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Supporting Information

Synergistic Enhancement and Mechanism Study of Mechanical and Moisture Stability of Perovskite Solar Cell Introducing Polyethyleneimine into $CH_3NH_3PbI_3$/HTM Interface

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Materials

A titanium diisopropoxide bis(acetylacetonate) solution (75 wt% in isopropanol), n-butanol (99.8%), 2-propanol (anhydrous, 99.5%), *N,N*-dimethylformamide (anhydrous, 99.8%), lead(II) iodide (99%), 4-*tert*-butylpyrididne (TBP, 96%), chlorobenzene (anhydrous, 99.8%), toluene (anhydrous, 99.8%), bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI, 99.95%) and branched polyethylenimine (PEI, average Mn ~10,000) were purchased from Sigma-Aldrich. 2,2′,7,7′-Tetrakis(*N,N*-di-p-methoxyphenyl-amine)-9,99-spirobifluorene (spiro-OMeTAD, Merck), TiO_2 paste (Dyesol 18NRT, Dyesol), methylammonium iodide (Dyesol), gold (Au, 99.99%, Itasco) were used to fabricate the perovskite solar cell device.

Perovskite solar cell fabrication

Etched fluorine doped tin-oxide (FTO) substrates (TEC-8, Pilkington) were cleaned with sonication in ethanol, isopropanol, and acetone, followed by UV-O_3 treatment for 20 min to eliminate residual organic compounds. A compact TiO_2 layer was then deposited onto the FTO substrate by spin-coating a titanium diisopropoxide bis(acetylacetonate) solution (75 wt% in isopropanol) diluted with n-butanol (1:11, volume ratio) at 500rpm for 5s, 1000rpm for 5s, and 2000rpm for 40s in a consecutive manner. After drying at 120 ^{o}C, the films were annealing at 500 ^{o}C for 30 min and cooled to room temperature. Then, mesoporous TiO_2 layers which were prepared from a commercial TiO_2 paste solution diluted in ethanol (2:7, weight ratio) was deposited onto as-prepared films by spin-coating at 3500 rpm for 40s and dried at 120 ^{o}C for 10min. After evaporation of residual solvents, the films were heated at 500 ^{o}C for 1h to form a mesoporous scaffold. The perovskite layer was then obtained by a sequential deposition method. A PbI_2 solution (1.0 M in DMF) was dissolved at 80 ^{o}C and kept heating during the entire procedure. PbI_2 layer was formed by infiltrating into the mesoporous scaffold for 30s, followed by spinning at 6500 rpm for 1 min and immediately, a CH_3NH_3I solution (10 mg/ml in 2-propanol) was spin-coated onto the PbI_2 layer at 1000 rpm for 10 s followed by annealing at 80^{o}C for 20min on a hot plate to form a $CH_3NH_3I_3$ perovskite layer. Onto the perovskite layer, a PEI solution (0.1 mg/ml in Toluene) was spin-coated at 5000 rpm for 1min. A HTM solution prepared by 1 ml of chlorobenzene solution dissolving 56 mg spiro-OMeTAD, 29 mg 4-*tert*-butylpyridine (TBP), and 5.6 mg lithium bis(trifluoromethane) sulfonamide (Li-TFSI) was then deposited by spin-coating at 2500 rpm for 20 s. Finally, a 100 nm layer of Au was thermally evaporated to form a back contact of the device. All perovskite solar cells without PEI were prepared as the same fashion except spin-coating the PEI solution between the perovskite and HTM layers.

Characterization

X-ray diffraction patterns (XRD, Dmax2500/server, Rigaku Corporation) were measured under a condition of 40 kV and 150 mA with a Cu Kα beam (λ = 1.54 Å) and with a 2 theta mode at a scan rate of 2 deg/min. X-ray photoelectron spectroscopy (XPS) was analyzed using a PHI 5000 Versa Probe (Ulvac-PHI) with the photon energy of hν = 1486.6 eV (monochromator Al-Kα) at a take-off angle of 45^o relative to the sample surface, where the investigated area was 100 x 100 μm^2 performed on a 1.2 x 1.2 mm^2 area for each sample, and 284.6 eV was calibrated as a C1s peak at a background pressure of $6.7x10^{-8}$ Pa. Depth profiling was performed by Dynamic secondary ion mass spectrometry (D-SIMS, IMS 4FE7, Cameca corporation) using a 14.5KeV Cs^+ primary ion beam operated at 20 nA and raster over a 150 x 150 μm^2 area of the sample surface. The absorption spectra of the films were accomplished using an UV/vis spectrometer (Lambda 35, PerkinElmer) over the wavelength from 300 nm to 900 nm. The static contact angles were measured by using a Portable Contact Angle Meter (PCA-1, KYOWA, Japan). Morphological and structural characterization of the films was carried out by scanning electron microscopy (SEM, Nova, Nano200) and atomic force microscopy (AFM, Park System, USA). Energy dispersive spectroscopy (EDS) was measured by using Hitachi (S-5000H).

Solar cell measurements

Current density and voltage curves were recorded with a Keithley model 2400 source meter under AM1.5G at sun light intensity (100 mW/cm^2) in ambient air. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita Denso) was used as a light source. Its light intensity was calibrated by using a NREL-calibrated Si solar cell coupled with a KG-5 filter. During the I-V curve measurement, the solar cells were covered with a metal aperture mask. External quantum efficiencies (EQEs) were measured by using a K3100 IPCE measurement system

(Mcscience corporation).The devices were illuminated under a light source from a xenon lamp (K240 XE300), and the illuminated light was hopped at 2Hz.

Photoluminescence lifetime measurements

Time-resolved PL (TRPL) measurements were carried out by inverted-type scanning confocal microscopy (MicroTime-200, PicoQuant) with a 20x objective. All film samples were excited using a 470 nm pulsed diode laser with a pulse width of ~100 ps and a fluence of < 1 μW. The PL data were collected using a dichroic mirror (490 DCXR, AHF), a long pass filter (HQ500lp, AHF), a 50 μm pinhole, and a single photon avalanche diode (PDM series, MPD) through a 700 nm long-pass filter. The exponential fitting of the PL decay was performed using the Symphotime software (version 5.3). The PL lifetime of the film was compared by τ_e , which is defined as the time taken after excitation for the initial population to decrease to 1/e.

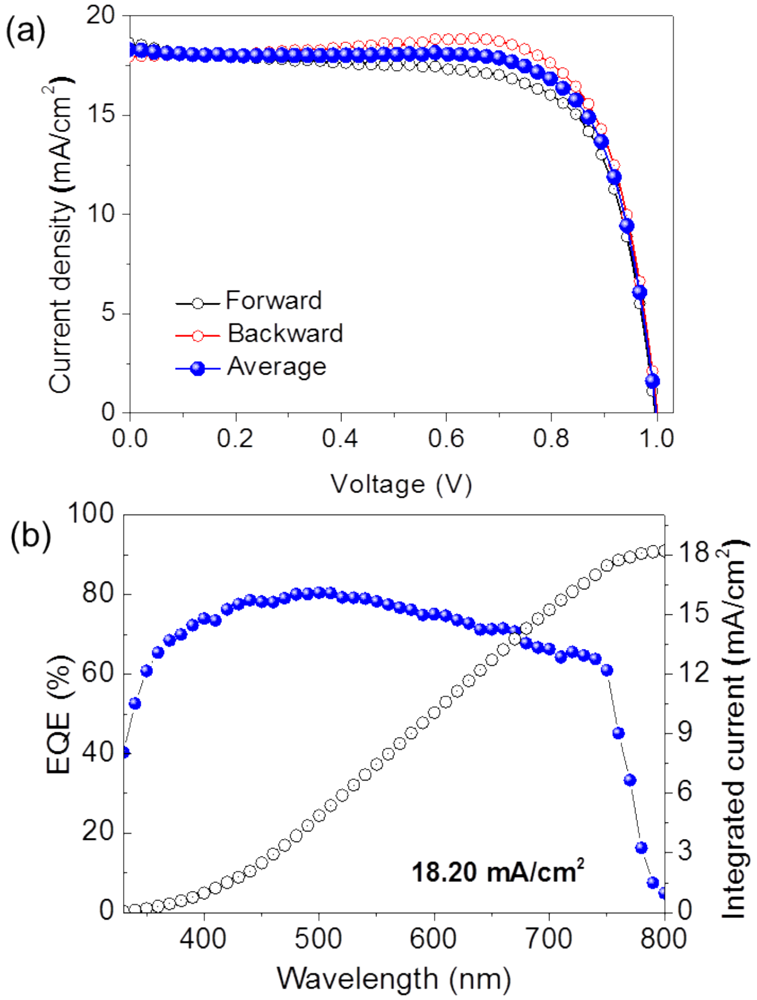


Figure S1. (a) *J*−*V* curves and (b) EQE spectra of the perovskite solar cell with PEI.

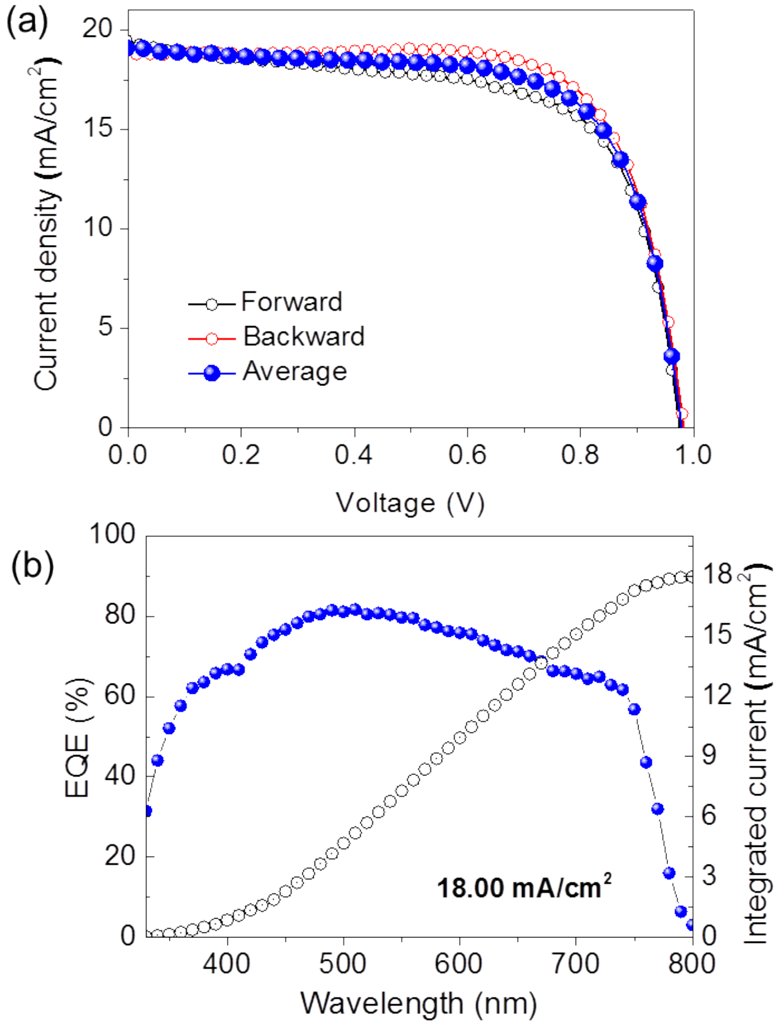


Figure S2. (a) $J-V$ curves and (b) EQE spectra of the perovskite solar cell without PEI.

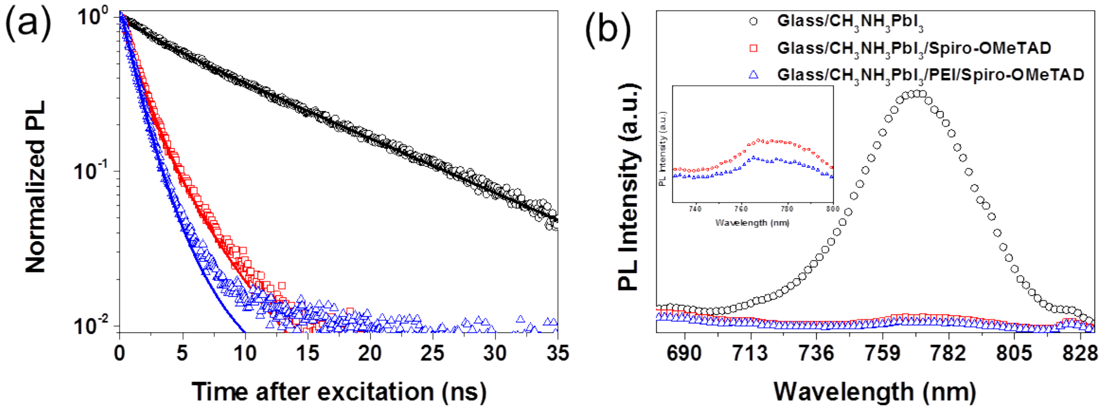
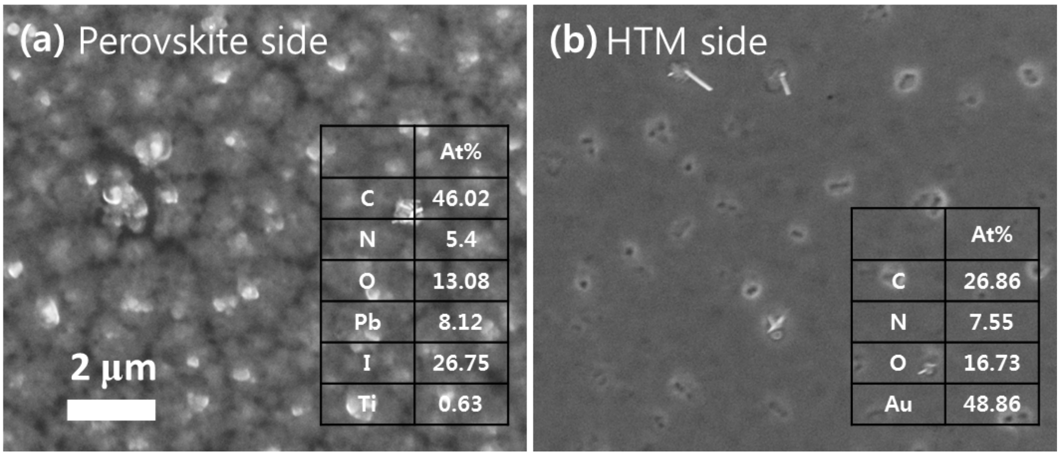


Figure S3. Photoluminescence response of $CH_3NH_3PbI_3$/HTM films with and without PEI. (a) Time-resolved PL decay transients and (b) steady-state PL spectra. PL decay transients were collected at the wavelength range above 700 nm for all films in vacuum after excitation at 470 nm.



	At%
C	46.02
N	5.4
O	13.08
Pb	8.12
I	26.75
Ti	0.63

	At%
C	26.86
N	7.55
O	16.73
Au	48.86

Figure S4. SEM images of the fractured surfaces of the device without PEI and surface atomic compositions (At%) determined from EDS analysis.

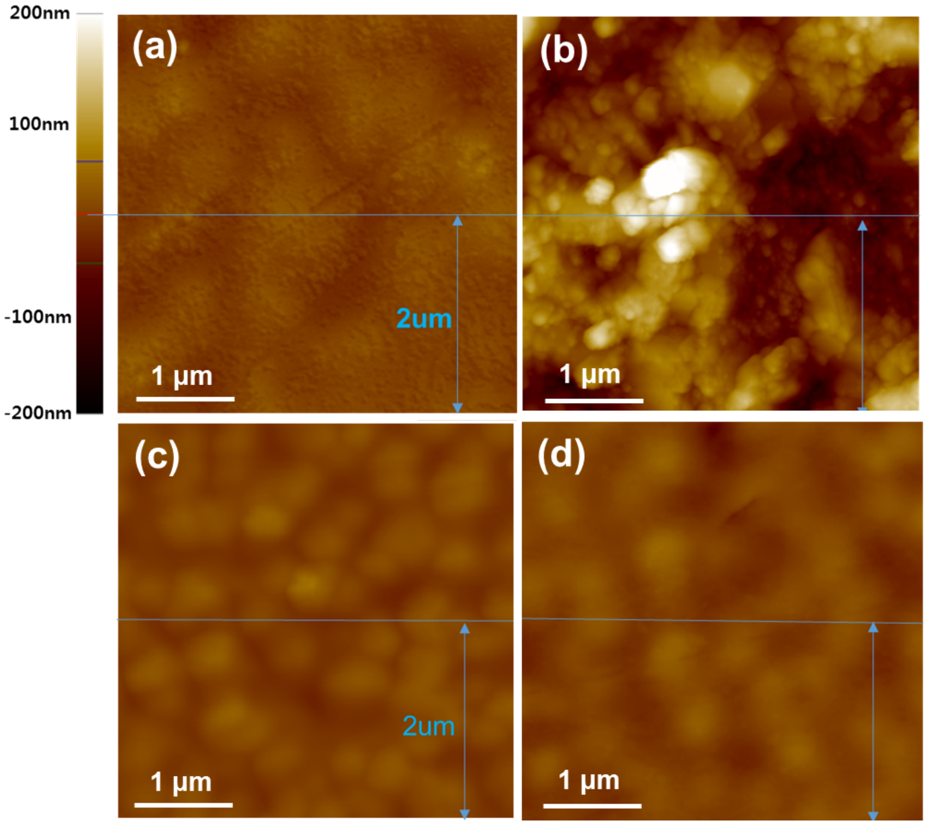


Figure S5. Top-view AFM images of the Au-uncovered areas in the devices without PEI (a, b) and with PEI (c, d). (a, c) images before degradation. (b, d) images after degradation.

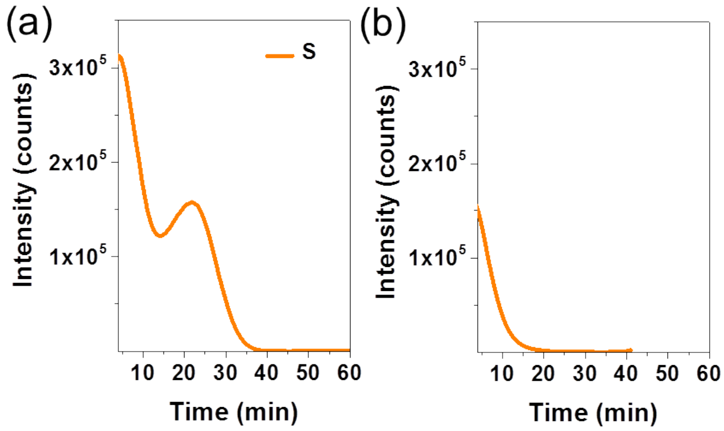


Figure S6. Dynamic-SIMS profiles (sulfur) of the perovskite solar cell device without PEI before (a) and after (b) degradation.

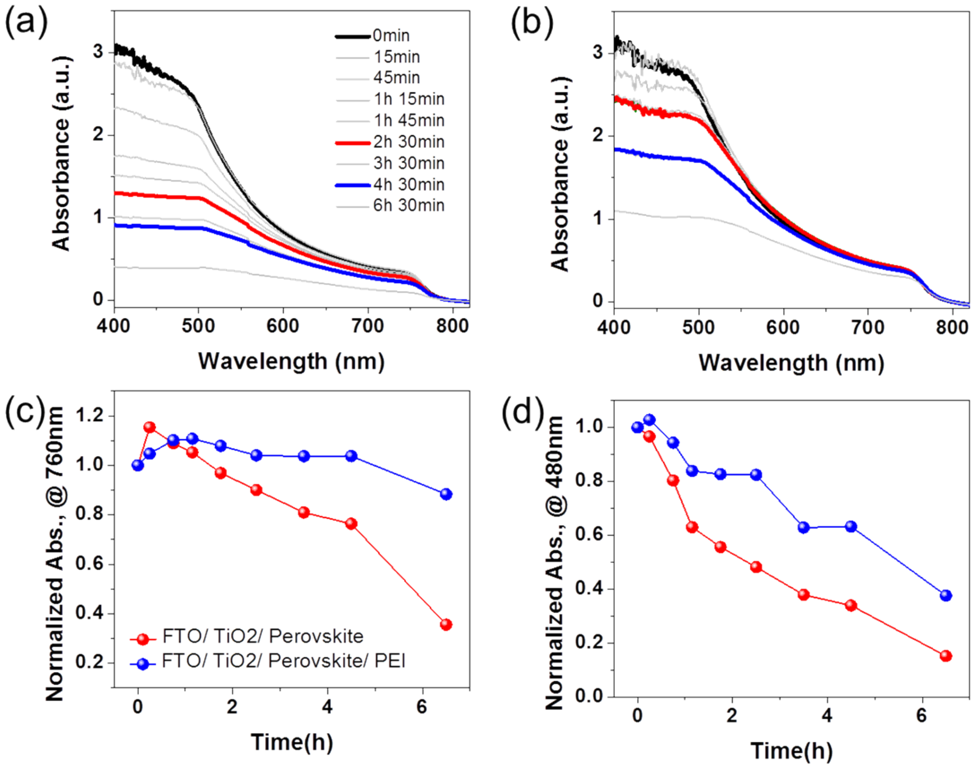


Figure S7. Normalized absorbance at (a) 760 nm and (b) 480 nm as a function of time for FTO/TiO2/Perovskite films exposed to 85% humidity.