Supporting Information

Conductive chelating agent treating electron transfer layer for environment-friendly and efficient perovskite solar cells

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1.Experimental sections:

Materials:

All of the chemicals and solvents were obtained commercially and were used without further purification. Methylammonium iodide (MAI), methylammonium bromide (MABr), methylammonium chloride (MACl), formamidinium iodide (FAI), lead iodide (PbI_2, 99.99%), cesium iodide (CsI, 99.999%), 4-*tert*-butylpyridine (99.9%), acetonitrile (99.9%) were purchased from Xi'an Polymer Light Technology Corp. PbI_2 and Spiro-OMe TAD are purchased from Liao'ning advanced election Technology Corp. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF) and isopropanol (IPA) were purchased from Sigma-Aldrich. Sodium p-styrenesulfonate (SSS) was purchased from TCI. Commercial tin (IV) oxide solution (SnO_2, 15% in H_2O colloidal dispersion) was purchased from Alfa Aesar.

Preparation of SnO_2 (SSS) colloidal solution:

Dilute the SnO_2 aqueous colloidal dispersion (15wt%) with deionized water to a concentration of 3.75 wt%. Subsequently, 0.4 mg of SSS were dissolved in 1 mL of diluted SnO_2 aqueous colloidal dispersion. Mix SnO_2 (SSS) solution in an ultrasonic cleaning machine for 2 hours to prepare SnO_2 (SSS) precursor solution.

Device Fabrication:

FTO substrate was sequentially ultrasonically cleaned by deionized water, acetone, ethanol, and isopropanol for 30 min, and then treated with UV/O_3 light for 60 min. SnO_2 colloidal solution solutions (3.75 wt%) doped with different concentrations of SSS (0.4 mg mL^{-1}) were spin coated on FTO substrate at 3000 rpm for 30 s to prepare SnO_2 layers, and then annealed at 150 ℃ in the environment for 30 minutes. The control device is based on a SnO_2 layer prepared from a SnO_2 colloidal solution (3.75 wt%) without SSS. Then, a 1.35 M PbI_2 and 0.0675 M CsI mixture solution (dissolved in DMF/DMSO (9:1, v/v) and stirred at 70 ℃ for 2 h) were spin-coated on the substrate at 3000 rpm for 30 s. Next, a mixed organic cation solution (600 mg of FAI, 75 mg of MAI, 30 mg of MABr, and 30 mg of MACl dissolved in 15 mL IPA) was spin-coated at 2800 rpm for 30 s and then annealed at 150 ℃ for 15 min in ambient environment. The hole transferer, Spiro-OMe TAD, was dissolved in chlorobenzene and LiTFSI and tert-butylpyridine (TBP) was used as the additive (167 mg Spiro-OMe TAD, 298 mg TBP, 10.3 mg in 1.00 mL chlorobenzene), and then the solution was deposited by spin-coating at 5000 rpm for 30 s. Finally, an Ag electrode with a thickness of 80 nm was

evaporated with a vacuum evaporation apparatus. The active area of the electrode is controlled by the mask to 0.09 cm^2.

Characterizations:

Current density versus voltage (*J-V*) testing was performed by measuring the solar cells under standard AM 1.5 sunlight with a solar simulator assembled with an electrochemical workstation (illumination 100 mW/cm^2, WXS-90L2, Wacom). The light intensity was calibrated using a standard monocrystalline silicon photovoltaic cell, and a single mask sheet with an area of 0.09 cm^2 was used to control the active area of the device. Surface morphology was characterized by an atomic force microscope (AFM; Brook Multimode 8). The absorption spectra of the as-prepared films were recorded using a UV-Vis-NIR spectrophotometer (UV-3600i, Shimadzu). The surface morphology of the perovskite films was observed by field emission scanning electron microscopy (FE-SEM; Quanta 250 FEG) and atomic force microscopy (AFM; Brook Multimode 8). The Space Charge Limited Current (SCLC) test was measured by linear cyclic voltammetry with the SourceMeter with sweep rates from -1 V to 1 V. Steady-state photoluminescence (PL) curves were obtained by a steady-state lifetime spectrofluorometer (Varian Cary Eclipse) at room temperature. The time-resolved photoluminescence decay spectra of the as-prepared perovskite films were characterized using a Horiba Fluorolog-3 time-correlated single photon counting (TCSPC) system. Mott-Schottky (MS) and Electrochemical impedance spectroscopy (EIS) were measured by an electrochemical station (CPE-2000) in the dark state.

Theoretical calculations:

Time-dependent density functional theory (DFT) theoretical calculations were performed using the Guassian 16 package to calculate and visualize electrostatic potential (ESP) maps for SSS using the 6-311G(d) level and to optimize SSS and Pb possible coordination modes. The corresponding frequency analysis was carried out, and the minimum vibration frequency was greater than zero, which proved that all the optimized structures are stable. Density functional theory (DFT) calculations were performed using the Gaussian 16 suite of programs, and geometry optimization was performed at the B3LYP/6-31G(d) theoretical level. Binding energy ΔE is calculated according to equation: $\Delta E = E_{Pb^{2+}/m} - E_m - E_{Pb^{2+}}$

Among them, $E_{Pb^{2+}/m}$, Em, and $E_{Pb^{2+}}$represent the energy of Pb^{2+} binding to molecules, the energy of molecules, and the energy of Pb^{2+}, respectively. M is H_2O or SSS.

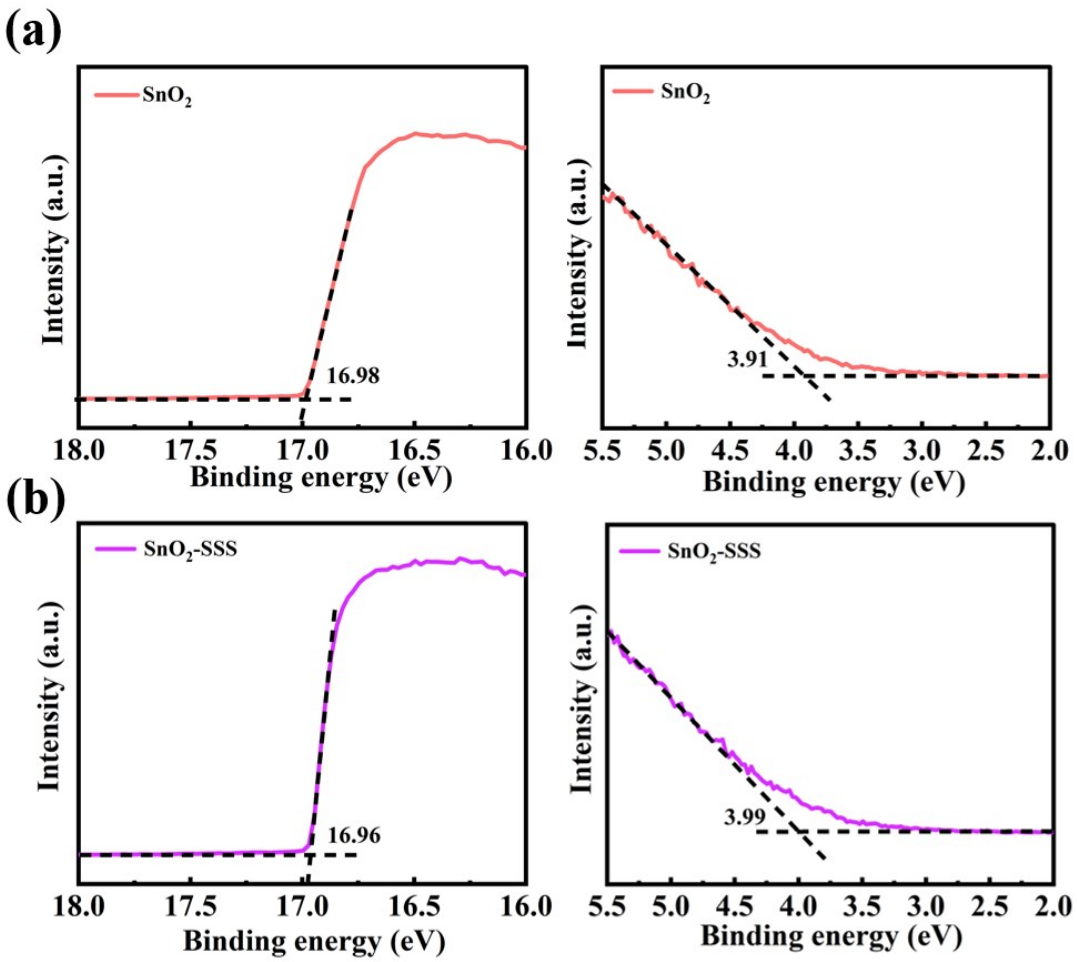

Figure S1. UPS analysis of SnO_2 (a) without the introduction of SSS and (b) with the introduction of SSS.

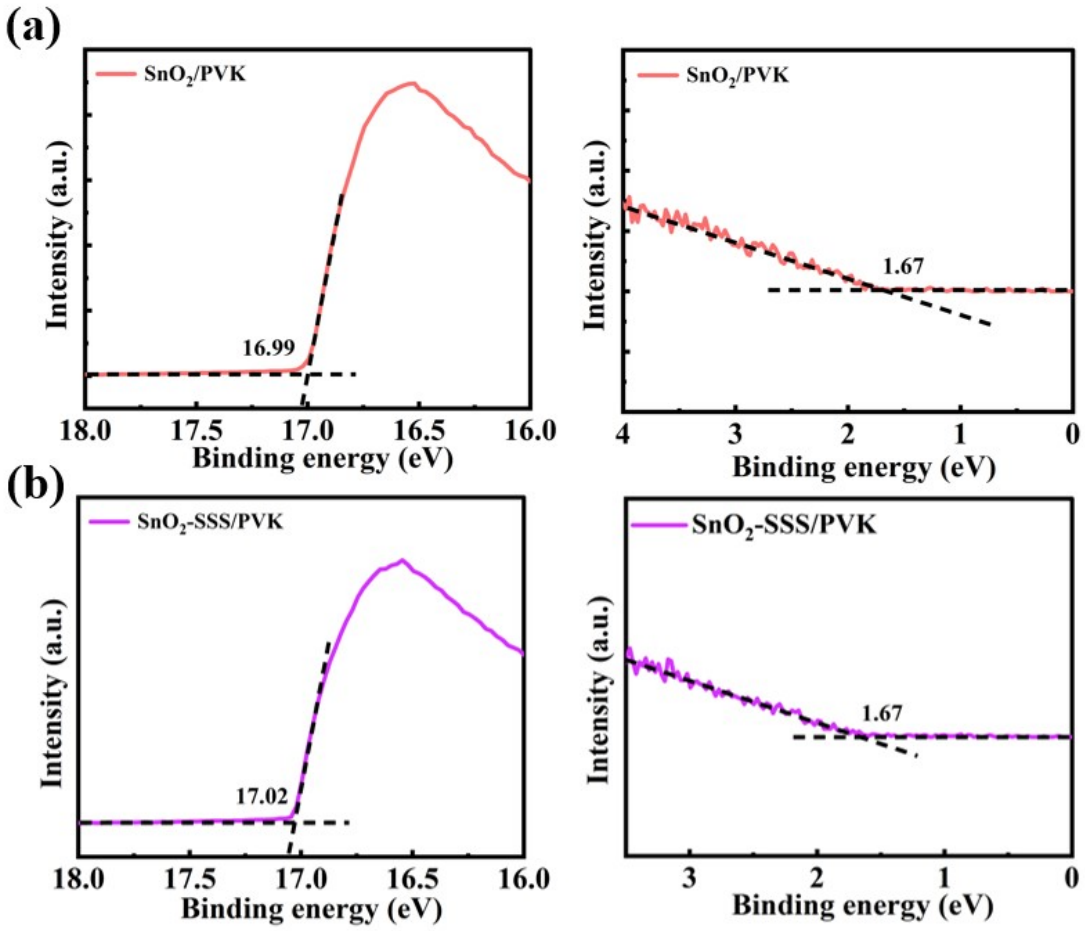

Figure S2. UPS analysis of perovskite layer (a) without the introduction of SSS and (b) with the introduction of SSS.

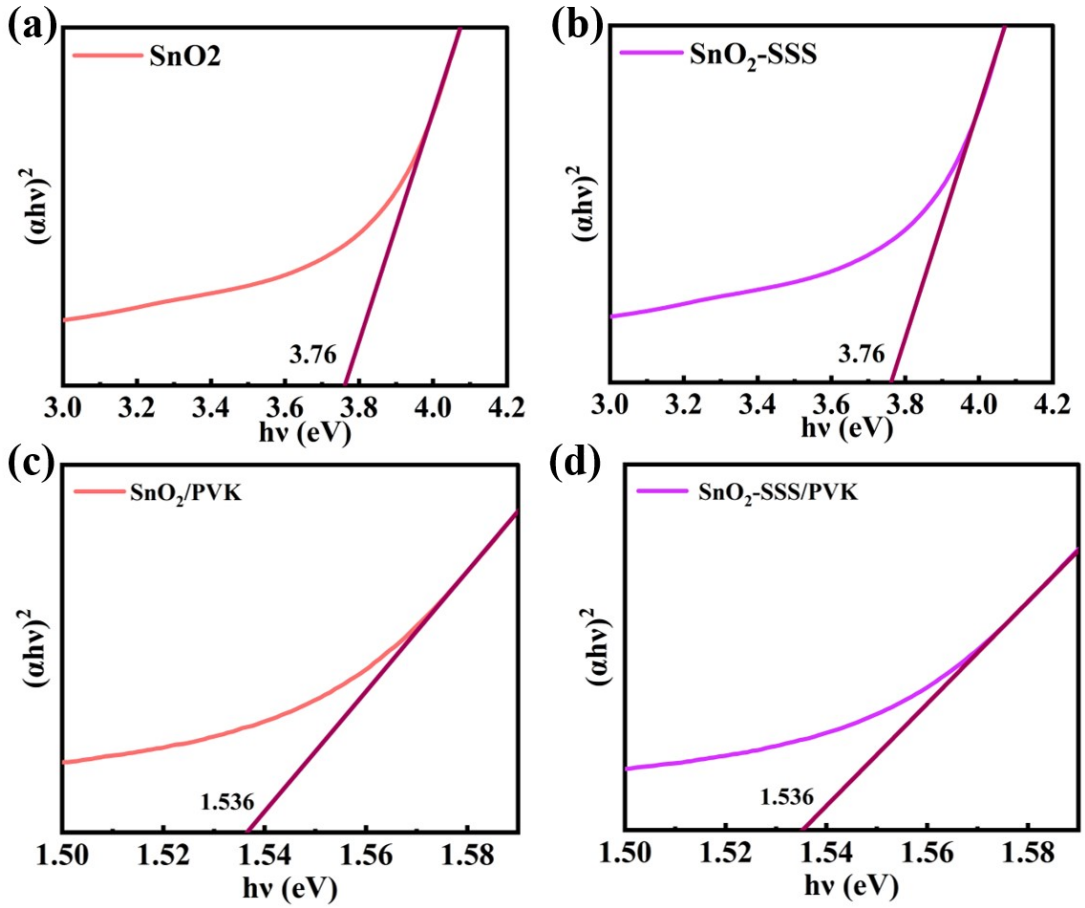

Figure S3. Tauc plot of SnO_2 (a) without SSS and (b) after the introduction of SSS. Tauc plot of perovskite films deposited on (c) SnO_2 without SSS and (d) SnO_2 with SSS.

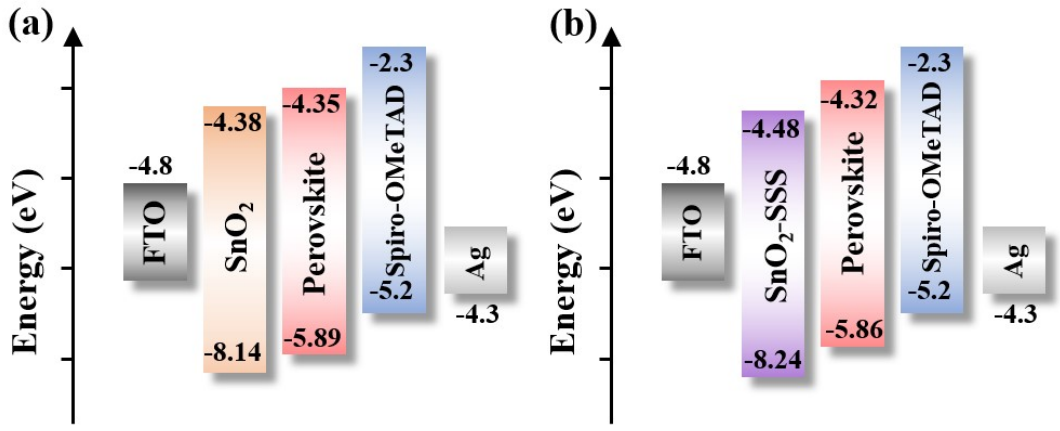

Figure S4. Schematic diagram of the energy levels of each functional layer (a) before and (b) after the introduction of SSS.

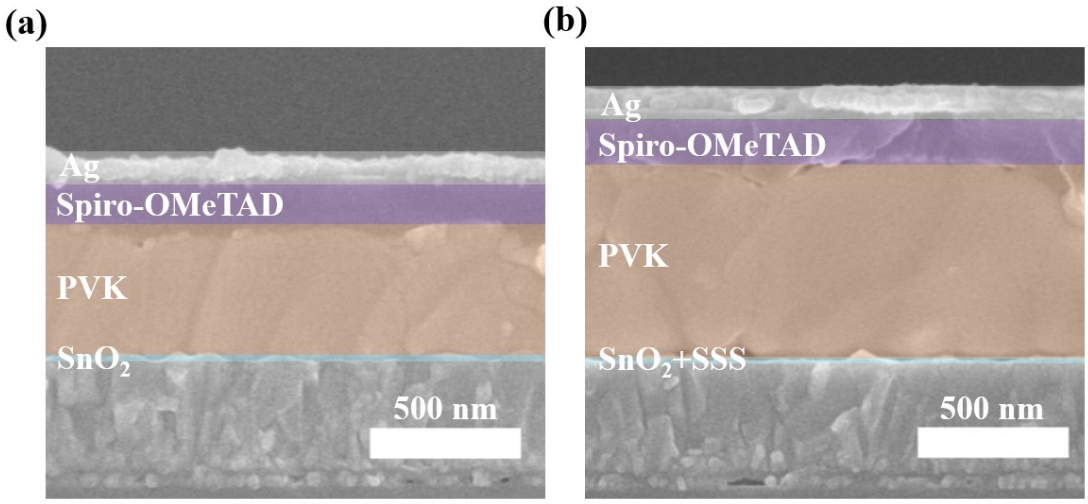

Figure S5. SEM cross-sectional images of the complete device (a) before and (b) after the introduction of SSS.

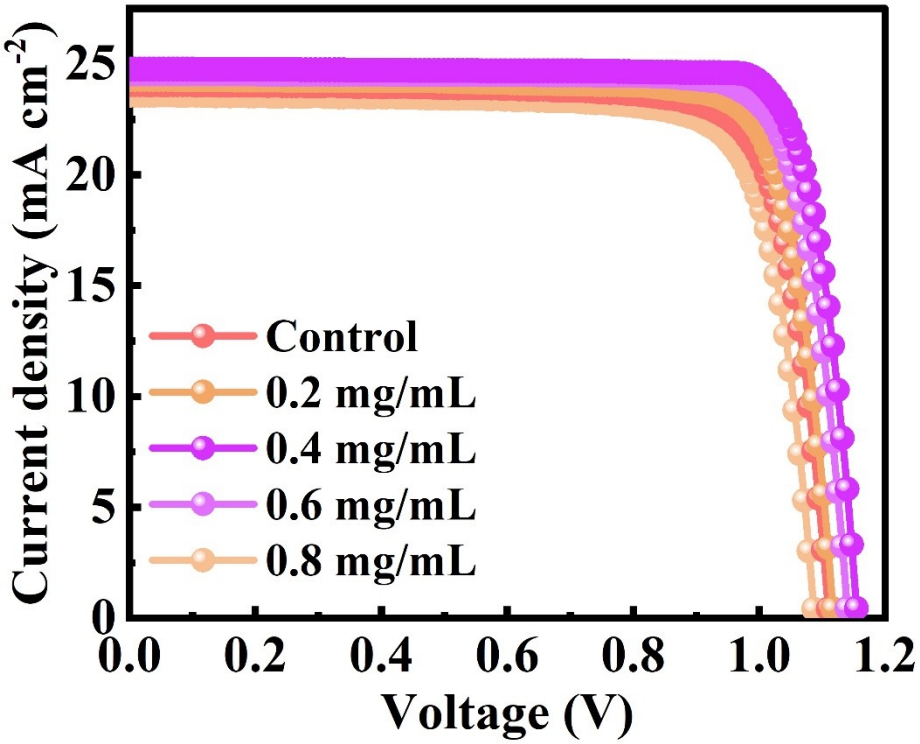

Figure S6. Reverse scanning *J-V* curves of PSCs with different SSS concentrations.

Table S1. The parameters of electrical conductivity (σ).

Sample	σ (mS cm^{-1})
SnO_2	5.56×10^{-3}
SnO_2 (SSS)	9.44×10^{-3}

The conductivity (σ) using the following equation: $\sigma = ID(AV)^{-1}$.

Table S2. The fitting parameter of TRPL spectra.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
SnO_2/PVK	0.95	3.81	0.093	9.38	4.89
SnO_2 (SSS)/PVK	1.04	1.12	0.008	6.58	1.35

$$\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Table S3. The parameters of the SCLC for sample with different ETLs.

Sample	V_{TFL} (V)	N_{trap} (cm^{-3})
SnO_2/PVK	0.171	2.13×10^{15}
SnO_2 (SSS)/PVK	0.114	6.32×10^{14}

The density of trap states can be calculated using the following formula: $N_{trap} = 2\varepsilon_r\varepsilon_0 V_{TFL}/eL^2$

Table S4. Photovoltaic parameters of PSCs based on pristine SnO_2 and SnO_2 (SSS) with different scanning direction.

Sample	Scan directions	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	HI (%)
SnO_2	Forward	1.07	23.67	80.82	20.67	3.63
	Reverse	1.12	24.05	79.65	21.45	
SnO_2 (SSS)	Forward	1.16	24.88	83.42	24.12	0.45
	Reverse	1.16	24.76	84.37	24.23	

The hysteresis index (HI) can be determined by Equation: $HI = (PCE_{reverse} - PCE_{forward}) / PCE_{reverse}$

Table S5. The detailed photovoltaic parameters of PSCs based on modified SnO_2 ETL with other SSS concentrations.

Sample	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0.2 mg mL^{-1}	1.11	24.30	82.53	22.26
0.6 mg mL^{-1}	1.13	24.55	83.67	23.21
0.8 mg mL^{-1}	1.08	23.58	80.62	20.53

Table S6. Fitted R_{tr} and R_{rec} of EIS parameters of PSCs based on pristine SnO_2 and SnO_2 (SSS)

Name	**R_{tr}**	**R_{rec}**
Control	9336	5.47E+06
SSS	8052	7.74E+06

Table S7. The parameter calculated by DFT.

Sample	Energy (a.u.)
Pb^{2+}	-192.1403
SSS	-1095.2349
Pb^{2+}/ SSS	-1287.9527

Binding energy ΔE is calculated according to equation: $\Delta E = E_{Pb^{2+}/m} - E_m - E_{Pb^{2+}}$.

Among them, $E_{Pb^{2+}/m}$, Em, and $E_{Pb^{2+}}$ represent the energy of Pb^{2+} binding to molecules, the energy of molecules, and the energy of Pb^{2+}, respectively. M is SSS.