

Electronic Supplementary Information

Enhanced compatibility between copper nanowire-based transparent electrode and hybrid perovskite absorber by poly(ethylenimine)

Hyewon Hwang,‡ Jihoon Ahn,‡ Eunsong Lee, Kyungmi Kim, Hyeok-Chan Kwon, and Jooho Moon*

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea

**E-mail: jmoon@yonsei.ac.kr*

Experimental section

Preparation of copper nanowire (CuNW) suspension

In order to prepare CuNW suspension, 0.013 M anhydrous copper chloride (CuCl_2 ; 97%, Sigma-Aldrich, St. Louis, MO, USA), 0.011 M anhydrous dextrose ($\text{C}_6\text{H}_{12}\text{O}_6$; Sigma-Aldrich), and 0.056 M 1-hexadecylamine ($\text{C}_{16}\text{H}_{35}\text{N}$; 98%, Sigma-Aldrich) were dissolved in 600 mL of deionized water. By stirring the solution at 600 rpm for 12 h, a sky-blue solution containing Cu-akylamine complex was obtained.^{S1} The solution was then heated in a hydrothermal reactor at 120 °C for 15 h, which yielded a reddish-brown aqueous CuNW suspension. The solution was centrifuged for 4 min at 12000 rpm and then washed several times with deionized water and a 1:2 (v/v) mixture of IPA (Duksan Pure Chemicals, Ansan-si, Gyeonggi-do, Korea) and hexane (Duksan Pure Chemicals) to remove unreacted residues.

Preparation of AZO/CuNWs/AZO composite electrode

The AZO/CuNWs/AZO composite transparent electrodes were prepared by the layer-by-layer deposition technique. First, the bottom AZO layer with a thickness of ca. 30 nm was deposited by magnetron sputtering using an AZO target at a constant dc power of 70 W, Ar flow of 24 sccm, and working pressure of 2 mTorr on a glass substrate with dimensions of 20 × 20 mm². The CuNW network was then deposited on the bottom AZO layer by vacuum filtration with lactic acid treatment.^{S2} The AZO/CuNW films were annealed at 200 °C for 30 min in N₂ atmosphere. The top AZO layer was deposited on the CuNW film using two-step deposition sequences. A 20 nm-thick AZO layer was then deposited under the same conditions as that of the bottom AZO layer. After the temperature of the sputtering chamber was elevated to 200 °C, an additional AZO layer with a thickness of ca. 20 nm was deposited at a dc power of 80 W, Ar flow of 17 sccm, O₂ flow of 8 sccm, and working pressure of 2.7 mTorr. Typically, the composite electrodes

possessed a transmittance of 87–88% at 550 nm and sheet resistance of 38–40 Ω/\square .

Fabrication of perovskite solar cells

On the transparent electrodes (TEC-15, Pilkington, UK; or AZO/CuNWs/AZO), a ca. 140-nm-thick ZnO layer was coated as an ETL by magnetron sputtering at a dc power of 60 W, Ar flow of 50 sccm, O₂ flow of 5 sccm, and working pressure of 1 mTorr. After the deposited ZnO electrodes were cleaned by a O₂ plasma cleaner (PDC-002, Harrick Plasma, New York, USA), a poly(ethylenimine) (PEI, branched, Mw ~25,000 by LS and Mn ~10,000 by GPC, Sigma-Aldrich) layer was spin-coated at 5000 rpm using 0.1 wt% PEI solution dissolved in 2-propanol. The PEI coated substrate was annealed at 105 °C for 10 min. The perovskite absorber layer was fabricated with a 53 wt% solution in dimethylformamide (DMF, Sigma-Aldrich). Lead iodide (PbI₂, Alfa-aesar, MA, USA), methylammonium iodide (CH₃NH₃I, Dyesol, Australia), and dimethylsulfoxide (DMSO, Sigma-Aldrich) were dissolved in the solution in the mole ratio of 1:1:1. This solution was spin-coated at 4000 rpm for 25 s, followed by drying at 65 °C for 3 min and annealing at 105 °C for 10 min. Further, the hole-transporting layer was prepared as follows: the precursor solution for the HTM was prepared using 54 mM 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD, Boron Molecular, Raleigh, NC, USA) in chlorobenzene, with 177.7 mM 4-*tert*-butylpyridine and 28.5 mM lithium bis-(trifluoromethylsulfonyl)imide in acetonitrile as additives. The solution was spin-coated at 1150 rpm for 30 s. Finally, Au electrode with 70 nm thickness was deposited on the top of the cell by evaporation.

Preparation of MAPbI₃ powder

In 1 ml of ethanol (Duksan Pure Chemicals), 922 mg of PbI₂ and 318 mg of CH₃NH₃I were poured together. Under vigorous stirring, dark solid products were formed in the solution. Solvent was evaporated with vacuum to obtain MAPbI₃ powder.

Reaction between MAPbI₃ powder and PEI

50 mg of PEI was put in a vial and 1 ml of anhydrous toluene (Duksan Pure Chemicals) was poured in the vial. 100 mg of MAPbI₃ powder was added to the mixture. The mixture was allowed to reaction for 3 h under vigorous magnetic stirring. Viscous product was obtained after the evaporation of toluene by vacuum. .

Measurement of chemical stability of the electrodes against perovskite

In order to examine the chemical stability of various AZO/CuNWs/AZO electrodes with and without ZnO and PEI layers against MAPbI₃, a MAPbI₃ layer was sequentially deposited and removed from the CuNW-based electrode substrate. The deposition procedure for the ZnO and MAPbI₃ layers is the same as described above. After the MAPbI₃ layer was deposited, it was aged for 120 h in ambient condition. Then, the MAPbI₃-coated substrate was immersed in γ -butyrolactone (GBL, Sigma-Aldrich) and ethanol (Duksan pure chemicals) for 3 min each, and the top layer was carefully wiped out with a cotton swab.

Finally, the MAPbI₃ layer was dissolved out, exposing the surface of the electrodes. The XRD profiles and sheet resistance of the electrodes were then recorded.

Characterization

SEM images were obtained using a field emission scanning electron microscope (FE-SEM, JSM-7001F, JEOL Ltd., Japan). The total transmittance was determined using a UV–visible spectrophotometer (V-670, Jasco, Japan) equipped with an integrating sphere (ARMN-735, Jasco, Japan). The sheet resistance was measured using a four-point probe meter (RS8, BEGA Technologies, Seoul, Korea), and XRD profiles were obtained using an X-ray diffractometer (D/MAX-2500, Rigaku, Tokyo, Japan). The photovoltaic properties were measured using a solar simulator (Sol3A Class AAA, Oriel Instrument, Irvine, USA) at 100 mW cm⁻² (1 sun) with a xenon arc lamp equipped with a 1.5G air mass sunlight filter. The selected area (0.06 cm²) covered by a hard mask was exposed to the light and scanned at a rate of 480 mV s⁻¹ and a delay time of 50 ms. The external quantum efficiency (EQE) was measured by a QEX 10 IPCE measurement system (PV measurements, Inc., Colorado, USA) in the wavelength range of 300–900 nm.

ESI References

S1 D. V. Ravi Kumar, I. Kim, Z. Zhong, K. Kim, D. Lee and J. Moon, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22107.

S2 Y. Won, A. Kim, W. Yang, S. Jeong and J. Moon, *NPG Asia Mater.*, 2014, **6**.

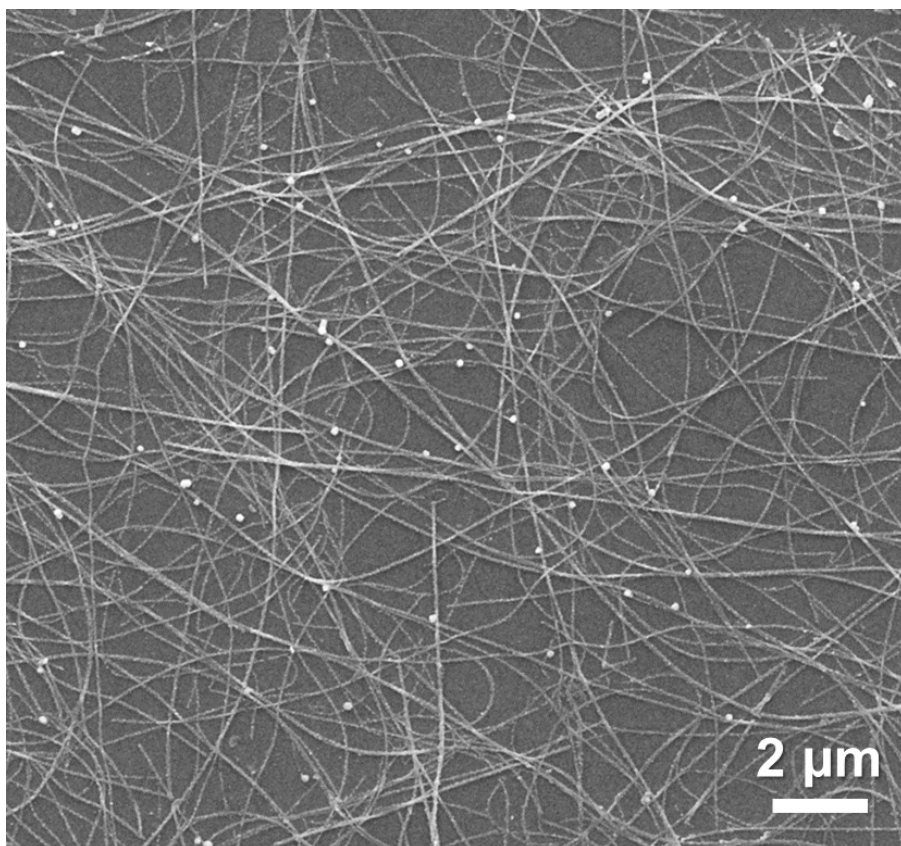


Fig. S1 SEM image of CuNW network film; CuNWs are few micrometers long with ca. 50 nm diameter.

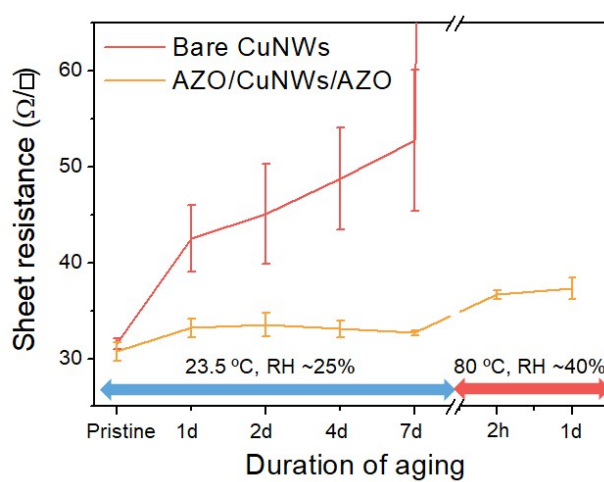


Fig. S2 Sheet resistance change of bare CuNWs network electrode and AZO/CuNWs/AZO composite electrode while stored in specific conditions (23.5 °C and relative humidity (RH) of ~25%; 80 °C and RH = 40 %).

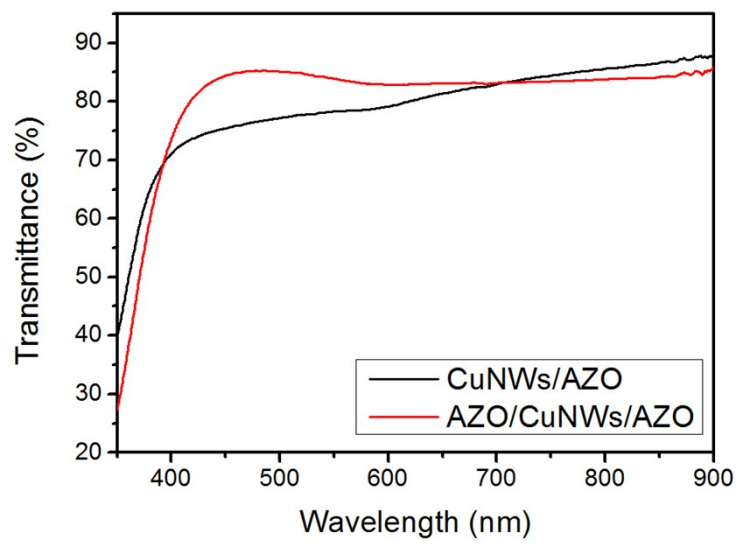


Fig. S3 Transmittance spectra of CuNWs/AZO and AZO/CuNWs/AZO.

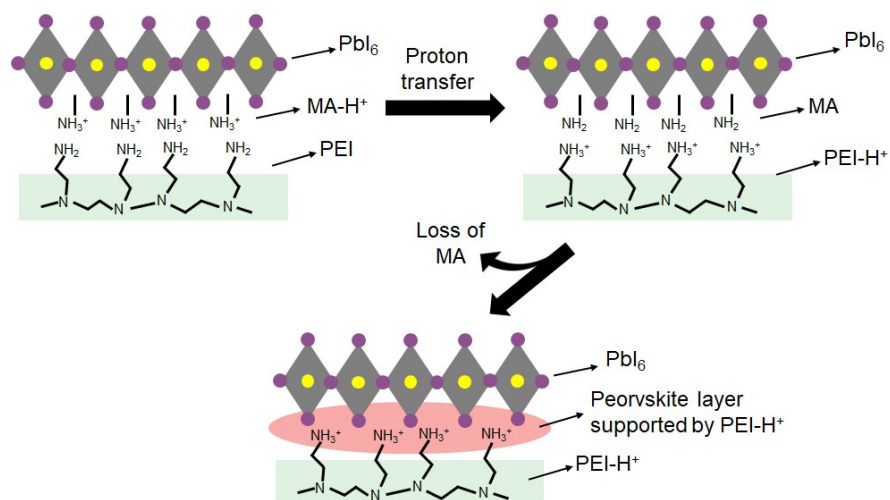


Fig. S4 Schematic illustration of the PEI-supported perovskite layer formation at the interface of PEI and perovskite.

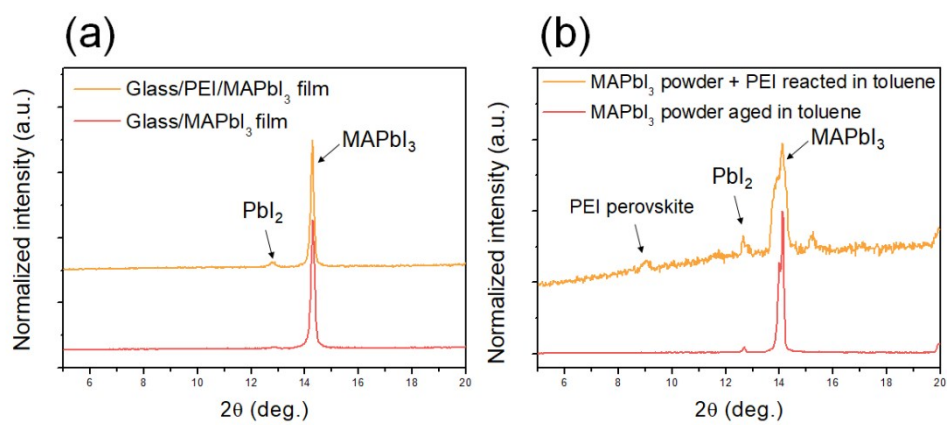


Fig. S5 XRD patterns of (a) glass/PEI/MAPbI₃ and glass/MAPbI₃ films, (b) MAPbI₃ powder mixed with PEI in toluene and only MAPbI₃ powder immersed in toluene.

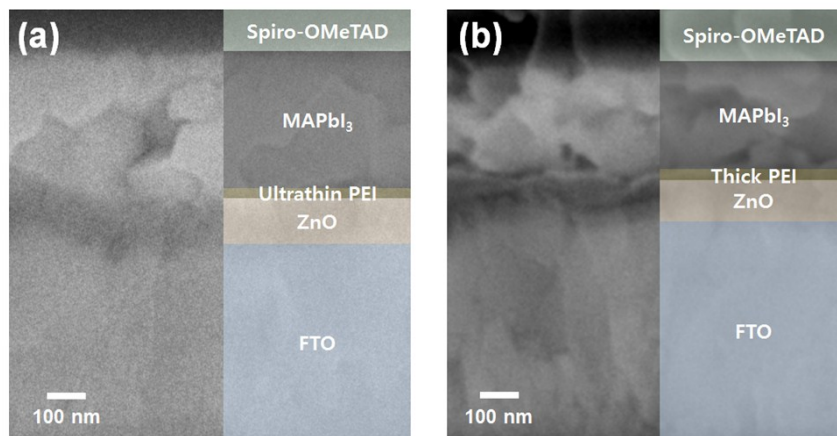


Fig. S6 Cross-sectional SEM images of FTO-based PSCs with (a) ultrathin PEI layer (coated using 0.1 wt% PEI solution) and (b) thick PEI layer (coated using 1.0 wt% PEI solution).

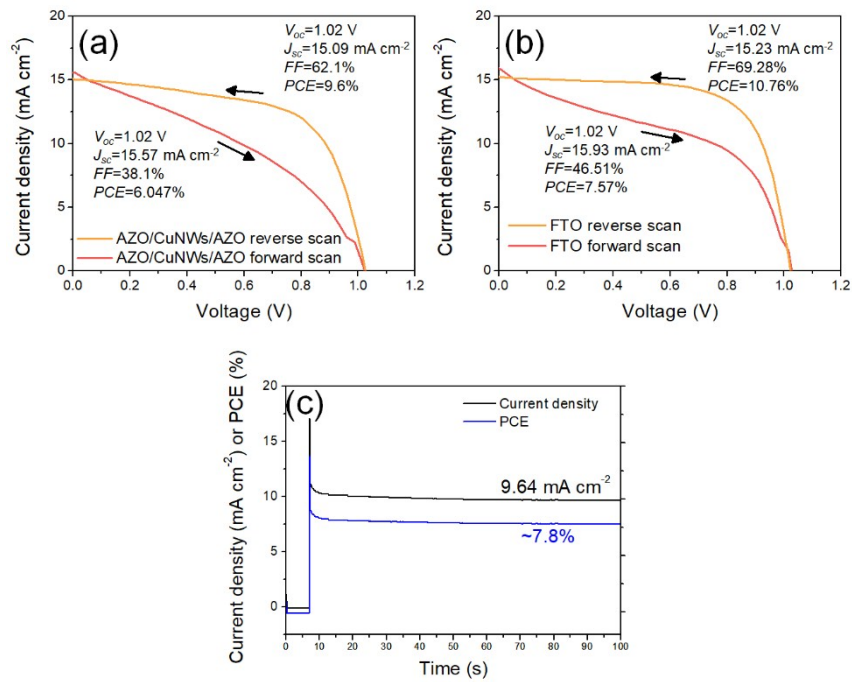


Fig. S7 Hysteresis behavior of PSCs with (a) AZO/CuNWs/AZO electrode and (b) FTO electrode (dwell time at each data point was 50 ms); (c) stabilized PCE and current density measured at 0.807 V.