECURSOR SOLUTION PREPARATION

Dissolve 0.0069g 5-AVAI, 0.1280g MAI, 0.3842g PbI₂ and different percent molar ratios of KPF₆ (0.5%, 1.0%, 1.5%) in 1 ml of γ -butyrolactone solution, stir on a hot table at 50°C for 4 h and then cool to room temperature and keep aside in a

desiccator.

DEVICE PREPARATION

Fluorine-doped tin oxide (FTO)-coated glass substrates were peeled by laser etching to form separate electrode patterns, which were successively ultrasonically cleaned with detergent, deionized water anhydrous ethanol and then dried and set aside. Subsequently, the dense TiO₂ layer was prepared by spray pyrolytic deposition by spraying an ethanol solution of isopropanol bis(acetylacetonate) titanium on the FTO at 450 °C and then cooled to room temperature. Then a mesoporous TiO₂ layer with a thickness of about 500 nm was printed on the dense TiO₂, and then a mesoporous ZrO₂ layer with a thickness of nearly 2-2.5µm was printed on it after annealing at 500 °C for 40 min and cooling to room temperature. Finally, the carbon electrode was printed and annealed at 400 °C for 30 min, cooled to room temperature, and the perovskite precursor solution was applied dropwise to the carbon film, left for ten minutes, and then annealed at 53 °C for 4 h on a hot bench.

CHARACTERIZATION

The surface morphology, cross-sectional morphology and the corresponding energy dispersive X-ray spectra of the perovskite films were observed with a field emission scanning electron microscope (FEI, Quanta FEG 450, USA). Absorption spectra were recorded using a UV-vis spectrophotometer (PerkinElmer, Lambda 365, USA). The crystal properties of the perovskite films deposited on FTO/mp-TiO₂ were examined using an X-ray diffractometer (Bruker, D8 Advance, Germany). Steady-state PL and time-resolved PL of chalcogenide films deposited on Glass/mp-ZrO₂ and FTO/mp-TiO₂ substrates were measured using a fluorescence spectrometer (Edinburgh, FS 5, U.K.). The surface potential was measured by KPFM and AFM (Bruker, multimode 8, Germany). The photocurrent density-voltage (J-V) curves of the devices were recorded by a Keithley 2400 source/instrument unit and solar simulator (SAN-EI, XES-40S3, Japan) with simulated AM 1.5G illumination of 100 mW⁻². The QE-R solar cell spectral response measurement system (Enlitech, QE-R,

China) was used to IPCE spectra were measured. XPS and UPS were performed by a Thermo Fisher Scientific.

XPS and UPS were performed by a Thermo Fisher Scientific (ESCALAB 250Xi) system using monochromatic Al K α X-ray excitation (1486.6 eV).

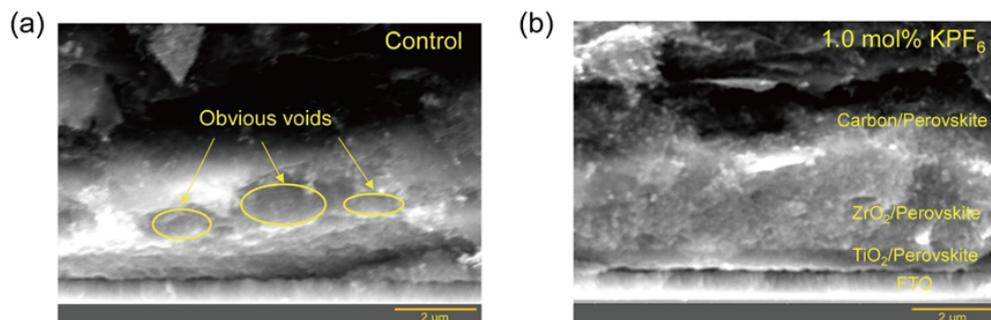


Figure S1. Cross-sectional SEM of the devices. (a) without KPF₆, (b) with KPF₆.

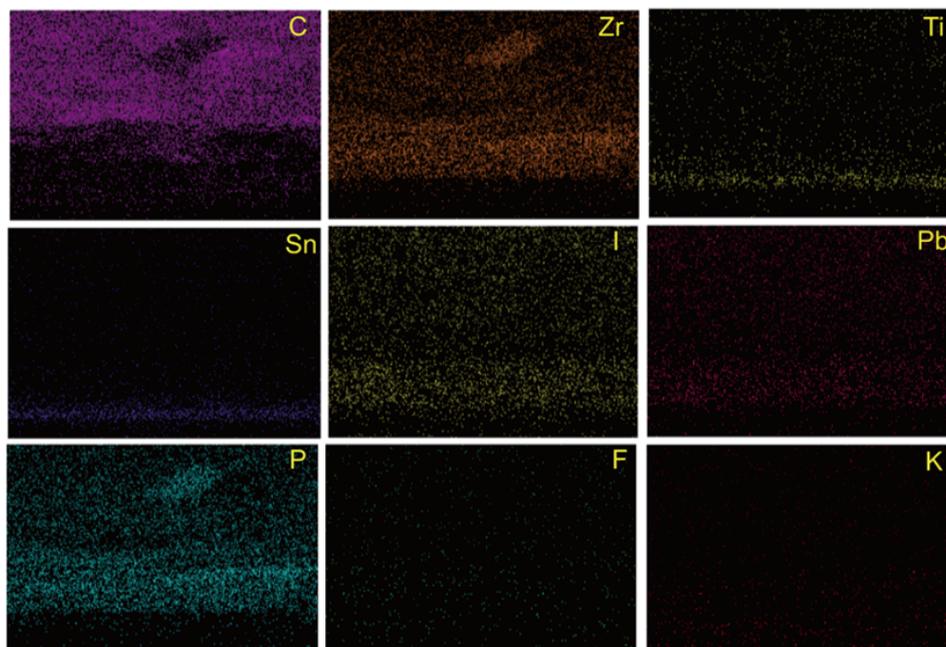


Figure S2. The cross sectional elements distribution (C, Zr, Ti, Sn, I, Pb, P, F and K) of the device with KPF₆ is measured by EDS.

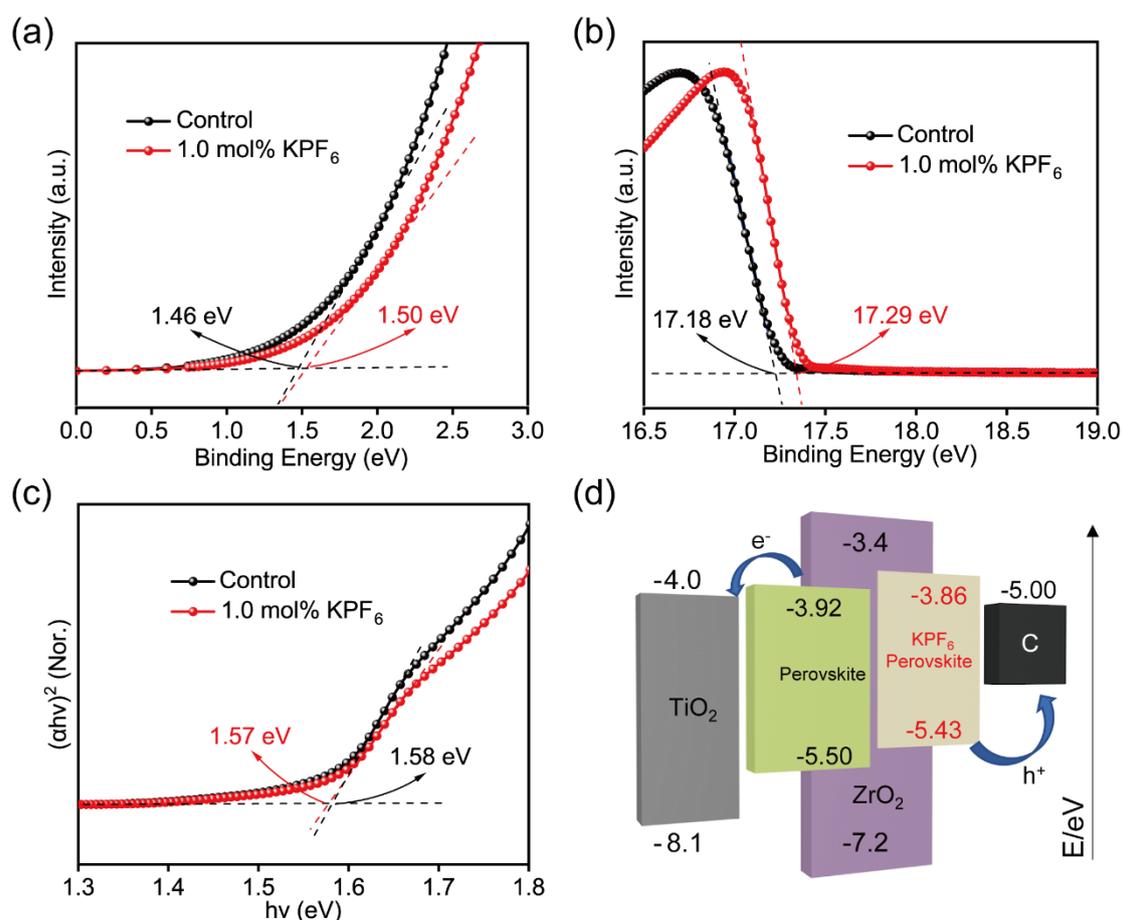


Figure S3. (a) Cut-off energy region of the UPS spectra of without and with 1.0mol% KPF_6 perovskite films. (b) Near Fermi edge region of the UPS spectra of without and with 1.0mol% KPF_6 perovskite films. (c) Tauc plots of the perovskite films without and with 1.0mol% KPF_6 . (d) Energy level change diagram of MPSCs.

Table S1. Fitting parameters of the Glass/mp-ZrO₂/perovskite with (1.0mol%) and without KPF_6 obtained from the TRPL spectra.

KPF_6	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
Without	0.58	1.76	0.42	13.60	11.81
With	0.63	2.57	0.37	22.33	19.03

Table S2. Fitting parameters of the Glass/mp-TiO₂/perovskite with (1.0mol%) and without KPF₆ obtained from the TRPL spectra.

KPF ₆ (mol%)	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{ave} (ns)
0	0.68	1.60	0.32	17.18	14.56
1.0	0.67	1.45	0.33	12.31	10.21

Table S3. Fitting values of EIS measurements for the without and with 1.0mol% KPF₆ MPSCs.

Device	Rs (Ω)	Rct (Ω)	CPEct (F)
Control	17.42	3644	2.56×10 ⁻⁸
1.0 mol% KPF ₆	16.63	1139	1.85×10 ⁻⁸

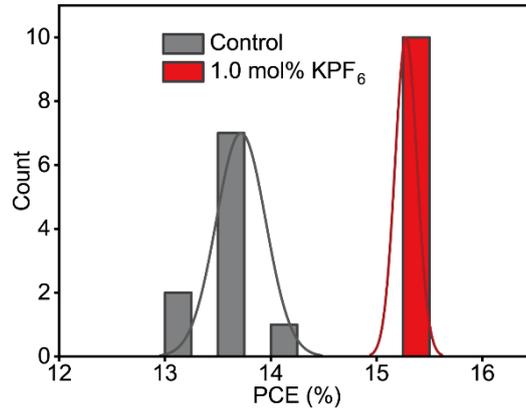


Figure S4. The PCE Statistical histogram of without and with 1.0mol% KPF₆ MPSCs.

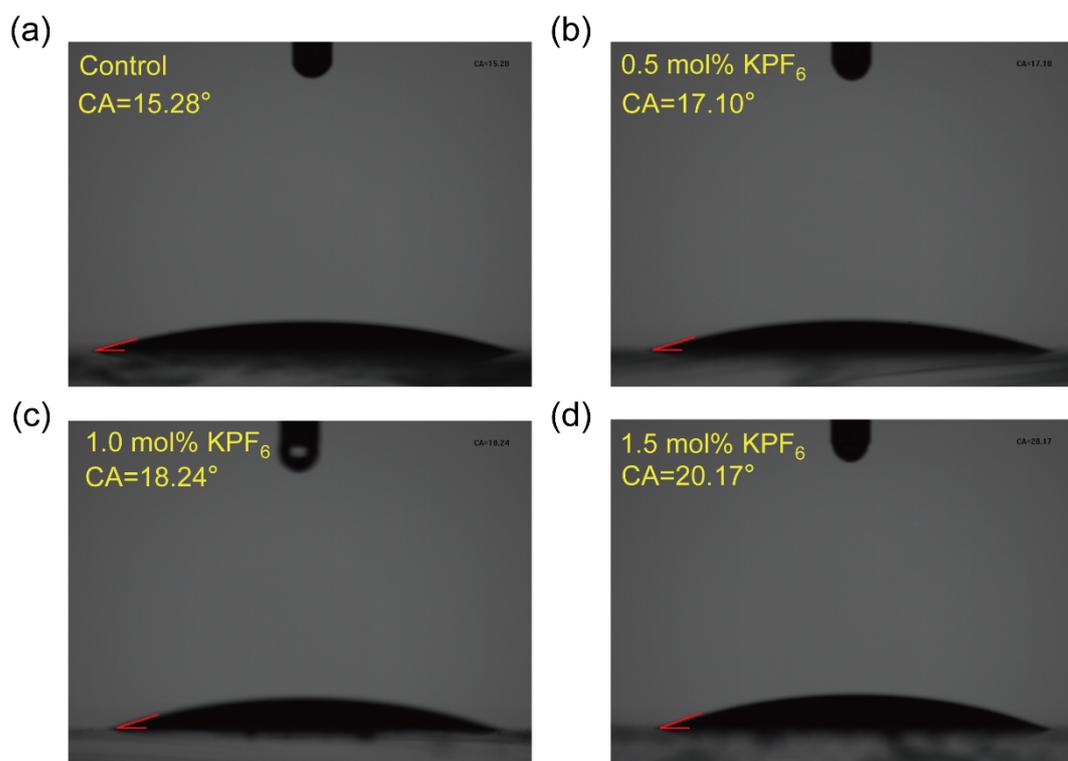


Figure S5. (a-d) Contact angle between water and carbon electrode containing different concentrations of KPF_6 .