In situ NbO_x as an Efficient Interfacial Layer on SnO_2 electron-transport layer for High-Performance and Stable Flexible Perovskite Solar Cells

Jun Jiang [a], Menghui Wang [a], Gonglv Yang [a], Hongwei Hu [c], Pengyun Huo [a], Lijun Wang [a], Lvzhou Li [b,*], Ningyi Yuan [a,**], Jianning Ding [b,***]

a. *School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Jiangsu Province Cultivation Base for State Key Laboratory of Photovoltaic Science and Technology, Changzhou University, Changzhou 213164, Jiangsu China.*
b. *Yangzhou Technological Innovation Institute for Carbon Neutralization, Yangzhou University, Yangzhou 225127, Jiangsu China.*
c. *School of Mechanical Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu China.*

Materials.

All the commercial materials were used as received without any future purification, including PbI_2 (99.99%, TCI), methylammonium Chloride (MACl, Xi'an Polymer Light Technology Corp.), $HC(NH_2)_2I$ (FAI, Xi'an Polymer Light Technology Corp.), anhydrous DMF (99.9%, Alfa Aesar), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), chlorobenzene (CB, 99.9%, Alfa Aesar), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Xi'an Polymer Light Technology Corp.), 2,2′,7,7′-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD, Xi'an Polymer Light Technology Corp.), ethanol niobium (99.9%, Alfa Aesar), SnO_2(15% in H_2O colloidal dispersion, Alfa Aesar), anhydrous ethyl alcohol (99.8%, Aladdin).

Experiment section.

Preparation of the SnO_2 ETL

Indium tin oxide (ITO) glass or ITO PET (polyethylene terephthalate) was cleaned with deionized water, acetone, and ethanol in turn. The ITO glass was dried and cleaned with UV ozone for 25 mins before use to increase surface passivation. The ITO substrate was then spin-coated with a dense layer of SnO_2 (2.67 %, diluted by deionized water) at 4000 rpm for 30 s before being annealed at 150 ◦C for 30 mins.

Preparation of the NbO_x layer

Ethanol-based niobium solution was prepared by dissolving ethanol niobium (0.45, 0.60, 0.75 mg) in 1 mL ethanol. The ethanol niobium solution was than spin-coated on the surface of SnO_2 substrate at 3000 rpm for 30 s, then annealed on a hot plate at 100 °C for 30 mins in a glove box, and finally, process with a UV Ozone cleaning machine for 1 hour.

Preparation of the perovskite film

Metal-halide perovskite precursor solution was prepared by dissolving 1.53 M PbI_2, 1.4 M FAI, 0.5 M MACl, and 0.0122 M $MAPbBr_3$ in 1 mL N, N-dimethyl formamide and dimethyl sulfoxide (8:1 v/v) mixed solvent. The dissolved perovskite precursor solution was spin-coated on the SnO_2 layer with 1,000 rpm for 10 s then 5,000 rpm for 30 s, and 100 μL of chlorobenzene was dropped on substrate15~20 s before the spinning procedure was finished. And finally, the substrate was transferred to the hot plate for annealing at 100 ◦C for 60 mins.

Preparation of the Spiro-OMeTAD film and top electrode

Spiro-OMeTAD solution was prepared by dissolving 101.9 mg of Spiro-OMeTAD in 1 mL chlorobenzene containing 24.36 μL Li-TFSI (520 mg Li-TSFI dissolved in 1 mL acetonitrile), 45.36 μL 4-tert-butylpyridine (4-tBP) and 49.6 μL Co-TFSI (300 mg Co-TSFI dissolved in 1 mL acetonitrile). And then, This Spiro-OMeTAD precursor solution 25 μL was spin-coated under the perovskite layer at 4,000 rpm for 30 s.

Finally, a ~80 nm metal (Ag/Au) film was deposited under the Spiro-OMeTAD layer by thermal evaporation.

Characterization.

The *J-V* curves of PSCs were measured by a Keithley 2400 source meter under AM1.5G illumination with a solar simulator (San-ei Electric XES-301S) with a scan rate of 50 mV/s. The intensity of 1000 W/m^2 was calibrated by a standard silicon reference solar cell. The atomic force microscopic (AFM) images were performed by an atomic force microscope (Bruker, Dimension Icon). The SEM were obtained by a field-emission scanning electron microscopy (FESEM; Hitachi,

SU8020). The X-Ray Diffraction measurements were conducted by an X-ray diffractometer (Bruker, D8 Advance). The ultraviolet photoelectron spectra were obtained by a photoelectron spectrometer (PHI-5000 Versaprobe III) with a He-discharge lamp (He I, hν=21.22 eV). Steady-state and time-resolved photoluminescence (PL) spectra were obtained by a photoluminescence spectrometer (Edinburgh, FLS 1000).

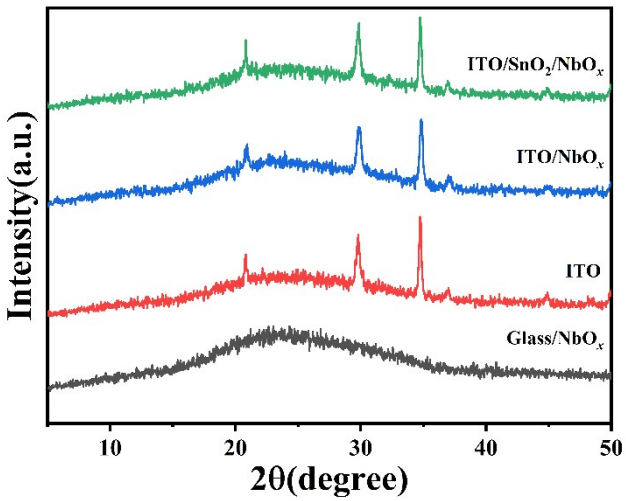

Fig. S1. X-ray diffraction patterns of NbO_x films grown on glass, on ITO glass, and on SnO_2.

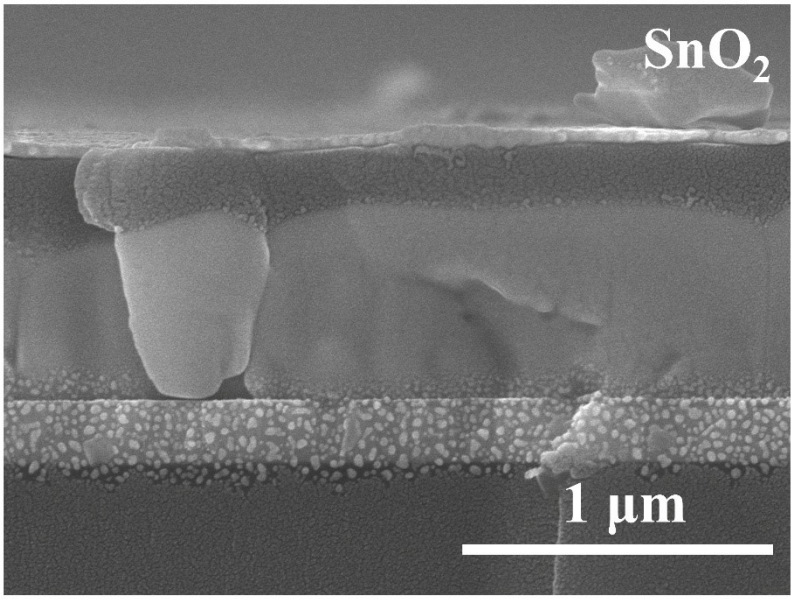

Fig. S2. Cross-sectional SEM image of PSCs based on SnO_2 film.

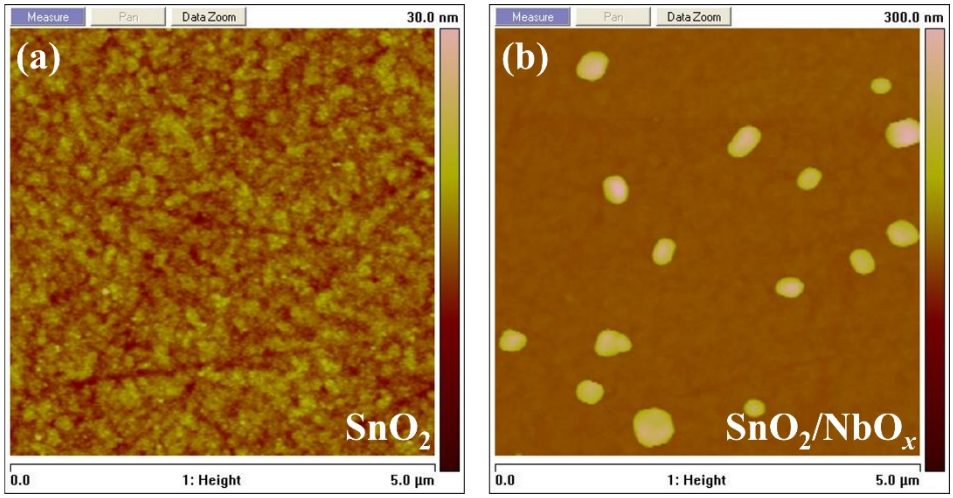

Fig. S3. AFM images of SnO_2 and SnO_2/NbO_x films.

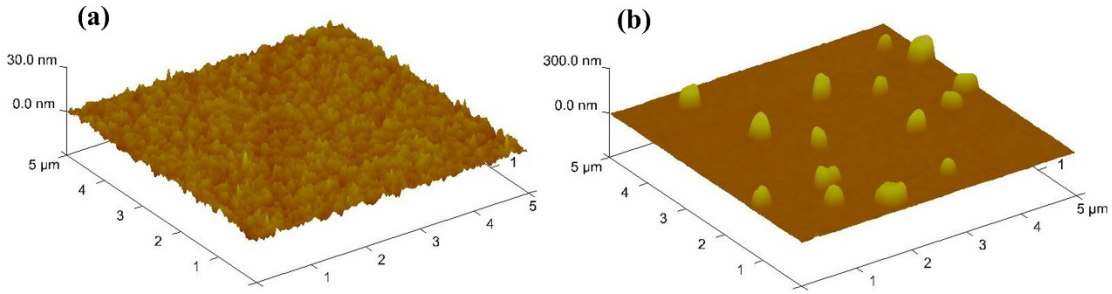

Fig. S4. 3D AFM image of the SnO_2 and SnO_2/NbO_x film.

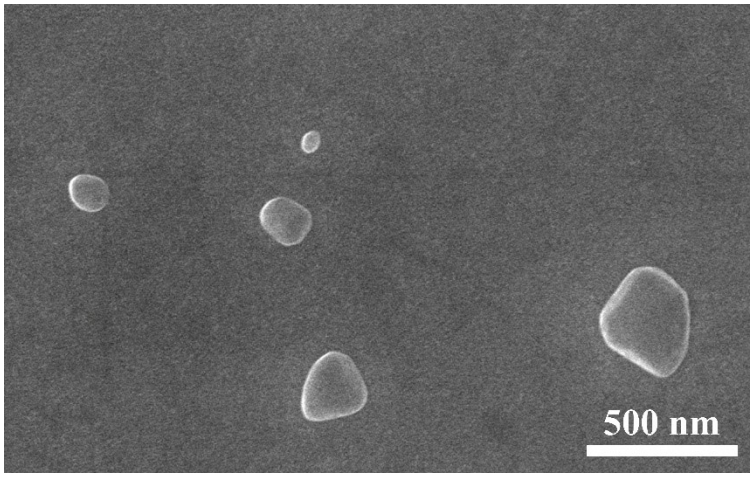

Fig. S5. Surface SEM image of the SnO_2/NbO_x film.

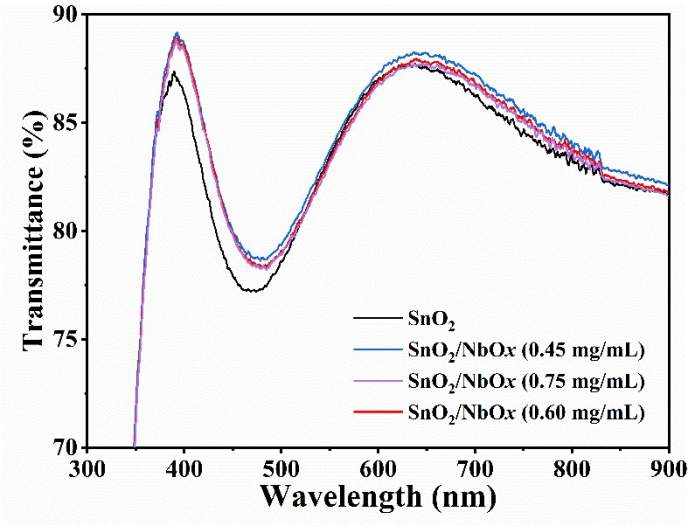

Fig. S6. Transmittance of the ITO substrates coated by SnO_2 and SnO_2/NbO_x films.

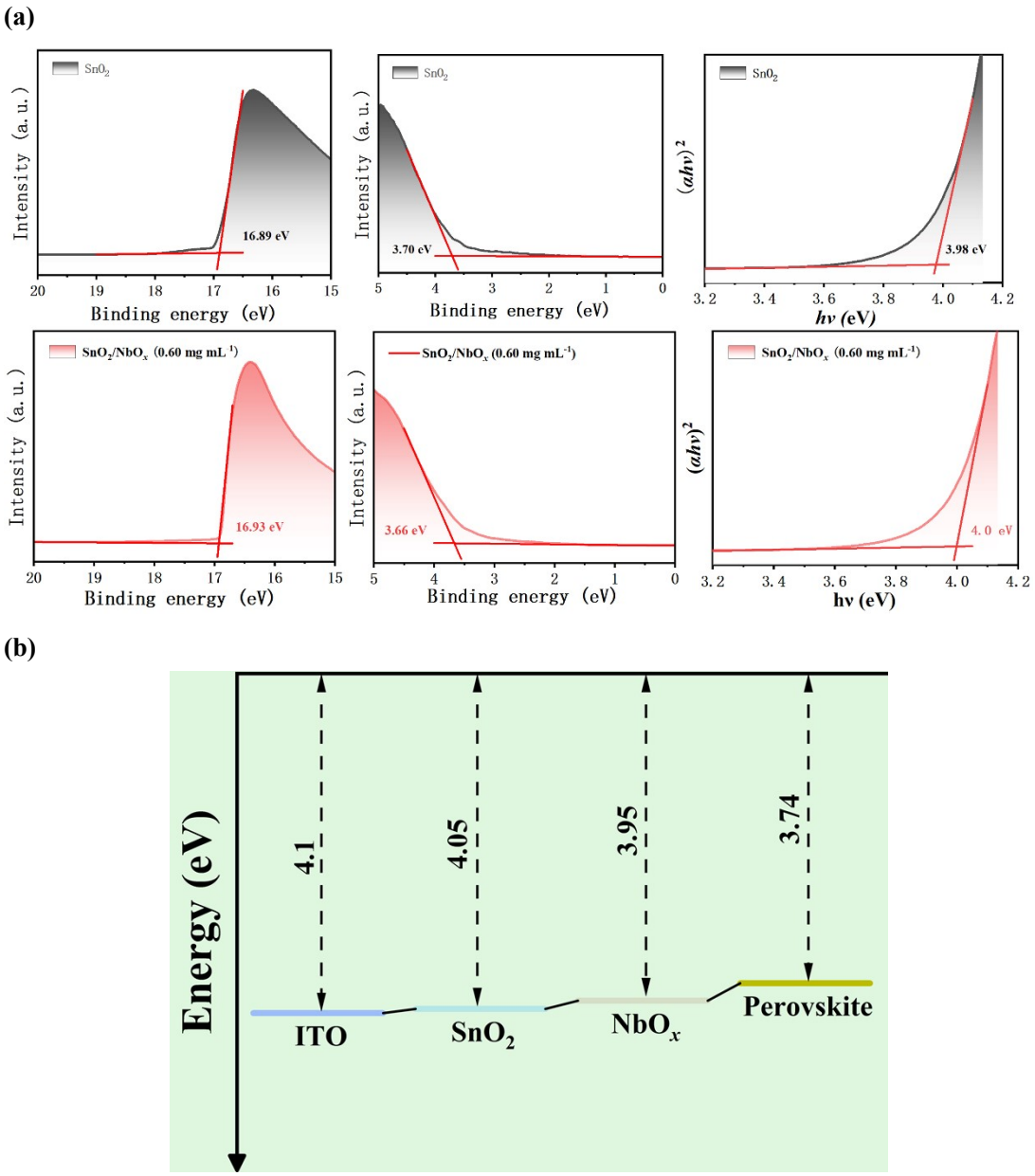

Fig. S7. (a) Valence band edges, cutoff regions and Tauc plots of for SnO_2 and SnO_2/NbO_x films. (b)Schematic energy level alignment.

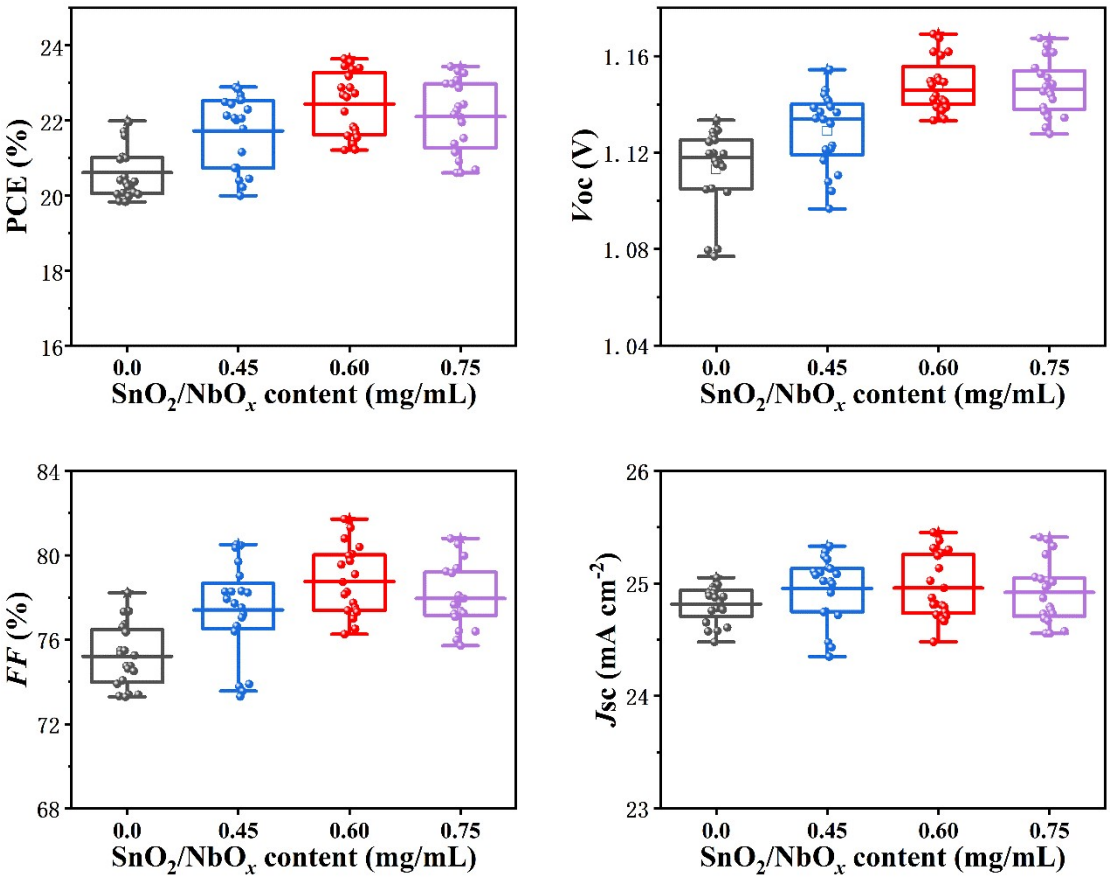

Fig. S8. Box charts of PCE, V_{OC}, FF, J_{SC} of PSCs with SnO_2 and SnO_2/NbO_x at different Ethanol niobium(0.45、0.60、0.75 mg/L).

Table S1. The full width at half maximum (FWHM) values of the corresponding XRD pattern of pristine and NbO_x-based thin films.

sample	FWHM of perovskite peaks	
	14°	**28°**
0 mg/mL	0.192	0.174
0.45 mg/mL	0.136	0.146
0.60 mg/mL	0.132	0.141
0.75 mg/mL	0.134	0.144

Table S2. The fitting parameters of the TRPL spectra for SnO_2/perovskite and SnO_2/NbO_x perovskite films.

	τ_1	A_1	τ_2	A_2	τ_{ave}
SnO_2	58.90	0.21	264.41	0.87	253.92
SnO_2/NbO_x (0.45 mg/ml)	19.79	0.31	173.47	0.69	165.98
SnO_2/NbO_x (0.6 mg/ml)	10.58	0.37	57.99	0.63	53.40
SnO_2/NbO_x (0.75 mg/ml)	16.72	0.31	106.58	0.69	100.66

Table S3. Schematic energy level alignment.

Sample	E_f (eV)	Ev(eV)	Ec(eV)	Eg(eV)
SnO_2	3.7	-8.03	-4.05	3.98
SnO_2/NbO_x (0.60 mg/mL)	3.66	-7.95	-3.95	4.0
Perovskite	1.67	-5.29	-3.74	1.55

Table S4. Photovoltaics parameters of perovskite solar cells with different concentrations (mg/mL) of ethanol niobium treating SnO_2 film measured under standard 1-sun illumination (reverse and forward scan).

	Scan direction	V_{oc}(V)	PCE (%)	*FF* (%)	J_{sc} (mA/ cm^2)
SnO_2	Reverse	1.13	22.08	79.97	24.52
	Forward	1.10	19.18	70.90	24.56
SnO_2/NbO_x(0.45 mg/mL)	Reverse	1.15	22.87	80.38	24.72
	Forward	1.12	19.89	71.87	24.76
SnO_2/NbO_x(0.60 mg/mL)	Reverse	1.17	23.64	81.31	24.87
	Forward	1.15	20.50	71.58	24.89
SnO_2/NbO_x(0.75 mg/mL)	Reverse	1.17	23.26	80.79	24.66
	Forward	1.13	19.56	70.06	24.67

Table S5. Photovoltaics parameters of flexible perovskite solar cells.

	$V_{oc}(V)$	PCE (%)	*FF* (%)	J_{sc} (mA/cm^2)
SnO_2	1.02	19.54	78.75	24.28
SnO_2/NbO_x	1.10	21.86	81.54	24.46