

Supporting Information

Microscopic Analysis of Inherent Void Passivation in Perovskite Solar Cells

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Experimental Section:

Perovskite film preparation: A 20~30 nm TiO₂ blocking layer was deposited on the cleaned FTO glass by spray pyrolysis at 450 °C from a precursor solution of titanium diisopropoxide and bis(acetylacetonate) in anhydrous isopropanol. A 100~200nm diluted 30mM particle paste (Dyesol) in ethanol, mesoporous TiO₂ was coated on the substrate by spin-coating at 4,500 r.p.m for 15s. After that, the substrate was dried on a 80 °C, and then the substrate were sintered at 500 °C for 30min. The perovskite film was deposited by spin-coating on to the TiO₂ substrate as follow: PbI₂ was dissolved in *N,N*-dimethylformamide (DMF) with a concentration of 462 mg ml⁻¹ (~1 M) under stirring at 70 °C. The solution was kept at 70 °C during the whole procedure. The mesoporous TiO₂ films were then coated with PbI₂ by spin coating at 6,500 r.p.m. for 90 s, and dried at 70 °C for 30 min. After cooling to room temperature, the films were dipped in a solution of CH₃NH₃I in 2-propanol (10 mg ml⁻¹) for 20 s, rinsed briefly with 2-propanol, and dried at 70 °C for 30 min again. The HTM was then deposited by spin coating at 4,000 r.p.m. for 30 s. The HTM was deposited by spin-coating a solution of spiro-OMeTAD, 4-tert-butylpyridine, lithium bis(trifluoromethylsulphonyl)imide and tris(2-(1H-pyrazol-1-yl)-4-

tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl). A 80 nm-thick gold counter-electrode was deposited by thermal evaporation.

X-ray Photoemission Spectroscopy (XPS) The chemical states were characterized by commercial XPS equipment (Quantum 2000 system) with AlK α x-ray source (h ν : 1486.6 eV) and hemispherical electron analyzer. The resulting XPS results provide the average chemical information on spatial area of 100 μ m diameter.

Reflection Electron Energy Loss Spectroscopy (REELS) were measured by Auger electron spectroscopy (AES; PHI 4700 system) with concentric hemispherical analyzer (CHA) . The primary energy of electrons for the AES measurement was 1.5 keV and the full width at half maximum (FWHM) of the elastic peaks of 1.5 keV was 0.8 eV.

Electron beam-induced current (EBIC) were performed immediately loaded into the with an FEI Sirion scanning electron microscope (SEM) vacuum chamber and Point electronic EBIC system. The gold contact was connected to the sample chamber and electron beam energy of 2 kV and a fixed current of 388 pA were used to excite a constant amount of carriers.

Current–voltage characteristics were measured using a solar simulator (Newport, Oriel 3A Class AAA, 64023A) equipped with a 450-W xenon lamp (Newport 6279NS) and a potentiostat (CHI 600D, CH Instruments). The light intensity was adjusted using a standard Si-reference cell (Oriel, VLSI standards; 1 sun is equivalent to 100 mA cm⁻²). The J – V curves of all devices were measured by masking the active area with a metal mask of area 0.096 cm².

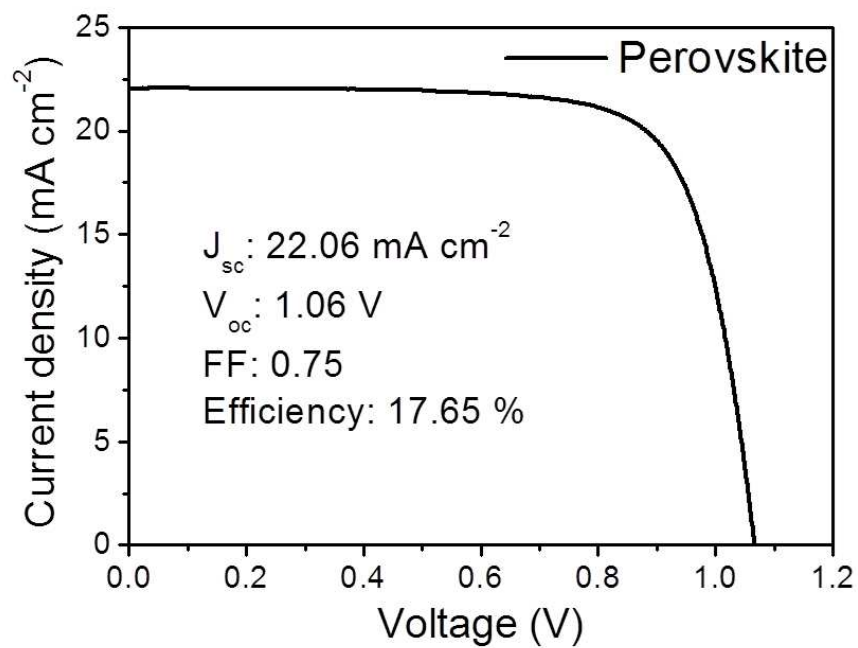


Figure S1. The J - V curve of the reference perovskite

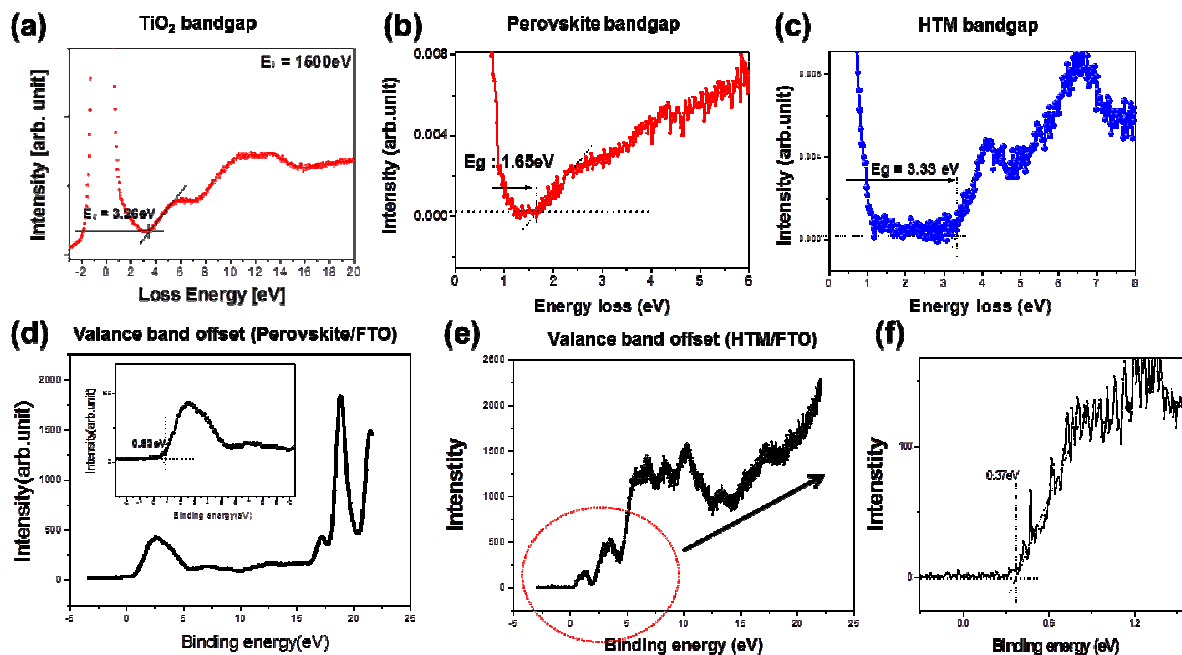


Figure S2. REELS spectra of TiO_2 (a), the perovskite layers (b), and HTM layers (c). XPS spectra of the perovskite and FTO layers (d), inset shows enlarged fitted data, and HTM and FTO layers (e). The circled region in Figure S2(e) is enlarged in Figure S2(f).

The band structures of the perovskite solar cells were investigated with reflection electron energy loss spectroscopy (REELS) and X-ray photoemission spectroscopy (XPS) in Figure S2. The band gaps of TiO_2 , the perovskite, and HTM layers are extracted from the REELS data and are displayed in Figure S2(a)-(c). The values are 3.26 eV (TiO_2), 1.65 eV (perovskite), and 3.33 eV (HTM), respectively. The XPS spectrum for the valence band offset between the perovskite and FTO layers is displayed in Figure S2(d). The valence band offset of the perovskite layer and

FTO was extracted: 0.83 eV. The XPS spectrum for the valence band offset between HTM and FTO layers is displayed in Figure S2(e). The valence band offset of HTM and FTO was extracted: 0.37 eV. With the extracted band gaps and valence band offsets values, the bands of the perovskite solar cells were aligned and are illustrated in Figure S3.

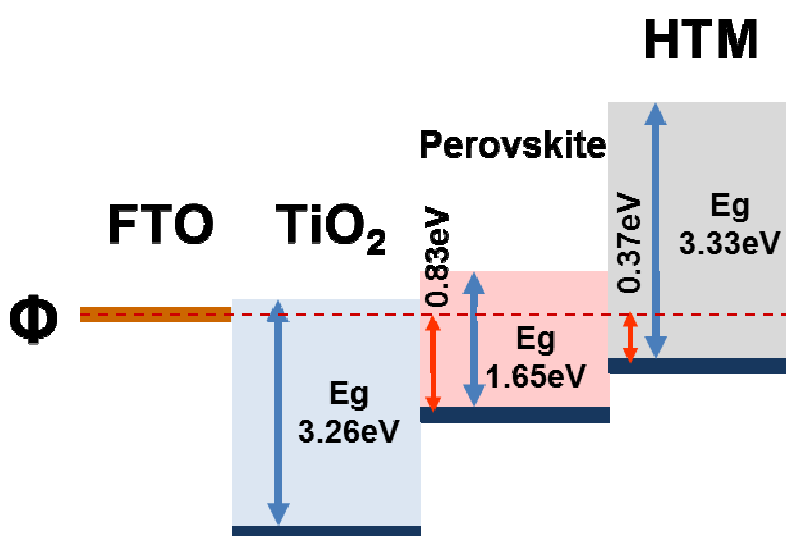


Figure S3. The schematic band diagram for the perovskite solar cell.