Supporting Information

Enhanced SnO_2 electron transport layer by Eu^{3+} for Efficient and Stable Perovskite Solar Cells

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Experimental Section

Materials. $SnCl_2 \cdot 2H_2O$ (99.99%) was purchased from Beijing psaitong Biotechnology Co., Ltd. Hydrochloric acid (36.0~38.0%, HCl) was purchased from Sinopharm Chemical Reagent Co., Ltd. Europium chloride hexahydrate ($EuCl_3 \cdot 6H_2O$), Mercapto acetic acid (TGA), Urea and Potassium chloride (98%, KCl) were purchased from Aladdin. PbI_2 (99.99%, trace metals basis) was purchased from Tokyo Chemical Industry (TCI). Formamidinium iodide ($CH(NH_2)_2)I$, FAI), methylammonium chloride (CH_3NH_3Cl, MACl), 4-methoxy-phenethylammonium iodide (MeO-PEAI), 2,2’,7,7’-Tetrakis[N,N-di(4-methoxy phenyl)amino]-9,9’-spirobifluorene (spiro-MeOTAD), tert-butylpyridine (tBP), li-bis(trifluoromethanesulfonyl)imid (Li-TFSI) were purchased from Xi'an Polymer Light Technology Co., Ltd. N, N dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropanol (IPA), acetonitrile (ACN), and chlorobenzene (CB) were purchased from Sigma-Aldrich. All chemicals were used directly without further purification.

Solution Preparation. 548 mg $SnCl_2 \cdot 2H_2O$, 2.5 mL HCl, 50 uL TGA and 2.5 g urea were dissolved in 200 mL of deionized water to prepare a precursor solution of SnO_2. Perovskite film prepared by a typical two-step sequential deposition method, 0.6915 g PbI_2 was dissolved in 1 mL DMF and DMSO (v/v=9/1), while 0.090 g FAI and 0.013 g MACl were dissolved in 1 mL IPA. Then, 4.5 mg MeO-PEAI was dissolved in 1 mL IPA for the passivating layer on top of the perovskite surface. The spiro-OMeTAD solution was prepared by combining 72.3 mg spiro-OMeTAD powder, 27.6 μL 4-tBP, and 17.5 μL Li-TFSI solution (520 mg/mL in ACN) in 1 mL CB.

Device Fabrication. Fluorine-doped tin oxide (FTO) glasses (8 Ω/sq) were ultrasonicated with detergent, ethanol, and DI-water for 15 mins in sequence. The cleaned FTO glasses were subsequently treated with UVO for 30 mins, then vertically place them in the dyeing vat. Following this, pour the SnO_2 precursor solution, diluted with deionized water at a ratio of 1:5, into the dyeing vat and place it in water bath kettle for chemical bath deposition at 90 ^{o}C for 8 hours to obtain SnO_2. To prepare Eu-SnO_2, different concentrations of $EuCl_3 \cdot 6H_2O$ (0.05, 0.14, 0.23 mM) were added to diluted SnO_2 precursor solution for subsequent in-situ chemical bath deposition, with an optimal concentration of 0.14 mM. After the chemical bath deposition, the as prepared ETL films sonicated twice with deionized water for 5 mins each time. Before use, anneal at 200°C for 1 h, then SnO_2 and Eu-SnO_2 treat with UVO for 10 mins before spin coating a 24 mM KCl aqueous solution at 3000 rpm for 30 s. After that, the substrates were treated with UVO for 10 mins and quickly transferred into N_2 glovebox, where the perovskite film was prepared. Firstly, the PbI_2 solution was spin-coated onto the prepared ETL substrates at 1500 rpm for 30 s, followed by annealing at 70°C for 60 s. Next, the mixed solution of FAI and MACl was spin-coated onto the PbI_2 film at 1800 rpm for 30 s and then annealed at 150°C in ambient air with a humidity of 30-40% for 15 mins. Then, the perovskite film was returned to the N_2 glovebox, where the MeO-

PEAI solution was dynamically spin-coated at 4000 rpm for 30 s, followed by the spin-coating of the Spiro-OMeTAD solution under the same parameters. Finally, an 80 nm layer of Au was deposited by thermal evaporation.

Characterization. XPS spectrums were characterized using an ESCALAB 250Xi system with Al Kα X-ray radiation (Thermo Fisher Scientific). Atomic force microscopy (AFM) images were characterized by an AFM system (Dimension Icon, Bruker). The SEM photography of SnO_2, PbI_2, and perovskite films was characterized using the SU8010 microscope (Hitachi). GIXRD measurements were conducted by Rigaku MicroMax-007HF equipped with a DECTRIS PILATUS3 R detector under an incident angle of 0.5°. XRD spectroscopy was conducted using XtaLAB mini (Rigaku) equipment. UV-visible absorption spectra were recorded using a Shimadzu UV-2600 spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) was performed using a ESCLAB Xi+ system equipped with a He I (21.22 eV) radiation source. The FLS980 fluorescence spectrometer (Edinburgh Instrument) equipped with a 450W Xe lamp and a picosecond pulse diode 405 nm laser (EPL-405) was used to characterize SSPL and TRPL. The Keithley 2400 source measuring instrument was used to measure the *J-V* curve under AM 1.5 illumination and calibrate it with a standard silicon solar cell. The device with an aperture area of 0.1 cm^2 undergoes reverse scanning at a speed of 0.06V/s under 1 sun in the atmosphere. EQE spectra were obtained using the QE-R system (Enli Tech.). EIS spectra were analyzed using the Zahner Zennium electrochemical workstation and fitted using ZSimpwin software.

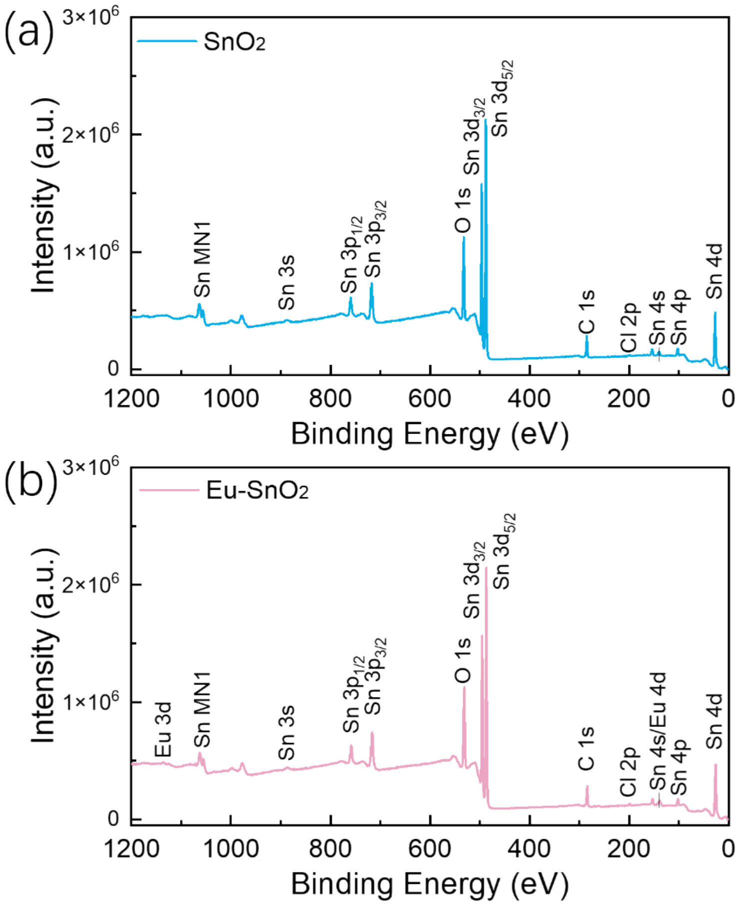

Figure S1. XPS survey of different SnO_2 ETLs.

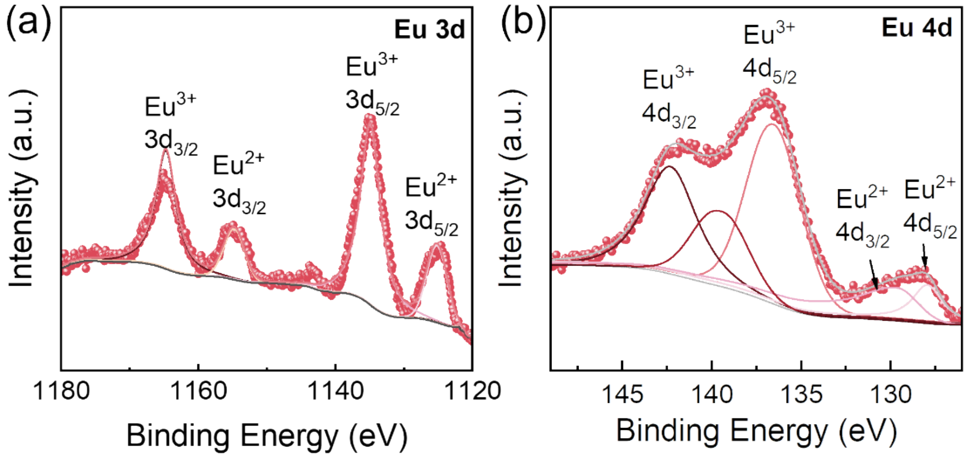

Figure S2. XPS survey of SnO_2 ETLs treated with 1.4 mM $EuCl_3{\cdot}6H_2O$.

Table S1. Calculated FWHM and crystallite size of SnO_2 dopped with different concentrations of $EuCl_3 \cdot 6H_2O$.

Conc. (mM)	**(hkl)**	**FWHM (°)**	**Crystal Size (nm)**
0	(110)	1.630	4.951
	(101)	1.719	4.777
	(211)	1.607	5.431
0.14	(110)	1.661	4.859
	(101)	1.817	4.520
	(211)	1.292	6.759
1.4	(110)	1.828	4.415
	(101)	2.280	3.600
	(211)	1.961	4.451

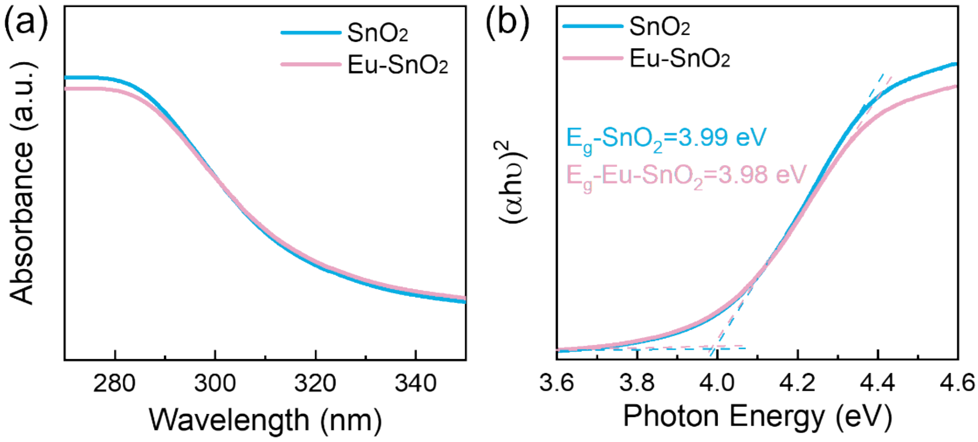

Figure S3. (a) Absorbance and (b) Tauc plots of SnO_2 and Eu-SnO_2 ETLs.

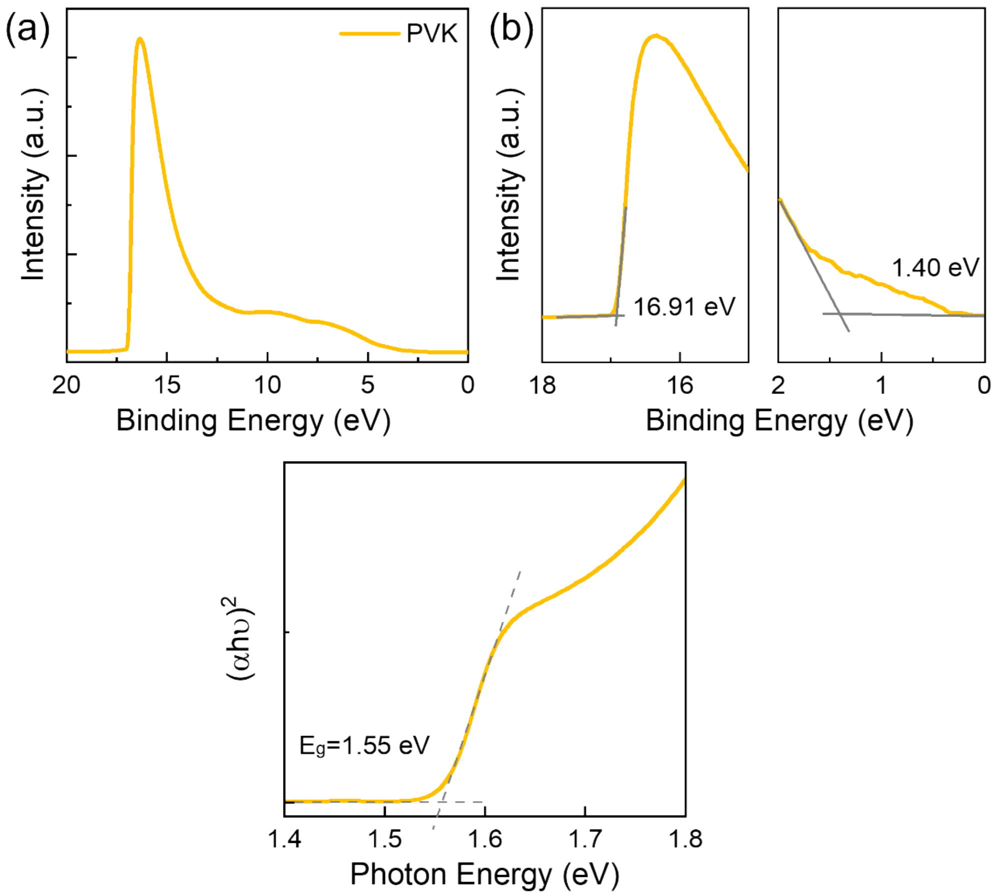

Figure S4. (a) Full spectra, (b) enlarged cut-off UPS spectra, and (c) Tauc plot of perovskite film.

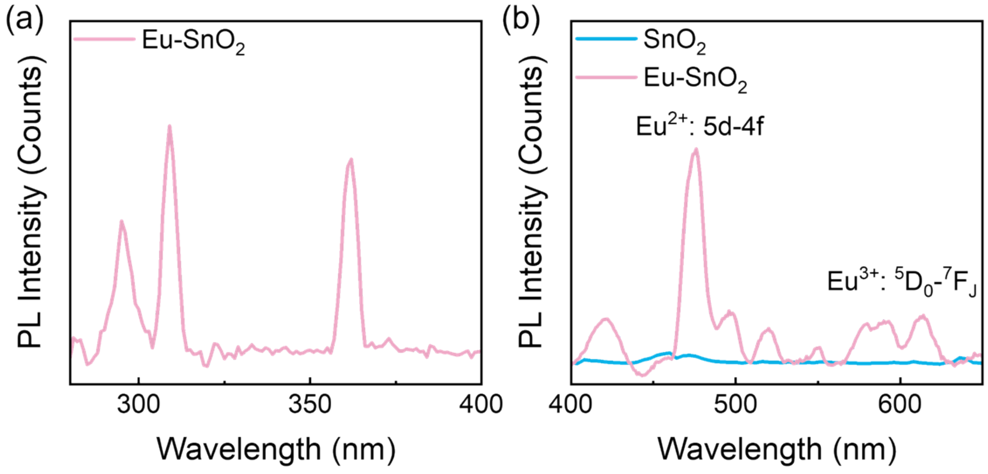

Figure S5. (a) Excitation spectra of Eu- SnO_2 under emission at 523 nm. (b) Emission spectra of SnO_2 and Eu- SnO_2 under excitation at 280 nm.

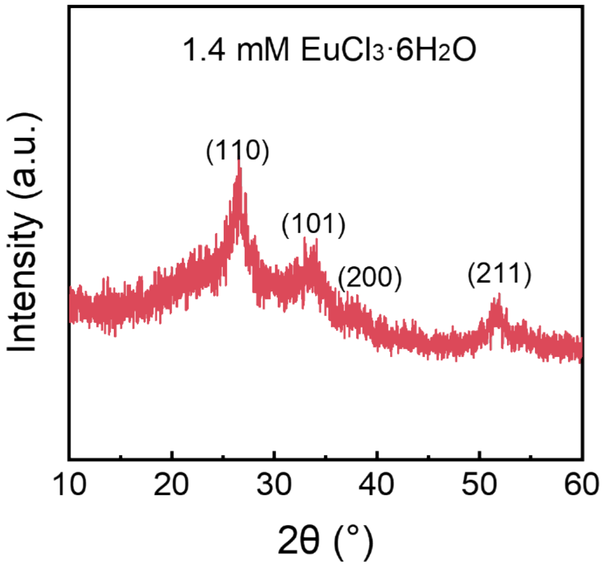

Figure S6. GIXRD pattern of SnO_2 dopped with 1.4 mM $EuCl_3 \cdot 6H_2O$.

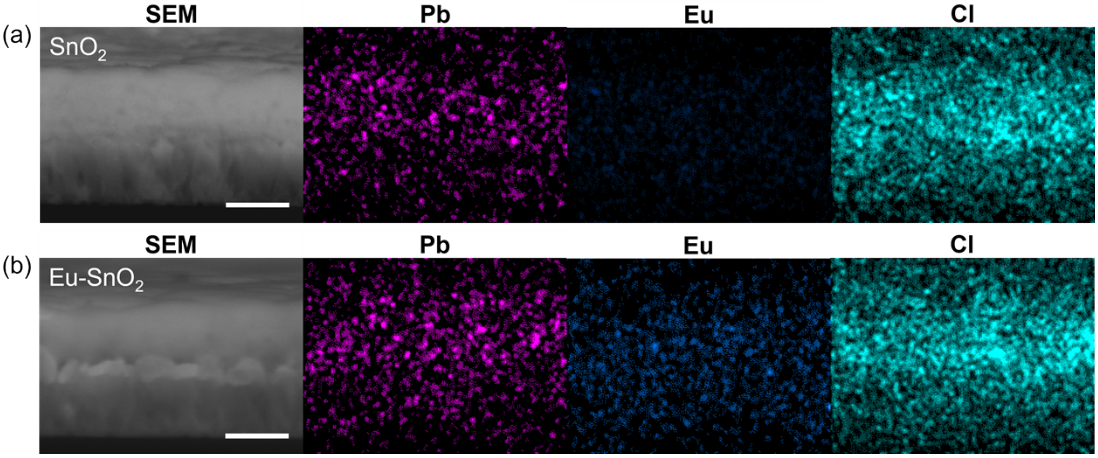

Figure S7. Cross-sectional EDS mapping of SnO_2 (a) and Eu-SnO_2 (b), the scale bar is 1 μm.

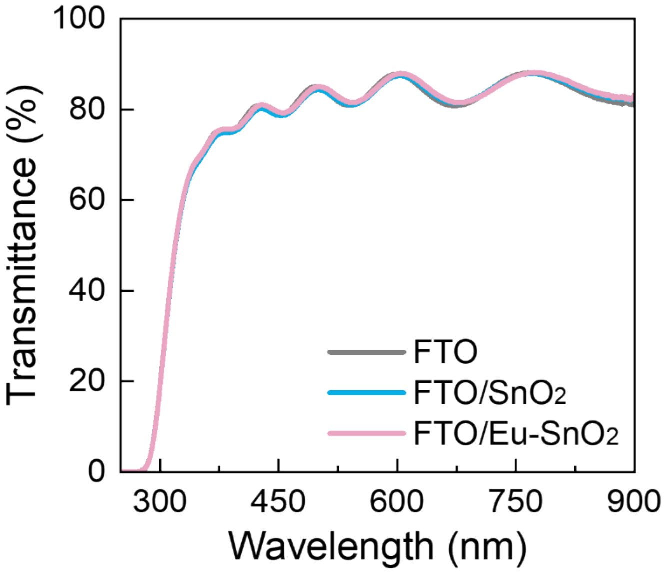

Figure S8. Transmittance of FTO, FTO/SnO_2, and FTO/Eu-SnO_2 substrates.

Table S2. Photovoltaic parameters of PSCs doped with different concentrations of $EuCl_3 \cdot 6H_2O$.

Conc. (mM)	**J_{SC} (mA/cm^2)**	**V_{OC} (V)**	**FF (%)**	**PCE (%)**
0	25.10	1.16	77.64	22.62
0.05	25.48	1.16	77.57	22.94
0.14	25.62	1.17	80.16	24.11
0.23	25.57	1.17	79.81	23.95

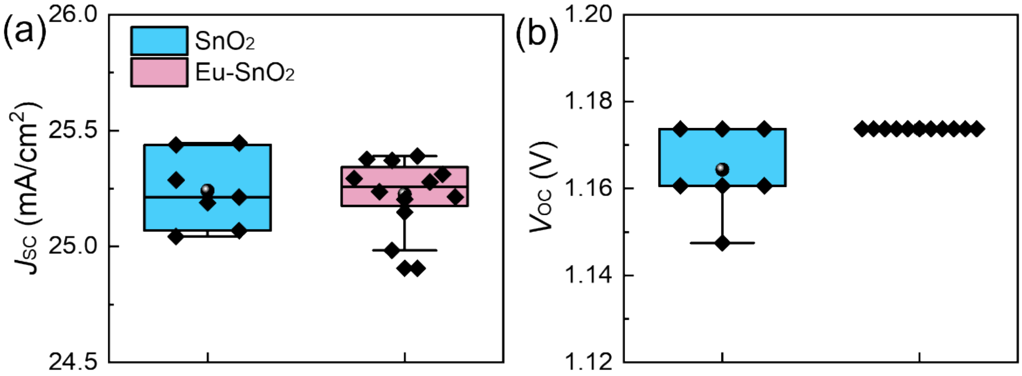

Figure S9. Statistical photovoltaic parameters of PSCs with different ETLs, including 7 SnO_2 samples and 11 Eu-SnO_2 samples: (a) J_{SC} and (b) V_{OC}.

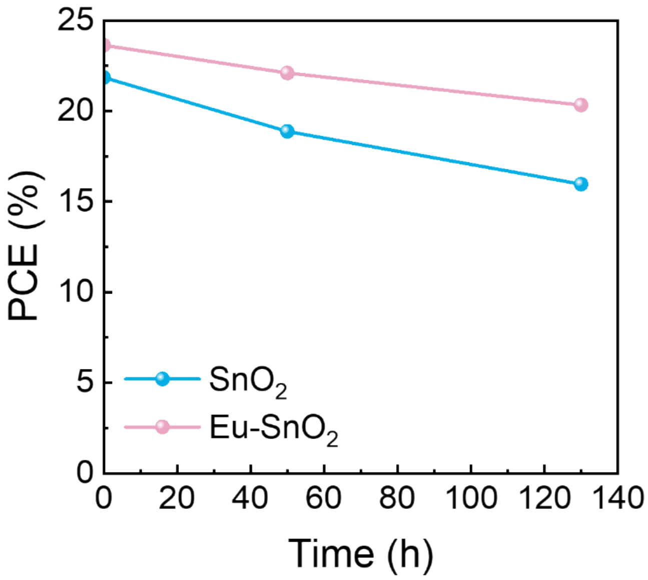

Figure S10: UV stability measurement of the PSCs exposed to UV light.

Table S3. Photovoltaic parameters of PSCs with different ETLs scanned at forward and reverse scan.

	Scan Direction	**J_{SC} (mA/cm^2)**	**V_{OC} (V)**	**FF (%)**	**PCE (%)**
SnO_2	Reverse	24.98	1.15	77.72	22.28
	Forward	25.01	1.12	72.34	20.29
Eu-SnO_2	Reverse	25.03	1.15	80.02	22.99
	Forward	25.00	1.12	78.41	21.98

Table S4. Photovoltaic parameters of PSCs with different ETLs before and after aging.

	Time (h)	**J_{SC} (mA/cm^2)**	**V_{OC} (V)**	**FF (%)**	**PCE (%)**
SnO_2	0	25.55	1.16	80.55	23.89
	2600	25.32	1.15	68.64	19.95
Eu-SnO_2	0	25.70	1.19	79.54	24.26
	2600	25.85	1.16	78.32	23.50

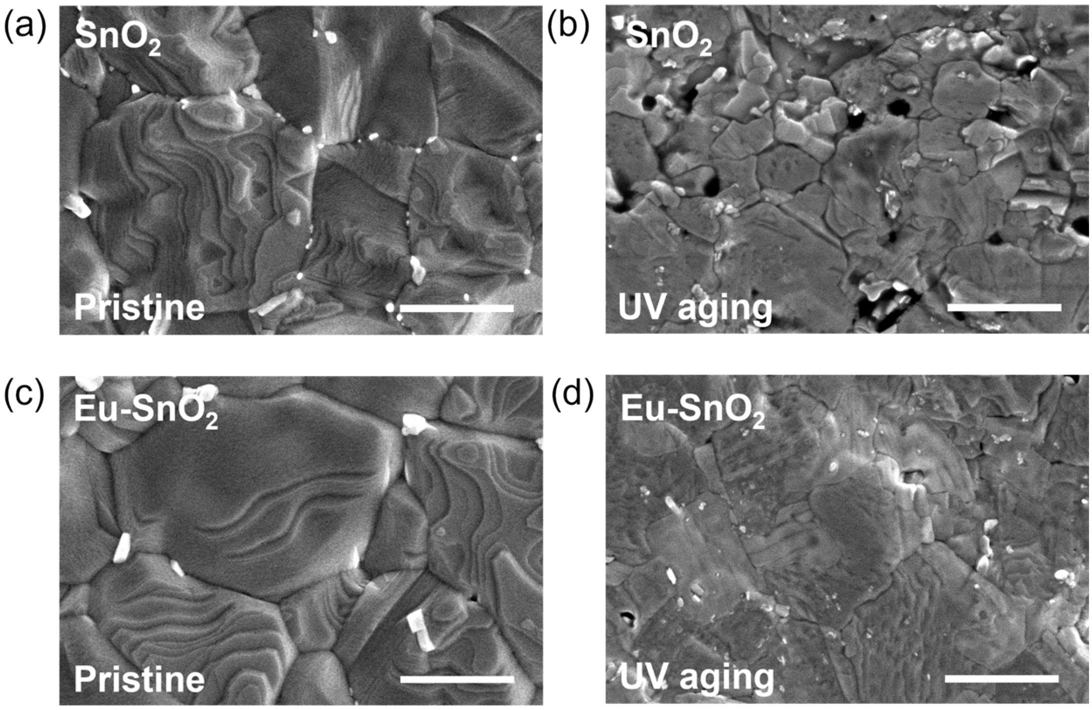

Figure S11: Top-view SEM images of perovskite film buried interfaces peeled from SnO_2 without (a) and with (b) UV aging. Top-view SEM images of perovskite film buried interfaces peeled from Eu-SnO_2 without (c) and with (d) UV aging. The scale bar is 1 μm.

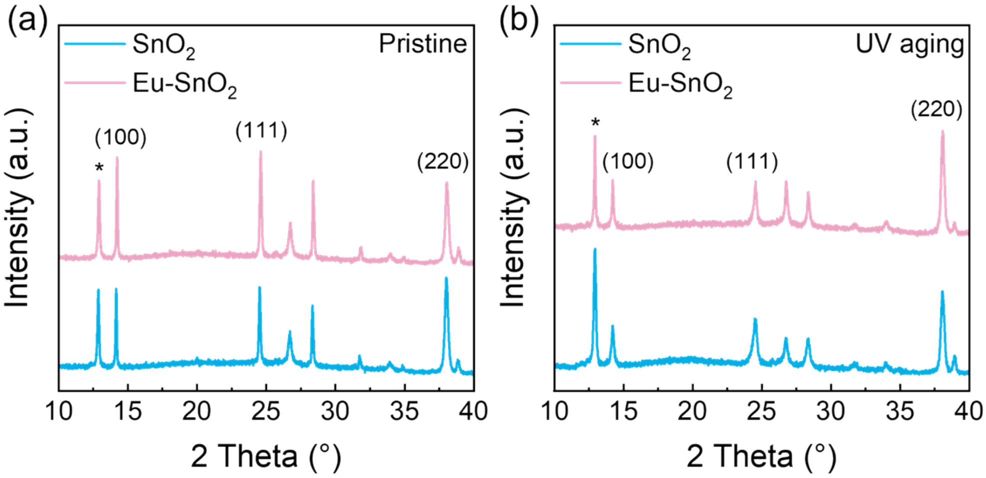

Figure S12: XRD patterns of perovskite film buried interfaces peeled from SnO_2 and Eu-SnO_2 without (e) and with (f) UV aging.