Supporting Information

Synergistic Dual-Layer Passivation Boosts Efficiency and Stability in Perovskite Solar Cells Using Naphthol Sulfonate

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Experimental Section

Materials

Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF), Isopropanol (IPA), Methylammonium bromine (MABr), Methylammonium chloride (MACl), Forma-iminium iodide (FAI), Lead iodide (PbI_2), Chlorobenzene (CB) and PTAA were purchased from Advanced Election Technology Co., Ltd. Dipotassium 7-hydroxynaphthalene-1,3-disulphonate (K-NDS) and Tris (pentafluoro phenyl) borane (TPFB) were obtained from TCI company. All materials in this study were used as received without further purification.

Solutions Preparation

The PbI_2 solution was obtained by dissolving 1.4 mM PbI_2 into 1 mL DMF/DMSO mixed solvent (volume ratio is 94:6). The FAI/MABr/MACl solution was prepared by dissolving 70 mg FAI, 3 mg MABr and 11 mg MACl into 1 mL IPA. The solutions were stirring overnight before use. The HTL precursor solution was prepared by dissolving 40 mg PTAA with 4 mg TPFB in 1mL CB. Mixing K-NDS with deionized water to obtain K-NDS solutions with different concentrations (2, 4, 6 mg/ml).

Device fabrication

The ITO substrates were first ultrasonically washed by ethanol, acetone, and deionized water for 30 min followed by drying under nitrogen stream and treatment with UV-ozone for 30 min to remove any organic residues and enhance the surface hydrophilicity. Then, the SnO_2 colloidal solution was diluted in deionized water (volume ratio is 1:6) and then spin-coated on ITO surface at the rate of 3000 rpm for 30 s, followed by annealing at 150 ℃ for 30 min. After cooling down to room temperature, another UV-ozone treatment was carried out for 30 min. The K-NDS solution with different concentrations (2, 4, 6 mg/ml) was spin-coated on the as-fabricated SnO_2 film at the rate of 2000 rpm for 30 s, following by annealing at 100 ℃ for 10 min. After cooling down to room temperature, another UV-ozone treatment was carried out for 30 min, then transferred into a nitrogen glove box. The PbI_2 solution was spin-coated on the SnO_2/K-NDS substrate at 1500 rpm for 30 s and annealed at 70 ℃ for 1 min. And the FAI/MABr/MACl solution was spin-coated on the substrate at 1800 rpm for 30 s, then the film was annealed outside the glove box at 150 ℃ for 10 min with 40% humidity, resulting in a $(FAPbI_3)_x(MAPbBr_3)_{1-x}$ perovskite film (x is 0.92 in the precursor). The PTAA solution was spin-coated on the perovskite film as a hole conductor. The devices were completed by evaporation 100 nm silver in a vacuum chamber (base pressure, 5×10^{-4} Pa).

The perovskite bottom interface can be exposed using the following process:

1. Spin-coat a layer of UV-curable adhesive onto the perovskite film.
2. Cure the adhesive using an ultraviolet lamp.
3. Remove the cured adhesive layer.

Characterization

The *J-V* characteristics of the photovoltaic cells were measured under ambient conditions using a Keithley 2400 source meter, with simulated AM 1.5G solar illumination (100 mW/cm^2). Dark current and steady-state power output were also measured using the Keithley 2400. Electrochemical impedance spectroscopy (EIS) and capacitance-voltage (*C-V*) measurements were conducted using an IM6e Electrochemical Workstation (ZAHNER).

X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed in an ultrahigh vacuum environment (base pressure of 1×10^{-10} mbar) using a Thermo Scientific Nexsa G2 system. XPS utilized a monochromatic Al Kα X-ray source (1486.6 eV), while UPS employed monochromatic He Iα radiation (21.22 eV). The ^{1}H NMR measurement in solution was carried out on the Bruker AVANCE III 400 (400 MHz)

spectrometer at room temperature. Deuterated DMSO was used as ^{1}H NMR solvent to dissolve the K-NDS and PbI_2 just before the ^{1}H NMR mearsurement.

Atomic force microscopy (AFM) measurements were conducted using a Dimension Icon-PT (Bruker). Fourier-transform infrared (FTIR) spectroscopy of the SnO_2 and perovskite films was performed in transmission mode using a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific). UV-visible (UV-vis) spectra were recorded using a UV-3600 spectrophotometer (Hitachi). X-ray diffraction (XRD) patterns were acquired using a PANalytical X-ray diffractometer with Cu Kα radiation.

Surface and cross-sectional scanning electron microscopy (SEM) images were obtained using a Nova Nano 230 instrument. Steady-state and time-resolved photoluminescence (PL) measurements were carried out using an FS5 spectrometer (Edinburgh Instruments). Water contact angle measurements were performed using a Krüss DSA100s drop shape analyzer.

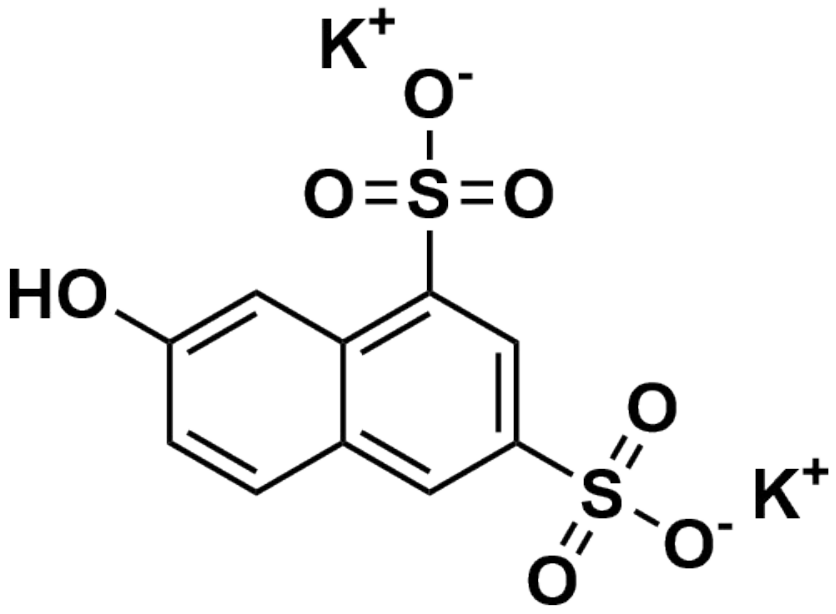

Figure S1. The structure of the K-NDS.

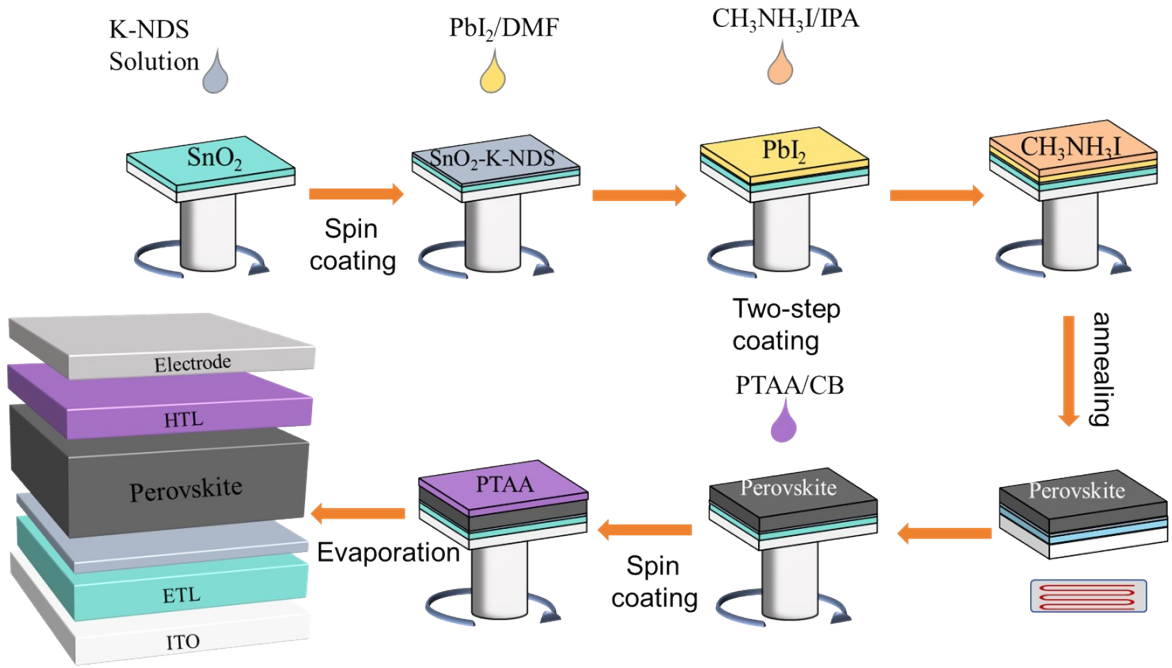

Figure S2. The fabrication of the PSCs.

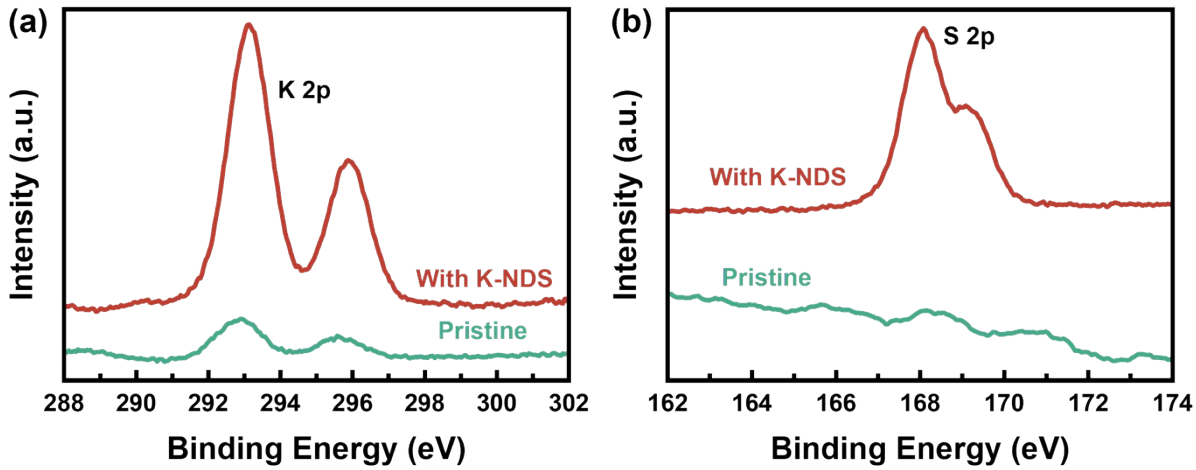

Figure S3. XPS high-resolution spectra of SnO_2 and SnO_2/K-NDS for (a) K 2p, (c) S 2p.

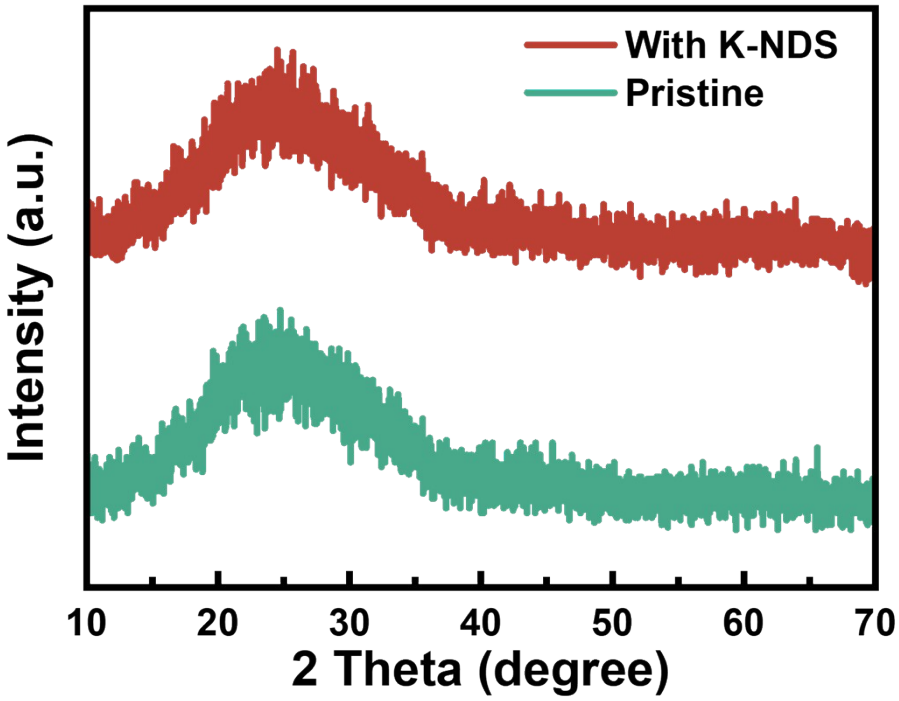

Figure S4. The XRD spectrum of SnO_2 and SnO_2/K-NDS.

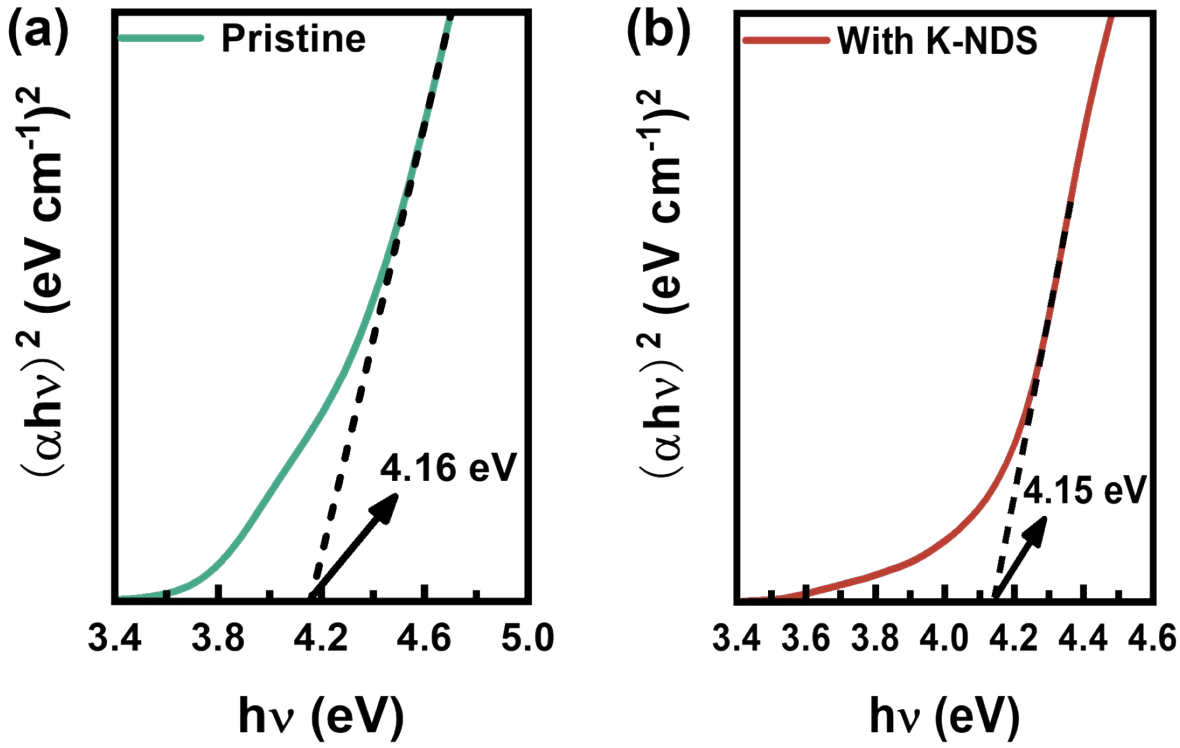

Figure S5. The Tauc plot of the SnO_2 and SnO_2/K-NDS.

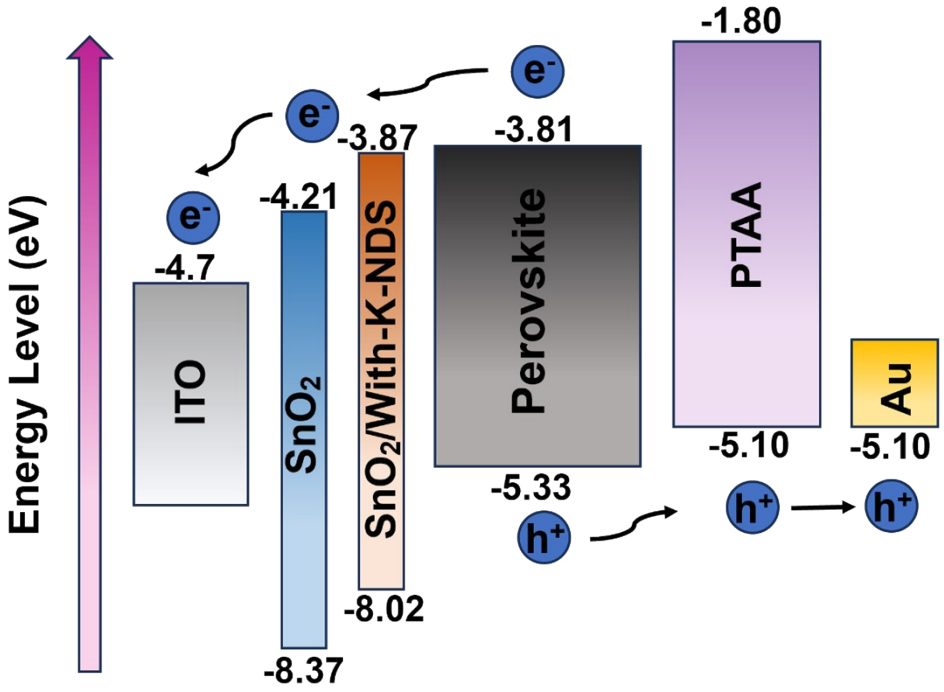

Figure S6. The Schematic illustration of energy level diagram in the PSCs.

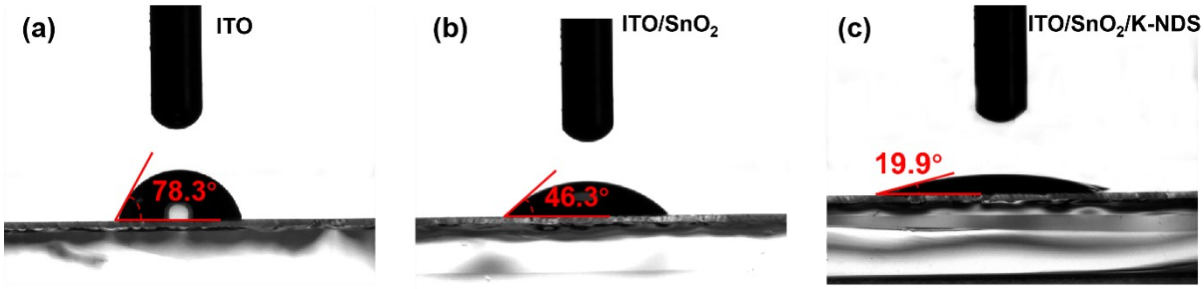

Figure S7. The contact angle measurements of (a) ITO, (b)ITO/SnO_2 and (c) ITO/SnO_2/K-NDS films.

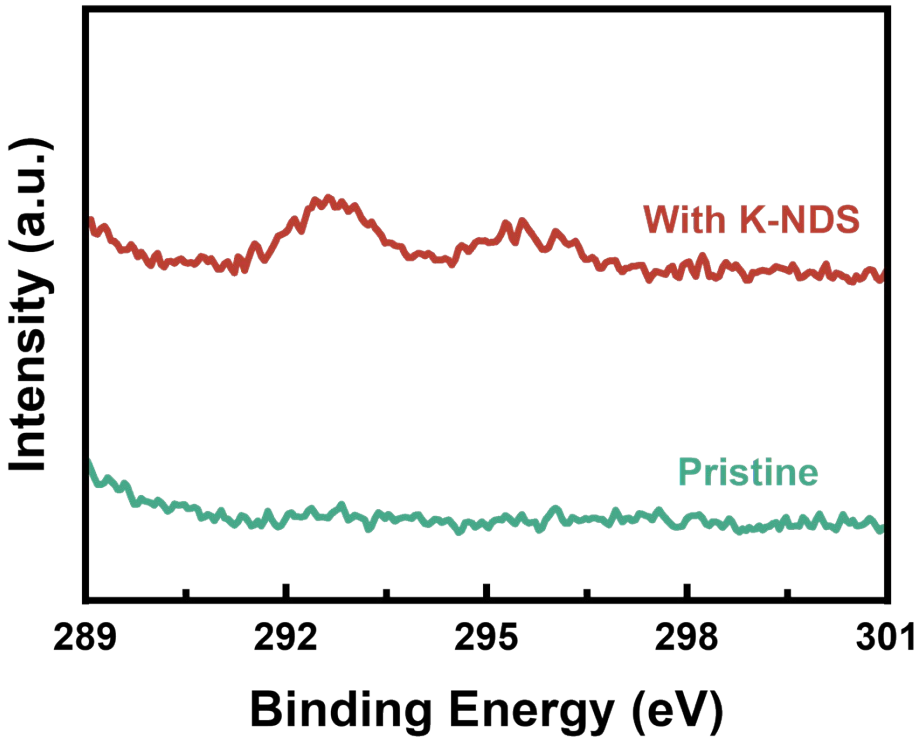

Figure S8. XPS high-resolution spectra of Perovskite and K-NDS/ Perovskite for K 2p.

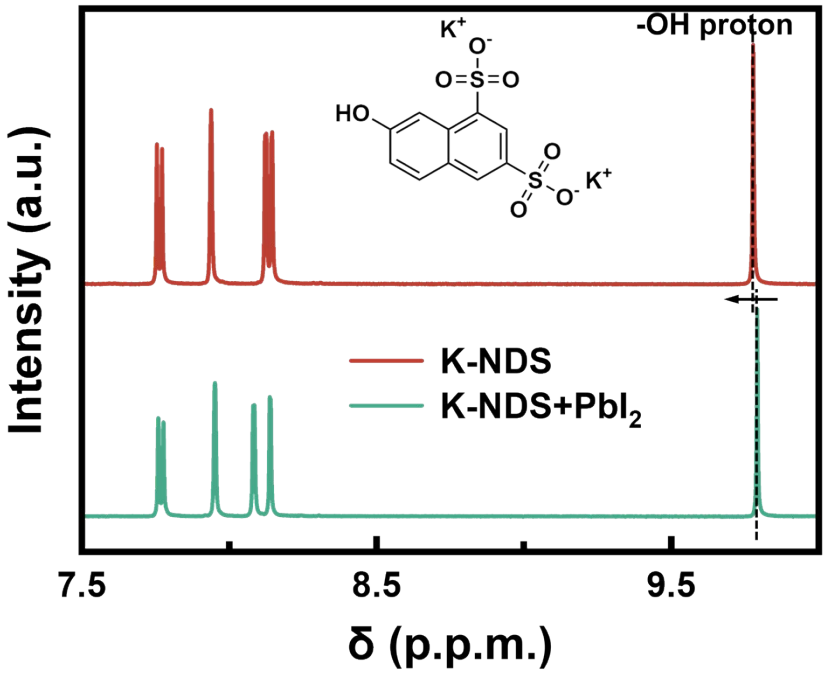

Figure S9. ^{1}H NMR spectra of K-NDS and its mixture with PbI_2 in deuterated DMSO solution.

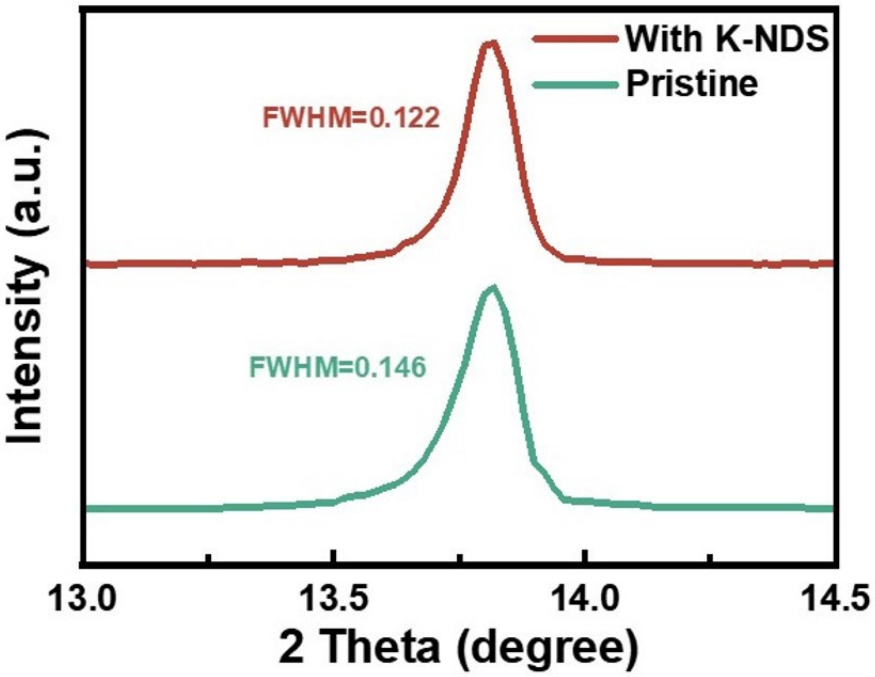

Figure S10. The FTHM of (100) crystallographic plane for perovskite and K-NDS/ perovskite.

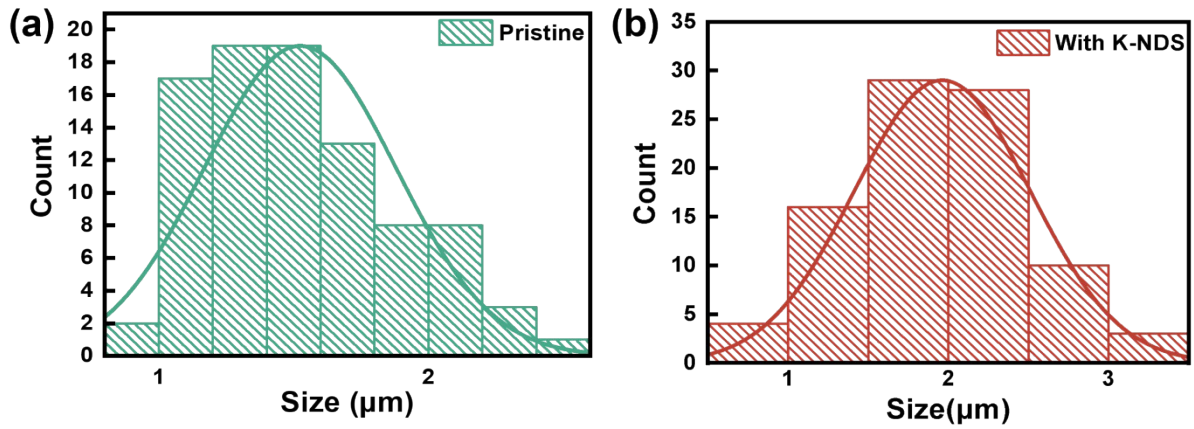

Figure S11. Statistical histogram of grain size of perovskite and K-NDS/perovskite.

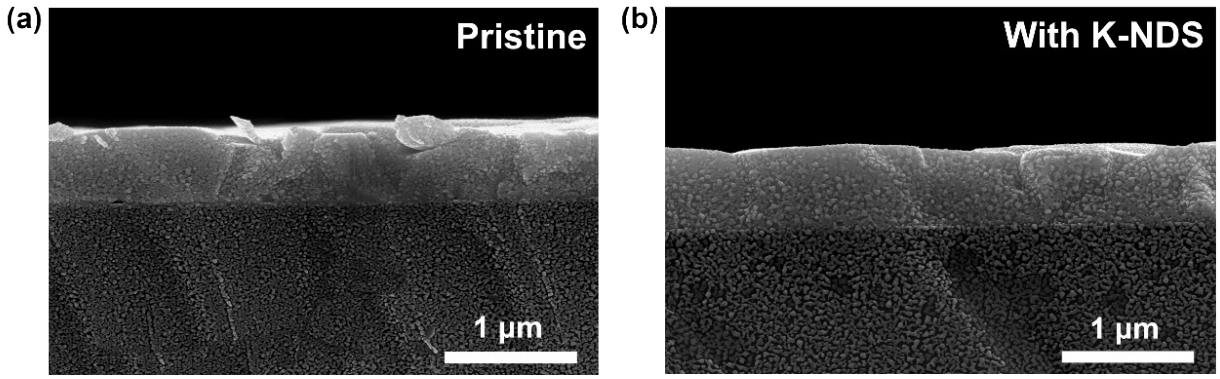

Figure S12. The cross-sectional SEM images of the perovskite on (a) SnO_2 and (b) SnO_2/K-NDS.

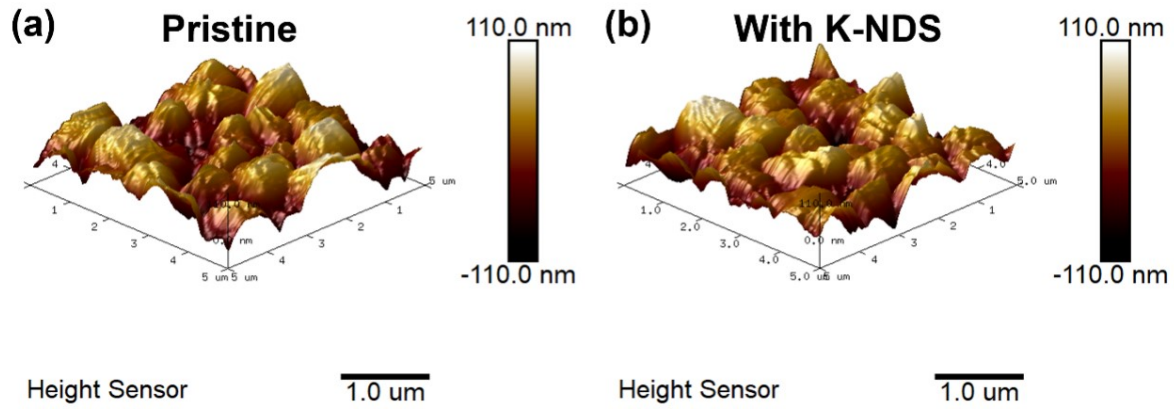

Figure S13. The 3D-AFM images of the perovskite on (a) SnO_2 and (B) SnO_2/K-NDS substrate.

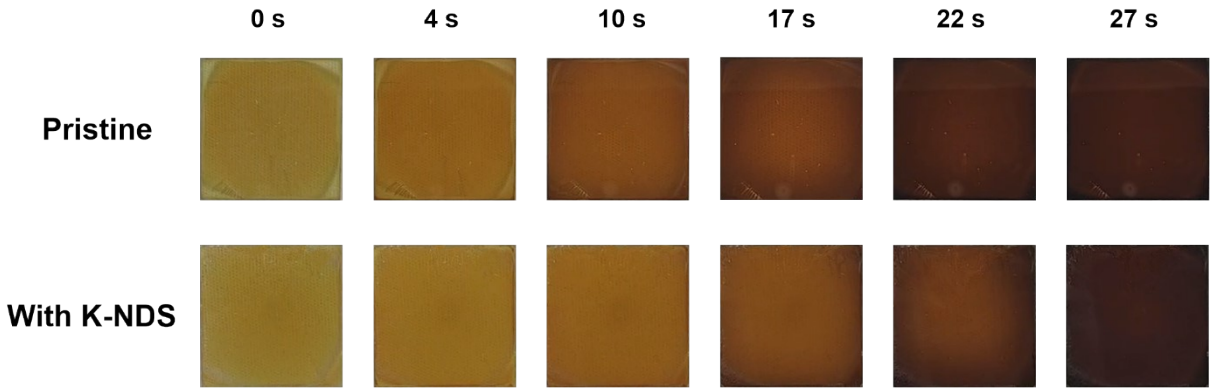

Figure S14. The annealing images of perovskite films deposited in SnO_2 and SnO_2/K-NDS.

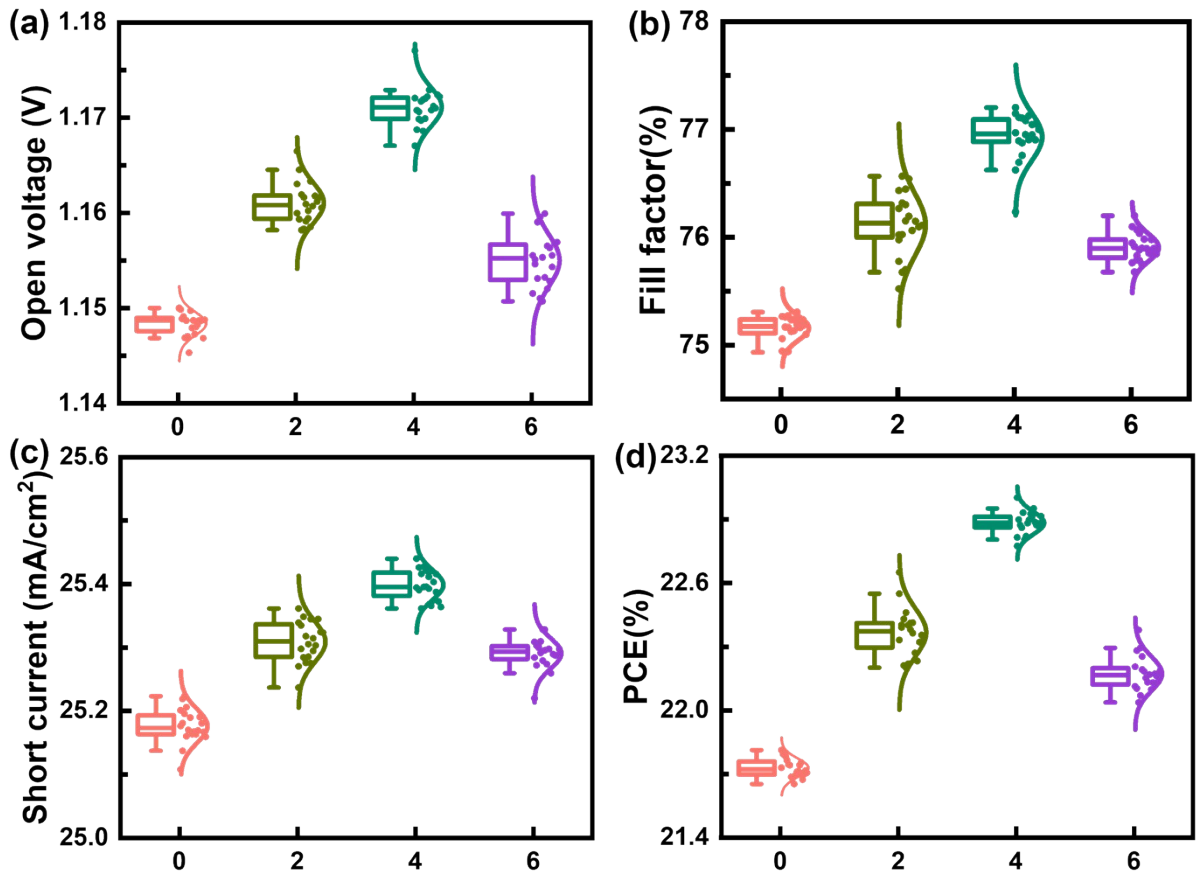

Figure S15. The statistics parameters distribution of PCSs devices (a) V_{OC}, (b) FF, (c) J_{SC} and (d) PCE.

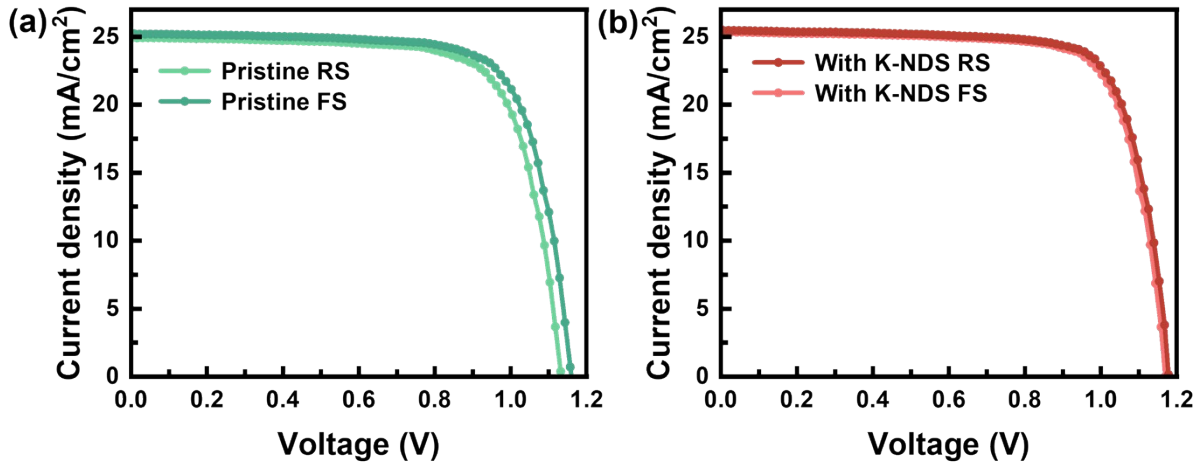

Figure S16. The RS and FS *J–V* curves of PSCs devices deposited on (a) SnO_2 and (b) SnO_2/K-NDS ETL.

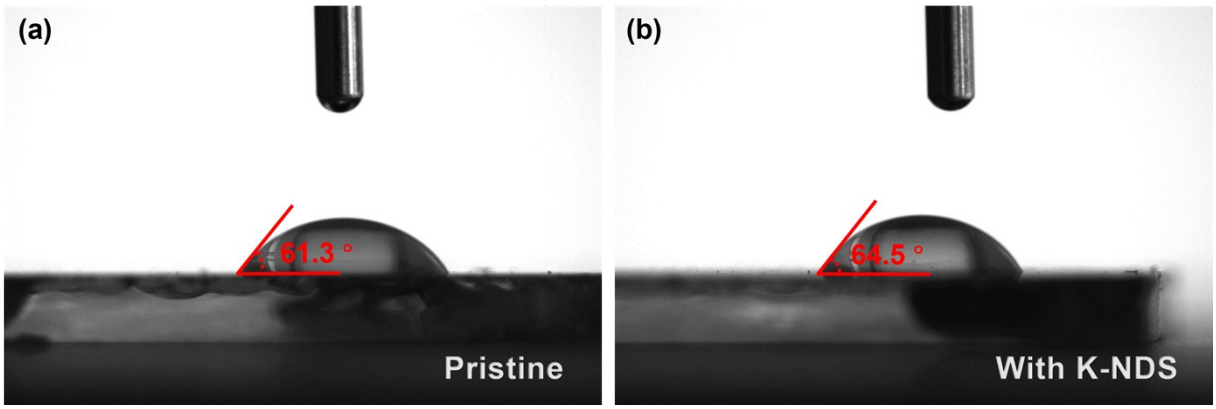

Figure S17. The contact angle measurements of perovskite film deposited on (a) SnO_2 and (b) SnO_2/K-NDS.

Table S1. O content of the surface of SnO_2 and SnO_2/K-NDS of O 1s high resolution spectra.

Peak	Atomic conc (%) Pristine	Atomic conc (%) With K-NDS
Sn-O	66.01	93.56
O_V/ O_{OH}	33.99	2.40
SO_3^-	0	4.04

Table S2. The calculation of the energy alignment.

Sample	E_{SEC} (eV)	E_{VBE} (eV)	E_F (eV)	E_g (eV)	VBM (eV)	CBM (eV)
Pristine	16.93	4.08	-4.29	4.16	-8.37	-4.21
With K-NDS	17.07	3.87	-4.15	4.15	-8.02	-3.87

Table S3. The parameters of TRPL measurement.

Device	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
Pristine	28.61	16.27	209.00	65.50	203.07
With K-NDS	36.57	21.69	191.33	59.61	181.27

Table S4. The calculated parameters and trap density (N_t) of perovskite films based on SnO_2 and SnO_2/K-NDS.

Device	L (nm)	V_{TFL} (V)	N_t (cm^{-3})
Pristine	547.96	0.26	3.063×10^{15}
With K-NDS	550.10	0.14	1.636×10^{15}

Table S5. Performance summary the champion PSCs devices with various K-NDS cocentration.

Device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0 mg/ml	25.20	1.150	75.27	21.81
2 mg/ml	25.36	1.166	76.56	22.64
4 mg/ml	25.44	1.172	77.15	23.00
6 mg/ml	25.30	1.160	75.98	22.29

Table S6. Performance summary the PSCs devices with and without K-NDS modification.

Device		J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	HI
Pristine	RS	25.20	1.150	75.27	21.81	0.0422
	FS	24.92	1.130	74.20	20.89	
With K-NDS	RS	25.44	1.172	77.15	23.00	0.0217
	FS	25.32	1.166	76.23	22.50	