Supporting information

Thiosemicarbazide-complexed SnO_2 electron transport layer for high-efficiency $MAPbI_3$ perovskite solar cells

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1. Experimental section

1.1 Materials:

Lead iodide (PbI_2, purity≥99%), methylammonium iodide (MAI, purity≥99.5%), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, purity≥99.5%), 4-tertbutylpyridine (4-TBP, purity≥96%) and li-bis-(trifluoromethanesulfonyl)imide (Li-TFSI) were all purchased from Xi'an Polymer Light Technology Corp.

Thiosemicarbazide (TSC, purity≥99.5%), dimethyl sulfoxide (DMSO, purity≥99.9%), chlorobenzene (CB, purity≥99.8%), acetonitrile (ACN, purity≥99.6%), dimethyl-formamide (DMF, purity≥99%) and Tin (IV) chloride solution ($SnCl_4$, 1.0 M in methylene chloride) were all purchased from Sigma-Aldrich.

Indium tin oxide (ITO) substrates were purchased from Liaoning Huite Photoelectric Technology Co., Ltd.

1.2 PSC device fabrication

The TSC-SnO_2 precursor solution was prepared by adding different amount of TSC (0 mg, 10 mg, 15 mg, 20 mg) into a mixed solvent of deionized water/ Tin (IV) chloride solution (5.5 ml/1 ml). After stirring at room temperature for 30 minutes, the precursor solution was placed in a Muffle furnace at 85 °C for 12 hours to form SnO_2 colloid. 35 μL SnO_2 colloid was spin-coated on ITO substrates at a speed of 4000 rpm for 30 s. After annealing at 150 ° C for 30 min, the SnO_2 ETL was formed.

The $MAPbI_3$ precursor solution was prepared by adding 159 mg MAI and 461 mg PbI_2 into the DMF/DMSO mixed solvent (635 μL/71 μL). The precursor solution was spin-coated on the SnO_2 layer at 5000 rpm for 36 s. 1 mL diethyl ether was dripped on the spinning substrate at 21 s after the start of the procedure. After annealing at 100 °C on a hotplate for 10 min, a dense $MAPbI_3$ film was obtained. For the hole transport layer, a Spiro-OMeTAD/CB solution (72.25 mg/mL) was employed with 28.75 μL 4-t-BP and 17.5 μL Li-TFSI/ACN solution (520 mg/mL) added. The precursor was spin-coated on the $MAPbI_3$ layer at 3000 rpm for 35 s to form Spiro-OMeTAD film. At last, the Ag layer (100 nm) was thermally evaporated on the top in vacuum (< 1.0×10^{-3} Pa).

The effective area of solar cells is determined to be 0.1 cm^2.

1.3 Characterization

The UV-Vis absorption data were collected using an ultraviolet spectrometer (UV-2600, Shimadzu). The morphologies of $MAPbI_3$ films were observed by the scanning electron microscope (SEM) (S-4800, Hitachi). High resolution transmission electron microscope (HRTEM) images were obtained with JEM-2100. The X-ray photoelectron spectroscopy (XPS) was measured by AXIS Supra (Kratos), and the binding energy in XPS is corrected by aligning C 1s peaks. The steady-state photoluminescence (PL) and the time-resolved photoluminescence (TRPL) spectra were obtained using the PL spectrometer (FluoTime 300, PicoQuant), excited by a 373 nm laser diode at a frequency of 20 MHz. Current density-voltage (*J-V*) characterization was conducted under AM 1.5 G condition at a light intensity of 100 mW cm^{-2}, using a sourcemeter (2400, Keithley) and a solar simulator (94022A, Newport). The *J-V* measurements were conducted by forward scan (from 0 to 1.2 V) and reverse scan (from 1.2 to 0 V), with a scan rate of 100 mV/s. The work function of samples was ascertained by ultraviolet photoelectron spectroscopy (UPS, AXIS Supra). Fourier transform infrared spectroscopy (FTIR) spectra were performed on Nicolet iS20 fluorescence spectrometer. Dynamic light scattering (DLS) was measured by Malvern Zetasizer Nano S.

2. Calculation of band structure for SnO_2 ETLs

The band structure of SnO_2 ETL could be calculated with the following equations:

$$E_F = E_{cutoff} - 21.22 \text{ eV} \quad (1)$$

$$E_{VB} = E_F - E_{onset} \quad (2)$$

$$E_{CB} = E_{VB} + E_g \quad (3)$$

where E_{onset} and E_{cutoff} stand for the onset and secondary electron cutoff binding energy of UPS spectra, E_g stands for bandgap, E_F, E_{VB}, and E_{CB} stand for the position of Fermi level, valence band maximum, and conduction band minimum, respectively.

The calculated results are listed in **Table S1**.

3. Figures

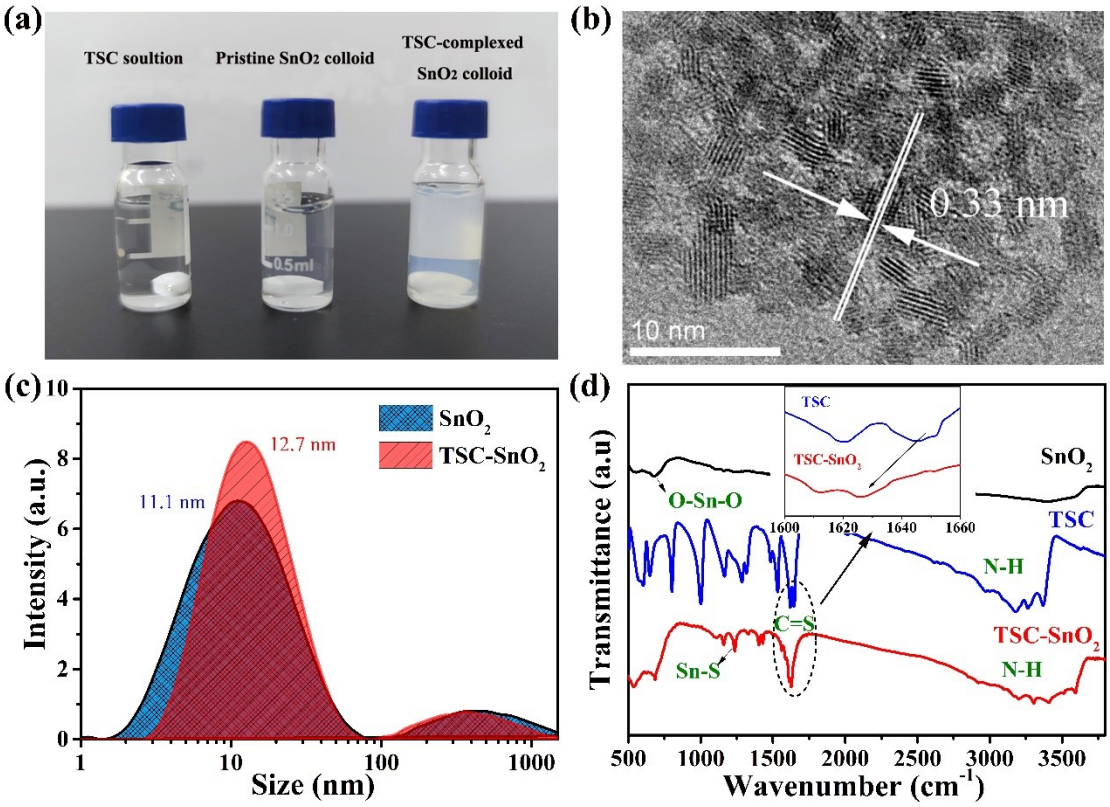

Figure S1. (a) The optical images of TSC solution, pristine SnO_2 colloid, and TSC-complexed SnO_2 colloid. (b) HRTEM image of TSC-complexed SnO_2 nanocrystals. (c) DLS spectra of pristine SnO_2 colloid and TSC-complexed SnO_2 colloid. (d) FTIR spectra of SnO_2, TSC, and TSC complexed SnO_2. The inset shows the enlarged spectra for the C=S peak.

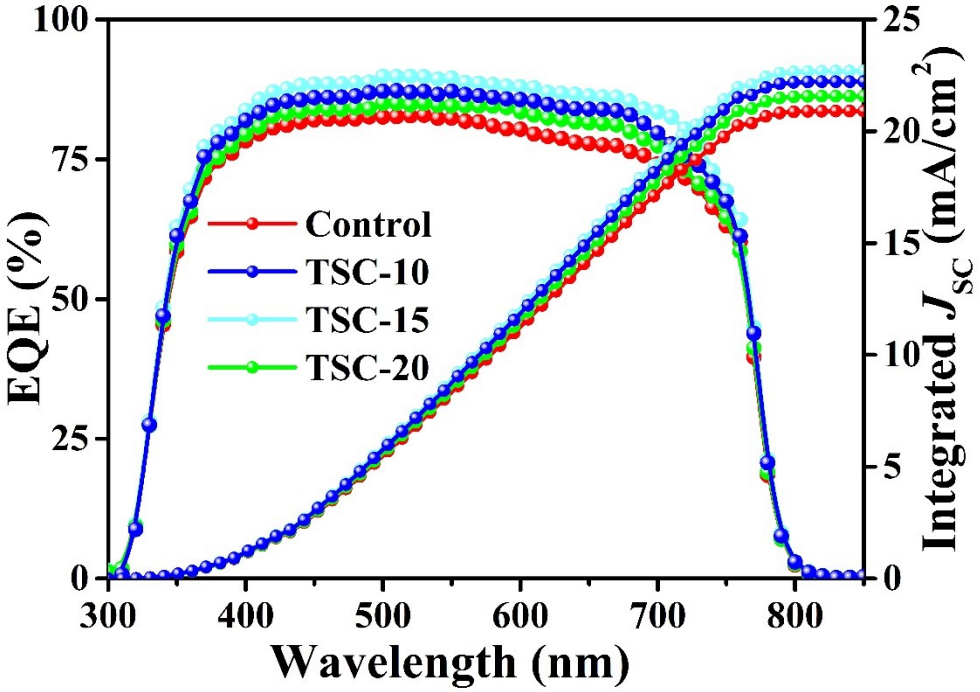

Figure S2. EQE spectra and corresponding integrated J_{SC} of PSCs based on different ETLs.

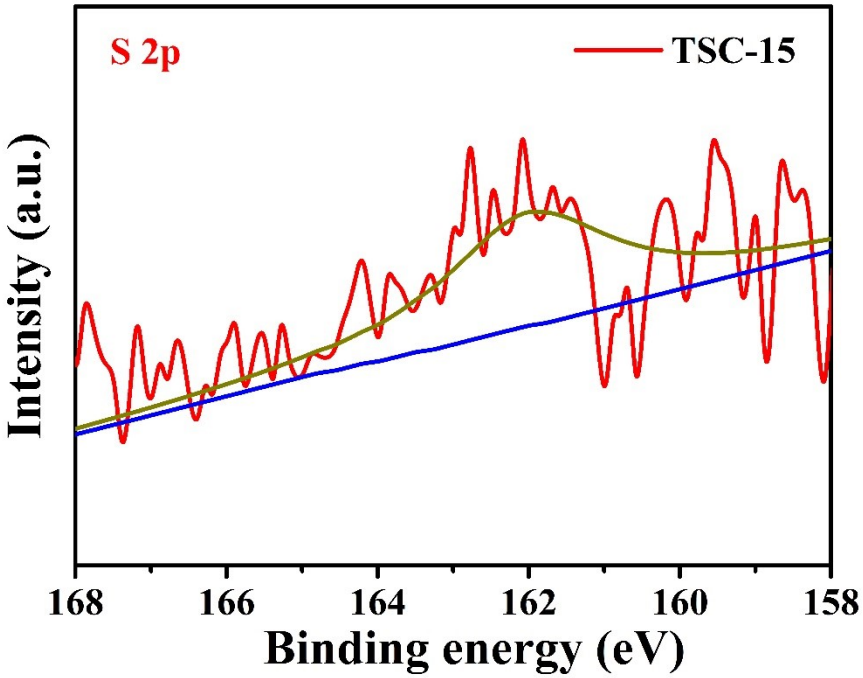

Figure S3. Detailed XPS spectra of S 2p peak for TSC-complexed SnO_2.

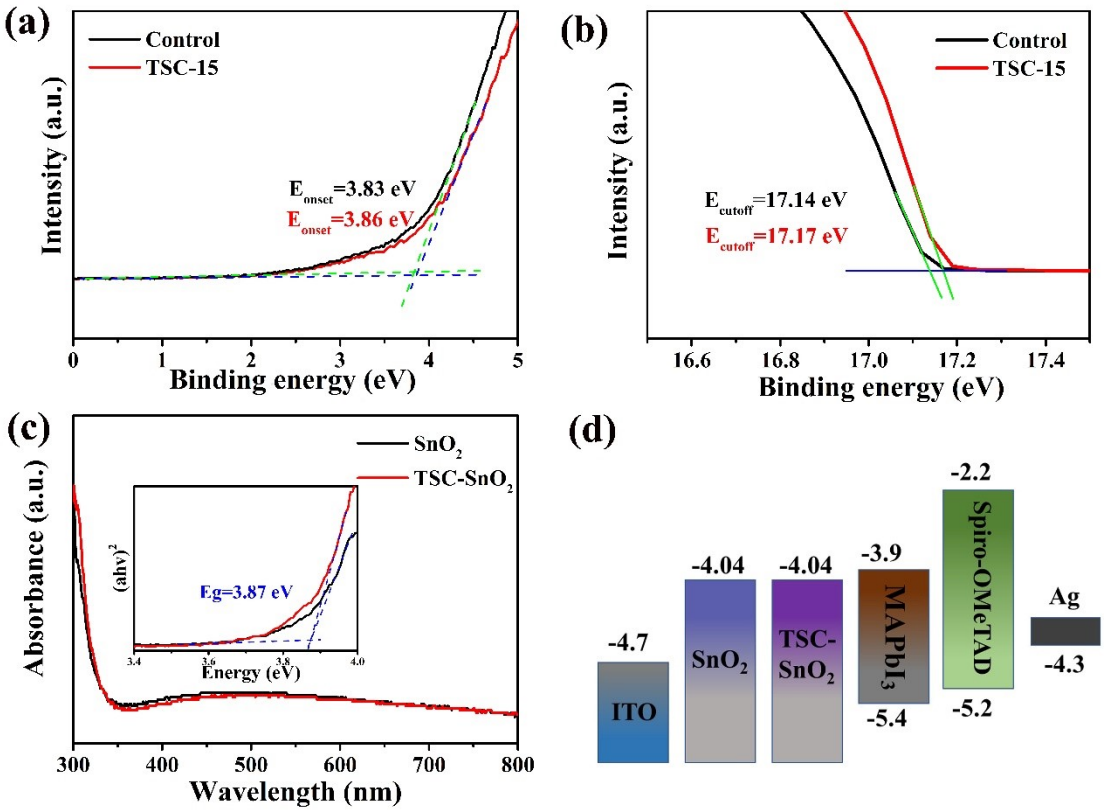

Figure S4. Onset (a) and secondary electron cutoff (b) of UPS spectra for control ETL and TSC-15 ETL. (c) UV-vis absorption spectra of control ETL and TSC-15 ETL. The inset shows the Tauc plots $((\alpha h\nu)^2$ vs photon energy) of the absorption spectra, where α, h, and ν stand for absorbance, Planck constant, and frequency of incident light, respectively. (d) Energy level diagram of perovskite solar cells.

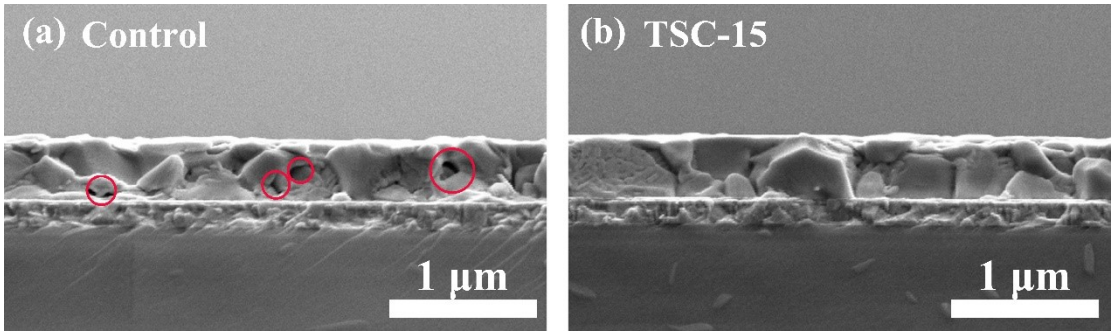

Figure S5. Cross-sectional SEM images of perovskite films deposited on different ETLs: (a) control and (b) TSC-15.

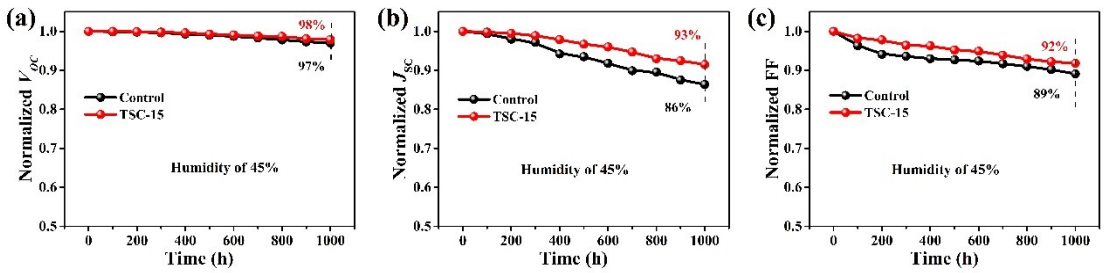

Figure S6. Normalized (a) V_{OC}, (b) J_{SC}, and (c) FF ageing curves of PSCs based on different ETLs.

3. Tables

Table S1. Parameters extracted from the UPS spectra and absorption spectra for control ETL and TSC-15 ETL.

Sample	E_{onset}	E_{cutoff}	E_g	E_F	E_{VB}	E_{CB}
Control ETL	3.83	17.14	3.87	-4.08	-7.91	-4.04
TSC-15 ETL	3.86	17.17	3.87	-4.05	-7.91	-4.04

Table S2. Fitting parameters of decay traces for perovskites deposited on different ETLs.

$MAPbI_3$ films with different ETLs	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
SnO_2	2322.15	25.23	8264.84	70.30	66.17
TSC-complexed SnO_2	11218.50	5.33	4728.38	54.36	45.11