

Supporting Information

***In Situ* Growth of Bifunctional Modification Material for Highly Efficient Electron- Transport-Layer-Free Perovskite Solar Cells**

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Experimental

Materials

Indium-tin-oxide (ITO) was purchased from Yingkou OPV Tech New Energy Co., Ltd. CsI (99.9%), PbBr₂ (99.9%), MABr (99.5%), FAI (99.5%) were purchased from Xi'an Polymer Light Technology Corp. Dimethyl sulfoxide (DMSO, 99.7%), N,N-dimethylformamide (DMF, 99.9%), Chlorobenzene (CB, 99.9%) and 3-aminopropyl trimethoxy silane (APS, 97%) were purchased from Sigma-Aldrich. Anhydrous ethanol (99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2',7,7'-Tetrakis-[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD, 99.86%) and PbI₂ (99.99%) were purchased from Advanced Election Technology Co., Ltd.

Devices fabrication

ITO substrates were cleaned by sequential ultra-sonication in detergent, deionized water, ethanol, acetone, and ethanol for 30 min each. The tri-cation perovskite material Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃ was composed of FAI (1.19 M), PbI₂ (1.31 M), MABr (0.21 M), PbBr₂ (0.21 M), and CsI (0.07 M), which were dissolved in a mixed solvent with a volume ratio of DMSO:DMF = 1:4. For the ETL-free structure device with the bare ITO, the perovskite precursor solution was directly spin-coated on the clean ITO after ultraviolet ozone (UVO) for 25 min. For the ETL-free structure device with the APS modified ITO, the UVO treated ITO was soaked in 2 μL·mL⁻¹ APS ethanol solution for 10 min. Later the substrates were rinsed with anhydrous ethanol and dried on the hotplate at 100 °C for 10 min. The perovskite precursors were spin-coated in two steps (1000 rpm for 10 s and 5000 rpm for 30 s). During the 15th second of the main step, 150 μL chlorobenzene was dropped onto the perovskite surface, followed by annealing at 100 °C for 75 min. Spiro-OMeTAD was utilized as the hole transport layer by spin-coated at 3500 rpm for 30 s. The solution of the HTLs was prepared by adding 72.3 mg spiro-OMeTAD, 28.8 μL 4-tert-butylpyridine (tBP), 17.5 μL of a stock solution of 520 mg·mL⁻¹ lithium bis(trifluoromethyl sulphonyl) imide (Li-TFSI), and 20.0 μL of a stock solution of 300

mg·mL⁻¹ tris(1-(pyridin-2-yl)-1H-pyrazol) cobalt(iii) tris(hexafluorophosphate) (FK102) in acetonitrile to 1 mL chlorobenzene. Finally, 50 nm of gold was deposited by thermal evaporation using a shadow mask to pattern the electrodes.

Characterizations

The properties of perovskite films were characterized by X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific, ESCLAB 250Xi, USA. The structural properties of perovskite films were performed by X-ray diffraction (XRD-7000 S, Shimadzu) from 5° to 60°. The energy level positions of perovskite materials were tested by Ultraviolet photoelectron spectroscopy (UPS), He I ($h\nu = 21.2$ eV) was used as the emission source and all measurements were calibrated with Au. The scanning electron microscopy (SEM) images were measured on a high-resolution field emission Nano SEM 450 (FEI, USA) to characterize the surface morphology of the perovskite films. The Nyquist chart tests were performed using an electrochemical workstation (Zennium Zahner, Germany) at 0.6 V forward bias voltages of Alternating current perturbation ranging from 100 mHz to 4 MHz meanwhile under light conditions. The incident photon to current conversion efficiency (IPCE) testing was achieved through a combination of Xenon lamps and computer-controlled monochrome (PEC-S20, Peccell). Photoluminescence (PL) spectra were obtained by using C5410 (Hamamatsu) at 517 nm excitation wavelengths. The absorbance was measured by a LAMBDA 950. The J-V characteristic curves were obtained by a solar simulator (Peccell-L15, Japan) under the condition of AM 1.5G (1000 W·m⁻², Keithley 2460, America) at 0.1 V·s⁻¹. Transient Photocurrent (TPC), Transient Photovoltage (TPV), Intensity-modulation photovoltage spectroscopy (IMVS), and Intensity-modulation photocurrent spectroscopy (IMPS) were also obtained using an electrochemical workstation.

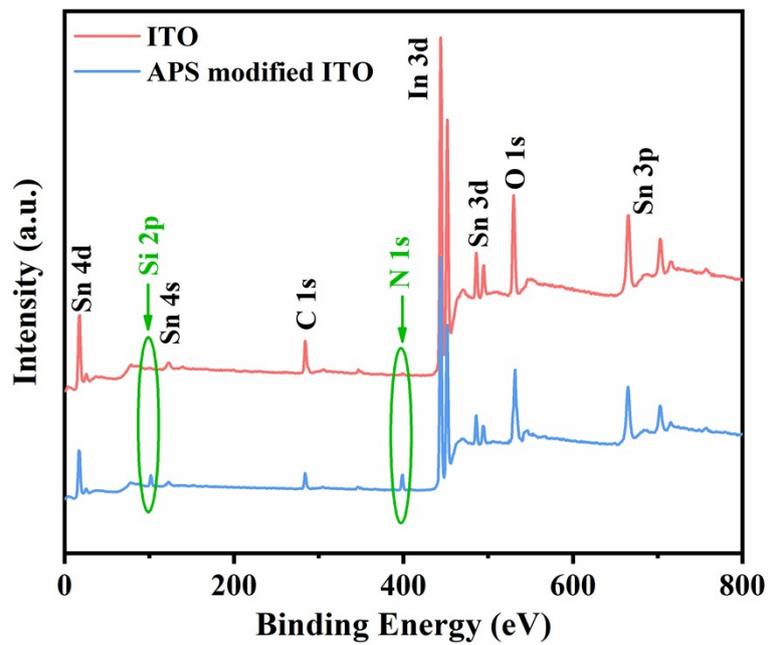


Figure S1. The full XPS spectrum of ITO and APS modified ITO.

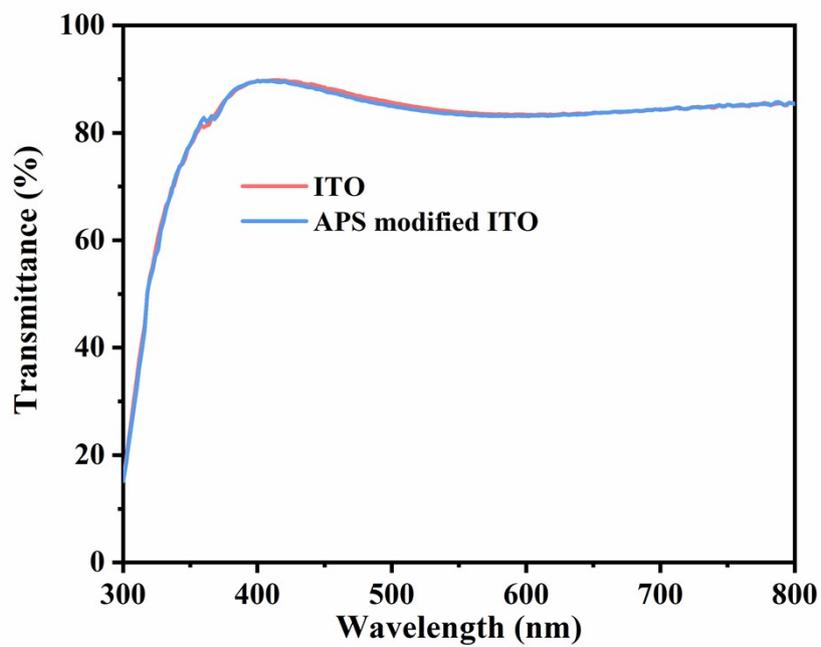


Figure S2. UV-vis transmittance of ITO and APS modified ITO.

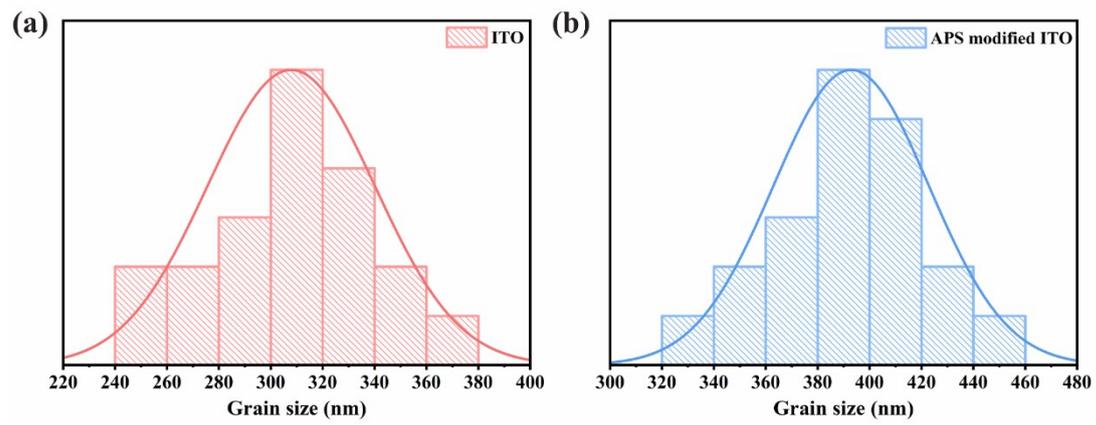


Figure S3. The distribution histogram of average grain size of perovskite films deposited on ITO and APS-modified ITO.

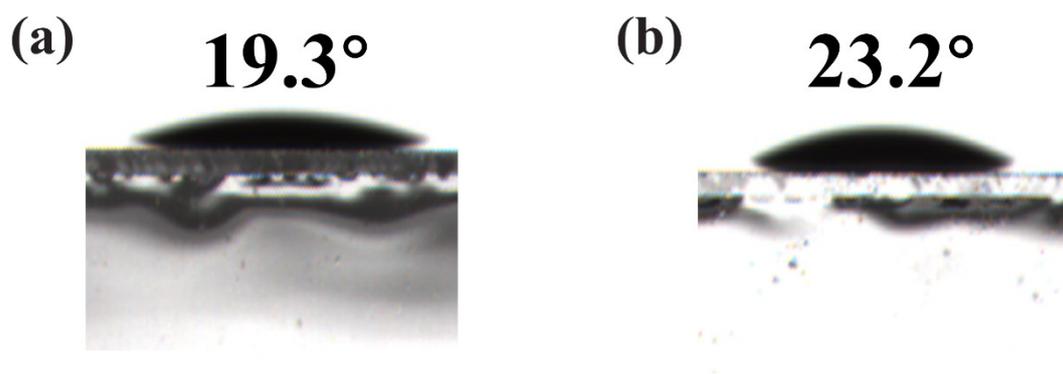


Figure S4. Contact angles of the perovskite films deposited on (a) ITO and (b) APS modified ITO.

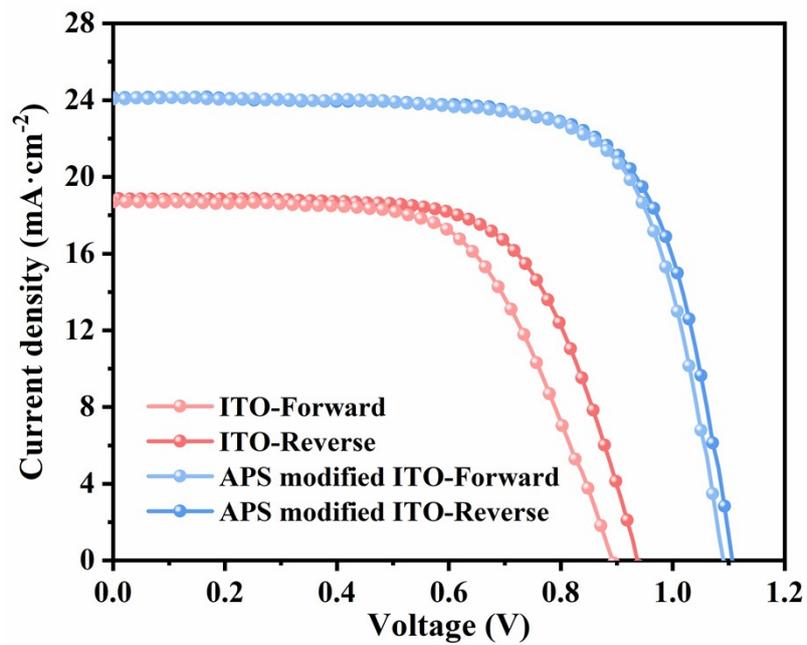


Figure S5. The forward and reverse scanning J - V curves of the champion ETL-free PSCs based on ITO and APS modified ITO.

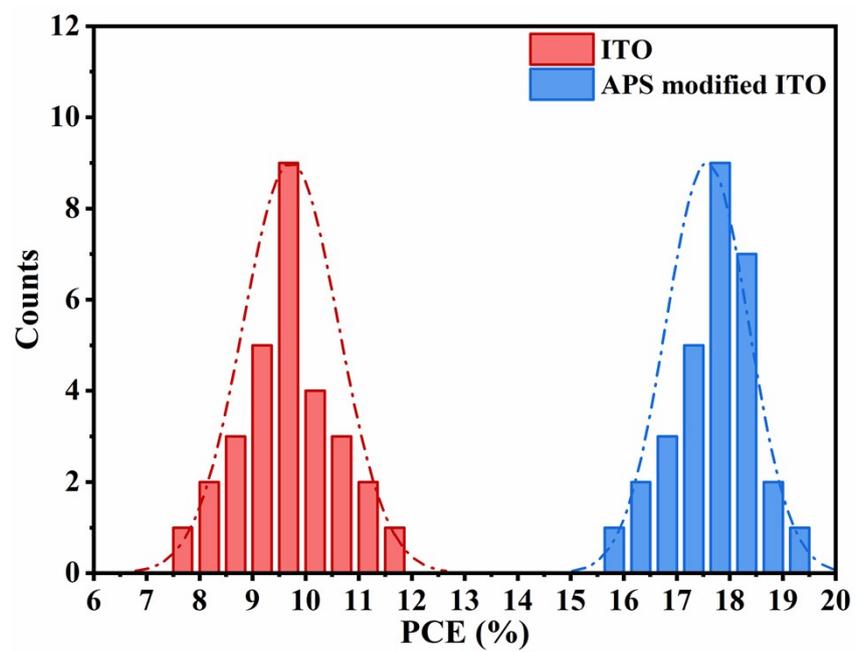


Figure S6. The histogram of PCE distribution of 30 ETL-free PSCs based on ITO and APS modified ITO.

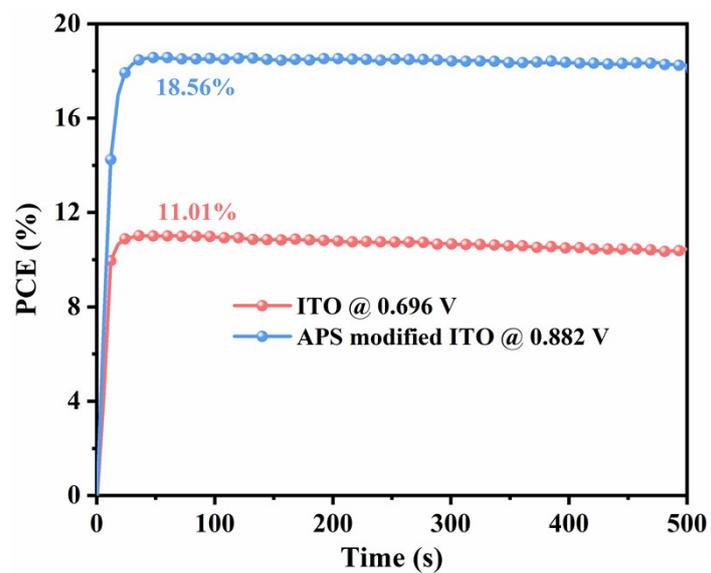


Figure S7. The output tracking of the devices based on ITO and APS modified ITO in the maximum power point under AM 1.5G illumination.

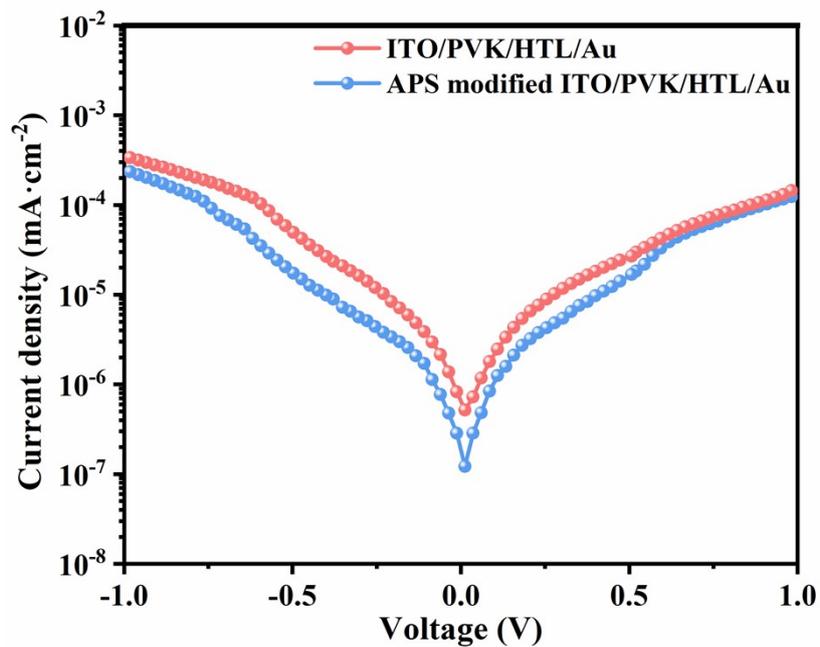


Figure S8. J - V characteristics of the ETL-free PSCs based on ITO and APS modified ITO measured in the dark.

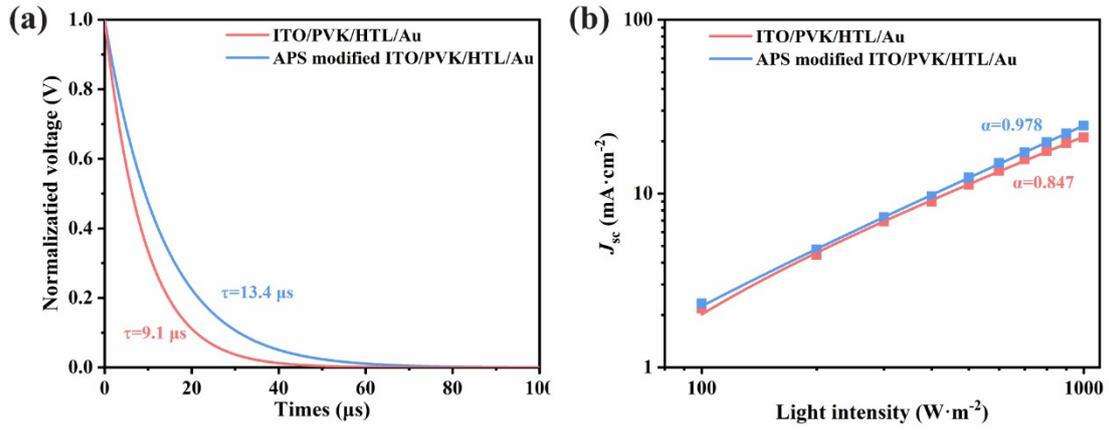


Figure S9. (a) Transient photovoltage decay curves and (b) Short-circuit current density (J_{sc}) plotted versus light intensity of ETL-free PSCs based on ITO and APS modified ITO.

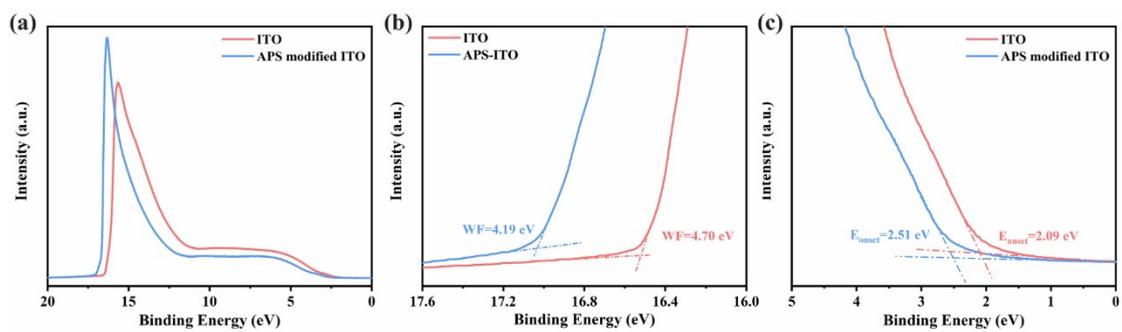


Figure S10. (a) The full UPS spectra, (b) the secondary-electron cut-off and (c) the onset region of ITO and APS modified ITO.

Table S1. Photovoltaic parameters of ETL-free PSCs based on ITO and APS modified ITO.

	Scan direction	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF	PCE(%)
ITO	Forward	0.88	18.70	0.63	10.39
	Reverse	0.93	18.88	0.66	11.65
APS modified ITO	Forward	1.08	24.12	0.72	18.86
	Reverse	1.10	24.13	0.72	19.09

Statistical Photovoltaic parameters of ETL-free PSCs based on ITO and APS modified ITO (30 cells).

	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF	PCE(%)
ITO	0.90±0.03	18.27±0.63	0.64±0.02	9.92±0.89
APS modified ITO	1.08±0.02	23.87±0.40	0.70±0.02	17.88±0.67