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Supporting Information

Antimony trifluoride incorporated SnO_2 for high-efficiency planar perovskite solar cells

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Keywords: Perovskite solar cells, High-performance, Hysteresis, Stability, Tin dioxide

Experimental Section

Materials:

The SnO_2 colloid precursor was purchased from Alfa Aesar. N, Ndimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chlorobenzene were purchased from Sigma-Aldrich. PbI_2, FAI, MABr, MACl, bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI), 4-tertbutylpyridine (TBP) and Spiro-OMeTAD were purchased from Xian Polymer Light Technology Corp. Antimony fluoride (SbF_3) was purchased from Aladdin.

Solar cells Fabrication:

The ITO glass substrate (1.78×1.78 cm) was cleaned with deionized water, acetone and isopropanol respectively for 15 minutes. Then the clean substrate was dried by a nitrogen stream, and treated with oxygen plasma for 5 minutes. The SnO_2 colloidal precursor was diluted with ultrapure water (volume ratio 1.2:6.5) to prepare the SnO_2 precursor (marked by SnO_2). SnO_2 precursors with different SbF_3 concentrations (0.2mg/mL, 0.4mg/mL and 0.6mg/mL) were also prepared (marked by SnO_2-SbF_3). The SnO_2 precursors without/with different SbF_3 concentrations were spin-coated on the ITO substrates at a speed of 3000 rpm for 35 s, and then annealed at 150°C for 30 minutes in the air (relative humidity RH=40%). SnO_2 film and SnO_2-SbF_3 film were consequently obtained. Then the substrate was transferred to a nitrogen glove box to prepare the perovskite film. The perovskite film was prepared by a two-step method. First, 760 mg PbI_2 and 18.2 mg CsI were dissolved in a mixed solvent of DMF (1 mL) and DMSO (160 μL), and then stirred at 60 °C for 15 h. The PbI_2 solution was filtered through a 0.22 μm pore PTFE filter, and then PbI_2 solution was spin-coated on the ETL/ITO substrate at a speed of 1600rpm for 20s and 4000rpm for 30s, respectively. Then the PbI_2 film was annealed at 70°C for 2 minutes. Second, 120 μL of mixed ammonium salt isopropanol solution (110 mg FAI, 11.5 mg MACl and 11 mg MABr dissolved in 1500 μL isopropanol) was spin-coated on the PbI_2 film at a speed of 2000 rpm for 23 s, the perovskite layer was obtained. The perovskite film was then taken out of the glove box and annealed at 140°C for 20 minutes in the air (RH =40%). After annealing, 120 μL isopropanol was used to clean the excess ammonium salt in the perovskite film. Spiro-OMeTAD solution was subsequently spin-coated on the perovskite layer at 4000 rpm for 30 s. After that, the prepared film was placed into a desiccator for 20 hours. Finally, 90 nm Au film was deposited as electrode by thermal evaporation.

Characterization:

XPS was measured by XPS machine (ESCALAB250XI, Thermo Fisher Scientific). The X-ray diffraction patterns were measured by using a Rigaku-2500 X-ray diffractometer with an X-ray tube (Cu Kα, λ =1.5406 Å). UPS was measured by UPS machine (AXIS ULTRA DLD, Kratos). The UV light source is He I, and the energy of He I is 21.22 eV. The basic

vacuum of the Analytical Chamber is 3.0×10^{-8} Torr, and the bias voltage is -9 V. The top-view and cross-sectional SEM images were attained using a scanning electron microscope (SEM, HITACH2100). EQE was recorded using a Newport Oriel QE-200 (Newport 300 W xenon lamp). All J−V curves were measured using a source meter (Keithley 2420, USA) under AM 1.5 sunlight at an irradiance of 100 mW cm^{-2} provided by a solar simulator (Newport, Oriel Sol3A Class AAA, 94043A). The device area was 0.04 cm^2. Light intensity was calibrated using a monocrystalline silicon reference cell with a KG5 window (Newport, Oriel 91150). Impedance spectroscopy (IS) was measured by Zennium (Zahner).

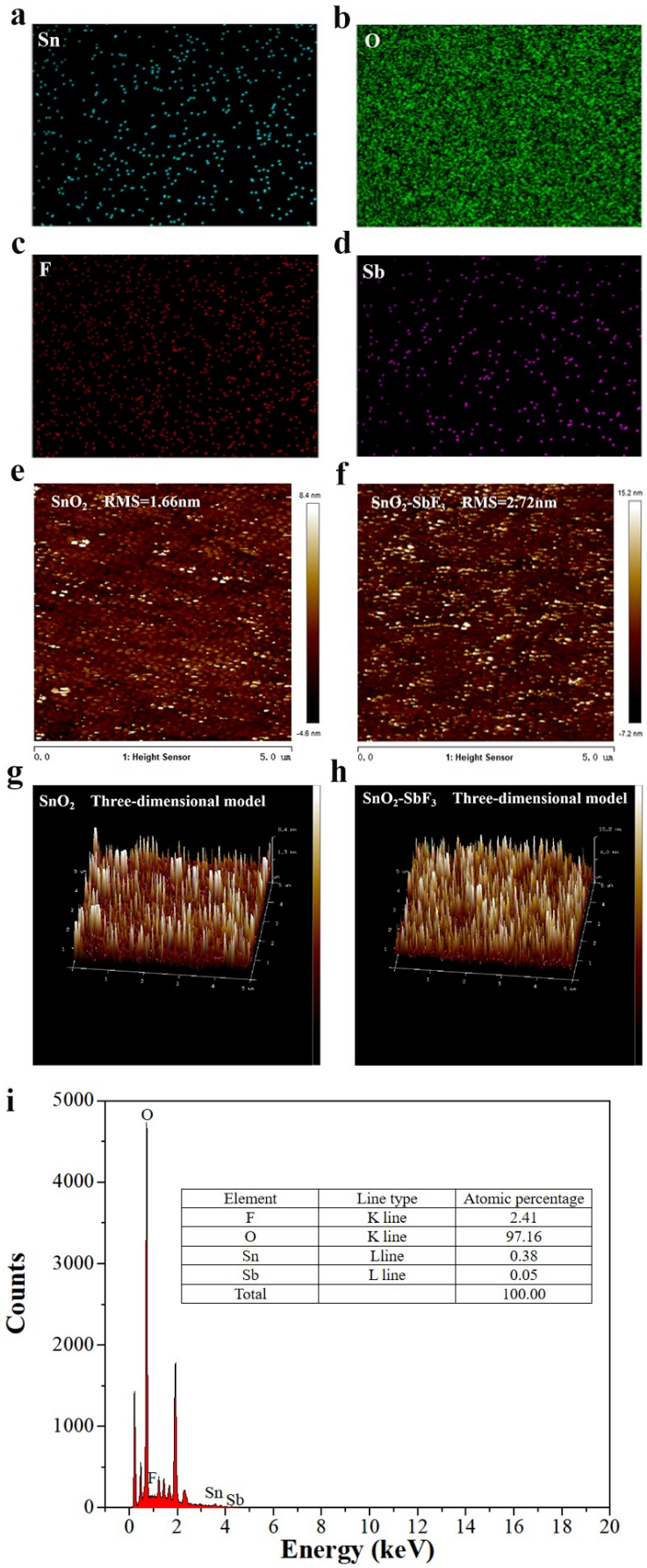

Figure S1. (a)-(d) and (i) EDS mappings of the SnO_2-SbF_3 film on glass, (e)-(h) AFM images of the SnO_2 and SnO_2-SbF_3 films.

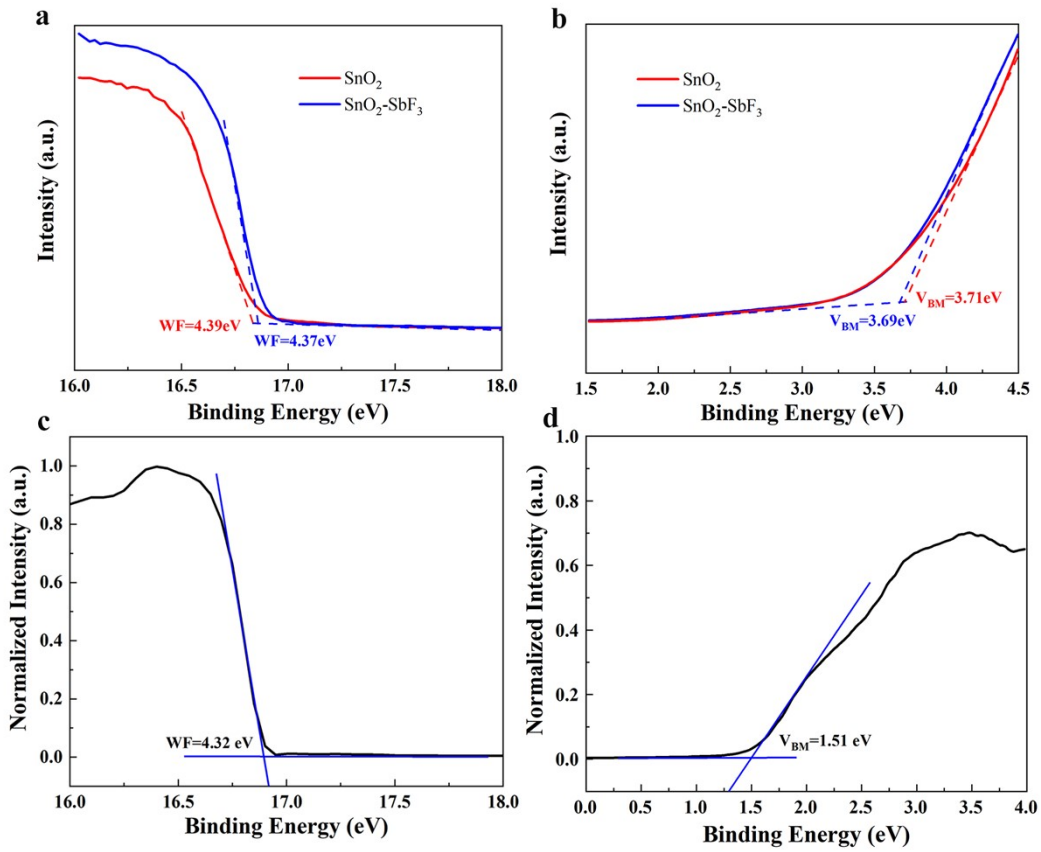

Figure S2. (a) UPS cutoff edge and (b) valence band spectrum of SnO_2, SnO_2-SbF_3. (c) UPS cutoff edge and (d) valence band spectra of the perovskite film.

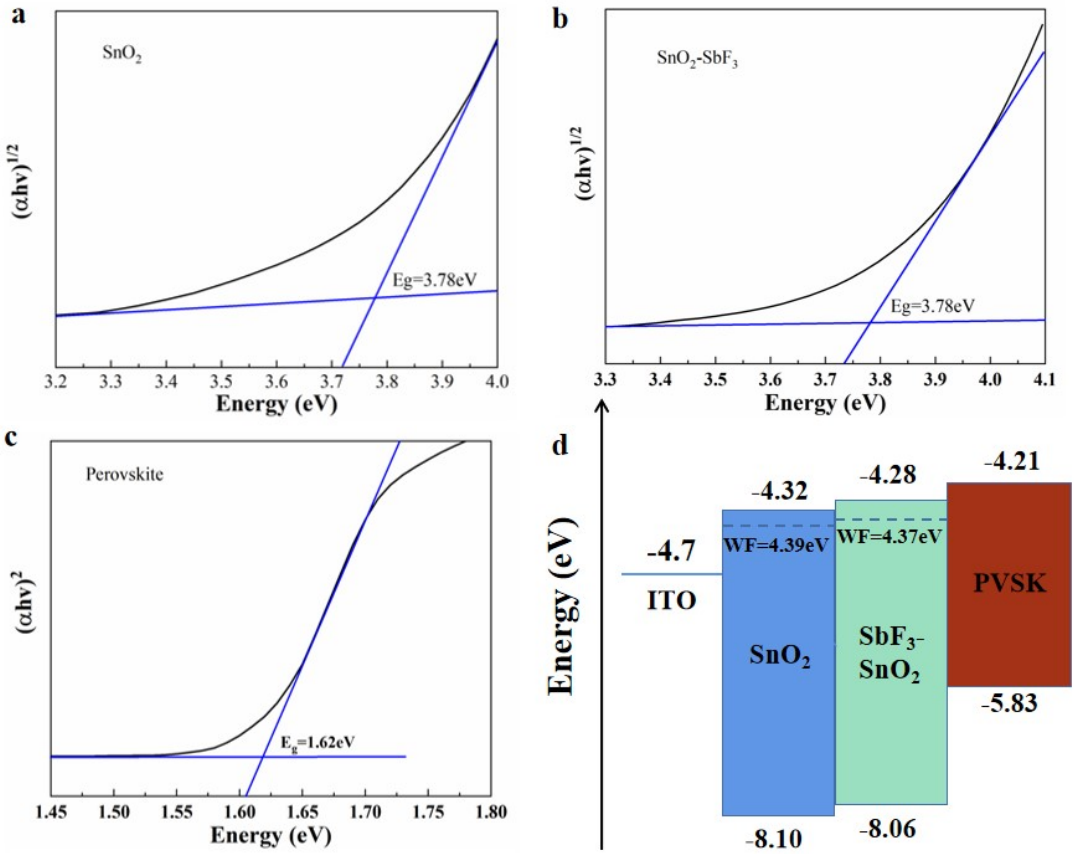

Figure S3. (a)-(c) Bandgap measurement and (d) schematic energy-level diagram.

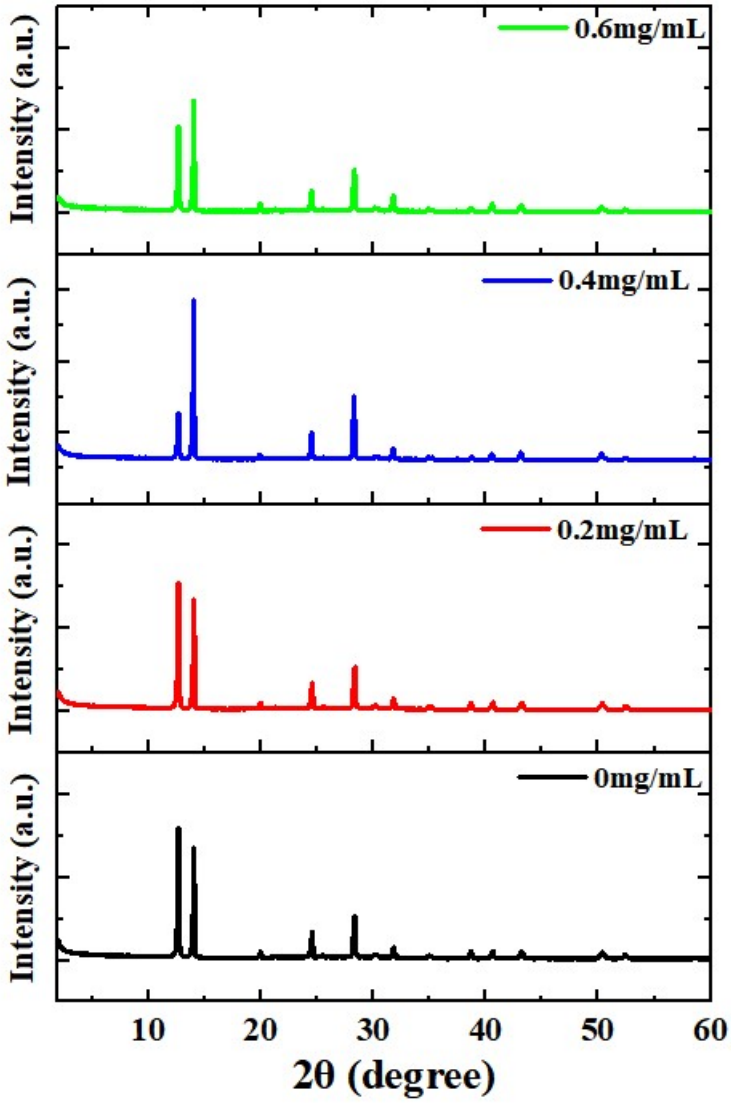

Figure S4. XRD patterns of perovskite films deposited on ETL with different SbF_3 amounts.

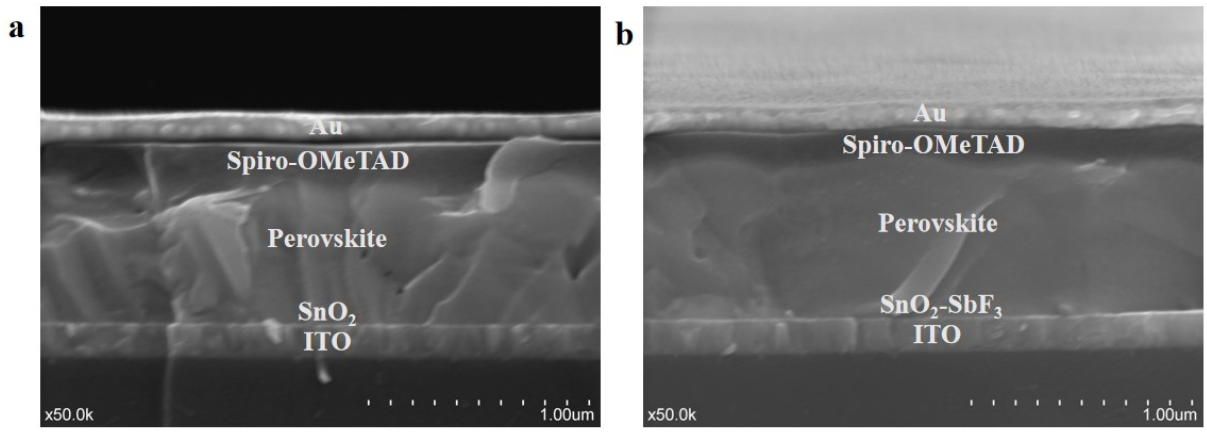

Figure S5. Cross-sectional SEM images of devices.

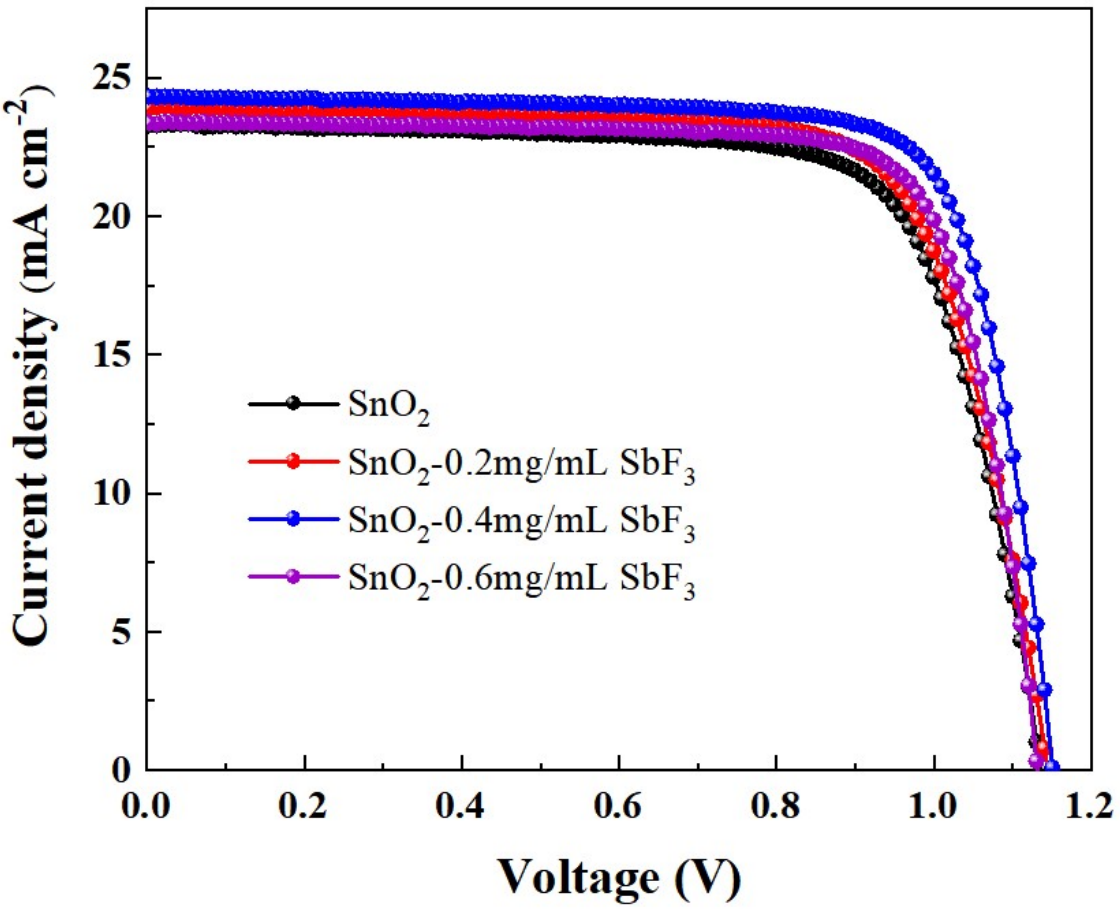

Figure S6. J-V curves of SnO_2-SbF_3 devices with different concentrations of SbF_3 aqueous solution.

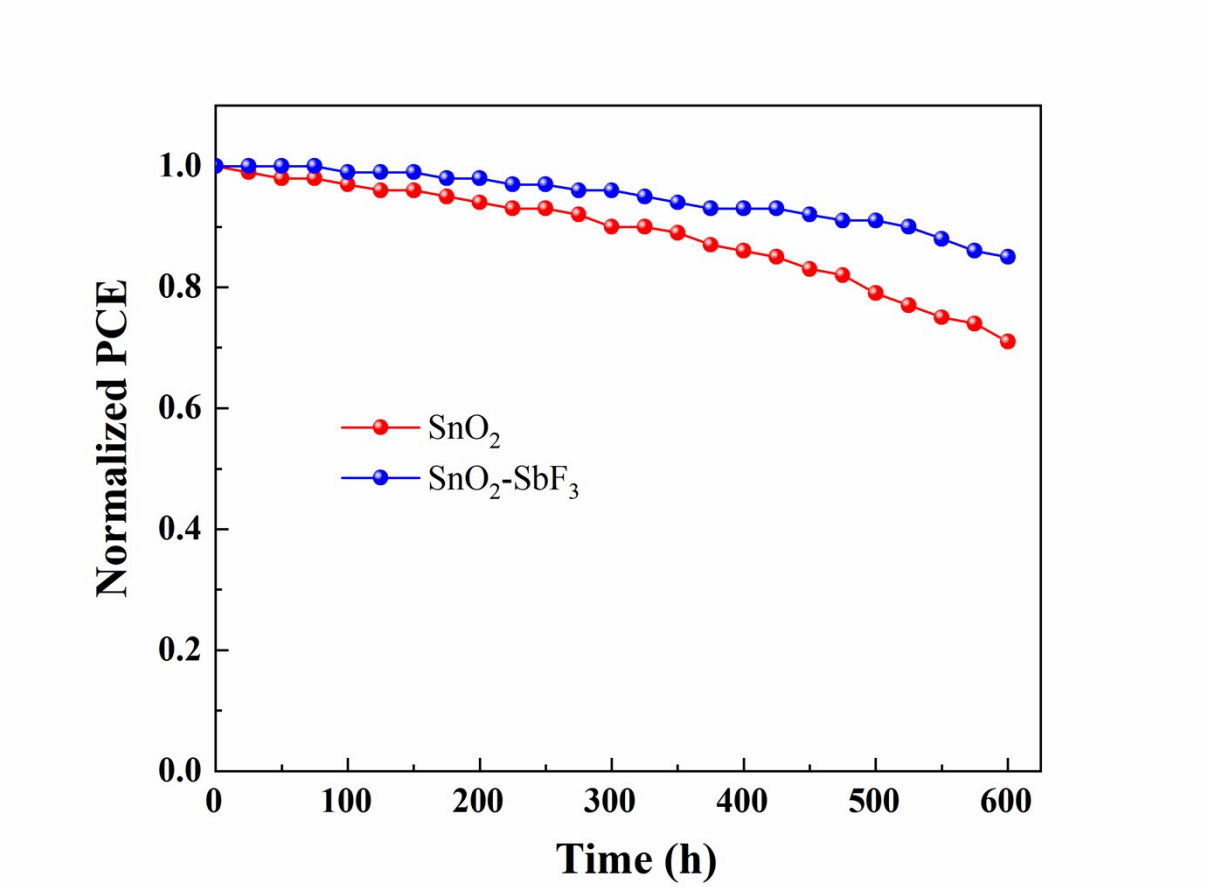

Figure S7. The long-term stability of PSCs based on SnO_2 or SnO_2-SbF_3.

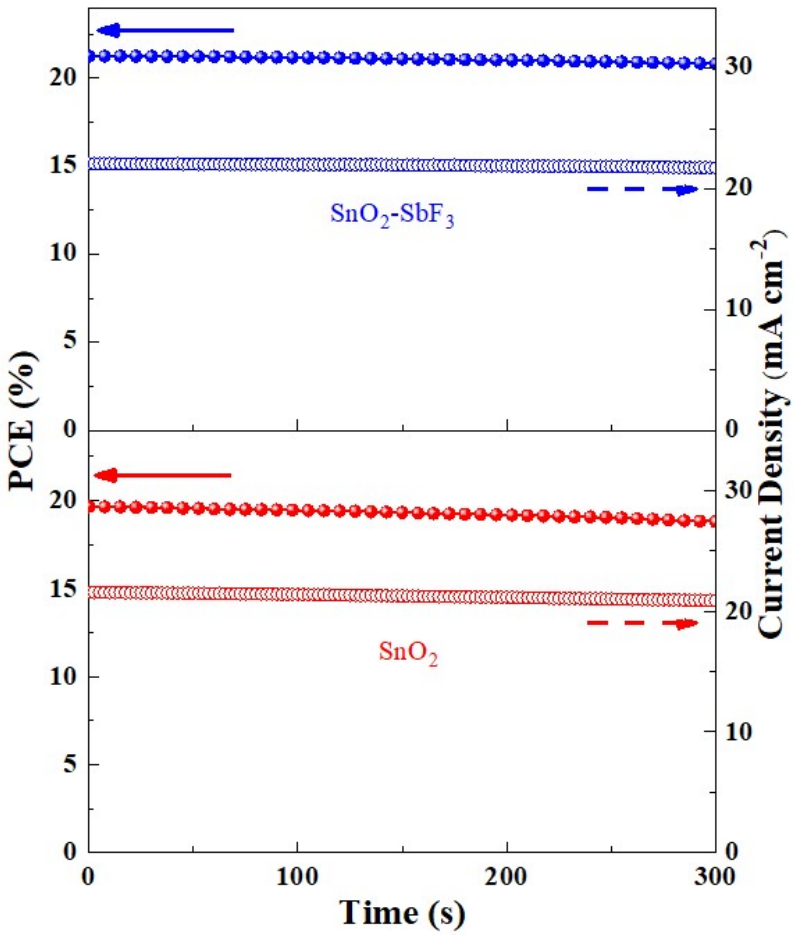

Figure S8. MPP tracking for PSCs under continuous AM 1.5 G illumination (The V_{MPP} of SnO_2 device is 0.918 V, and the V_{MPP} of SnO_2-SbF_3 device is 0.948 V).

The electron mobility of the ETL was determined by using a space charge finite current (SCLC) model with the ITO/Al/ETL/Al structure (ETL was SnO_2 film or SnO_2-SbF_3 film). Here, we calculate the electron mobility by using the following Equation:[1]

$$\mu_e = \frac{8JL^3}{9\varepsilon_0\varepsilon_r(V_{app} - V_r - V_{bi})^2}$$

where μ_e, J, L, ε_0, ε_r, V_{app}, V_r, and V_{bi} are electron mobility, current density, thickness of ETL, , vacuum permittivity, relative dielectric constant of ETL, applied voltage, voltage drop and built-in voltage, respectively. The calculated parameters and electron mobility are listed in Table S1 as follows.

Table S1 The calculated electron mobility of the ETL.

ETL	Mobility [$cm^{-2}V^{-1}S^{-1}$]	Thickness [nm]
SnO_2	2.38×10^{-4}	32.7
SnO_2-SbF_3	4.35×10^{-4}	34.8

The structures composed of ITO/ETL/Au were fabricated to study the conductivity of ETLs. Figure 2b shows the current-voltage (I-V) characteristic curves. We calculated the conductivity (σ) using the following Equation:[2]

$$\sigma = \frac{Id}{VA}$$

where A is the area and d is the thickness of the ETL. The calculated parameters and conductivity are listed in Table S2 as follows.

Table S2 The calculated electron conductivity of the ETL.

ETL	Slop [I/V]	Thickness [nm]	Conductivity [$mScm^{-1}$]
SnO_2	46.5	32.7	3.80×10^{-3}
SnO_2-SbF_3	59.7	34.8	5.19×10^{-3}

The average recombination lifetime was estimated from the TRPL spectra fitted by a bi-exponential decay function, the equation is as follows:[3]

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

where τ_i is decay times and A_i is amplitudes.

Table S3 Parameters for the TRPL spectra of the perovskite films deposited SnO_2 or SnO_2-SbF_3.

Sample	τ_1 [ns]	A_1	τ_2 [ns]	A_2	τ_{ave} [ns]
ITO/SnO_2/perovskite	77.21	194.03	276.32	152.77	224.17
ITO/SnO_2-SbF_3/perovskite	67.04	166.43	233.54	143.75	191.98

Table S4 Calculated perameters and trap density (Nt) of the perovskite films deposited on SnO_2 or SnO_2-SbF_3.

Sample	L [nm]	ε	V_{TFL} [V]	N_t [$\times 10^{15}$cm^{-3}]
SnO_2	720	42.3	0.626	5.65
SnO_2-SbF_3	720	42.3	0.433	3.91

Table S5 EIS parameters of the SnO_2 and SnO_2-SbF_3 devices.

Substrates	R_s [Ω]	R_{tr} [kΩ]	C_{tr} [F]	R_{rec} [kΩ]	C_{rec} [F]
SnO_2	35.1	54.5	9.416E-10	2904.2	5.119E-8
SnO_2-SbF_3	34.3	45.2	1.078E-9	3492.3	6.289E-8

Table S6 Parameters of the devices with different SbF_3 concentrations.

SnO_2-SbF_3	V_{oc} [V]	J_{sc} [mA/cm^2]	FF(%)	PCE(%)
0mg/mL	1.132	23.42	75.03	19.89
0.2mg/mL	1.144	23.85	75.59	20.62
0.4mg/mL	1.146	24.24	77.10	21.42

0.6mg/mL	1.133	23.51	75.80	20.19

References

[1] Z. G. Liu, K. M. Deng, J. Hu, and L. Li, ***Angew. Chem. Int. Ed.*** 2019, 58, 11497-11504.

[2] J. H. Heo, M. H. Lee, H. J. Han, B. R. Patil, J. S. Yu, and S. H. Im, ***J. Mater. Chem. A*** 2016, 4, 1572.

[3] J. Zhuang, P. Mao, Y. G. Luan, X. H. Yi, Z. Y. Tu, Y. Y. Zhang, Y. P. Yi, Y. Z. Wei, N. L. Chen, T. Lin, F. Y. Wang, C. Li, and J. Z. Wang, ***ACS Energy Lett.*** 2019, 4, 2913.