Electronic Supplementary Information

Dual Functional Additive for HTM Layer in Perovskite Solar Cells

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1. Experimental Details

Materials and Reagents: Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. Spiro-MeOTAD was purchased from Lumtec. CH₃NH₃I was synthesized according to a reported procedure¹. N-butyl-N'-(4-pyridylheptyl) imidazolium bis(trifluoromethane)sulfonimide (BuPyIm-TFSI) was kindly supplied by Prof. Feng Yan and used as received. The molecular structure of BuPyIm-TFSI was characterized by NMR spectra as following.

¹H NMR (400MHz, CDCl₃, δ ppm): 8.95 (s, 1H, NCHN), 8.46 (d, 2H, Hpy), 7.25 (d, 2H, Hpy), 7.11 (d, 2H, Hmi), 4.18-4.22 (t, 4H), 2.59-2.62 (t, 2H), 1.58-1.66 (m, 4H), 1.30-1.39 (m, 10H), 0.95-0.98 (t, 3H). ¹³C NMR (400MHz, CDCl₃, δ ppm): 152.01 (Cpy), 148.88 (Cpy), 149.33 (Cpy), 136.13 (NCN), 124.09 (Cpy), 124.20 (Cpy), 122.00 (Cim), 121.00 (Cim), 50.30 (CH₂), 50.13 (CH₂), 35.10 (CH₂), 32.01 (CH₂), 30.06 (CH₂), 29.96 (CH₂), 28.69 (CH₂), 28.58 (CH₂), 25.99 (CH₂), 19.41 (CH₂), 13.25 (CH₃).

2. Device fabrication

To fabricate the devices, Fluorine-doped tin oxide (F:SnO₂) coated glass (15 Ω /sq, Pilkington, US) was patterned by etching with Zn powder and 2 M HCl diluted in deionized water. The etched substrate was then cleaned with 2% hellmanex diluted in deionized water, rinsed with deionized water, acetone, isopropanol and deionized water and dried with clean dry air. A thin layer of compact anatase TiO₂ was formed through spin coating TiO₂ organic sol on the clean substrates at 3000 rpm for 30 s, followed by a sintering process in a furnace at 450°C for 2 h. TiO₂ organic sol for TiO₂ compact layer was prepared according to the reported procedure.³ Then, mesoporous TiO₂ layer were prepared by spin coating a commercial TiO₂ paste (Dyesol-18NRT, Dyesol) diluted in ethanol (2:7, weight ratio) at 5000 rpm for 30s. After drying at 125°C, the TiO₂ films were gradually heated to 500°C, baked at this temperature for 30 min and cooled to room

temperature. The sintered films were then treated with 40 mM TiCl₄ aqueous solution at 70°C for 30 min followed by calcinations at 500°C for 30 min. The mesoporous TiO₂ films were then infiltrated with PbI₂ by spin coating at 6500 rpm. for 5 s and dried at 75°C for 30 min. After cooling to room temperature, the films were dipped in a solution of CH₃NH₃I in 2-propanol (10mg ml⁻¹) for 60s, rinsed with 2-propanol and dried at 75°C for 30 min The peroviskite films were dried on a hot plate at 70°C for 30 min. The HTMs were then deposited by spin coating at 3000 rpm for 30 s. HTM₁ was prepared by dissolving 72.3 mg spiro-MeOTAD in 1 ml chlorobenzene. HTM₂ was prepared by dissolving 72.3 mg spiro-MeOTAD and 40 ul a solution of 48.11mg ml⁻¹ N-butyl-N'-(4-pyridylheptyl) imidazolium bis(trifluoromethane)sulfonimide (BuPyIm-TFSI) in acetonitrile in 1 ml chlorobenzene. HTM₃ was prepared by dissolving 72.3 mg spiro-MeOTAD and 40 ul a solution of 48.11mg ml⁻¹ no 28.8 ml 4-*tert*-butylpyridine, 17.5ml of a stock solution of 520 mg ml⁻¹ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile in 1 ml chlorobenzene. Finally, 100 nm Ag was thermally evaporated on top of the device to form the back contact. The active area of this electrode was fixed at 0.06 cm². All devices were fabricated in glove box.

3. Characterization

NMR spectra were taken with VARIAN INOVA 400 MHz (USA) using TMS as standard. The thermal analysis was performed through TGA (TGA/SDT851, Switzerland) at a heating rate of 10 °C min⁻¹ in a temperature range of 40 °C to 500 °C under nitrogen atmosphere. The sample morphology and energy dispersive X-ray (EDX) spectroscopy were observed using scanning electron microscopy(SEM, FEI QUANTA 450). The *J-V* characteristics of the DSCs were measured under simulated AM 1.5 illumination (100 mWcm⁻², PEC-L15, Japan) with a Keithley digital source meter (Keithley 2601, USA). IPCE values were recorded using the monochromatic light from a system made of a xenon lamp, a monochromator, and appropriate filters. The linear sweep voltammetry curve was derived from an electrochemical workstation system (CHI630, Chenhua, Shanghai) at a scan rate of 10 mV s⁻¹. X-ray diffraction (XRD) measurements were carried out using an automatic X-ray diffractometer (D/Max 2400, Rigaku) with Cu K α radiation (γ =0.154 nm).



Fig. S1. X-ray Diffraction (XRD) spectra of $CH_3NH_3PbI_3$ deposited on $TiO_2/glass$ by sequential deposition method and heated to 70°C before measured.

X-ray diffraction results are in accordance with those in the related references, ¹ which showed that the material synthesized have the perovskite crystalline structures. The CH₃NH₃PbI₃

sensitized film gives diffraction peaks at 14.04° , 28.32° , 31.70° , 40.52° and 43.04° which can be assigned to the (110), (220), (310), (224) and (314) planes of the tetragonal perovskite structure with a =8.872 and c =12.637.



Fig. S2. Cross-sectional scanning electron micrograph (SEM) of a ~750 nm thick device(left), and energy dispersive x-ray (EDX) spectroscopy with elemental mapping of (right) titanium, oxygen, lead, iodine.

Reference

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- 2 H. Yu, S. Zhang, H. Zhao, B. Xue, P. Liu, and G. Will, J. Phys. Chem. C, 2009, 113, 16277.