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Supporting Information

Ammonium sulfate treatment at TiO_2/perovskite interface boosts operational stability of perovskite solar cells

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Experimental section

Materials

Titanium (IV) butoxide, acetylacetone, cesium iodide (CsI), bis(trifluoromethylsulfonyl)amine lithium salt (LiTFSI), 4-*tert*-butylpyridine (TBP), ammonium sulfate, and anhydrous 2-methoxyethanol, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile and chlorobenzene (CBz), used in this study were purchased from Sigma-Aldrich. Lead iodide (PbI_2) and lead bromide ($PbBr_2$) were obtained from Tokyo Chemical Industry (TCI). Methylammonium bromide (MABr), formamidinium iodide (FAI), FK 209 Co (III) TFSI salt and mesoporous TiO_2 paste were purchased from Greatcell Solar.

Solar cell fabrication

Fluorine-doped tin oxide (FTO) substrates were washed with 1.5% (by volume) Hellmanex III soap solution (aq.), water, and ethanol in ultrasonication bath for 15 min in each step. FTO substrates were dry by hot air gun and then UV-ozone treated for 15 minutes before coating with compact titanium oxide blocking layer ($cTiO_2$) precursor. The $cTiO_2$ precursor was prepared by mixing titanium butoxide, 2-methoxyethanol, and acetylacetone. The $cTiO_2$ film was then dried at 100 ^oC then baked at 500 ^oC for 1 hour with ramp heating 10 ^oC/min. Next, mesoporous titanium oxide ($mTiO_2$) was spin-coated at 6000 rpm for 20 s. The precursor was made by diluting TiO_2 paste with absolute ethanol (VWR Chemicals) with ratio 1 is to 5.5 by weight. The $mTiO_2$ film was annealed at 325, 450, and 500 degrees Celsius for 10, 15, and 15 minutes, respectively. Sulfate treatment was applied by coating 0.08 mL ammonium sulfate solution on $mTiO_2$ layer with 3-second delay before spinning at 3000 rpm. The treated $mTiO_2$ film was then annealed again at 150 ^oC for 15 minutes to eliminate the solvent and ammonia species. Subsequently, $mTiO_2$ films were UV-ozone treated before brought to argon-filled glovebox for perovskite and spiro-OMeTAD hole transport layer deposition. To prepare the perovskite precursor solution, 18 mg of CsI, 25.4 mg of MABr, 84.7 mg of $PbBr_2$, 198.5 mg of FAI and 585.1 mg of PbI_2 are mixed with 0.8 mL DMF and 0.2 mL DMSO. Mixture was stirred over 2 hours before filtered through PTFE membrane. The HTL precursor solution was made of 59 mM of spiro-OMeTAD solution doped with TBP and LiTFSI dopants. Triple-cation perovskite was deposited by two-step spin-coating at 1000 rpm (10 s) and 5000 rpm (22 s). Just 5 seconds before the end of the second step, 0.25 mL CBz was dripped on the spinning substrate. The sample was then annealed at 100 ^oC for about an hour and cooled down to room temperature before HTL coating. The spiro-OMeTAD solution was coated at 4000 rpm for 20 s. The fabrication was completed with 80-nm thermally evaporated Au contact.

Characterization

X-ray diffraction (XRD) measurements were carried out by Bruker D8 Advance diffractometer. XPS and UPS measurements were conducted by using AXIS SUPRA photoelectron spectrometer with He I (21.22 eV) light source. The perovskite films morphologies were assessed by JEOL JSM-7600F field emission scanning electron microscope (SEM). For solar cell measurement, Newport solar simulator with one-sun AM 1.5G (100 mW/cm^2) was used with Keithley 2612 as the source meter. During the stability tracking measurements, the temperature of solar cell devices during the measurements were also measured using a non-contact temperature infrared gun. Shimadzu UV-3600 and HORIBA Fluoromax-4 were used to obtain absorbance and photoluminescence profiles of perovskite films. TRPL measurement was carried out by using a Picoquant PicoHarp 300 time-correlated single photon counting (TCSPC) setup. The samples were excited at 405 nm with pulsed laser-emitting diode at 40 MHz repetition rate. The full width half maximum of the TRPL setup's response function is about 50 ps.

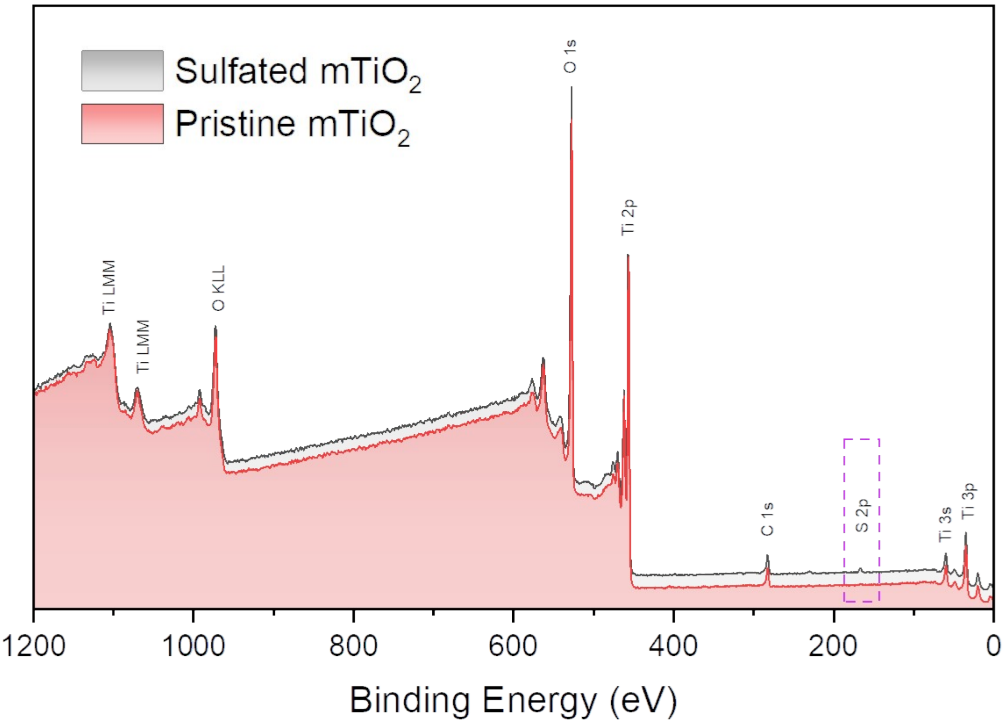

Fig. S1 Full XPS spectrum of sulfated and pristine ETL films. Dashed square highlights the presence of S 2p orbital peak originated from sulfate species incorporation.

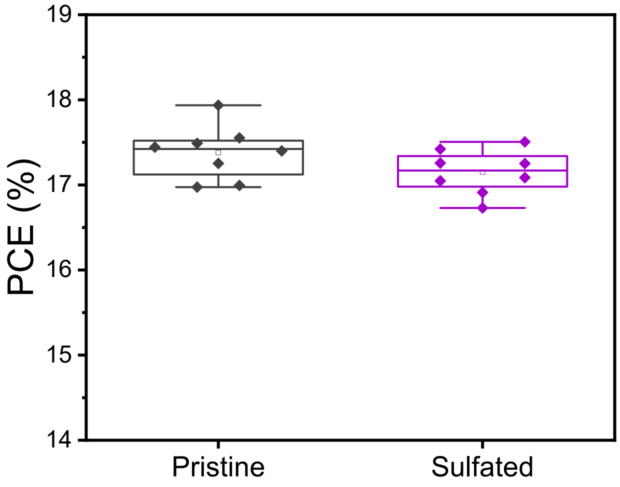

Fig. S2 Statistical distribution of power-conversion efficiencies (PCE) of pristine and sulfated devices with similar average PCE values of 17.4% and 17.2%, respectively.

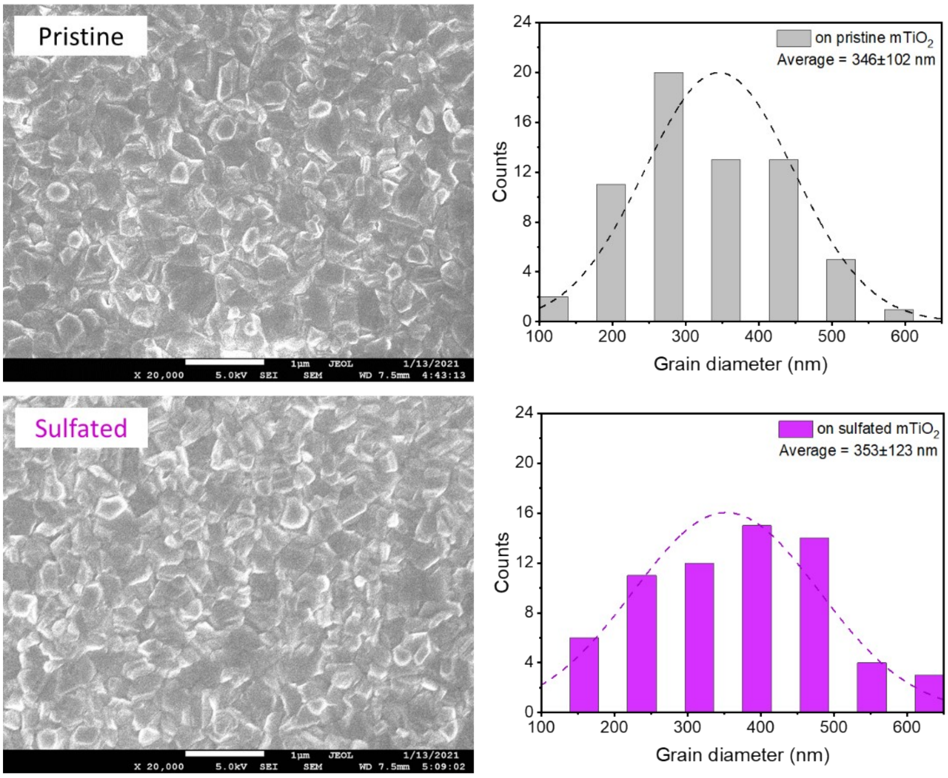

Fig. S3 Grain size distribution comparison between perovskite layers grown on top of pristine and sulfate $mTiO_2$ films.

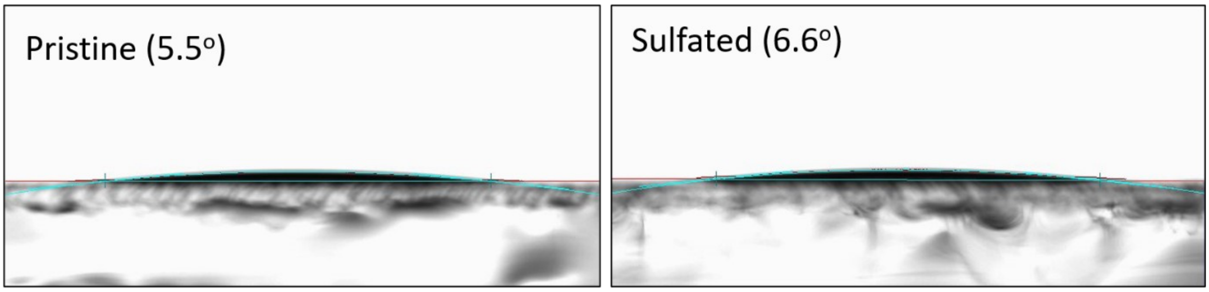

Fig. S4 Water-droplet contact angle measurement on pristine and ammonium sulfate-treated mesoporous TiO_2 films. The contact angle values presented is the average from 3 to 4 water droplets measured.

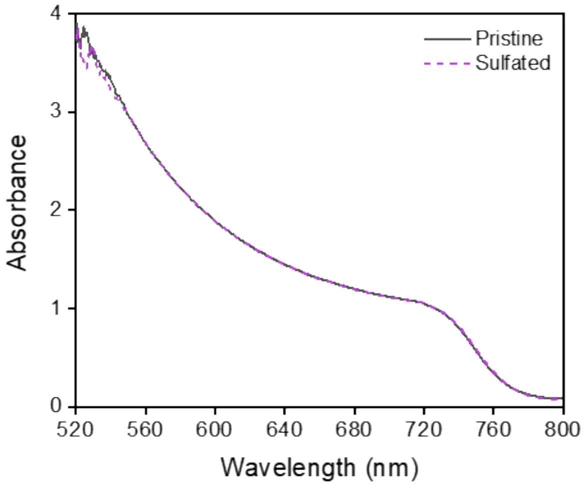

Fig. S5 Absorbance spectra of perovskite films coated on pristine and sulfated ETL films.

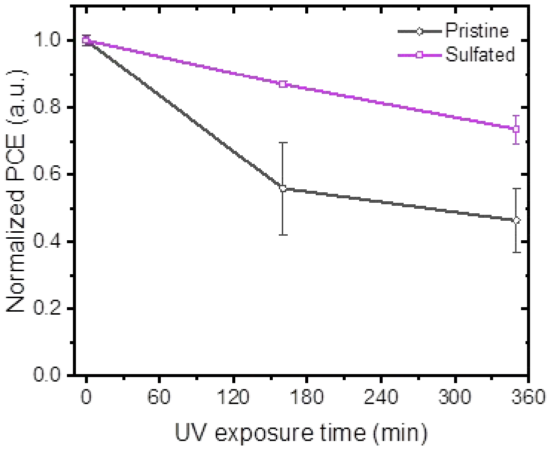

Fig. S6 The stability tracking of unencapsulated devices over about 6 hours of UV exposure time (λ_{UV}=365 nm) using 6-Watt UV light source.

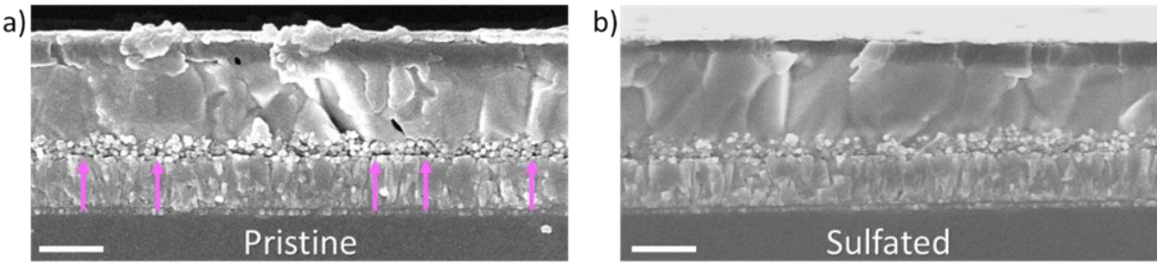

Fig. S7. Cross-sectional SEM images of a) pristine and b) sulfated devices after thermal aging at 60 ^{o}C for 25 days.

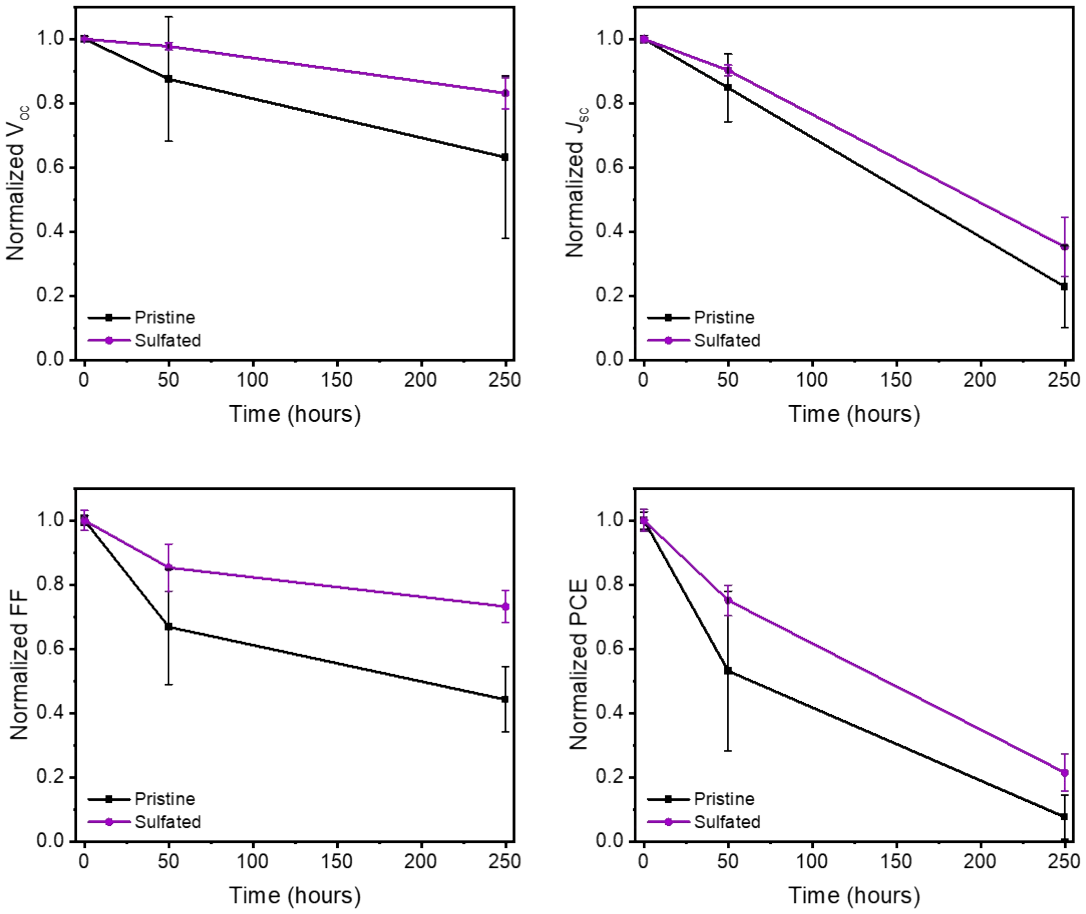

Fig. S8 Photovoltaic performance parameters of unencapsulated pristine and treated devices over thermal aging at 85 °C for 250 hours.

Table S1. Composition of O species (from fitting of O 1s spectra, atomic %) of pristine and sulfate $mTiO_2$ films.

Sample	**M-O**	**M-OH**	**SO_4**	**Organic O**
Pristine mTiO_2	82.45	5.68	0	11.87
Sulfate mTiO_2	80.71	2.75	6.13	10.41

Table S2. Device performance summary.

Conditions	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	**FF (%)**	**PCE (%)**
Pristine	1.073±0.009	21.50±0.12	75.3±1.1	17.4±0.3
5 mM	1.076±0.005	21.44±0.17	73.4±1.1	17.2±0.3
10 mM	1.028±0.020	21.49±0.16	72.7±0.8	16.1±0.3
20 mM	0.998±0.031	21.54±0.07	71.7±2.2	15.4±0.7

Table S3. Time-resolved photoluminescence decay time constants of perovskite films coated on ETL films and bare glass substrate.

Conditions	**A_1**	**τ_1 (ns)**	**A_2**	**τ_2 (ns)**	**τ_{ave} (ns)**

Bare glass	0.33	3.4	0.67	68.3	46.9
Pristine $mTiO_2$	0.44	14.2	0.56	3.6	8.3
Sulfated $mTiO_2$	0.62	1.3	0.38	5.7	3.0

Table S4. Percentage of perovskite, lead iodide and hydrate perovskite components in thermal aged perovskite samples.

ETL	**Hydrate (%)**	**PbI_2 (%)**	**Perovskite (%)**
Pristine	12.5	63.5	24.0
Sulfated	0	63.3	36.7