Supporting Materials for

Enhanced charge carrier extraction and transport with interface modification for efficient tin-based perovskite solar cells

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Materials and Methods

Materials

All chemicals were used as received without further purification. Tin (II) iodide (SnI_2, 99.99%), tin (II) fluorine (SnF_2, 99%), dime-thylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, ≥99.9%), chlorobenzene (CB, 99.8%), ethanol (EtOH, ≥99.5%) and isopropanol (IPA, 99.5%) were purchased from Sigma Aldrich. Formamidinium iodide (FAI) and phenethylammonium bromide (PEABr) were purchased from Great Cell Solar (Australia). Poly(3,4-ethylenedioxythiophene) poly-styrenesulfonate (PEDOT:PSS, Clevious PVP AI 4083), Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA, average Mn 7,000-10,000 (GPC)), bathocuproine (BCP) and indium tin oxides (ITO) were purchased from Advanced Election Technology Co., Ltd. (Yingkou, China). 1,1,4,4-Tetrahydro-di [1,4] methanonaphthaleno [1,2:2,3,56,60:2,3] [5,6] fullerene-C60 (indene-C60 bisadduct, ICBA) were purchased from 1-Materials. Trifluoroethanol (TFE, 99%) were purchased from J&K Scientific. Silver (Ag) and gold (Au) were obtained from commercial sources.

Device Fabrication

The glass substrates coated with indium tin oxide (ITO) were cleaned with detergent, deionized water, acetone, isopropanol and ethanol by ultrasonication for 15 min each. After drying with nitrogen flow, the ITO substrates were treated with ultraviolet-ozone for 20 min. PEDOT:PSS, a hole transport layer, was then spin-coated onto the ITO at 5000 rpm for 40 s and annealed at 150 ℃ for 10 min. After that, the substrates were transferred into a glove box filled with nitrogen. 60μL IPA/ TFE/ EtOH solvent was spin-coated onto PEDOT:PSS film at 8000 rpm for 60 s. 0.8 M control

perovskite precursor solution was prepared by dissolving SnF_2, PEABr, FAI and SnI_2 at a molar ratio of 0.10:0.15:0.85:1.00 in mixed solvent of DMF (800 μL) and DMSO (200 μL). 40 μL precursor was spin-coated onto the substrate at 5000 rpm for 40 s with 100 μL chlorobenzene dripped onto the perovskite film at 25 s. Then the as-prepared films were annealed at 80 ℃ for 10 min. The ICBA layer was spin-coating (21 mg mL^{-1} in chlorobenzene) at 1200 rpm for 30 s and then annealing at 70 ℃ for 10 min. Saturated BCP in isopropanol was spin-coated at 6000 rpm for 30 s, and the as-prepared film thermally annealed at 70 ℃ for 10 min. All precursors were filtered with 0.22 μm polytetra-fluoroethylene (PTFE) filters before spin-coating. Afterwards, Ag (100 nm) were sequentially deposited via thermal evaporation under 2×10^{-4} Pa, resulting in an active area of 0.1 cm^2. Devices were encapsulated with cover glass and ultraviolet-curable epoxy. The hole only devices for space charge limited current (SCLC) measurement were fabricated with the structure of ITO/ PEDOT:PSS/ Perovskite/ PTAA/ Au.

Device characterization

The current-voltage curves were measured in a glove box at AM 1.5G using a Keithley 2400 source-measure unit. The cells were illuminated by a 150 W xenon lamp class AAA solar simulator (XES-40S3-TT). The simulator's power was calibrated to 100 mW cm^{-2} by a silicon reference cell associated with a KG5 filter certified by NPVM (Chinese national PV industry measurement and testing center). The devices were measured in a forward scan from -0.05 V to 1.0 V with identical interval, under a mask t of 0.1 cm^2. The EQE spectra were recorded by an Enli Technology (Taiwan) EQE measurement system (QE-R), and the light intensity was calibrated with a standard single-crystal Si-cell. Long-term device stability tests for PSCs were performed by measuring the J-V curves periodically for a certain period of storage in the N_2 atmosphere.

Film Characterization

The top-view scanning electron microscopy (SEM) images were taken by Cold FE-SEM, SU8220, Hitachi. The cross-sectional SEM images of inverted PSCs were taken with Hitachi SU8220. Kelvin probe force microscopy (KPFM) images were performed using Bruker Demension Icon. Photoluminescense (PL) was measured using a Horiba Fluorolog-3 system with a petite integrating sphere. Timeresolved PL (TRPL) measurments was taken using a Horiba time-correlated single-photon counting system. Ultraviolet Photoelectron Spectroscopy (UPS) was performed by PHI 5000 VersaProbe III with He I source (21.22 eV) under an applied negative bias of 9.0 V. The grazing-incidence wide-angle X-ray scattering (GIWAXS) studies were performed at the beamline 7.3.3 of Advanced Light Source (LBNL), America, using beam energy of 10 keV (λ = 1.24 Å).

FIGURES

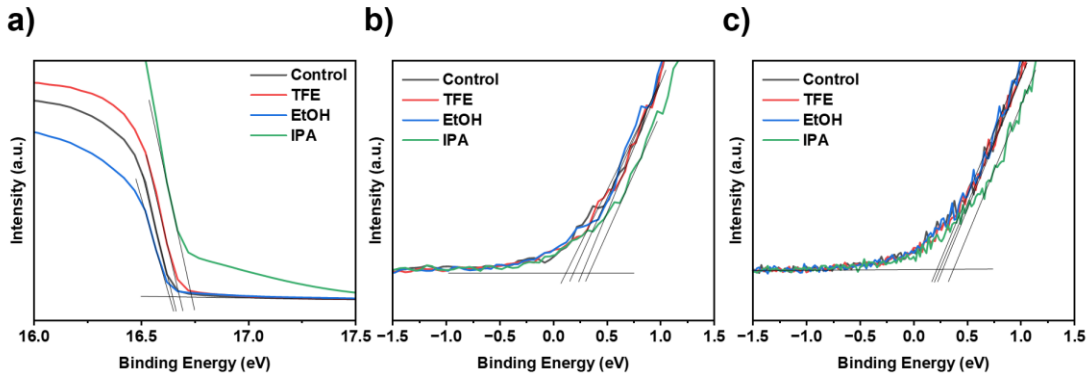

Fig. S1. UPS spectra of a) cutoff edge with bias, b) valence band with bias and c) valence band without bias.

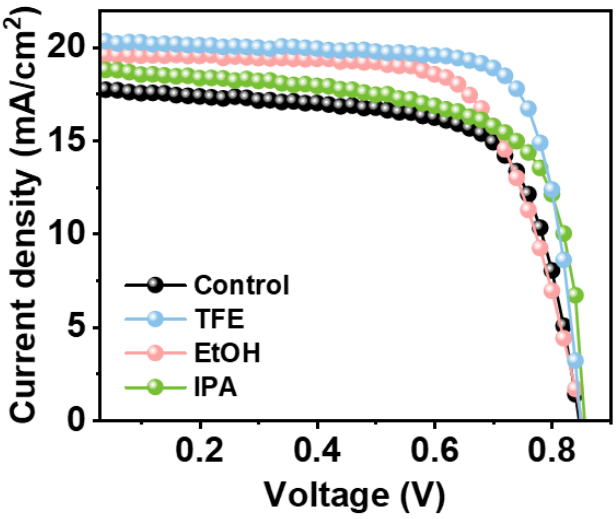

Fig. S2. *J-V* curves of of control and post-treated devices.

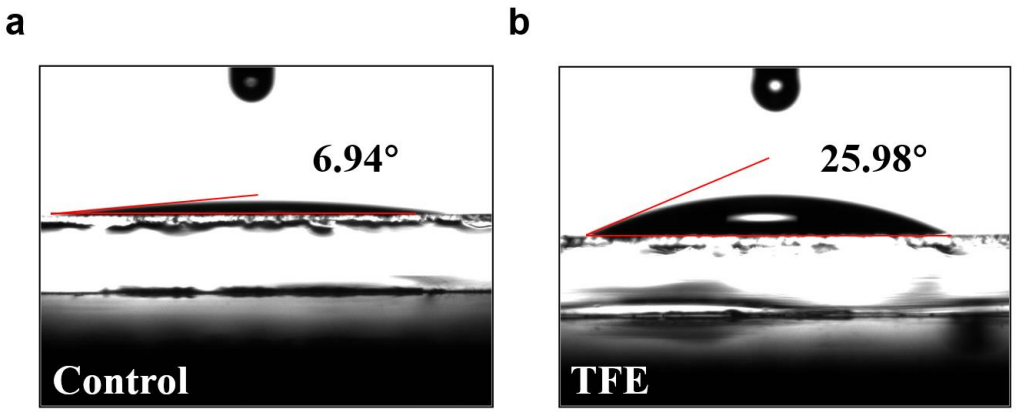

Fig. S3. Contact angles of (a) control and (b) TFE-treated PEDOT:PSS films.

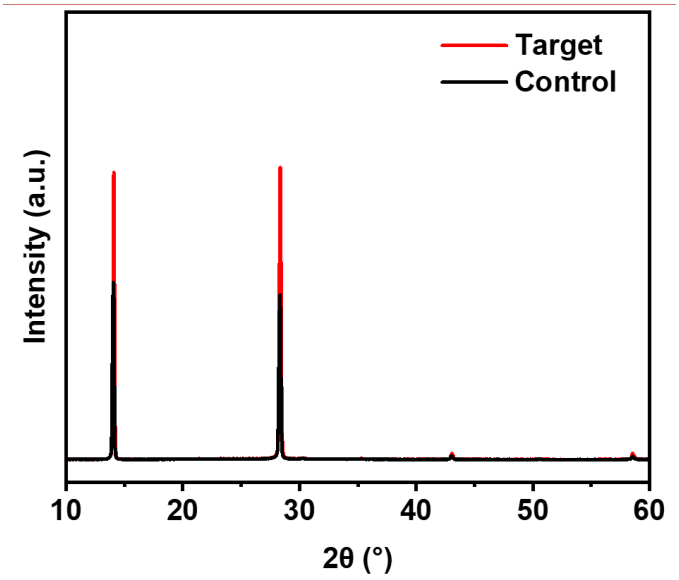

Fig. S4 XRD results of control and TFE-treated PEDOT:PSS films.

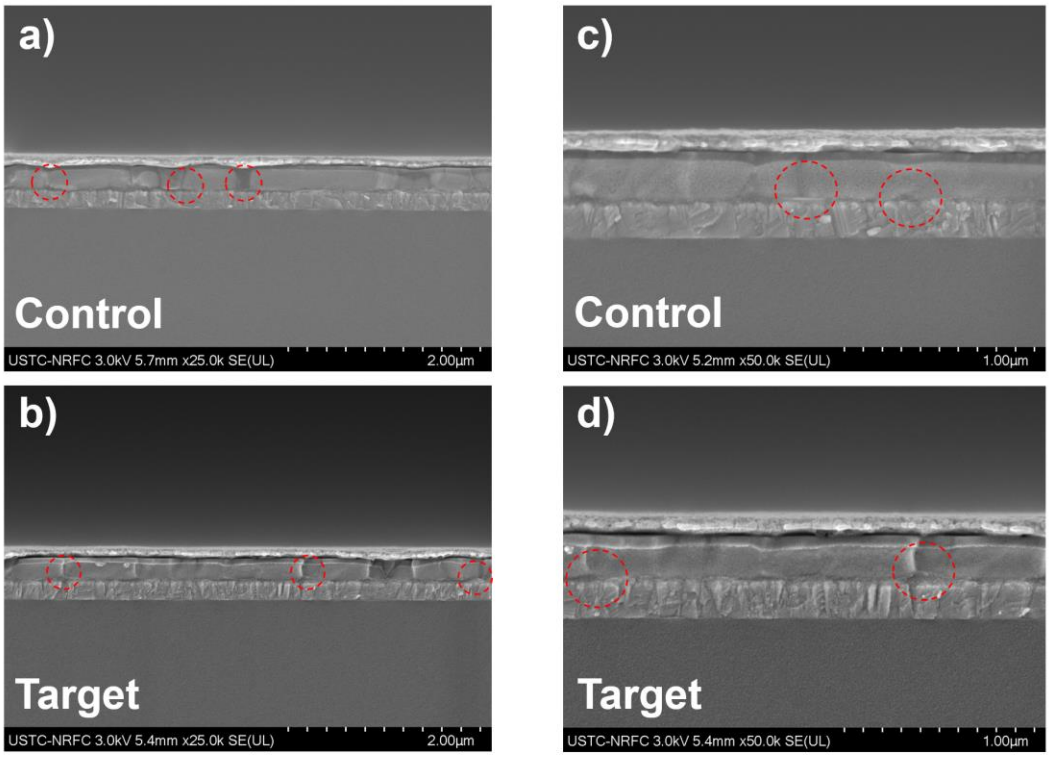

Fig. S5 SEM cross-sectional images of control and TFE-treated PEDOT:PSS films.

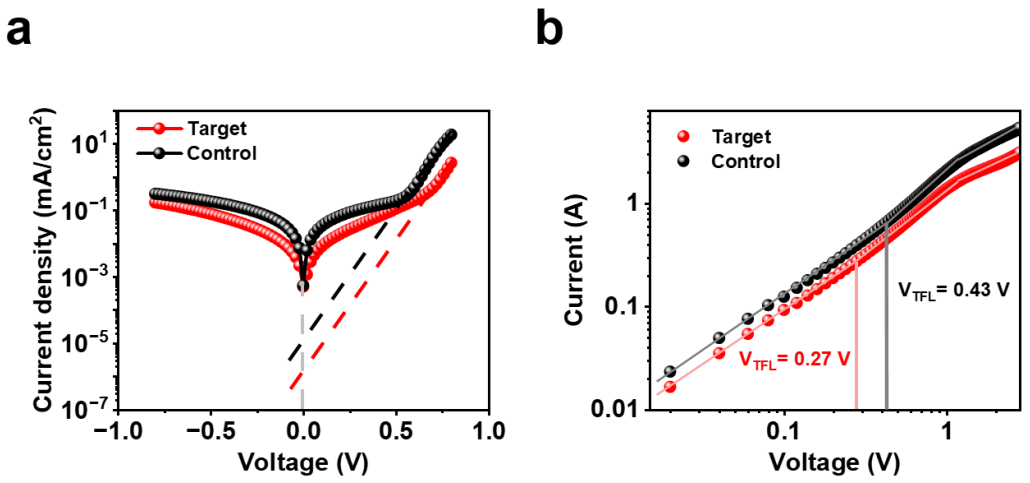

Fig. S6. (a) Dark J-V curves of the control and target devices. (b) SCLC results for the hole-only devices used to retrieve the trap-state density.

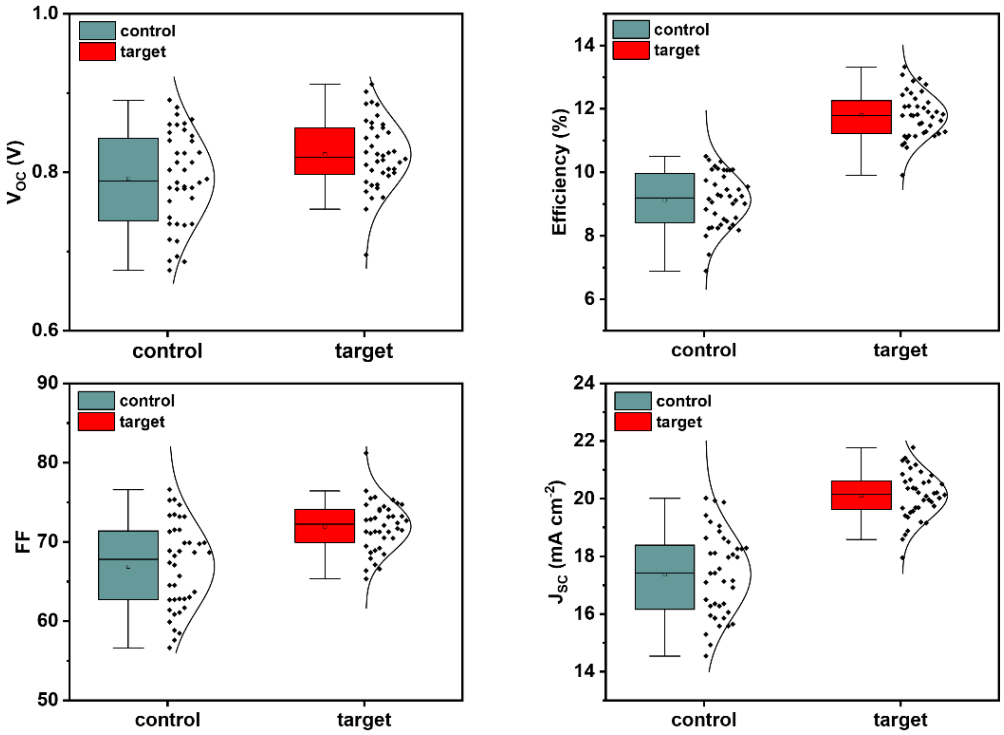

Fig. S7 Efficiency statistics of 80 Sn- based perovskite solar cells.

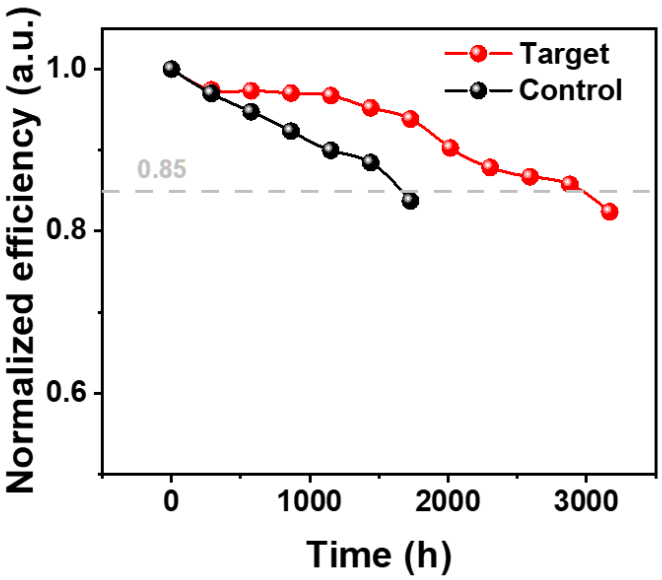

Fig. S8. (a) Store stabilitity in nitrogen atmosphere.

Tables

Table S1: Crystallite sizes, stacking distances, and the PEDOT ratios in PEDOT:PSS films treated by different solvents.

solvent treatment	d-spacing of PSS (Å)	d-spacing of PEDOT (Å)	PSS crystal size (Å)	PEDOT crystal size (Å)	PEDOT/Total ratio
Control	4.66	3.41	15.09	13.59	0.38
TFE	4.66	3.41	14.76	13.80	0.40
EtOH	4.64	3.39	15.07	13.69	0.42
IPA	4.64	3.38	15.23	13.66	0.39

Table S2: Cut-off edge with bias, valence edge with and without bias of UPS test, valance band maximum and Fermi level of PEDOT:PSS with IPA/ EtOH/ TFE solvent treatment and without solvent treatment.

solvent treatment	cut-off edge with bias (eV)	valence edge with bias (eV)	valence edge without bias (eV)	valance band maximum (eV)	Fermi Level (eV)
Control	16.6486	0.1924	0.2728	-4.7638	-4.4910
EtOH	16.632	0.2216	0.225	-4.8096	-4.5846
IPA	16.7411	0.3675	0.3721	-4.8464	-4.4743
TFE	16.6812	0.2855	0.2729	-4.8243	-4.5514

Table S3: Time-resolved photoluminescence fitting value of perovskite films based on PEDOT:PSS with IPA/ EtOH/ TFE solvent treatment and without solvent treatment.

solvent treatment	A1	T1 (ns)	A2	T2 (ns)	τ (ns)
control	0.11	0.58	0.89	7.14	7.07
TFE	0.48	1.41	0.55	3.12	2.62
IPA	0.16	1.47	0.85	3.70	3.54
EtOH	0.22	1.97	0.78	4.15	3.89

Table S4: Specific parameters of *J-V* curves in Fig. S2.

solvent treatment	Control	EtOH	IPA	TFE
V_{OC}	0.8459	0.8507	0.8554	0.8495
J_{SC}	18.1052	19.6620	19.0670	20.5001
FF	0.6827	0.6892	0.6811	0.7638
Efficiency	10.4557	11.5279	11.1087	13.3015