

Electronic Supplementary information

KF-doped SnO₂ as an electron transport layer for efficient inorganic CsPbI₂Br perovskite solar cells with enhanced open-circuit voltages

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Materials

The SnO₂ colloid solution (tin (IV) oxide, 15% in H₂O colloidal dispersion liquid) was purchased from Alfa Aesar. Potassium fluoride (KF, 99.5%) was purchased from Aladdin. Lead (II) bromide was purchased from TCI (Shanghai) Development Co. Ltd. Chlorobenzene (anhydrous, 99%), acetonitrile (anhydrous, 99.8%), and dimethyl sulfoxide (DMSO, 99.8%) were purchased from Acros. Lead (II) iodide (PbI₂, 99.9%), cesium iodide (CsI, 99.9%), 4-*tert*-butylpyridine (TBP, 96%), and tris(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine) cobalt (III) tri(bis(trifluoromethylsulphonyl) imide) (FK 209) were purchased from Xi'an Polymer Light Technology Corp. 2,2',7,7'-Tetrakis [N, N-di(4-methoxyphenyl)amino]-9,9'-spiro-bifluorene (Spiro-OMeTAD) was purchased from Shenzhen Feiming Science and Technology Co. Ltd.

Preparation of the solutions

Precursor for electron transport layer (ETL): The 15 wt% SnO₂ solution was diluted with pure water to obtain the dilute solution with a concentration of 3 wt%. And for different SnO₂-KF solutions with various concentrations of KF, KF (4-8 mg) was dissolved in 1 mL of dilute SnO₂ solution.

CsPbI₂Br precursor: The perovskite precursor solution (1.2 M) was prepared by dissolving 0.3118 g of CsI, 0.2202 g of PbBr₂, and 0.2766 g of PbI₂ in 1 mL of DMSO, and then stirred for 2 hours at 60 °C.

Spiro-OMeTAD: 72.3 mg of Spiro-OMeTAD, 28.8 μL of TBP, and 28.8 μL of FK209 (300 mg/mL in acetonitrile) were dissolved in 1 mL of chlorobenzene.

Fabrication of photovoltaic solar cells

The indium tin oxide (ITO)-coated glass was sequentially cleaned with water, acetone, and isopropyl alcohol for 30 minutes at each step, and then dried in the oven at 75 °C. Before use,

the ITO substrates were pretreated by UV-O₃ for 15 min. The ETL solution was spin-coated on the ITO at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min. After cooling, the substrates were transferred into a glove box for the preparation of the perovskite layer. CsPbI₂Br perovskite layers were deposited on the ETL with a one-step spin-coating (3000 rpm for 30 s). Next, the perovskite film was annealed at 42 °C for about one minute and then at 160 °C for 10 minutes. After the resulting film was cooled to room temperature, Spiro-OMeTAD solution was spin-coated at 4000 rpm for 20 s on the CsPbI₂Br. Finally, MoO₃ (10 nm) and metal silver electrode (100 nm) were deposited by thermal evaporation.

Characterization

The particle size distributions of the SnO₂ and SnO₂-KF solution were measured by Laser Particle Size and Zeta Potential Analyzer (BI-200SM, BROOKHAVEN). The AFM images were measured by Scanning Probe Microscope, SPM (Dimension Icon, Bruker). UV-vis absorption spectroscopy was performed by using a Lambda35 spectrophotometer. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al K α source (15 kV, 10 mA). X-Ray diffraction (XRD) spectra were measured by a Rigaku MiniFlex II diffractometer equipped with a Cu K α radiation. Top-view scanning electron microscope (SEM) images were recorded on a SU-8010. Photoluminescence (PL) and time-resolved PL were measured with an Edinburgh Instruments FLS 980 spectrometer equipped with a 450 W xenon lamp and a 60 W μ F flash lamp as the excitation sources. Perovskite solar cells were performed in air (with relative humidity of \sim 60%) with encapsulation and the active areas were fixed at 6.25 mm². The *J-V* curves were measured using an Oriel Sol3A simulator (Newport) under AM 1.5 irradiation (100 mW/cm²), and recorded using a Keithley 2400 source measurement unit. The light intensity was calibrated by a standard Si reference solar cell that has been certified by the National Renewable Energy Laboratory (NREL). For device stability testing, all the PVSCs were stored and periodically tested in air under ambient conditions. The ambient conditions for the device storage in air were the darkness, temperature of 25 °C, and relative humidity of \sim 60%. EQE measurements were conducted by using a Newport EQE measuring system. The electron mobility is calculated by the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8d^3}$$

where J is the current density, ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant of ETL, μ is the electron mobility, V is the voltage, d is the thickness of ETL.¹ The trap state density is calculated by the following equation:

$$N_t = \frac{2\varepsilon_0\varepsilon_r V_{TFL}}{eL^2}$$

where ε is the relative dielectric constant of the perovskite layer, ε_0 is the vacuum permittivity, V_{TFL} is the trap-filled limit voltage, e is the electronic charge, and L is the thickness of perovskite layer.²

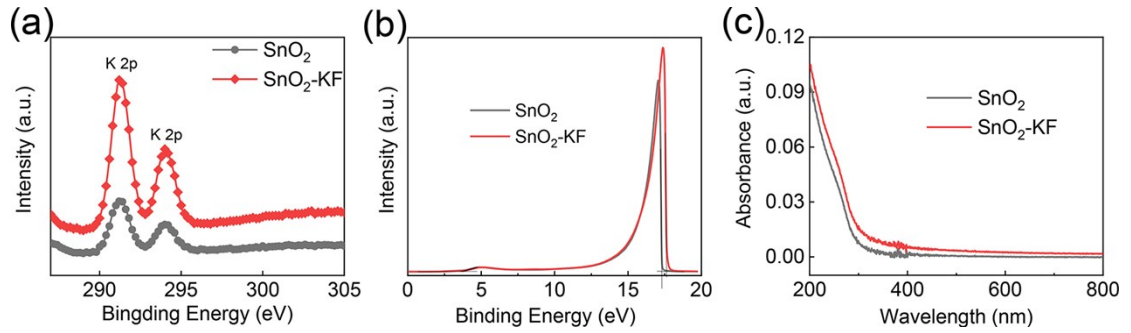


Fig. S1. (a) The XPS spectra of the K 2p orbital of SnO₂ and SnO₂-KF films. (b) The full UPS spectra of SnO₂ and SnO₂-KF films. (c) The absorption spectra of SnO₂ and SnO₂-KF films on the glass substrate.

Table S1. UPS parameters for SnO₂ and SnO₂-KF films.

Sample	$E_{\text{cutoff}}/\text{eV}$	$E_{\text{onset}}/\text{eV}$	VBM /eV	E_g/eV	CBM /eV
SnO ₂	17.32	3.38	7.28	4.05	3.23
SnO ₂ -KF	17.63	3.70	7.29	3.95	3.34

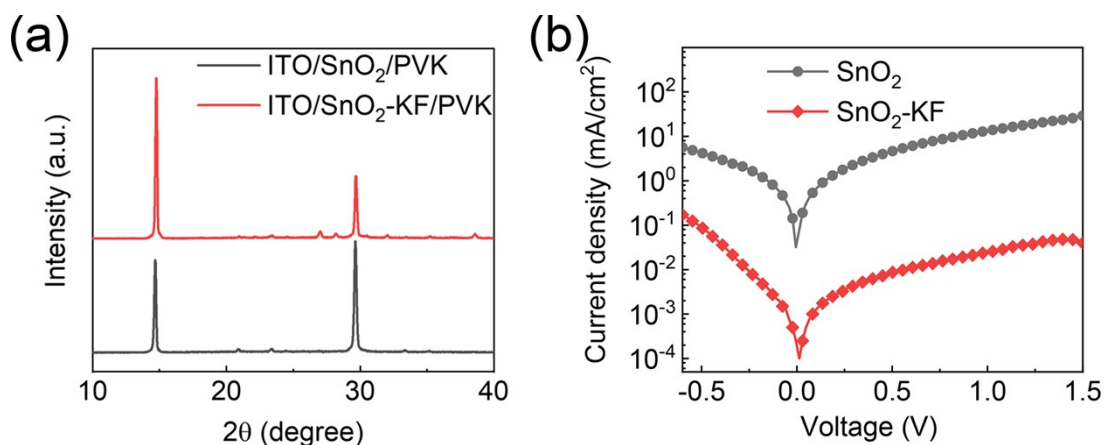


Fig. S2. (a) XRD patterns of the perovskites deposited on different ETLs. (b) J - V curves of perovskite solar cells based on SnO_2 and SnO_2 -KF under dark.

Table S2. TRPL decay parameters of the CsPbI_2Br films on SnO_2 film and SnO_2 -KF film.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{avg} (ns) ^a
SnO_2 /Perovskite	0.6818	47	1.642	53	1.38
SnO_2 -KF/Perovskite	0.2831	2.6	13.34	97	13.33

$$^a \tau_{avg} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$

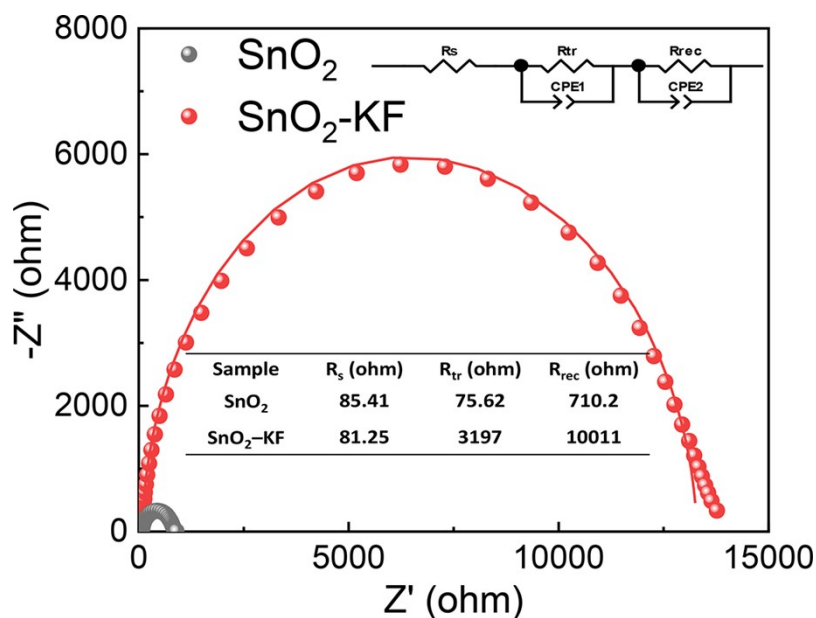


Fig. S3. Nyquist plots of the PVSCs based on two different ETLs.

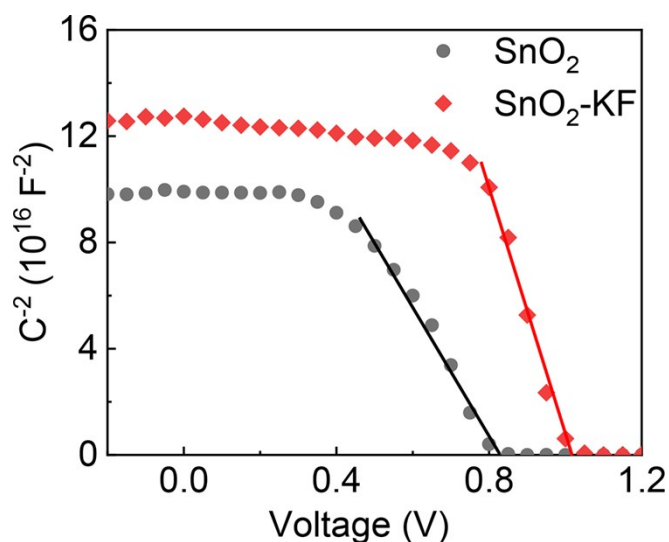


Fig. S4. Mott–Schottky plots of the PVSCs based on two different ETLs.

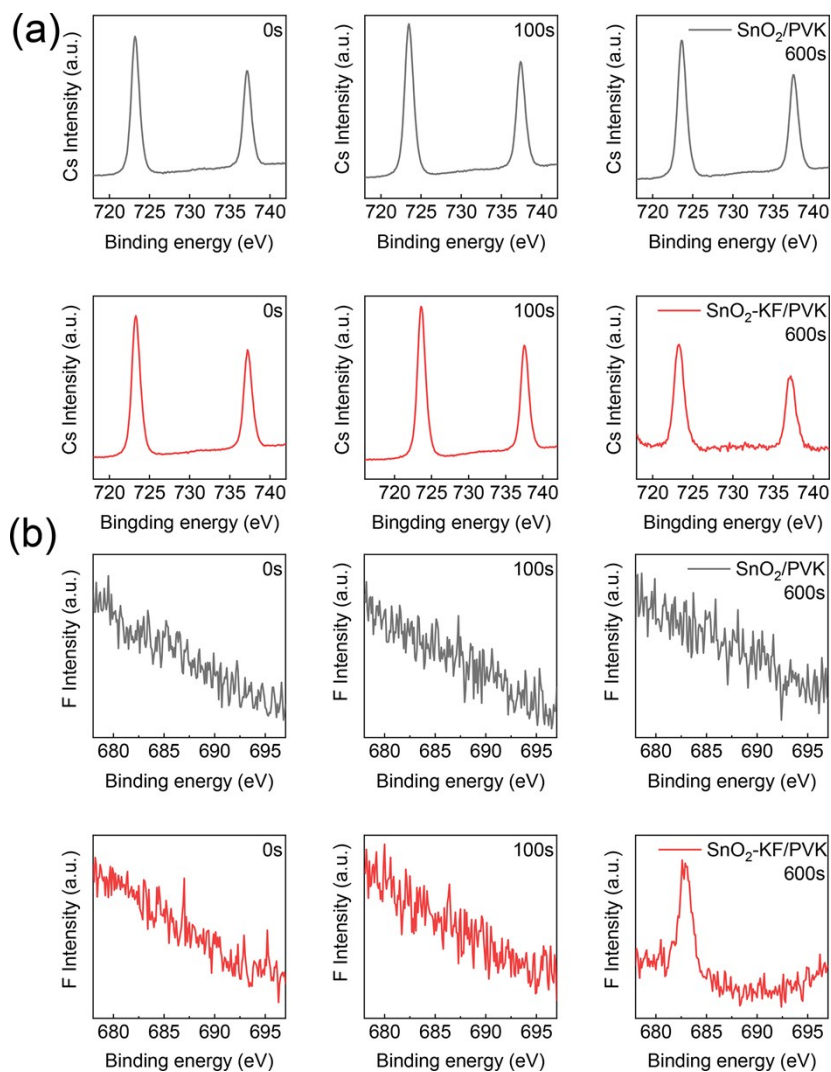


Fig. S5. XPS spectra of (a) Cs 3d orbital and (b) F 1s orbital of CsPbI₂Br films deposited on SnO₂ and SnO₂-KF at different etch-times.

Table S3. The photovoltaic parameters of using SnO₂-KF with different concentrations of KF as ETLs.

ETL		V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
SnO ₂ -KF (0 mg/mL)	Max	1.18	14.59	77.74	13.40
	Average	1.15 ± 0.01	14.98 ± 0.29	74.75 ± 1.98	12.90 ± 0.34
SnO ₂ -KF (4 mg/mL)	Max	1.21	14.20	75.28	12.94
	Average	1.21 ± 0.01	14.01 ± 0.16	75.10 ± 0.78	12.72 ± 0.17
SnO ₂ -KF (6 mg/mL)	Max	1.31	14.79	79.15	15.39
	Average	1.30 ± 0.01	15.06 ± 0.21	75.61 ± 2.02	14.85 ± 0.29
SnO ₂ -KF (8 mg/mL)	Max	1.19	12.31	61.01	8.92
	Average	1.11 ± 0.13	11.84 ± 0.49	60.62 ± 9.10	7.89 ± 0.65

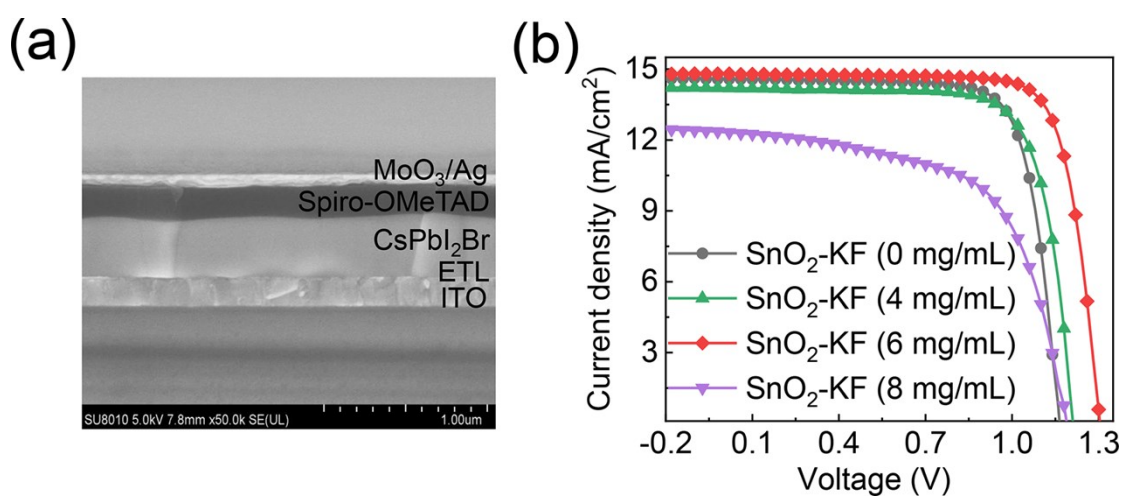


Fig. S6. (a) Cross-section SEM image of the PVSC. (b) *J-V* curves of the best-performance devices with different concentrations of KF.

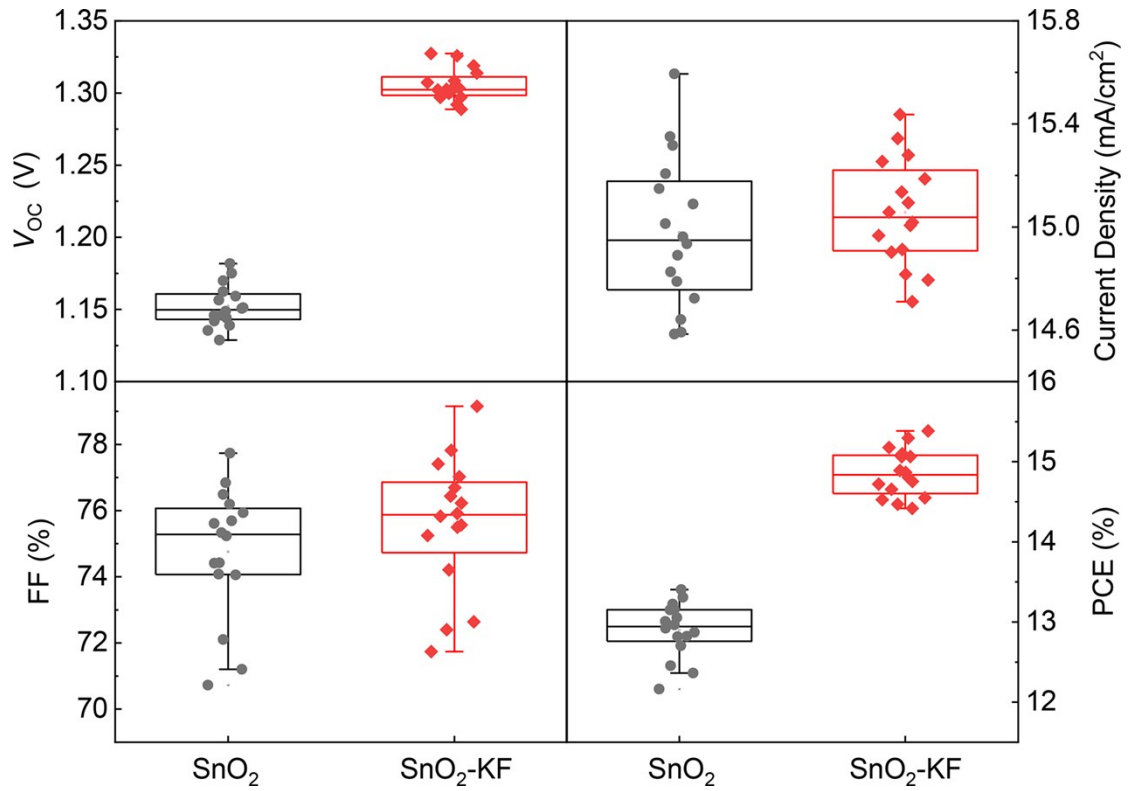


Fig. S7. Statistic distributions of photovoltaic parameters (V_{OC} , J_{SC} , FF and PCE) of solar cells based on $\text{SnO}_2\text{-KF}$ and SnO_2 .

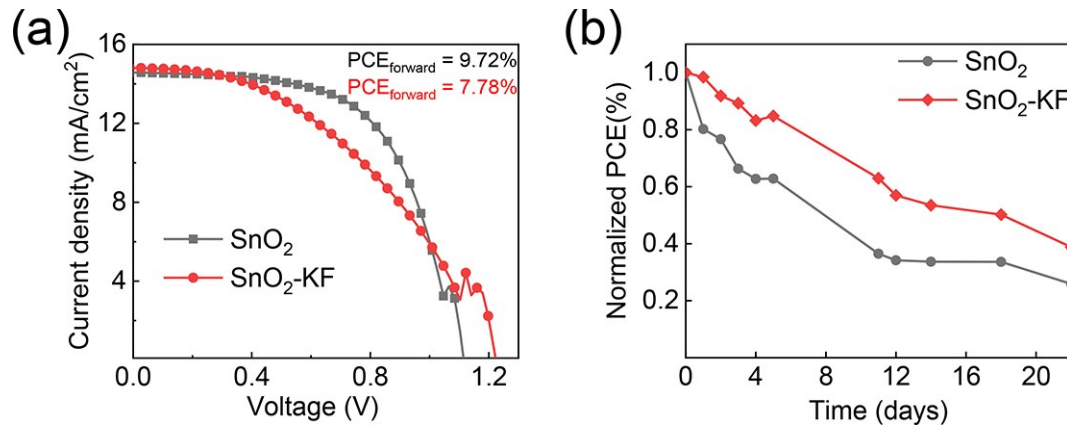


Fig. S8. (a) The forward scan of champion devices using SnO_2 and $\text{SnO}_2\text{-KF}$ as ETLs. (b) Normalized PCE for PVSCs in ambient condition (with humidity around 60% at room temperature) as a function of the storage time.

References

1. P. W. M. Blom, M. J. M. deJong and M. G. vanMunster, *Phys. Rev. B*, 1997, **55**, R656-R659.
2. R. H. Bube, *J. Appl. Phys.*, 1962, **33**, 1733-1737.