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Supporting information

The identification and characterization of defect states in hybrid organic-inorganic perovskite photovoltaics

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CH3NH3I Synthesis. Hydroiodic acid (Sigma Aldrich, 57 wt %), DMF (Sigma Aldrich, 99+%), lead(II) iodode (Sigma Aldrich, 98%), methylamine (Sigma Aldrich, 33 wt % in absolute ethanol) were used without further purification. CH_3NH_3I was synthesized according the reported procedures (reference 6).

Thin Film and Solar Cell Fabrication. Substrate preparation was carried out under ambient conditions. Fluorine-doped tin oxide coated glass (13 Ω/sq, Sigma Aldrich) was patterned by etching with Zn powder and 2M HCl diluted in deionized water. The substrates were then cleaned with detergent diluted in deionized water, rinsed with deionized water, acetone and ethanol, and dried with clean dry air. After oxygen plasma treatment, the substrates were spin-coated with 0.15 M and 0.3 M titanium diisopropoxide bis(acetylacetonate) (Sigma Aldrich) at 3,000 r.p.m. for 30 s subsequently. After drying at 125 °C for 10 min, they were sintering at 550 °C for 15 min in air. The substrate was immersed in 50 mM $TiCl_4$ (Sigma Aldrich) aqueous solutions for 30 min at 70

°C and washed with distilled water and ethanol, followed by annealing at 550 °C for 30 min in air to form a compact n-type layer of TiO2 (c-TiO2). The solution of 400 mg/mL PbI_2 in DMF were spin coated on the FTO/c-TiO2 substrates at 2,000 r.p.m. for 30s, and dried at 110 °C for 15 min. CH_3NH_3I powder was spread out around the PbI_2 coated substrates with a petridish covering on the top , and heated at 150 °C for desired time. Both the deposition of PbI_2 film and vapor treatment of PbI_2 film were carried out in the glovebox. After cooling down, the as-prepared substrates was washed with isopropanol, dried and annealed. The FTO/c-TiO_2/Perovskite substrates was deposited by spin-coating a hole transport layer (HTL) solution at 2000 r.p.m for 30s, where a spiro-OMeTAD (Lumtec)/chlorobenzene (180 mg/1 mL) solution was employed with addition of 50 μL Libis(trifluoromethanesulfonyl) imide (Li-TFSI, Sigma Aldrich)/acetonitrile (170 mg/ 1 mL) and 20 μL tert-butylpyridine (tBP, Sigma Aldrich). Finally, the counter electrode was deposited by thermal evaporation of gold under a pressure of 5×10^{-5} Torr.

Device Characterization. An emission SEM (The Nova 230 NanoSEM) was used for collecting the SEM images. The instrument uses an electron beam accelerated at 500V to 30 kV, enabling operation at a variety of currents. The current density (J)-voltage (V) curves were measured using a Keithley 2401 source-measure unit under AM1.5G illumination at 100 mW/cm^2 provided by an Oriel Sol3A solar simulator. Light intensity was determined by a calibrated KG-5 filter diode as a reference cell. The solar devices were masked with a metal aperture to define the active area of about 0.11 cm^2, and measured in a sample holder to minimize any edge effects. Admittance spectroscopy was conducted using a Hewlett-Packard 4284A LCR Meter. Electrical contact to the devices during LCR measurements was provided by a Janis cryogenic probe station with an

attached Lakeshore 331 temperature controller. The temperature was monitored using a thermocouple placed in contact with the sample location.