

Supporting Information

Synergistically modifying electron transport layers and bottom buried perovskite layers of perovskite solar cells

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Experimental Section

Materials

Lead iodide (PbI_2 , 99.99%), Methylamine iodide (MAI, 99.5%), Methylamine chloride (MACl, 99.5%) and Formamidinium iodide (FAI, 99.9%) were purchased from Xi'an Polymer Light Technology Corp, 3-O-Ethyl-L-ascorbic acid (ELAA, 99.5%) was purchased from TCI, Isopropanol (IPA, 99.5%), N, N-dimethylformamide (DMF, 99.5%), ethyl acetate (EA, 99.0%) and dimethyl sulfoxide (DMSO, 99.5%) were purchased from Aladdin. SnO_2 colloidal dispersion (diluted 15% in H_2O) was purchased from Advanced Election Technology CO.,Ltd. Unless otherwise specified, all powders and solutions are used directly without further purification.

Device fabrication

Firstly, ultrapure water, acetone, and ethanol are used to clean FTO substrate in an ultrasonic cleaner for 30 minutes in turn and then put into a UV cleaning box for the mixed treatment of UV and O_3 for about 30 min. For the SnO_2 electron transport layer, firstly, the used solution was prepared from SnO_2 nanocrystal solution (diluted to 5.5% with H_2O), then spin-coated on the FTO substrate for 35 s at 4,500 rpm/s, and finally heated at 155 °C in an air environment annealed for 25 minutes. For the SnO_2 film modified by ELAA, firstly, different concentrations of ELAA powder were dissolved in IPA, then dripped on the fresh SnO_2 film cooled to room temperature, spin-coated at the speed of 4000 rpm/s for 30 s, and then heated on a hot plate for 5min. For the preparation of perovskite thin films, 0.23 g FAI, 0.65 g PbI_2 , 0.045 g MAI and 0.03g MACl were mixed in 1 mL DMSO and DMF mixed solvent (6:1, v/v), and the $\text{FA}_x\text{MA}_{1-x}$.

$x\text{PbI}_3$ perovskite precursor solution with a concentration of 1.3 M was prepared, which was then put into a stirrer and stirred at 60 °C for 6 hours until it was completely dissolved. The perovskite precursor solution was dropped onto the SnO_2 substrate or SnO_2/ELAA substrate and spin-coated at 4000 rpm/s for 40 s. The anti-solvent was added dropwise during spin coating by adding 200 μL of EA dropwise after spinning for 15 seconds. Then, the perovskite films were annealed in a nitrogen atmosphere for 15 minutes with a hot plate temperature of 150 °C. The hole transporter, dissolving the hole transport material spiro-OMeTAD in a mixed solution of tert-butylpyridine (TBP) and chlorobenzene (0.22 g spiro-OMeTAD in 0.046 g TBP and 1.06 mL chlorobenzene), and the additive bistrifluoromethanesulfonimide lithium salt (LiTFSI) was added, the solution was then spin-coated on the device surface for 40 s at 4000 rpm/s. Finally, the top electrode was covered with a mask, and 80 nm thick Ag electrodes were deposited by thermal evaporation deposition coating equipment.

Characterization

Characterization of large instruments: FTIR spectra were measured by IRTracer-100 (Shimadzu, Japan). The ultraviolet-visible spectrum of the sample was recorded by ultraviolet-visible-near infrared spectrophotometer (UV-3600i, Shimadzu). Surface morphologies of perovskite thin films were observed by atomic force microscopy (Bruker AFM Multimode 8) and scanning electron microscopy (FEI NOVA NanoSEM 450). The XRD of the samples was measured on an Empyrean X-ray diffractometer (PANalytical B.V. Co., Netherlands) with Cu K α radiation. The steady-state PL spectra of the samples were measured using Steady State & Transient State Fluorescence Spectrofluorometer FluroMax-4P with an excitation light source wavelength of 405 nm. TRPL measurements were performed by Time-Resolved Fluorescence Spectrofluorometer TemPro-01 with an excitation light source wavelength of 478 nm. X-

ray photoelectron spectroscopy (XPS) Measurement of samples by K-alpha (Thermo Scientific, USA). The linear scanning current-voltage curve of PSC was measured with Keithley 2400 digital source meter under the standard sunlight simulator (100 mw cm⁻², Solar Simulator 94023A, Newport). Photo stability was tested under a solar simulator (XES-40S1, SAN-EI ELECTRIC) equipped with a 150 W Xe lamp. For stability, unencapsulated perovskite films and devices were placed in an air environment at 25 °C and 40 ± 5% relative humidity (RH) for long-term monitoring.

Theoretical calculations: Density functional theory (DFT) calculations were performed using the Gaussian 16 Revision A.03 suite of programs, and geometry optimization was performed at the B3LYP/6-31G(d) theoretical level. ^[1,2]

Figures and Tables

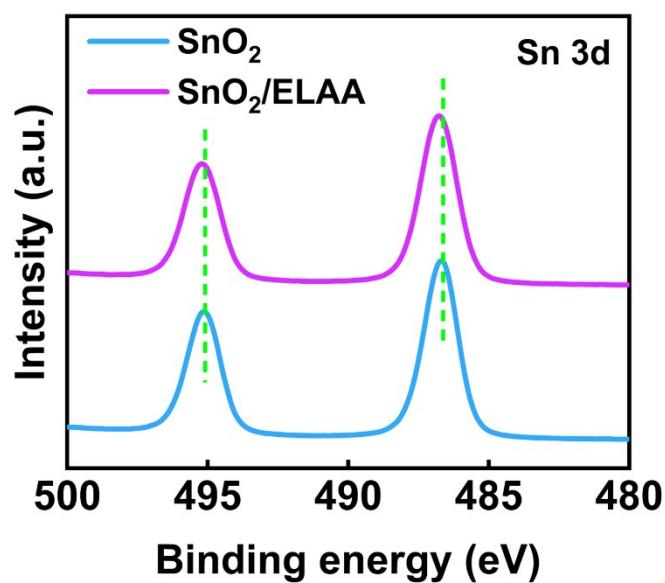


Fig. S1 XPS spectra of Sn 3d core levels of the unmodified SnO₂ and ELAA-modified SnO₂.

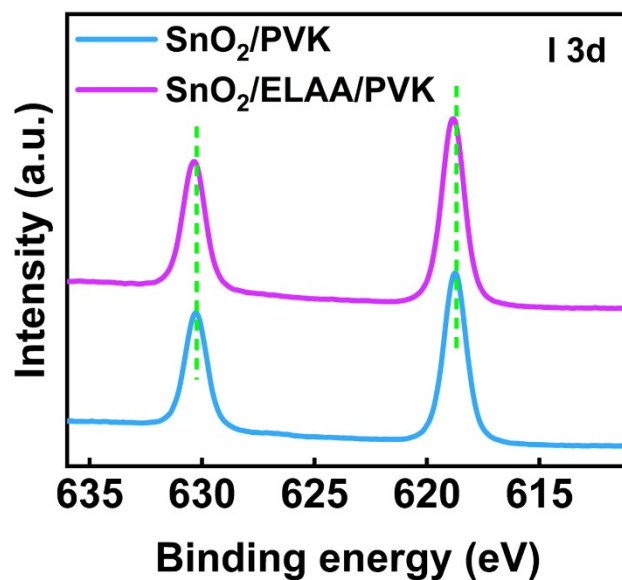


Fig. S2 XPS spectrum of core energy level of PVK I 3d deposited based on unmodified SnO₂ and ELAA modified SnO₂.

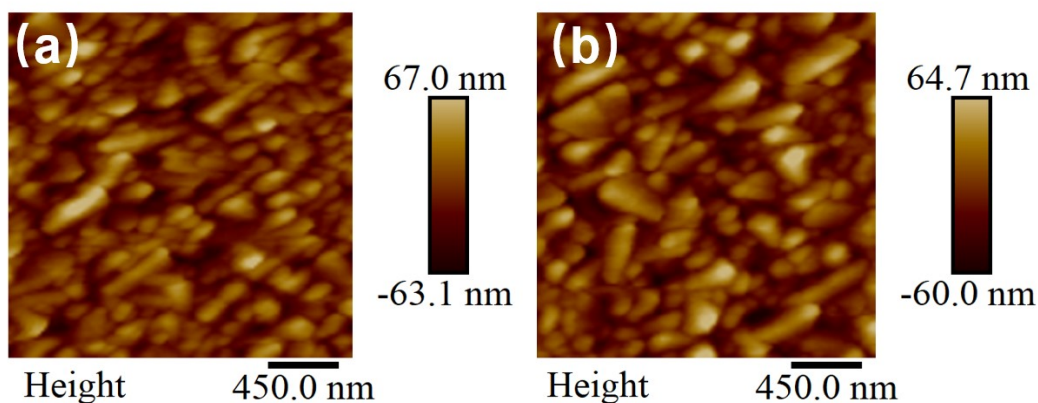


Fig. S3 AFM images of (a) unmodified and (b) ELAA modified SnO₂ films.

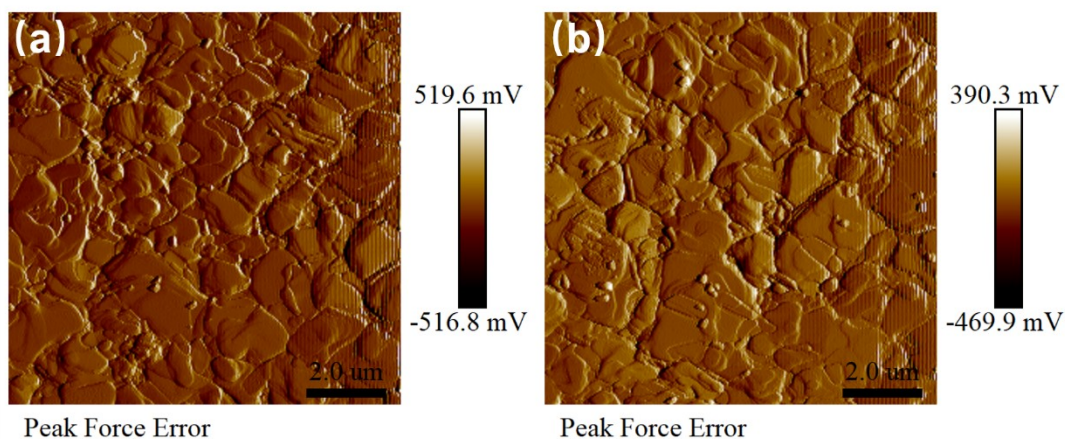


Fig. S4 AFM Peak force error mode image of PVK deposited based on (a) unmodified SnO₂ and (b) ELAA modified SnO₂.

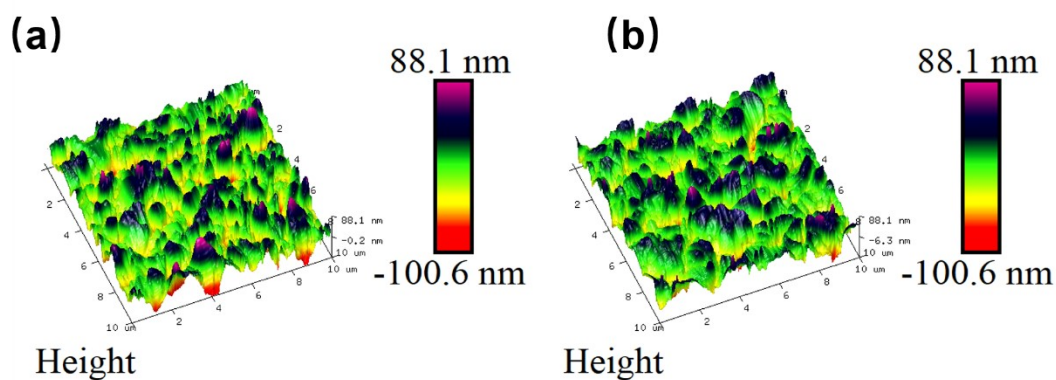


Fig. S5 3D AFM image of PVK deposited based on (a) unmodified SnO₂ and (b) ELAA modified SnO₂.

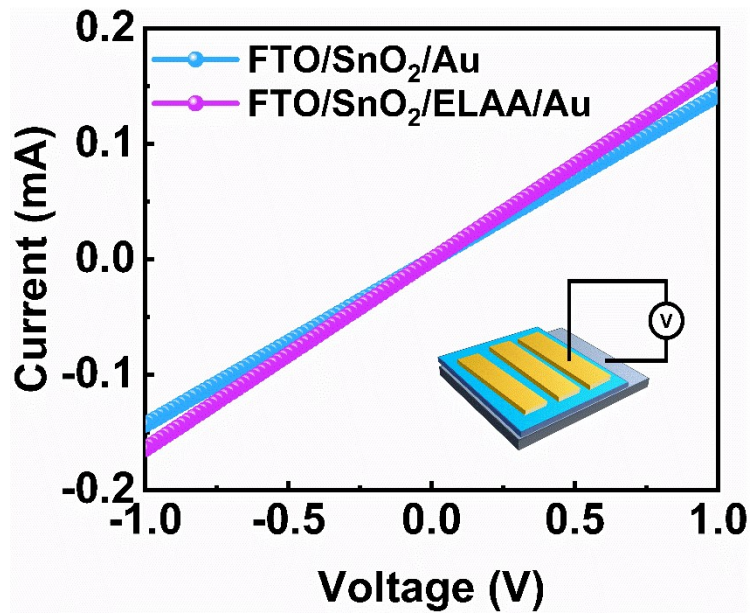


Fig. S6 Vertical conductivity of different cell structures without/with ELAA optimization.

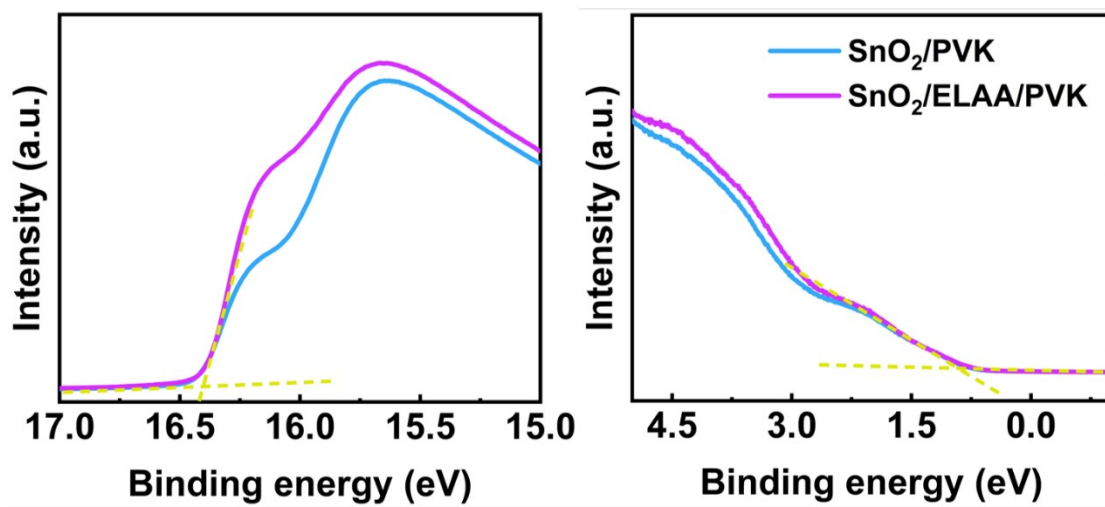


Fig. S7 (a) UPS of PVK based on SnO₂ of without/with ELAA modification.

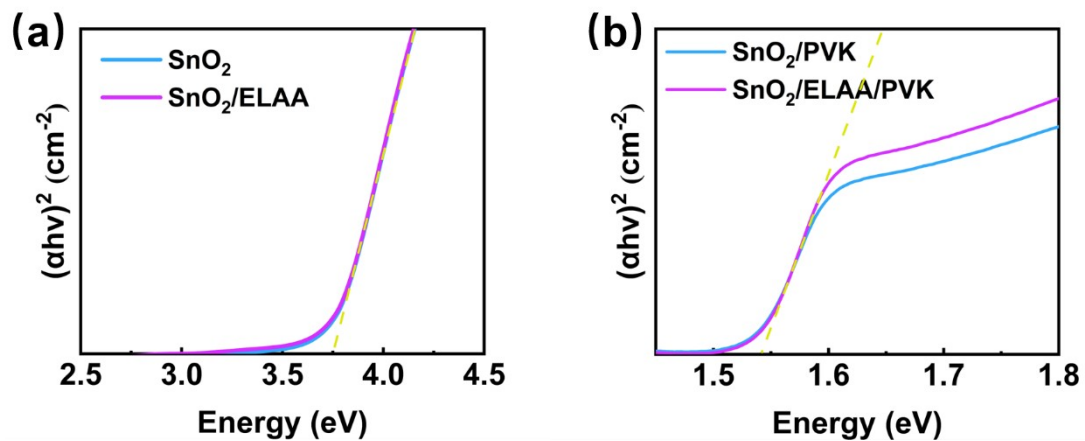


Fig. S8 Optical band gap Tauc spectra of (a) SnO_2 films without and with ELAA modification, (b) PVK films deposited based on unmodified SnO_2 and ELAA modified SnO_2 .

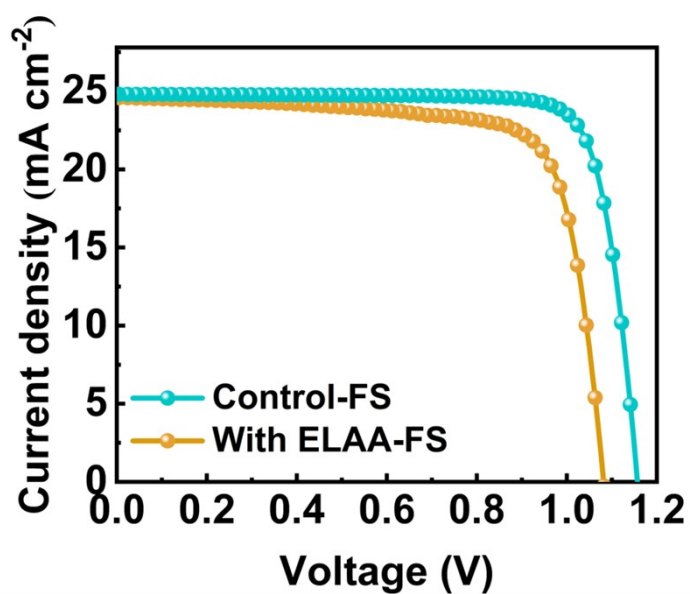


Fig. S9 Forward scanning (FS) $J-V$ curve of the best small PSCs without/with 5mM ELAA optimization.

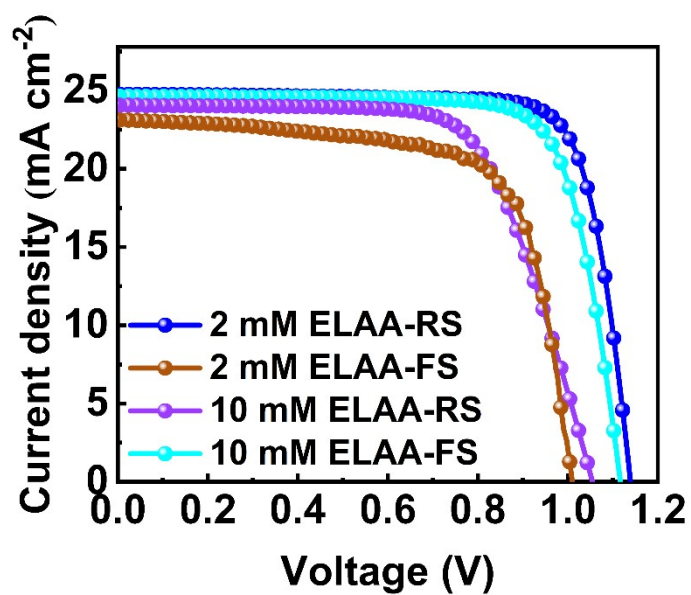


Fig. S10 J-V curves of the best small PSCs with other ELAA concentrations.

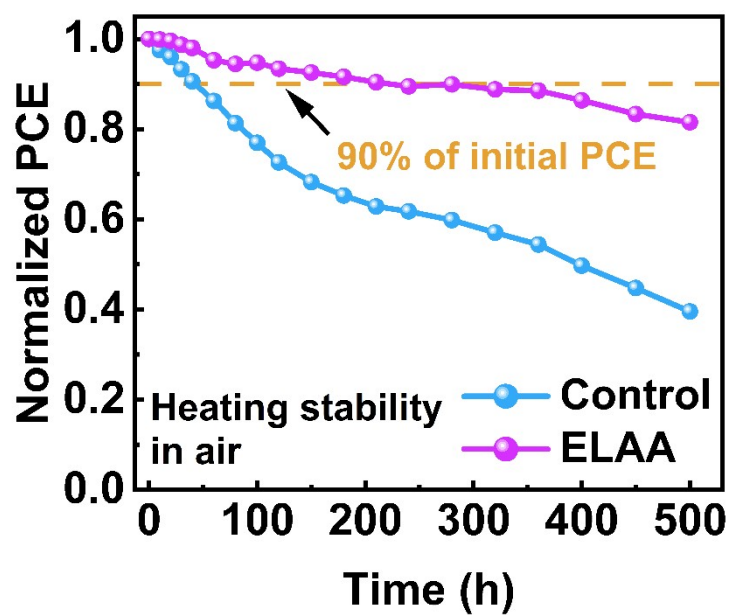


Fig. S11 Monitor the heating stability of PSCs without/with ELAA modification in air environment. The air environment conditions are 25°C and 40±5% RH.

Table S1 TRPL parameters of PVK thin films based on different structures.

Name	A ₁	τ ₁ [ns]	A ₂	τ ₂ [ns]	τ _{ave} [ns] ^{b)}
SnO ₂ /PVK	0.8372	7.52097	0.59043	220.18542	95.47336
SnO ₂ /ELAA/PVK	0.819	2.56156	0.57989	70.62028	30.77434
Glass/PVK	0.87214	62.8747	0.52872	1810.70754	722.55103
Glass/ELAA/PVK	0.95148	83.62355	0.56959	2080.8657	831.52414

b) $\tau_{ave} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$

Table S2 EIS Parametric statistics based on unmodified and ELAA modified devices.

Name	R _{ct}	R _{rec}
SnO ₂ /PVK	4.29E+04 ^{c)}	2.14E+05
SnO ₂ /ELAA/PVK	3.69E+04	5.26E+05

c) E+01: × 10¹

Table S3 Statistics of performance parameters of cells with different optimal concentrations of ELAA under the effective area of 0.09 cm².

concentration of ELAA [mM]	Scan direction	J _{sc} [mA cm ⁻²]	V _{oc} [V]	FF [%]	PCE [%]	HI [%] ^{a)}
0	Reverse	24.64	1.12	75.91	20.95	7.39
	Forward	24.51	1.08	74.57	19.40	
2	Reverse	24.77	1.14	78.85	22.27	5.76
	Forward	24.62	1.12	76.28	20.98	
5	Reverse	24.88	1.17	80.49	23.43	2.57
	Forward	24.79	1.16	79.32	22.83	
10	Reverse	24.05	1.05	71.19	17.98	11.93
	Forward	23.18	1.01	67.62	15.83	

a) $HI = (PCE_{Rev} - PCE_{For}) \times 100 / PCE_{Rev}$

Table S4 Statistics of performance parameters of cells without/with optimal concentrations of ELAA under the effective area of 1.01 cm².

Name	J _{sc} [mA cm ⁻²]	V _{oc} [V]	FF [%]	PCE [%]
SnO ₂ /PVK	23.82	1.05	73.23	18.32
SnO ₂ /ELAA/PVK	24.01	1.11	77.46	20.64

References

- [1] J.B. Foresman, Æ. Frisch, Exploring Chemistry, Gaussian Inc., Pittsburg, USA, 1996.
- [2] M. Frisch, GAUSSIAN16. Revision A. 03, Gaussian Inc., Wallingford, CT, USA, 2016.