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Support Information

Interface engineering via an insulating polymer for highly efficient and environmentally stable perovskite solar cells

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Experimental Section

Material Preparation

2,2’,7,7’-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9’-spirobifluorene (Spiro-OMeTAD), Lead iodide (PbI_2), Polystyrene (PS, average Mw=35,000), N,N-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chlorobenzene were obtained from the Sigma-Aldrich. Other chemicals were supplied by the Fisher Scientific. All the reagents were used without any purification post-treatment, and the deionized (DI) water was used throughout the process.

Synthesis of Methtylammonium iodide (CH_3NH_3I). CH_3NH_3I was synthesized following the previous method.[1] Typically, the methylamine (9.3 mL, 40% in methanol, TCI) and hydroiodic acid (10 mL, 57 wt% in water, Aldrich) were mixed during the continuous stirring at 0 °C for 2 h. The precipitate was recovered by the evaporation process at 50 °C for 1 h. Subsequently, the power was recrystallized with diethyl ether for about three times, and finally vacuum dried at 60 °C for 24 h before using.

Solar device fabrication

The fluorinated tin oxide glasses (FTO glass, 7 S/sq, 85% transmittance in the visible spectrum) partially etched by the zinc powder and 2 M hydrochloric acid were adequately cleaned by the ultrasonic bath. After being exposed to the UV-O_3 for 15 min, a uniform TiO_2 blocking layer was deposited by the spin-coating with titanium diisopropoxidebis(acetylacetonate) solution (0.15 M in 1-butanol). After drying at 125 ^oC for 5 min, they were further sintered at 500 ^oC for 30 min. After cooling to the room temperature, they were subjected into 40 mM $TiCl_4$ aqueous solutions at 70 ^oC for 30 min, and washed with DI water adequately. Then, the mesoporous TiO_2 scaffold was spin-coated with a diluted TiO_2 paste (Dyesol DSL18NR-T) with ethanol (2:7, weight ratio), and calcined at 500 ^oC for 30 min. A uniform and pinhole-free perovskite ($CH_3NH_3PbI_3$) layer was deposited onto the above substrate by the Lewis base adduct of PbI_2 following the reported method.[2] For the tunnelling contact at the perovskite/HTM interface, the PS suspension (10 mg /mL in chlorobenzene) was drop-coated on the perovskite sublayer at 2000 rpm for 30 s and 5000 rpm for 20 s without any further annealing treatment. Subsequently, the spiro-OMeTAD-based HTM (72.3 mg/mL) with such dopants as Li-TSFI as well as TBP was spin-coated on the $CH_3NH_3PbI_3$ layer at 4000 rpmfor 30 s. Finally, an Au counter electrode of 100 nm was further thermally evaporated after the device being stored in the desiccators overnight. For comparison, the control device was assembled with the same procedures besides the PS tunnelling contact. The active area of the electrode was fixed at 0.014 cm^2 via the metal mask.

Device characterization

The surface morphology was examined by the field emission scanning electron microscope (FE-SEM, Hitachi S4800). X-ray diffraction patterns were obtained using the Philips X'pert X-ray diffractometer (XRD) with Cu Ka radiation (λ=1.54 Å) to evaluate the crystal structures.The FTIR spectrum was recorded by the Bruker Hyperion FT-IR Spectrometer & Microscope (VERTEX 70). The light absorption behaviour was measured by UV-visible spectroscopy (Varian; UV-Visible spectrophotometer, Cary 5000). Current-voltage (J-V) characteristics were recorded from a solar simulator equipped with a Keithley 2400 source meter and 300 W collimated Xenon lamp (Newport) calibrated with the light intensity up to 100 mW/cm^2 at AM 1.5 G solar light condition by a certified silicon solar cell. The electrochemical impedance spectroscopy (EIS) measurement was carried out in the frequency range from 0.1 Hz to 100 KHz in the dark condition, in which the potential bias was fixed at 0.9 V.

Results and discussion

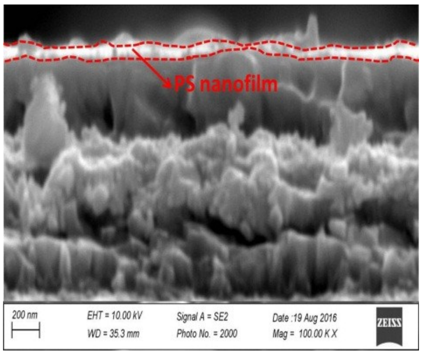

Fig. S1 The cross-sectional SEM image of substrate with PS uplayer;

For the interface modification, the PS suspension with a concentration of 10 mg/mL was drop-coated on the perovskite sublayer at 2000 rpm for 30 s and 5000 rpm for 20 s. For the limited instrument resolution for SEM measurement, the ultrathin PS layer cannot be detected even though they exist over the perovskite substrate. In this case, a continuous spin-coating up to 40 cycles has been processed, and the cross-sectional SEM measurement was conducted to estimate the thickness of PS ultrathin film as depicted in Fig. S1. Accordingly, the average thickness of PS ultrathin film in this work was estimated to be 2-3 nm.

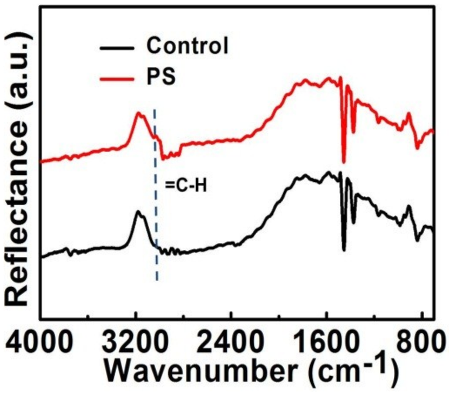

Fig. S2 FTIR spectrum of the perovskite before and after the PS incorporation;

The FTIR spectre was conducted to demonstrate the successful deposition of PS as well as its interaction with perovskite as depicted in Fig. S2. Clearly, an evident appearance of adsorption peak at ca. 3040 cm^{-1} can be assigned to =C-H stretching resulting from the PS ultrathin film, indicating that the PS was successfully coated onto the perovskite surface by the drop-coating method. Moreover, compared to the unmodified perovskite, no other corresponding peak change was detected for the PS-coated perovskite, suggesting the simple physical contact rather than the chemical interaction between the bilayers, in accordance with the previous result.[3]

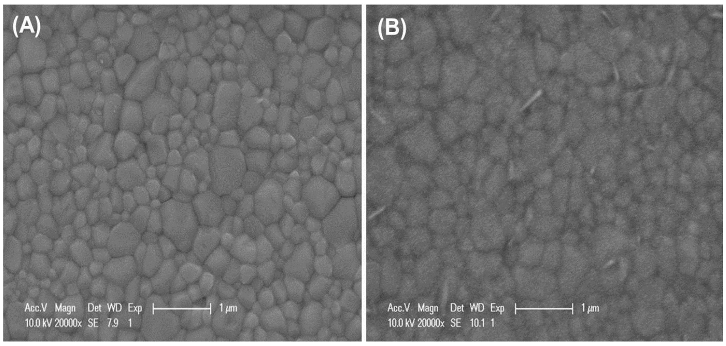

Fig. S3 SEM images of perovskite before (A) and after (B) the PS incorporation;

The surface morphology of different substrates was investigated by the SEM measurement as illustrated in Fig. S3. Clearly, a highly dense perovskite layer with the full coverage on the Mp-TiO_2 scaffold was developed by the Lewis base adduct of PbI_2 following the previous work.[2] For developing as a tunnelling junction at the perovskite/HTM interface, the PS suspension (10 mg/mL in in chlorobenzene) was drop-coated on the perovskite sublayer. As expected, a thin PS layer was successfully covered on the perovskite surface in a large domain without the exposed perovskite region, which was revealed to act as the tunnelling contact for perovskite/HTL interface as well as the water-resistant proof.

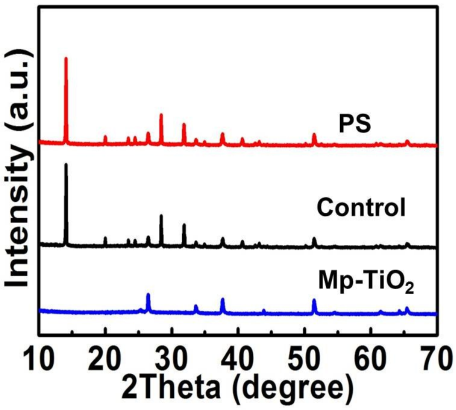

Fig. S4 XRD patterns of different substrates;

The effect of drop-coating PS interlayer on the crystalline property of the perovskite sublayer was characterized by the XRD measurement as depicted in Fig. S4. Clearly, the perovskite layer displayed the excellent crystalline property, and the incorporation of PS interlayer at the perovskite/HTL interface maintained the crystalline property of perovskite well.

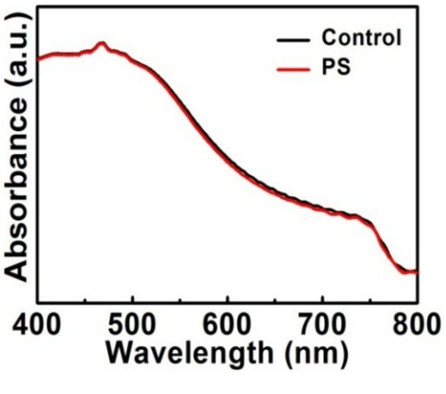

Fig. S5 The UV-Vis spectra of perovskite layer before and after the PS incroporation;

The absorption property of perovskite film before and after the surface modification with the insulating PS layer was investigated by the UV-Vis spectra as presented in Fig. S5. Clearly, the PS-coated perovskite film displayed a similar absorbance behavior to the pristine one.

Notes and references

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2. N. Y. Ahn, D. Y. Son, I.-H. Jang, S. M. Kang, M. Choi and N.-G. Park, *J. Am. Chem. Soc.*, **2015**, 137, 8696-8699.
3. S. Dong, Y. Wan, Y. Wang, Y. Yang, Y. Wang, X. Zhang, H. Cao, W. Qin, L. Yang, C. Yao, Z. Ge and S. Yin, *RSC Adv.*, 2016, DOI: 10.1039/c6ra09976a.