Electronic Supplementary Information

Poly(vinylpyrrolidone)-doped SnO$_2$ as an electron transport layer for perovskite solar cells with improved performance

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Materials

The SnO$_2$ colloid precursor was purchased from Alfa Aesar (Tin (IV) oxide, 15% in H$_2$O colloidal dispersion). Lead iodide and lead bromide were purchased from TCI. Cesium iodide and methyl ammonium bromide (MABr) were purchased from Xi'an Polymer Technology Crop., and formamidinium iodide (FAI) was obtained from Yingkou OPV Tech New Energy Co., Ltd. Polyvinylpyrrolidone (PVP) was purchased in Sigma-Aldrich. All the solvents were obtained from Sigma-Aldrich. 2, 2´,7,7´-Tetrakis(N,N´-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Shenzhen Feiming Science and Technology Co., Ltd.

Fabrication of ETLs and the resulting PVSCs

The ITO substrates were cleaned by using detergent, distilled water, acetone, and isopropanol in sequence, then dried in an oven at a temperature of 130 ℃. Before the deposition of electron transport layers, the ITO substrates were further cleaned by ultraviolet ozone treatment for 15 min. The SnO$_2$ precursor was obtained by mixing 1 mL of the SnO$_2$ colloid precursor with 1 mL of H$_2$O. For the P-SnO$_2$ precursor (15wt % in H$_2$O), PVP (3-12 mg/mL in H$_2$O) was added into 1 mL of the SnO$_2$ dispersion. Both SnO$_2$ and P-SnO$_2$ precursors were stirred at room temperature for two hours. The electron transport layer was obtained by spin-coating the SnO$_2$ or P-SnO$_2$ precursor on the ITO glass, then annealed at 120 ℃ for 10 min and then 150 ℃ for 20 min. After cooling, the substrates were subjected to ultraviolet ozone treatment for 5 min and then transferred into a glove box for solution deposition of the perovskite layer. The precursor solution of triple cation perovskite was prepared by mixing FAI (1.1 M), PbI$_2$ (1.15 M), MABr (0.14 M), PbBr$_2$ (0.2 M) and CsI (0.07 M) in mixed solvent of DMF:DMSO = 4:1 (volume ratio) and stirred at 60 ℃ for 4 hours. The perovskite films were deposited onto the SnO$_2$- or P-SnO$_2$-coated substrates with two-step spin-coating process. The first step was 2000 rpm for 10 s and the second step was 5000 rpm for 25 s. During the second step, 150 μL of chlorobenzene was dropped on the spinning substrate at 10 s before the end of spinning. The substrate was then immediately

transferred on a hotplate and heated at 150 °C for 10 min. After cooling down to room temperature, Spiro-OMeTAD solution (72.3 mg in 1 mL of chlorobenzene containing 28.8 μL of *tert*-butylpyridine and 17.5 μL of bis(trifluoromethane)sulfonimide lithium salt in acetonitrile (520 mg/mL)), was subsequently coated on the top of the perovskite film at 4000 rpm for 20 s. Finally, 80 nm of gold was deposited as electrode on top of the hole transporting layer by thermal evaporation.

Characterizations of ETLs and PVSCs

The scanning electron microscope (SEM) images of SnO_2, P-SnO_2, and the perovskite films were obtained by using the field-emission SEM (JSM6700-F). X-ray diffraction (XRD) patterns of the perovskite films were obtained with a Rigaku Ultima-IV diffractometer. Steady state photoluminescence (PL) and time-resolved PL spectra were measured by a fluorescence spectrometer (Edinburgh Instruments, FLS980). The *J*–*V* characteristics of the devices were obtained using a Keithley 2400 Source Meter under simulated AM 1.5G illumination (100 mW cm^{-2}) with an Oriel Sol3A simulator (Newport), and the light intensity had been accurately calibrated with a National Renewable Energy Laboratory (NREL)-certified silicon reference cell. For the shelf-stability test, the devices were tested every several days and stored in the ambient. The external quantum efficiency (EQE) was measured using an EQE measurement system (Newport). The absorption and transmission spectra were obtained by using a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 365). The root-mean-square (RMS) roughnesses of SnO_2 films were investigated by Scanning Probe Microscope (Bruker, Dimension Icon). X-ray photoelectron spectra (XPS) and ultraviolet photoelectron spectra (UPS) for the thin films were carried out by using X-ray Photoelectron Spectroscopy (Thermo Fisher, ESCALAB 250Xi). To explore the charge transport ability of the SnO_2 ETLs, we fabricated electron-only devices using the device configuration of ITO/Al/ETL/Al as shown in Figure 1b. 100-nm Al was deposited on glass, then SnO_2 (~50 nm) layer was coated on the glass/Al. Finally, 100-nm Al was deposited on top of SnO_2. We also fabricated electron-only devices (ITO/ETLs/perovskite/PCBM/Ag) to evaluate the mobility and defect density of the perovskite based on different ETLs. The thickness of perovskite was about 500 nm. The electron mobilities were calculated by the formula of $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where ε_0 is the permittivity of free space, ε_r is the dielectric constant of perovskite or SnO_2,[1,2] μ is the carrier mobility, V is the voltage drop across the device, and L is the thickness. The charge carrier trap densities of the perovskite films were calculated by the formula of $n_{trap} = 2\varepsilon_r\varepsilon_0 V_{TFL}/eL^2$, where ε_r is the relative dielectric constant of perovskite, ε_0 is the vacuum permittivity, V_{TFL} is the onset voltage of the trap-filling limited region, e is the electronic charge, and L is the thickness of the perovskite film.[2]
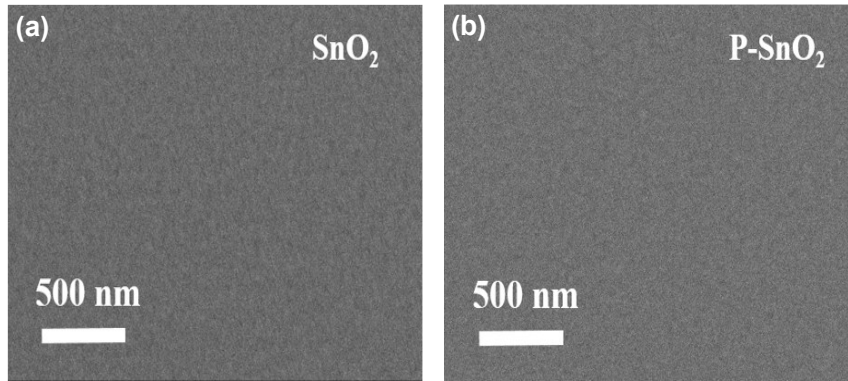
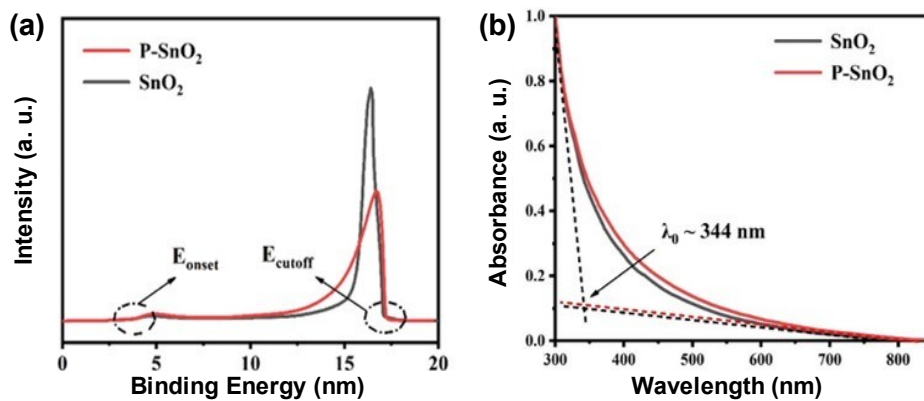**Figure S1**. SEM images of SnO_2 (a) and P-SnO_2 (b) films.

Figure S2. (a) UPS spectra for the SnO_2 and P-SnO_2 films. (b) UV-Vis absorption spectra for SnO_2 and P-SnO_2 films deposited on glass.

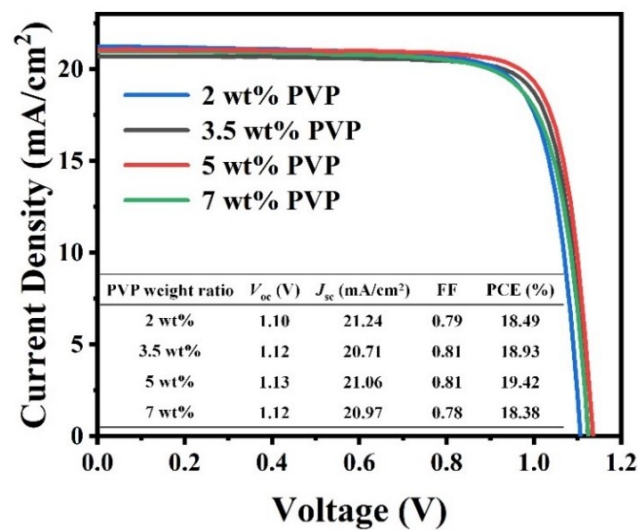| PVP weight ratio	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
2 wt%	1.10	21.24	0.79	18.49
3.5 wt%	1.12	20.71	0.81	18.93
5 wt%	1.13	21.06	0.81	19.42
7 wt%	1.12	20.97	0.78	18.38

Figure S3. *J-V* characteristics of PVSCs based on SnO_2 ETL with various amounts of PVP.

Table S1. TRPL decay parameters of the perovskites on various substrates

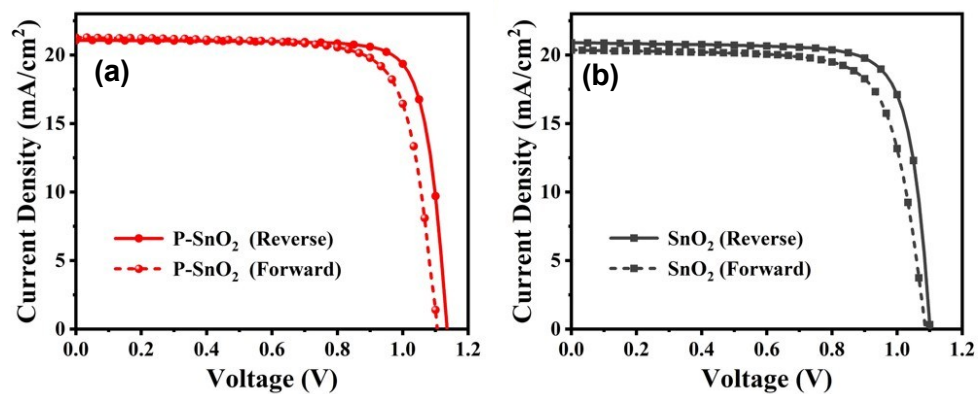| Samples	$\tau 1$ (ns)	Rel %	$\tau 2$ (ns)	Rel %	$\tau_{average}$ (ns)
Glass/Perovskite	123	18.58	397	81.42	346
Glass/SnO$_2$/Perovskite	55.2	13.02	216	86.98	195
Glass/P-SnO$_2$/Perovskite	20.1	9.03	115	90.97	106

Figure S4. *J-V* curves of devices using P-SnO$_2$ (a) and SnO$_2$ (b) as ETLs under reverse and forward scans.

References

1.   H. J. V. Daal, *J. Appl. Phys.*, 1968, **39**, 4467.
2.   T. Bu, X. Liu, Z. Yuan, J. Yi and J. Zhong, *Energy Environ. Sci.*, 2017, **10**, 2509-2515.