

Supporting Information

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Periodic Acid Modification of Chemical-Bath Deposited SnO₂ Electron Transport Layers for Perovskite Solar Cells and Mini Modules

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Materials

All the chemical reagents were directly used without further purification. Cesium iodide (99.999%), lead bromide (PbBr₂, 99.999%), Tin(II) chloride dihydrate (>99.995%), N,N-Dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, >99.9%), chlorobenzene (anhydrous, 99.8%), acetonitrile (anhydrous, 99.8%), bis(trifluoromethane) sulfonamide lithium salt (Li-TFSL, 99.95%), and 4-*tert*-butyl pyridine (t-BP, 98%), urea (99.0-100.5%) were purchased from Sigma-Aldrich. Formamidinium iodide (FAI, >99.99%) and methylammonium

iodide (MAI, >99.99%) were purchased from Greatcell Solar. Lead iodide (PbI₂, 99.99%), and thioglycolic acid (>95.0%) were purchased from Tokyo Chemical Industry (TCI). Periodic acid (99%) was purchased from Macklin. Hydrochloric acid (HCl), ethanol, and 2-propanol were purchased from Beijing TongGuang Fine Chemicals Company. FTO glass (12-14 Ohm/□) was purchased from Advanced Election Technology Co., Ltd. Methylamine chloride (MACl, 99.5%) was purchased from Xi'an Polymer Light Technology Co., Ltd. Spiro-OMeTAD (99.5%) and FK209 Co(III) TFSI salt (>99%) were purchased from Lumtec.

Preparation of SnO₂ layer by chemical bathing deposition (CBD)

The CBD solution was prepared by dissolving 0.5 g urea in 40 mL deionized water, followed by the addition of 10 μL thioglycolic acid and 500 μL HCl (37 wt%). After sonication for 5 minutes, 0.11 g SnCl₂·2H₂O (99.995%) was dissolved in the CBD solution. The solution was stored at 8~10 °C for 72 h before use. 20 mL CBD solution was diluted with 100 mL de-ionized water, followed by sonication for 5 minutes. The temperature during the sonication process needs to be carefully controlled below 30 °C to prevent the occurrence of the chemical reaction.

FTO glasses were etched and cleaned in detergent, deionized water, acetone, ethanol, and 2-propanol. Before use, the substrates were dried with N₂ and exposed to an O₂ plasma atmosphere for more than 20 min. As-cleaned FTO glasses were horizontally placed in the CBD solution, followed by a heating process at 70 °C for 4 h. The FTO glasses were cleaned with deionized water 3~4 times. For the PAPT-modified samples, the FTO glasses were immersed in periodic acid solutions with different concentrations varied from 1 mM to 4 mM for 5 minutes. All the FTO glasses were dried with N₂ and annealed on a hot plate at 150 °C for 40 minutes.

Fabrication of perovskite solar cells

1.45M perovskite precursor solution (CsI: FAI: MAI: PbI₂: PbBr₂: MACl=0.05: 0.81: 0.04: 0.98: 0.02: 0.20) were dissolved in DMF: DMSO=4: 1 solvent, as previously reported.^[1] The precursor solution was spin-coated on the FTO substrate with a SnO₂ layer at 1000 rpm for 12 s and 5000 rpm for 28s. 160 μL chlorobenzene was dropped at 10s before the end of the second spinning process, followed by

annealing at 100 °C for 10 min and 150 °C for 10 min. The Spiro-OMeTAD solution was prepared by dissolving 0.1260 g Spiro-OMeTAD, 32 μ L Li-TFSI solution (520 mg/mL in acetonitrile), 14 μ L Co-TFSI (375 mg/mL in acetonitrile), 55 μ L t-BP in 1.4 mL chlorobenzene. The spiro-OMeTAD solution was spin-coated on the perovskite film at 4000 rpm for 30 s. Finally, a 70 nm thick gold electrode was deposited by thermal evaporation.

Fabrication of perovskite solar modules (PSMs) via slot-die coating:

For the fabrication of PSMs, FTO substrates with areas of 3×3 cm² were first etched with a 1024-nm CO₂ laser (P1 scribing). Then, the SnO₂ films were fabricated by the CBD method. The slot-die machine was purchased from DaZheng (Jiangsu) Micro-Nano Tech. Co., Ltd. (China). Then, the perovskite precursor ink was diluted to a molar concentration of 0.8 M and slot-die coated on the substrates accompanied by a gas-quenching process (with a substrate-moving speed of 2 mm/s). The blowing gas pressure from the gas knife was 0.1 MPa. After that, the substrate was transferred onto a hot plate and annealed at 150 °C for 10 mins. Then, the Spiro-OMeTAD solution was slot-die coated at a speed of 2 mm/s. P2-scribe was conducted using a 532-nm-laser. Then, the P2-scribed substrate was evaporated with a mixed top electrode of MoO_x (5 nm)/ copper (100 nm). Afterward, the module was scribed again to complete the series connection using the same laser scriber. The ratio of the dead-area width to the active-area width was 1:9 (0.05mm to 0.45 mm), leading to a GFF of 90%.

Computational methods

First-principle calculations were performed with the density functional theory (DFT) as implemented in Vienna ab-initio Simulation Package (VASP) package.^[2] The augmented wave (PAW) method^[3, 4] was used for the interactions between ions and valence electrons with Perdew-Burke-Ernzerhof (PBE)^[5, 6] functional. The plane wave energy cutoff was set to 450 eV. A sufficiently large vacuum layer of 15 Å was used to avoid the periodic image interactions along the z-direction. The atomic force and energy convergence criteria thresholds were set to 0.02 eV and 1×10^{-5} eV/ Å, respectively. The k-point mesh of $3\times 3\times 1$ was employed for SnO₂ surface geometric

optimization and adsorption energy calculation. The van der Waals (vdW) interaction was taken into account with the Grimme type at the DFT-D3 level.^[7]

Characterization

The morphology of the perovskite films was observed by field-emission scanning electron microscopy (FESEM, LEO1530, Zeiss, Germany) and atomic force microscopy (AFM, Cypher, Oxford Instruments, UK). The crystal structures were characterized by X-ray diffraction (XRD, D8 Advance Diffractometer, Bruker, Germany) with Cu K α (1.5406 Å) radiation operating at 40 kV. The Ultraviolet-Visible light spectrum was obtained using a UV-Vis spectrophotometer (Lambda 1050, Perkin Elmer, USA). The photoluminescence (PL) spectra were characterized by a fluorescence spectrometry (FLS920, Edinburgh Instruments, UK). For steady-state PL spectra, the spectra were obtained by illuminating the sample with a monochromatic xenon lamp source (λ_{exc} =460 nm). For time-resolved PL (TRPL), the spectra were acquired with samples photoexcited by a pulsed laser beam (405 nm). The XPS spectra were recorded by an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher SCIENTIFIC INC., UK) with Al K α radiation ($h\nu = 1486.6$ eV) as the illumination source. The photoelectron spectroscopy in the air (PESA) was performed with the AC-2 instrument (AC-2, RIKEN Instruments, Japan). The Fourier transform infrared spectroscopy (FTIR) measurements were performed on the infrared spectrometer (VERTEX 70V, Bruker, Germany) in ATR (Attenuated Total Reflection) mode. The photocurrent density-voltage (J - V) curves were obtained by a digital source meter (2400, Keithley Instruments, USA). The perovskite solar cells were illuminated under AM 1.5G (100 mW/cm²) by solar simulators (91192 and 94082A, Newport, USA) calibrated with a standard crystalline silicon solar cell. The monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra were obtained by the quantum efficiency system (QEX10, PV measurements, USA) in a DC mode.

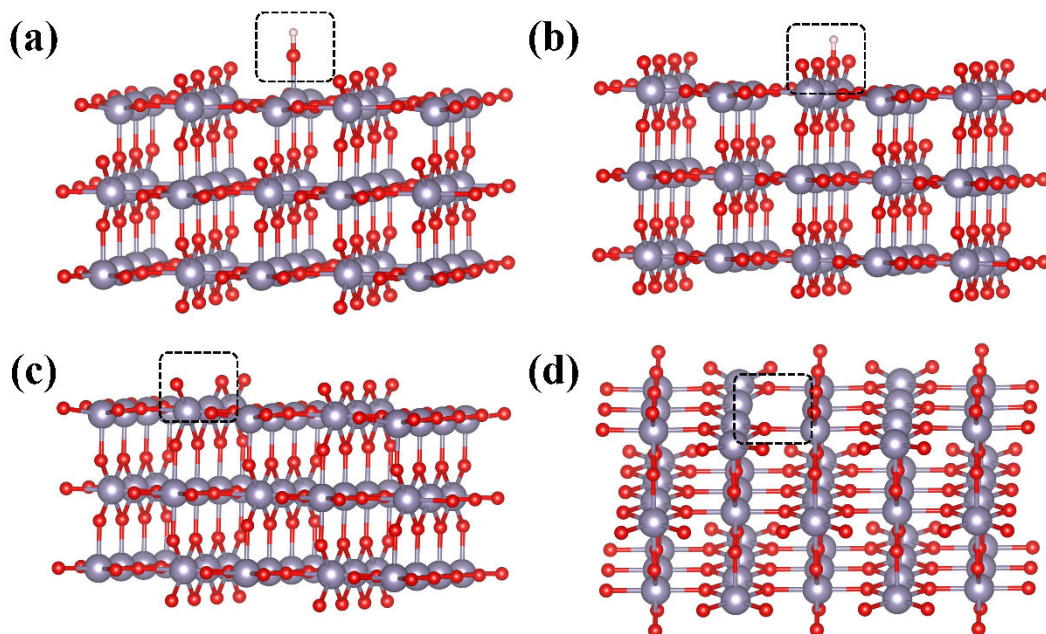


Figure S1 The structure image of four kinds of oxygen defects on the surface of CBD-coated SnO₂ films: (a) terminal hydroxyl (b) bridge hydroxyl (c) bridge-oxygen vacancy (d) deep oxygen vacancy.

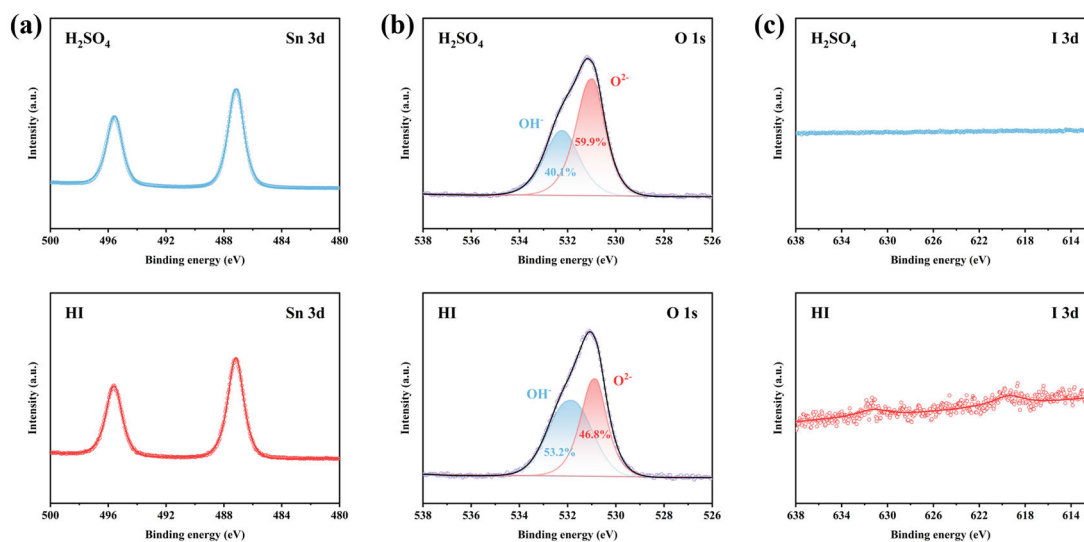


Figure S2 XPS spectra of SnO₂ films treated with H₂SO₄ and HI: (a) Sn 3d (b) O 1s (c) I 3d

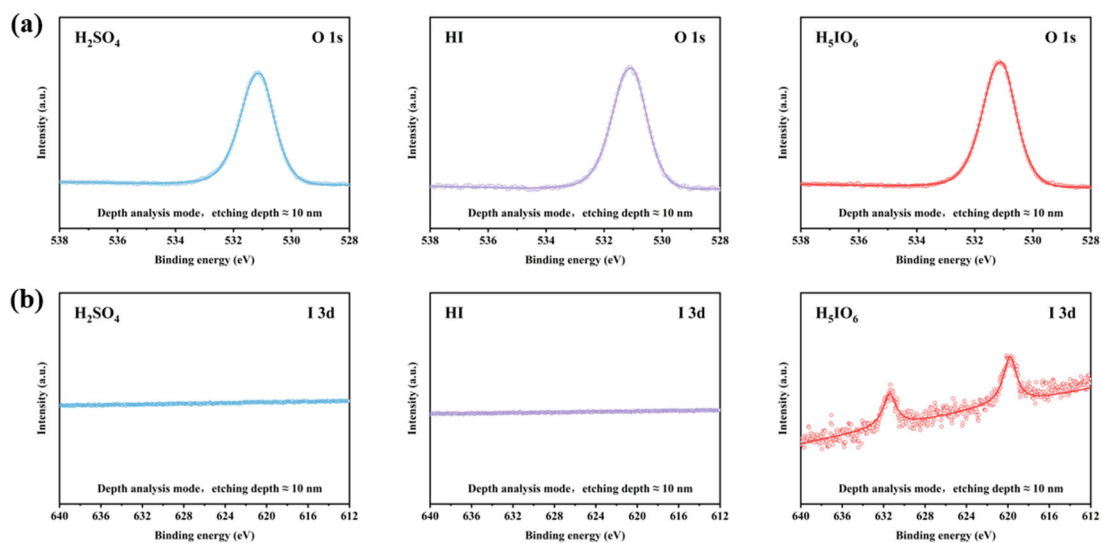


Figure S3 XPS spectra on depth analysis mode of SnO_2 films treated by several acids. (a) Sn 3d (b) I 3d

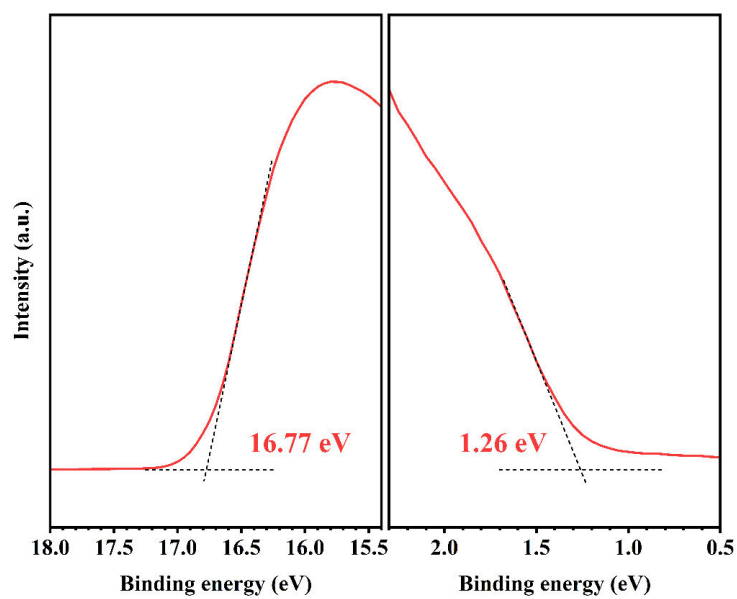


Figure S4 UPS spectrum of the corresponding perovskite film.

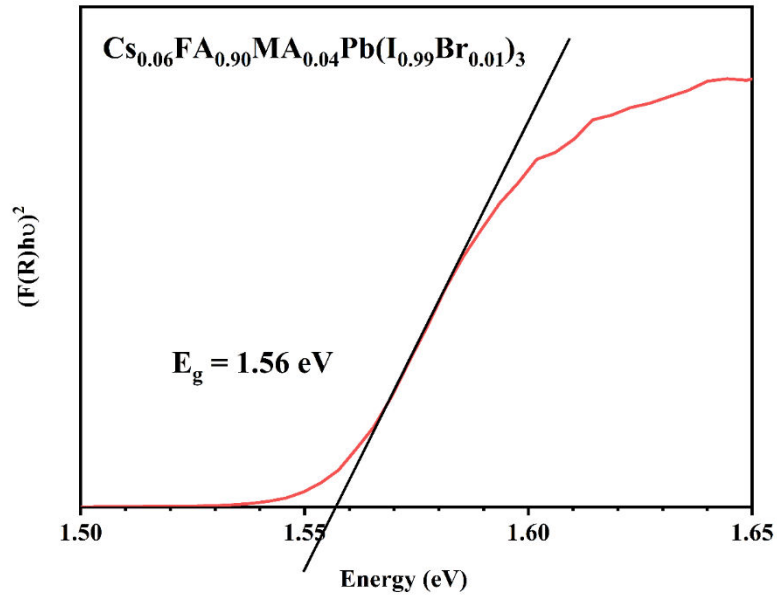


Figure S5 Optical bandgap calculated by Tauc plot of the perovskite films.

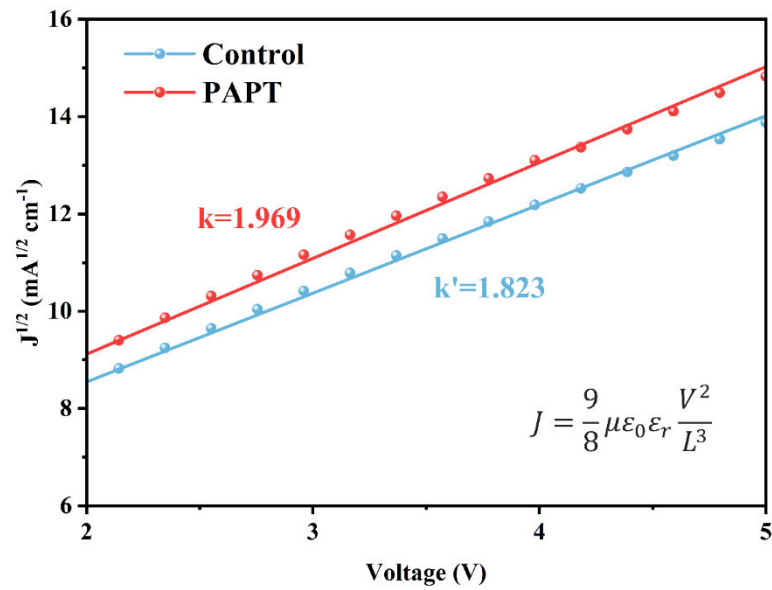


Figure S6 Mott-Gurney curves ($J^{1/2}$ - V) for the calculation of electron mobility in pristine SnO₂ and PAPT-modified SnO₂ layer based on a device structure of FTO/ETL/Ag.

The electron mobility can be calculated by Mott-Gurney Law:

$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{L^3}$$

Where μ is free carrier mobility, ϵ_0 is permittivity of free space, ϵ_r is the dielectric

constant of the material, V is the applied voltage and L is the distance between electrodes.^[8]

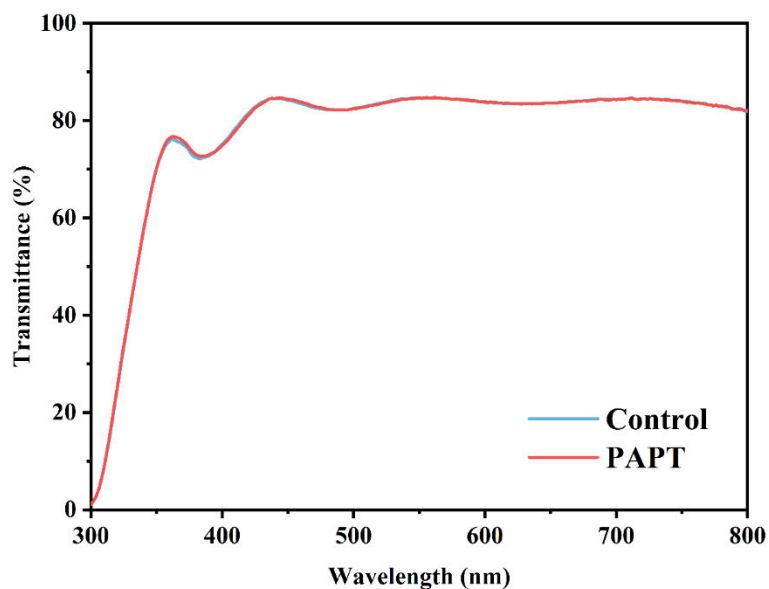


Figure S7 Transmittance spectra of control and PAPT-modified SnO₂ films.

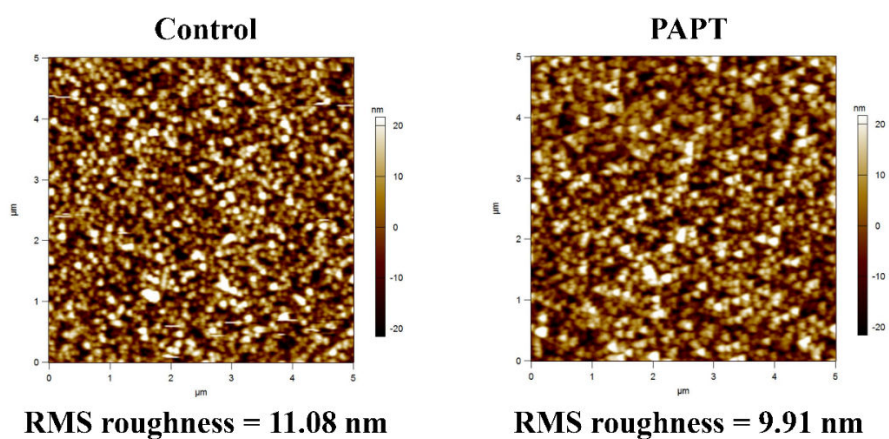


Figure S8 AFM images of pristine SnO₂ films and PAPT-modified SnO₂ films.

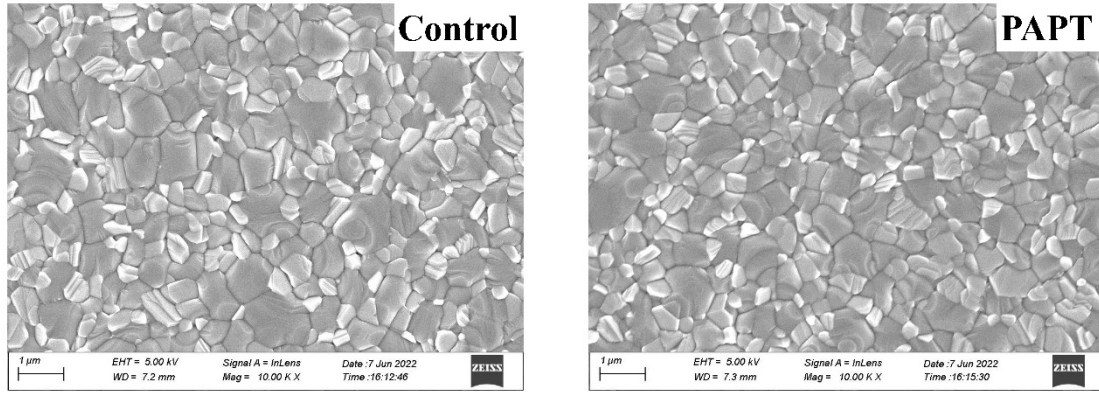


Figure S9 SEM image of perovskite films on control and PAPT-modified SnO₂ films.

Table S1 Fitting parameters of the bi-exponential decay function in TRPL spectra of the corresponding perovskite films deposited on the FTO/SnO₂ substrate using a 460 nm excitation light source.

Samples	<i>A1</i>	τ_1 (ns)	<i>A2</i>	τ_2 (ns)	τ_{avg} (ns)
Control SnO ₂	0.48	12.42	0.52	146.92	82.70
PAPT-modified SnO ₂	0.64	6.30	0.36	128.91	50.55

The average carrier lifetime (τ_{avg}) was calculated according to the equation:

$$\tau_{avg} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$$

Table S2 R² value of the dark J-V characteristics of the electron-only devices.

Samples	Ohmic region	TFL region	SCLC region
Control SnO ₂	0.9983	0.9997	0.9997
PAPT-modified SnO ₂	0.9999	0.9987	0.9991

Table S3 The champion photovoltaic performance of PSCs with/without Phe addition

Conditions	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
Control	25.09	1.06	74.28	19.77
1 mM PAPT	23.96	1.09	79.67	20.81
2 mM PAPT	25.02	1.09	81.55	22.25
3 mM PAPT	24.97	1.09	79.06	21.58
4 mM PAPT	24.91	1.06	78.47	20.77

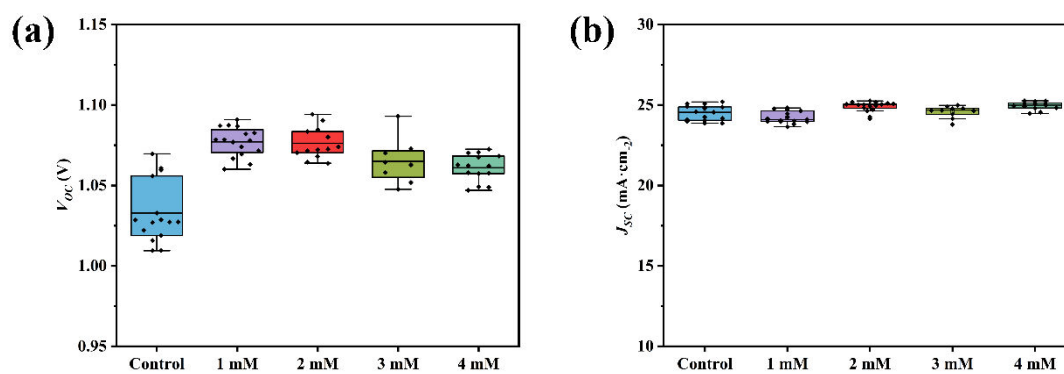


Figure S10 V_{OC} and J_{SC} statistic distribution of PSCs with different amounts of periodic acid treatment.

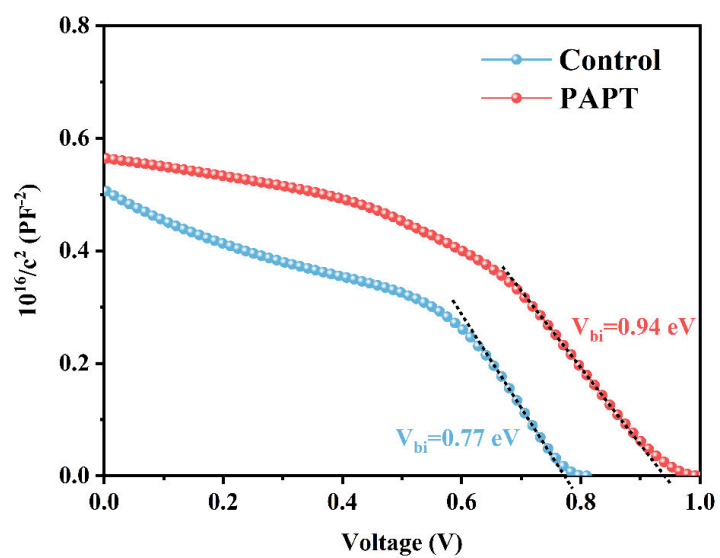


Figure S11 Electric capacity-voltage ($C-I$) measurement of the corresponding devices.

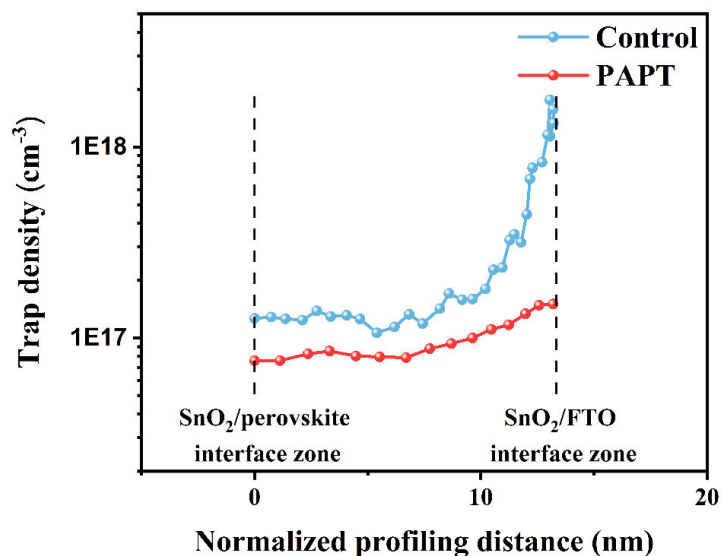


Figure S12 DLCP measurements of corresponding devices. Note: The x-axis has been adjusted to start from the SnO₂/perovskite interface.^[9]

Table S4 EIS fitting results for PSCs based on different SnO₂ films under dark condition.

Samples	R_s (Ω)	R_{rec} (Ω)
Pristine SnO ₂	29.49	240.6
PAPT-modified SnO ₂	23.96	399.7

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