

Supporting Information

Surface-functionalized perovskite films for stable photoelectrochemical water splitting

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Experimental Section

Precursor synthesis: $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was synthesized according to the literature by reacting 24 mL of methylamine solution (CH_3NH_2 , 33 wt % in ethanol, Aldrich), 10 mL of hydroiodic acid (HI, 57 wt % in water, Aldrich), and 100 mL of ethanol (99.7%, Shanghai Lingfeng Chemical reagent) in a 250 mL round-bottom flask under nitrogen atmosphere at 0 °C for 2 h with stirring. The white precipitates were recovered by evaporation at 50 °C for 2 h then dissolved in ethanol followed by recrystallized from diethyl ether, and finally dried at 60 °C in a vacuum oven night. $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution was prepared by reacting MAI powders and PbI_2 (Aldrich) at 1:1 mol ratio in DMF (Aldrich) at 60 °C for 12 h with stirring.

Device Fabrication: FTO-coated glass substrates (Nippon Sheet Glass, Japan, 8 Oper square) were patterned by etching with Zn powder and 2 M HCl diluted in Milli-Q water. Then cleaned by ultrasonication with soap, acetone, Milli-Q water, and ethanol. To make a compact layer of TiO_2 , the FTO glasses were coated with mildly acidic solution of titanium isopropoxide in ethanol by the spin-coating method at 3000 rpm for 30 s, followed by a thermal treatment at 500 °C for 30 min.

For anti-solvent method of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer synthesis, 90 μL of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution was first dropped onto a TiO_2 -coated FTO substrate and spin-coated at 4000 rpm for 30 s. At the fourth second, anhydrous chlorobenzene (2 mL) was fast dropped onto the center of the substrate, which instantly changed the sample color from transparent to brown. The obtained film was then dried at 90 °C for 10 min, and the final color of the perovskite film was dark brown. Perovskite was functionalized with a dipping process in 25 mM ammonium iodine isopropanol solution for 20 s, and then raised with pure isopropanol for three times. The resulting products were dried at 50 °C for 2 min and subsequently annealed at 100 °C for 10 min.

The HTM was deposited by spin-coating at 4000 rpm for 30 s. The spin-coating formulation was prepared by dissolving 72.3 mg of spiro-MeOTAD, 18 μL of a stock solution of 500 mg mL^{-1} lithium bis(trifluoromethylsulfonyl)imide in acetonitrile, and 29 μL of 4-tert-butylpyridine in 1 mL chlorobenzene. Finally, silver was thermally

evaporated onto the HTM layer as the back contact. The devices were left in a desiccator overnight before being tested. All the device fabrication process were carried out in an Ar-filled glovebox. Finally, an 80 nm thick Ag layer and an 80 nm Ni layer were sequentially deposited on the HTM layer by vapor deposition.

Characterizations: The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800). Crystallographic information of the thin film was obtained with X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu K α radiation, 40 kV). The optical absorption spectra of the samples were recorded in a UV/Vis spectrophotometer. The $^1\text{H-NMR}$ curves were

Solar cells: The current–voltage tests of solar cells were performed using a solar light simulator (Oriel, 91160, AM 1.5 globe) and the power of the simulated light was calibrated to 100 mW cm^{-2} using a Newport Oriel PV reference cell system (model 91150 V). The cells were measured using a Keithley 2400 source meter. Devices were masked with a metal aperture to define the active area of 0.0625 cm^{-2} .

PEC measurements: Photoelectrochemical measurements were taken with a potentiostat in a three-electrode configuration. The three electrodes were the working electrode, a Pt foil counter electrode and Ag/AgCl in saturated KCl solution as reference electrode. The electrode was immersed in $0.1 \text{ M Na}_2\text{S}$ and the linear sweep voltammetry was scanned from -0.6 V to 0.8 V at 10 mV s^{-1} vs. Ag/AgCl. The stability measurements were performed in the same system at 1.23 V vs. Ag/AgCl.

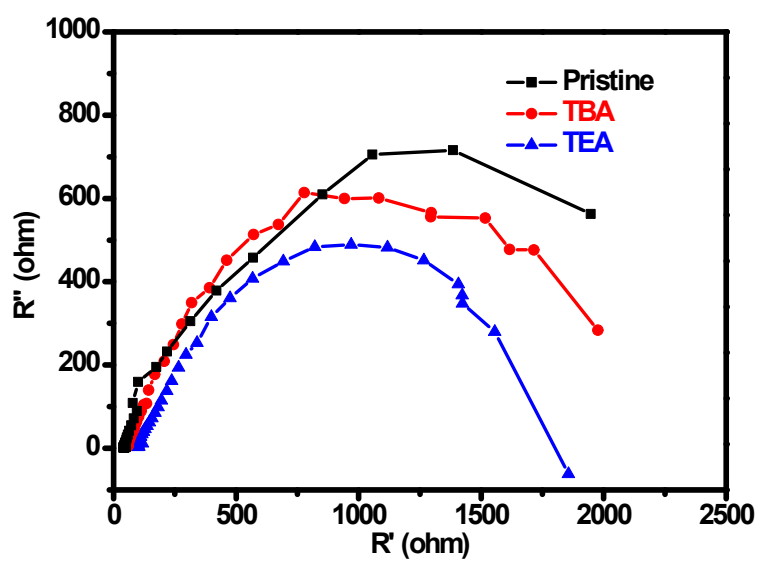


Figure S1. EIS measurements for pristine, TEA and TBA modified perovskite films. All electrodes display similar R_{ct} for water splitting and TEA treated film exhibits slight increase in R_s .

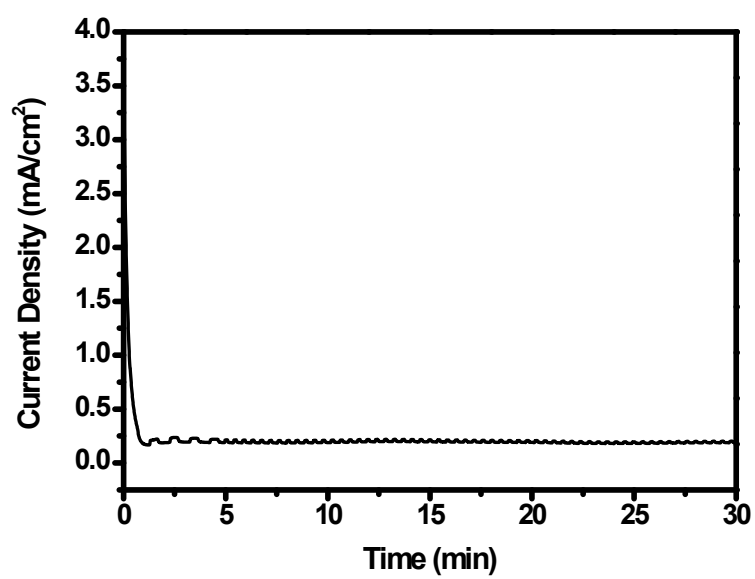


Figure S2. I-t curves measured for TBA modified film. The photocurrent quickly decay to around 0.2 mA/cm², indicating the instability of as-prepared electrode.

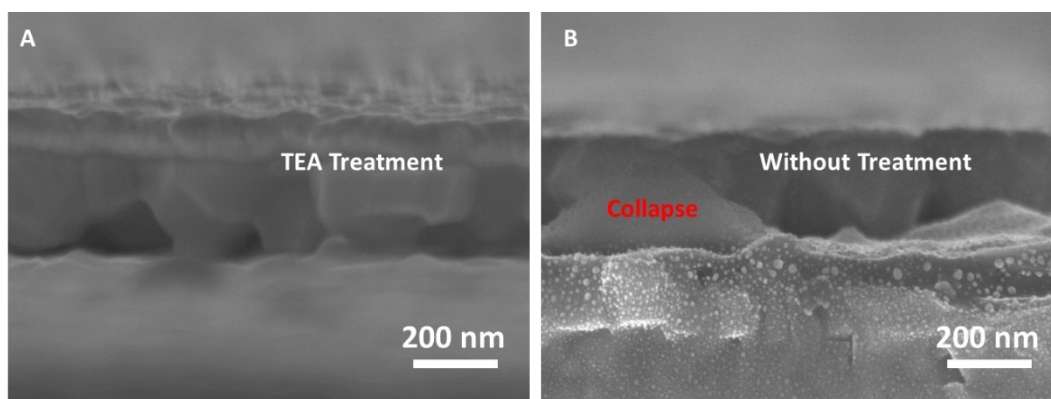


Figure S3. Cross-section SEM images measured for (A) pristine and (B) TEA modified perovskite electrodes after the stability measurements. Collapse can be observed for pristine perovskite film with Ni proactive layer while no significant alteration occurred in TEA modulated electrode after the chronoamperometry measurement.

Table S1. Photovoltaic parameters of solar cells based on pristine, TEA and TBA modified perovskite films. All the J-V curves were measured under 100 mW cm⁻² simulated AM 1.5G sunlight.

Sample	Jsc (mA cm ⁻²)	Voc (mV)	FF (%)	PCE (%)
Pristine	19.36	1018.51	57	11.23
TEA	18.61	1028.78	57	10.85
TBA	17.9	1049.07	56	10.69