Regulating Crystallization of Tin Oxide Nanoparticles by Environmental-friendly Poly-aluminium Chloride Additive for a High-Quality Electron Transport Film in Perovskite Solar Cells

Author: Xueqi Zhang[1], Disheng Yao[*1,2], Haiyue Dong[1], Junzhe Han[1], Wenwen Zheng[1], Bing Zhou[1], Nan Tian[1], Yong Peng[3], Guoyuan Zheng[*1,2], Fei Long[1,2]

Experimental Section

Materials: SnO_2 colloidal dispersion (tin (IV) oxide, 12% in H_2O) was purchased from Xi'an Yuri Solar Co. Ltd. N,N-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.9%), isopropanol (IPA, 99.9%), 4-tert-butylpyridine (tBP, 99%), lithium bis (trifluoromethanesulphonyl) imide (Li-TFSI), Spiro-OMETAD, lead iodide (PbI_2, 99.99%), formamidinium iodide (FAI, 99.9%), methylammonium iodide (MAI, 99.99%), methylammonium chloride (MACl, 99.99%), methylammonium bromide (MABr, 99.99%), cesium iodide (CsI, 99.99%) were purchased from Advanced Election Technology in China. Cobalt (III) FK 209 TFSI salt was purchased from TCI. Acetonitrile (anhydrous, 99.8%) was supplied by Aladdin. Polyaluminum chloride (PAC) was purchased from Adamas. All chemical reagents were used as received without further purification.

Device fabrication: The ITO glass was cleaned sequentially with soapy water, deionized water, acetone and anhydrous ethanol for 20 minutes each. Then UV-ozone was treated for 15 min. To prepare the SnO_2 precursor, the 12 wt% SnO_2 aqueous colloidal solution was diluted by deionized water to the concentration of 6 wt%. Then, the PAC was dissolved in deionized water and stirred at 40 °C for 1 h. The PAC solution was added into the diluted SnO_2 solutions to obtain the concentration required for SnO_2 preparation (SnO_2 6 wt% and PAC 1.0 to 3.0 mg/mL), which were mixed by ultrasonication for 1 h. The pristine and modified SnO_2 solutions were deposited on the ITO substrates at 4000 rpm for 30 s. After then, the substrates were annealed at 150 ℃

for 30 min in ambient air. After UV treatment, the ITO substrates were transferred to the glove box. The composition of the perovskite is $(Cs_{0.05}FA_{0.54}MA_{0.41})Pb(I_{0.98}Br_{0.02})_3$. 50 μL of mixture (1.3M PbI_2 and 5% CsI dissolved in DMF/DMSO=9/1, v/v) was spin-coated on the cooled substrate at 2500 rpm for 30 s, the films were annealed at 70 ℃ for 1 minute. 50 μL of organic solution (FAI 0.23M: MAI 0.12M: MACl 0.07M: MABr 0.05M in 1 mL IPA) was deposited on the PbI_2 film at speed of 2300 rpm for 30 s. Then, the films were annealed at 150 °C for 15 minutes at a relative humidity of 40±5% in ambient air. The Spiro-OMeTAD was prepared by mixed with 0.0500 g Spiro-OMeTAD, 12 μL Li-TFSI (520 mg/mL in acetonitrile), 7 μL Co-TFSI (300 mg/mL in acetonitrile), 20 μL tBP in 1 mL chlorobenzene, followed by depositing on the perovskite at speed of 4000 rpm for 25 s. Finally, the monolithic device was fabricated by evaporating 100 nm Au as the back electrode.

Characterization: All measurements involving PAC dopant were carried out at a concentration of 2.0 mg mL^{-1}. Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS) analysis were measured with Thermal Scientific ESCALAB 250Xi. The surface morphologies of perovskite films were tested by Atomic Force Microscope (AFM, Bruker Metrology Nanoscope III-D). Root-Mean-Square roughness (RMS) was calculated from atomic force microscopy (AFM) height images (Bruker Metrology Nanoscope III-D). The top-view and cross-sectional SEM images of the all samples were attained using a field-emission Scanning Electron Microscopy (S4800). The contact angle test was carried out on a contact angle analyzer

SL200B/K of American Kenor Co.Ltd. The X-ray Diffraction (XRD) patterns of all perovskite films were characterized using an X-ray diffractometer (XRD, PANalytical B.V., X Pert PRO). Optical absorption/transmission spectra of samples were measured by a UV−vis spectrometer (Shimadzu 3600). The steady state PL and Time-resolved PL spectra were measured by an Edinburgh FLS 1000 spectrometer. The EIS measurements were performed by an electrochemical workstation (CHI660E). External quantum efficiency (EQE) measurement was carried out using a QE-R (Enlitech). All the devices were tested with a defined active area of 0.0625 cm^2 and a scan rate of 10 mV s^{-1}.

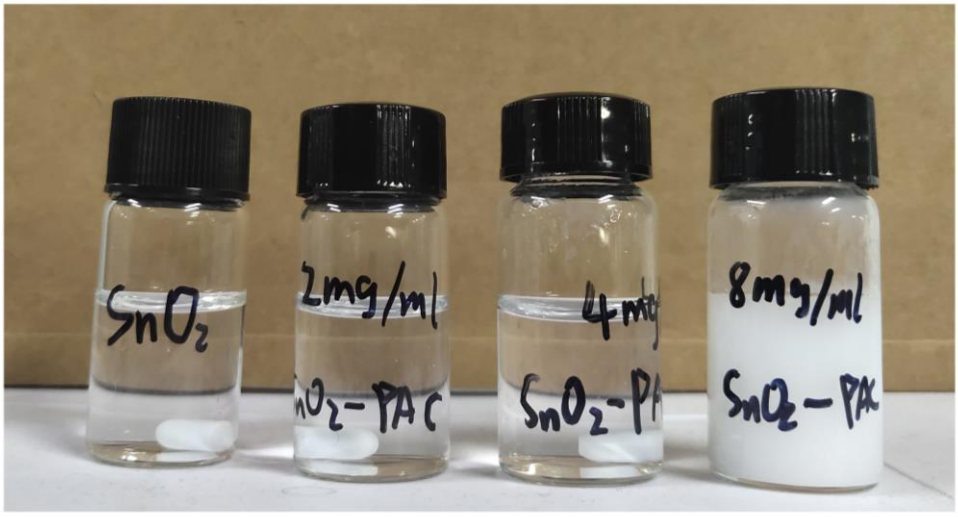
Calculations: The UPS results were calculated from the follow equations:

$$E_F = E_{cut\text{-}off} - 21.22 \quad \textbf{(1)}$$

$$E_{VB} = E_F - E_{F,\ edge} \quad \textbf{(2)}$$

$$E_{CB} = E_{VB} + E_g \quad \textbf{(3)}$$

Here, the photon energy of Type I for Helium is given as 21.22 eV.



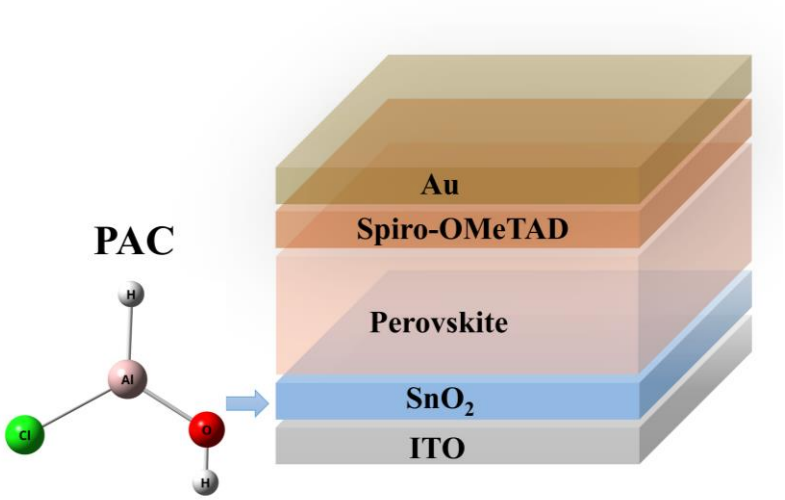


Figure S1. Photographs of SnO_2 solution with different concentrations of PAC and schematic device structure of the PSCs.

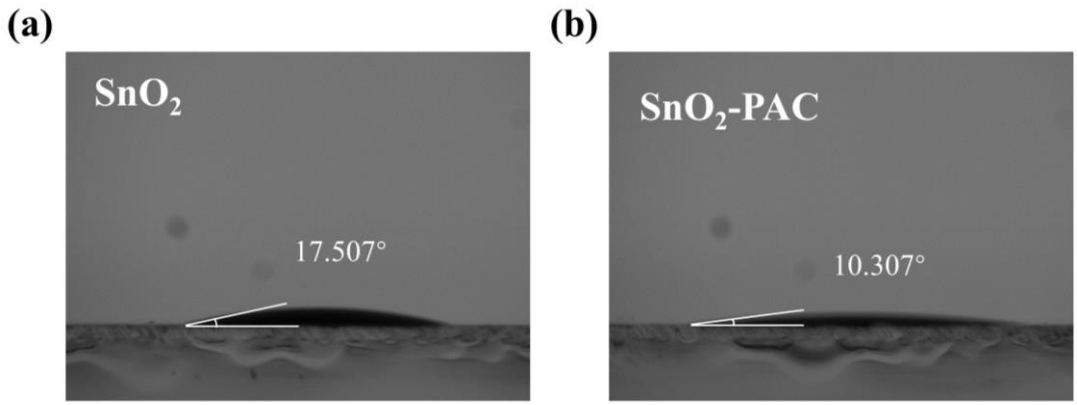


Figure S2. Contact angles of DMF on SnO_2 and SnO_2-PAC films.

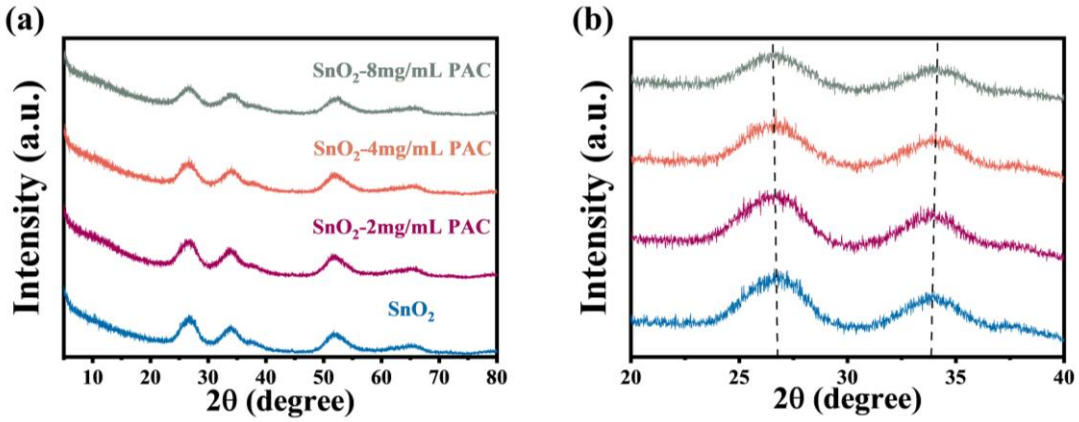
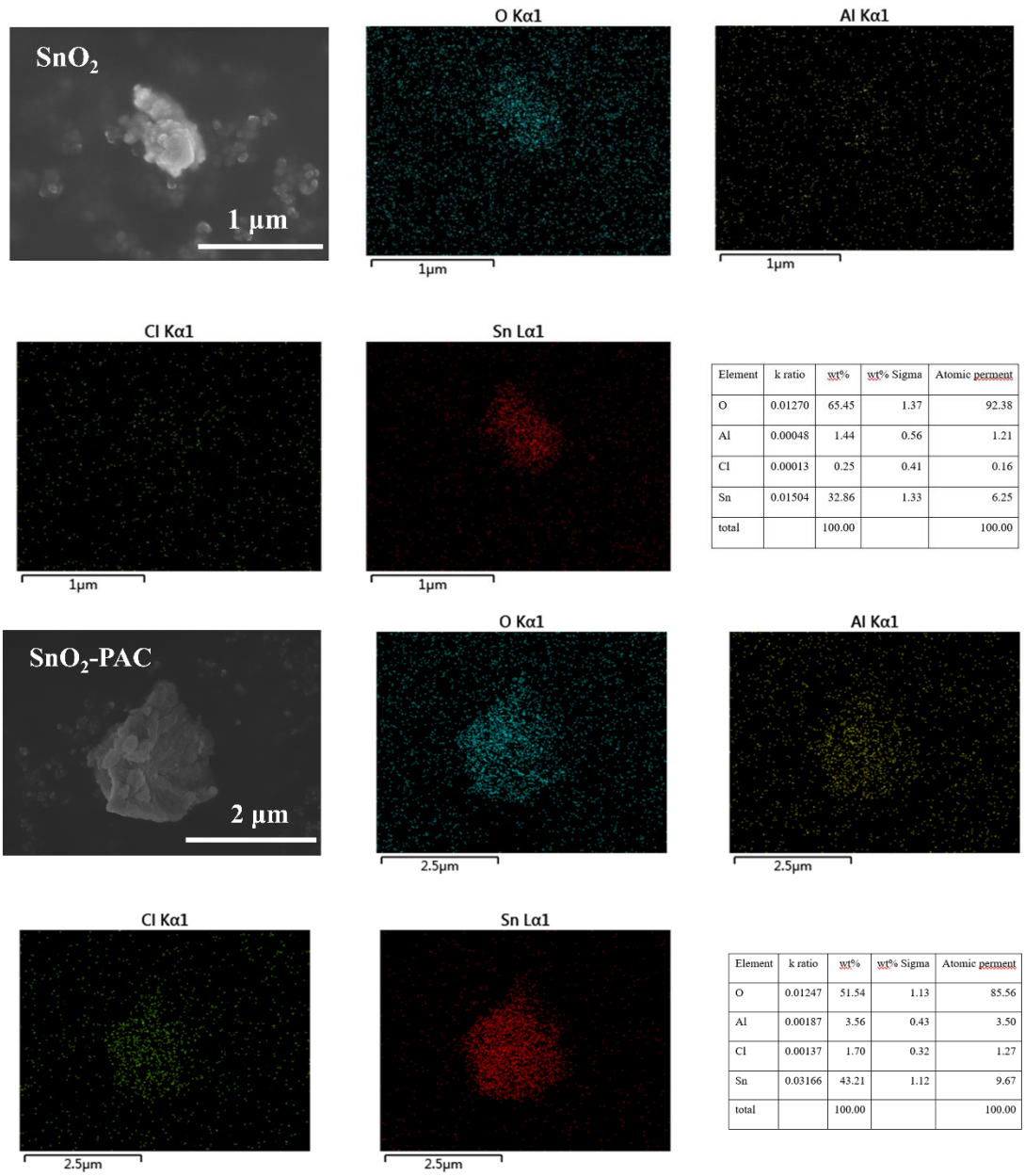


Figure S3. XRD patterns of SnO_2 powders with different concentrations of PAC.



Element	k ratio	wt%	wt% Sigma	Atomic perment
O	0.01270	65.45	1.37	92.38
Al	0.00048	1.44	0.56	1.21
Cl	0.00013	0.25	0.41	0.16
Sn	0.01504	32.86	1.33	6.25
total		100.00		100.00

Element	k ratio	wt%	wt% Sigma	Atomic perment
O	0.01247	51.54	1.13	85.56
Al	0.00187	3.56	0.43	3.50
Cl	0.00137	1.70	0.32	1.27
Sn	0.03166	43.21	1.12	9.67
total		100.00		100.00

Figure S4. EDS of SnO_2 and SnO_2-PAC powders.

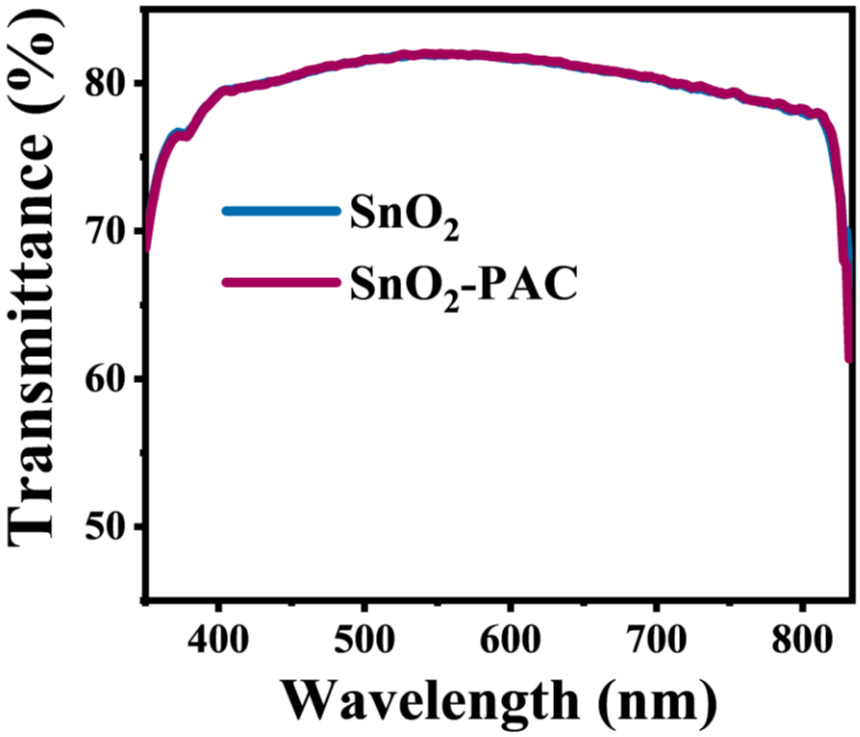


Figure S5. Spectra of light transmittance of different ETL films.

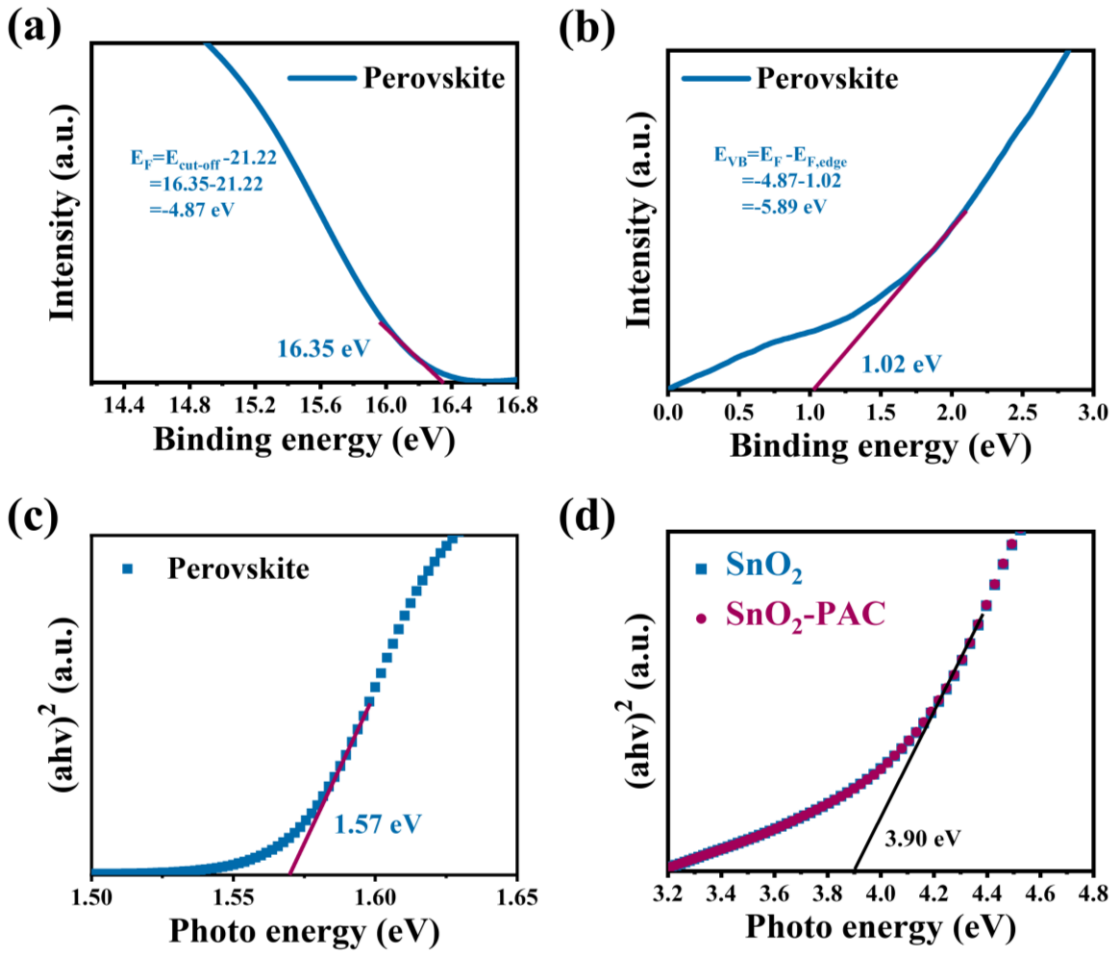


Figure S6. (a, b) UPS of the perovskite film. (c) and (d) are the Tacu curves of perovskite film and SnO_2 films with or without PAC.

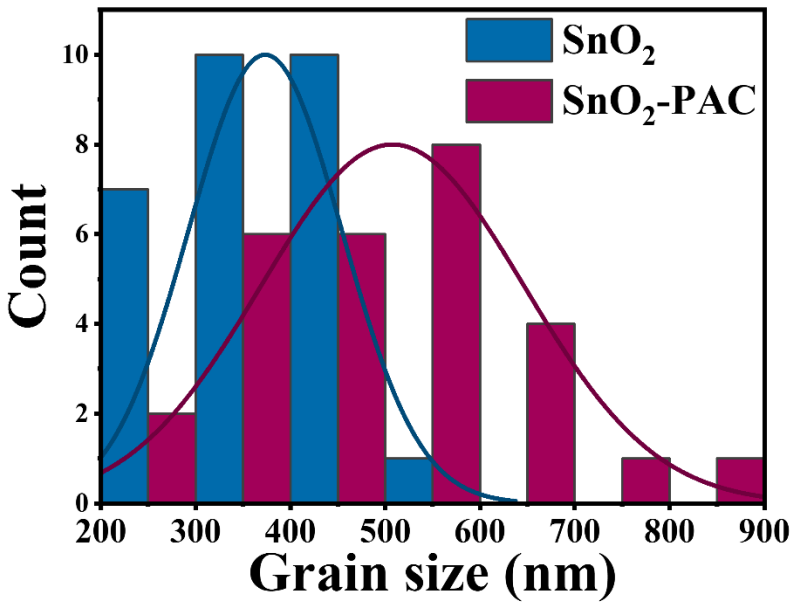


Figure S7. Grain size histograms for perovskite films prepared on pristine SnO_2 and SnO_2-PAC.

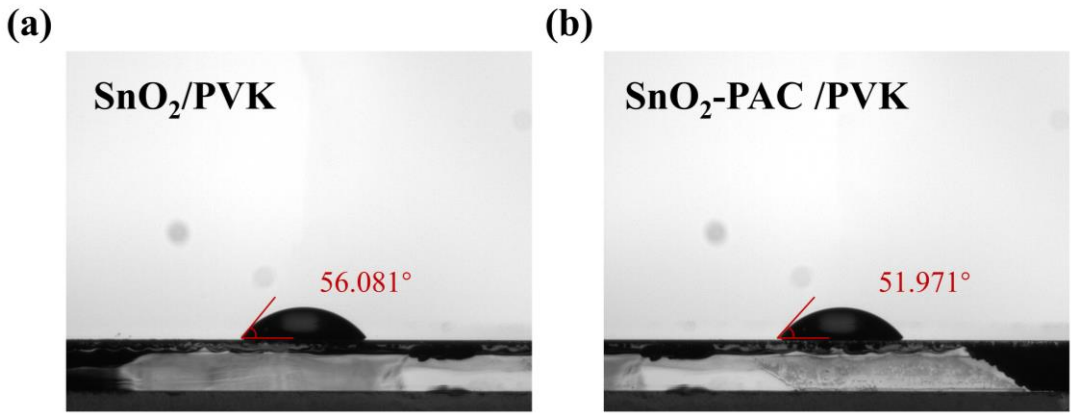


Figure S8. Contact angles of perovskite films deposited on the SnO_2 and SnO_2-PAC.

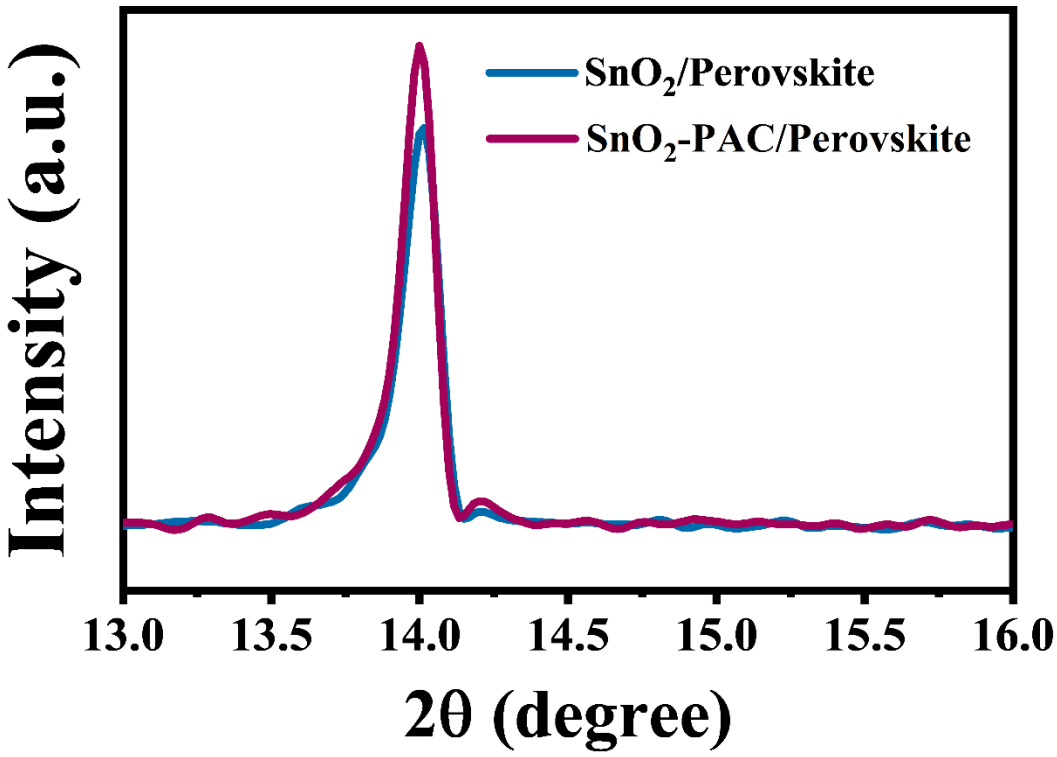


Figure S9. XRD patterns of the perovskite films at (110) plane.

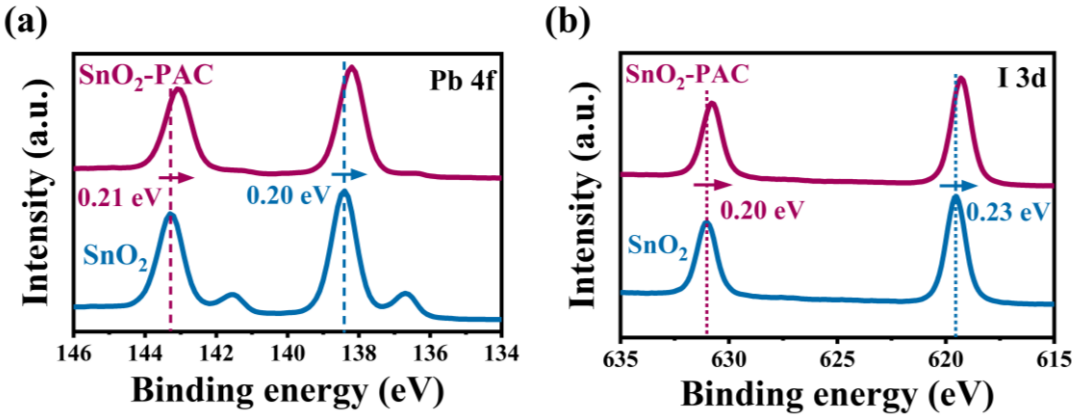


Figure S10. XPS spectra of the perovskite films: (a) Pb 4f and (b) I 3d.

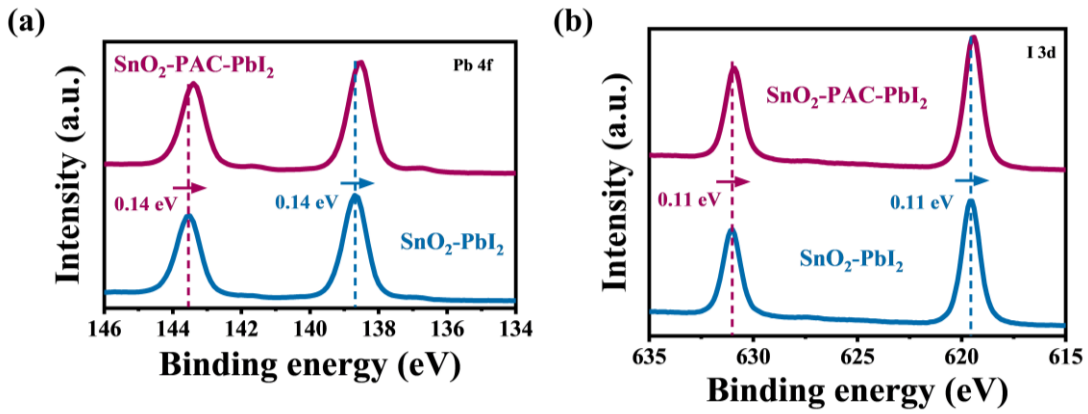


Figure S11. XPS spectra of the PbI_2 films: (a) Pb 4f and (b) I 3d.

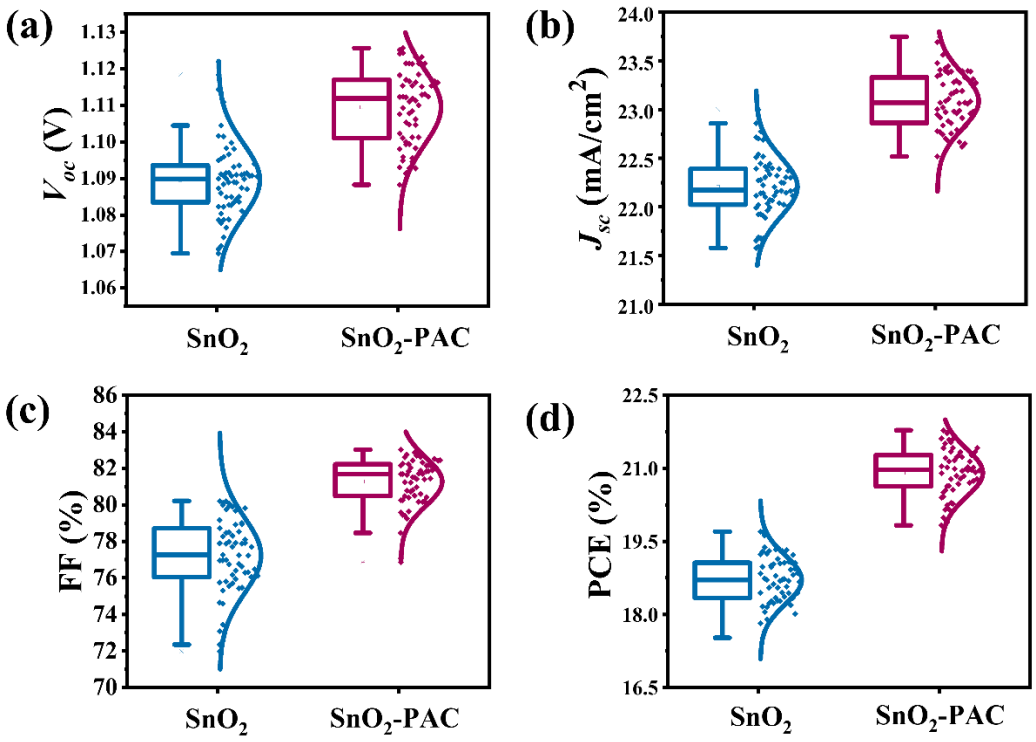


Figure S12. Statistics of (a) V_{oc}, (b) J_{sc}, (c) FF, and (d) PCE for PSCs made by using SnO_2 and SnO_2-PAC as ETL.

Table S1. the full width at half maximum (FWHM) parameters of prominent peaks of the perovskite films deposited on pristine SnO_2 and SnO_2-PAC.

Sample	**FWHM (110)**	**FWHM (121)**	**FWHM (220)**
SnO_2	0.162	0.177	0.195
SnO_2-PAC	0.156	0.135	0.157

Table S2. Electrochemical impedance parameter table of SnO_2 and SnO_2-PAC.

PSCs with different ETLs	R_s (Ω)	R_{rec} (Ω)	CPE (F)
SnO_2	10.98	30527	1.16×10^{-8}
SnO_2-PAC	4.78	47866	1.12×10^{-8}

Table S3. Fitted results of TRPL spectra of the perovskite films deposited on pristine SnO_2 and SnO_2-PAC.

ETL	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
SnO_2	0.45	22.87	0.51	94.15	81.57
SnO_2-PAC	0.29	19.49	0.66	63.93	59.19

Table S4. Performance parameters of PSCs made by using different concentrations of PAC in SnO_2 solutions.

PAC (mg/mL)		V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
0	Champion	1.11	23.38	77.06	20.02
	Average	1.11	23.54	76.23	19.86
1	Champion	1.13	22.02	82.03	20.31
	Average	1.11	22.10	80.13	19.60
2	Champion	1.13	24.72	81.24	22.67
	Average	1.11	23.59	80.76	21.17
2.5	Champion	1.12	23.81	78.65	21.02
	Average	1.11	22.67	79.84	20.07
3	Champion	1.10	22.47	81.11	20.06
	Average	1.10	22.16	79.87	19.54

Table S5. The hysteresis behavior of two representative PSCs without and with PAC treatment.

ETLs	Scan direction	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	HI (%)
SnO_2	Reverse	1.11	23.38	77.06	20.02	6.0%
	Forward	1.11	23.08	73.36	18.81	
SnO_2-PAC	Reverse	1.13	24.72	81.24	22.67	3.3%
	Forward	1.13	24.07	80.61	21.93	