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Effects of Highly Conductive PH1000 Anode Combining with Ethylene Glycol Additive and H_2SO_4 Immersion Treatments on Photovoltaic Performance and Photo stability of Polymer Solar Cells

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2. Experimental details

2.1 Materials

PH1000 solution and PEDOT:PSS solution (CLEVIOS^{TM} AI 4083) were purchased from H. C. Starck, ethylene glycol (EG) 1,8-Diiodooctane (DIO), isopropyl alcohol, H_2SO_4 and o-dichlor-obenzene (ODCB) were purchased from Sigma-Aldrich. PTB7 was purchased from 1-material Inc. $PC_{71}BM$ and the PFN were purchased from Luminescence Technology Corp. MoO_3, Ag, Al and Au were purchased from Alfa Aesar Co. ZnO nanoparticles were synthesized following the Pacholski method [1].

The PH1000 solutions were diluted by blend solution of isopropyl alcohol and deionized water, and the PH1000 concentration is 30 mg ml^{-1} and was filtered through a 0.45 μm syringe filter to remove large-size particles. PTB7:$PC_{71}BM$ (1:1.5, w:w, the PTB7 concentration of 10 mg ml^{-1}) were dissolved in ODCB solution. 3 wt% (1,8-diiodooctane (DIO) were used as additive. The PFN were dissolved in methanol solutions and add a small amount of acetic acid (the PFN and acetic acid concentration are 0.2 mg ml^{-1} in methanol 2 μl ml^{-1} respectively).

2.2 Device preparation and characteristics

The glass substrate and ITO glass were ultrasonicated washing treatment, the dried under a stream of nitrogen and UV-ozone treatment for 15 min. PH1000 solution were mixed with EG as additive (the EG concentration is 8 wt%) and the PH1000-EG solution was spin-cast onto 3×3 cm^2 glasses substrates and to fabricated the PH1000-EG layer based on glass substrate, and then dried at 120 °C for 15 min at the air condition and the thickness is around 30 nm. For the post-treatments, the PH1000-EG

layer were immersed into the H_2SO_4 solutions for 10 min. Then, the PH1000-EG-H_2SO_4 layer were sufficiently washed in a deionized water bath to remove the residual EG and H_2SO_4 solution and dried at 120 °C for 10 min to remove residual water. The control ITO/PEDOT:PSS composite anode were fabricated by spin-coating PEDOT:PSS solution (AI 4083) on the top of ITO glass and dried at 120 °C for 10 min at the air condition. After transferring to a nitrogen-filled glove box, PTB7:$PC_{71}BM$ photoactive layer were formed by spin coating their blend solution at 1400 rpm for 60 s and then annealed at 130 °C for 15 min. After that, the PFN solutions were spin-coated on the top of PTB7:$PC_{71}BM$ layer and thermal annealed at 130 °C for 5 min to form PFN layer. The Al layer was deposited on the PFN film by thermal evaporation under 10^{-4} Pa through a shadow mask to define the photoactive area of the devices (3×3 mm^2). The PH1000-EG-H_2SO_4-based PSCs and control PSCs structure are shown at figure S1a and b. The average photovoltaic parameter values are calculated by the five devices.

The current-voltage (*J-V*) characteristics were measured in a glovebox under 100 $mW \cdot cm^{-2}$ simulated AM 1.5 G irradiation and using a standard source measurement unit (Keithley 2400). All the measurements were performed in a glove box at room temperature. The external quantum efficiency (*EQE*) was detected under monochromatic illumination.

The SCLC devices were fabricated according to the above procedure. The SCLC hole-only device with the structure of PH1000-EG-H_2SO_4/PTB7:$PC_{71}BM$/Au. The control hole-only SCLC device have a structure of ITO/PEDOT:PSS (AI

4083)/PTB7:$PC_{71}BM$/Au. The dark current of the SCLC devices was measured by the below formula [2]:

$$J_D = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_e\frac{V^2}{L^3}$$

Where ε_0 and ε_r are the permittivity of free space and relative permittivity of the material (the ε_r value are assumed to be 3), and L is the distance between anode and cathode and the value was measured using step profiler. The devices structure are shown at figure S1c.

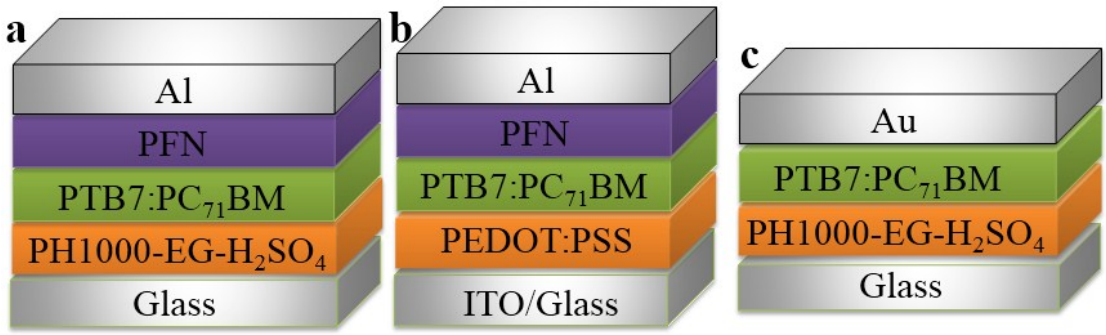

Figure S1. The schematic diagram of PH1000-EG-H_2SO_4-based PSCs and control PSCs for (a) and (b), hole-only SCLC devices configuration for (b).

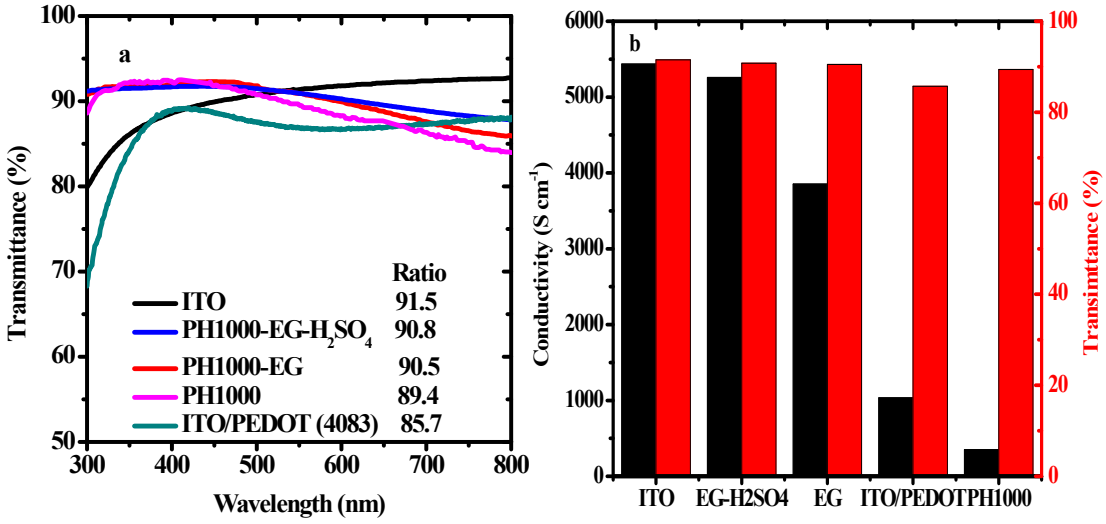

Figure S2. Transmittance spectra and transmittance ratio (%) of neat PH100, clean ITO, PH1000-EG-H_2SO_4 thin films, PH1000-EG thin films and ITO glass with

PEDOT:PSS (AI 4083) coating thin films (a). Transmittance ratio and Conductivity (S cm^{-1}) (b).

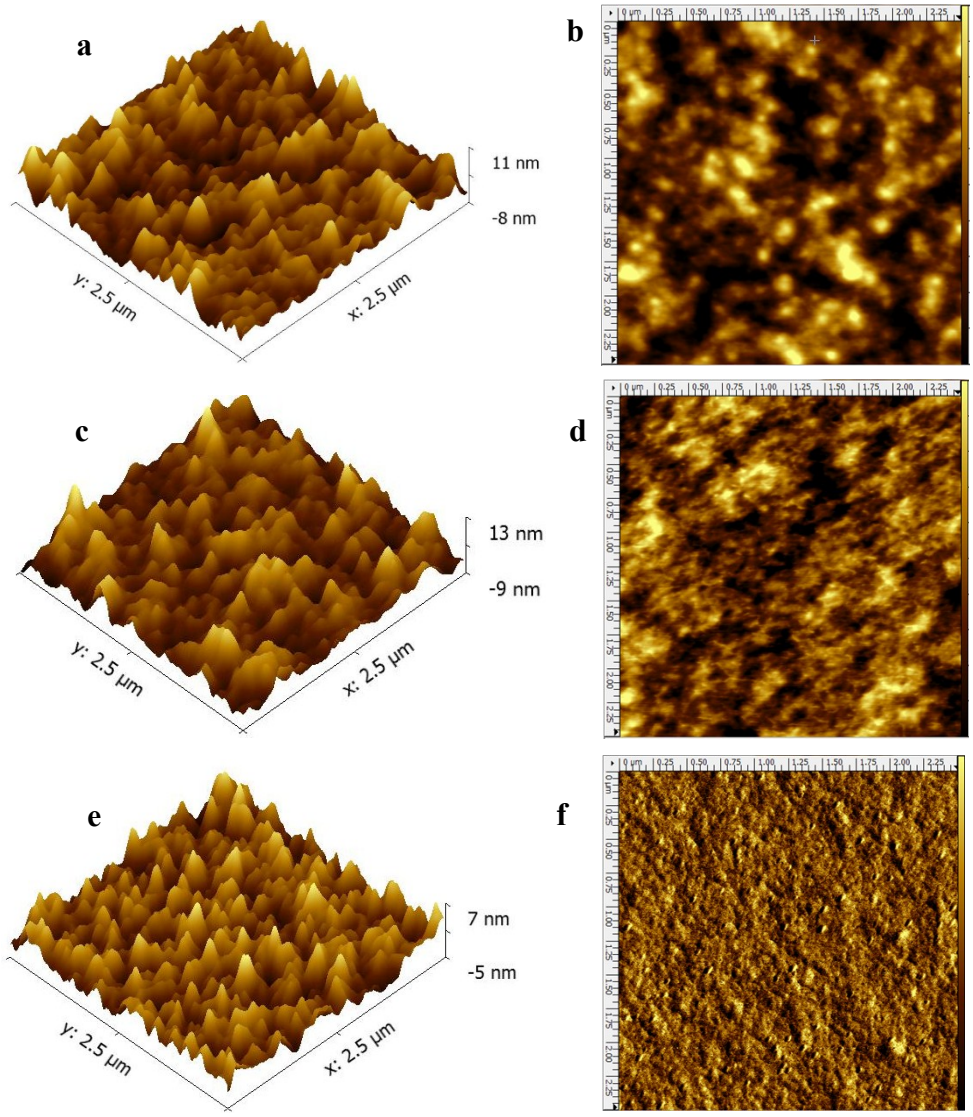

Figure S3. 3D AFM images and phase images for the three PH1000 thin films. (a and b) neat PH1000 thin films; (c and d) PH1000-EG thin films; (e and f) PH1000-EG-H_2SO_4 thin films.

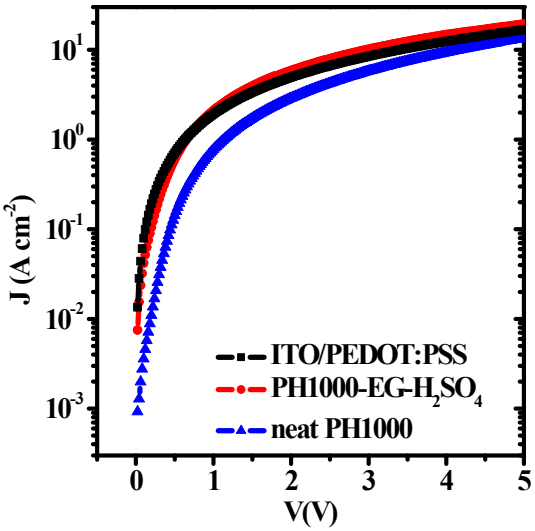

Figure S4. *J-V* characteristic curves based on the neat PH1000 and PH1000-EG-H_2SO_4 thin films as transparent electrodes for hole-only current, and the control SCLC devices with the ITO/PEDOT:PSS (AI 4083) as the transparent electrode.

Table S1. Calculated hole mobilities (μ_h) from Figure S4.

Transparent Electrode	μ_h [$\times 10^{-3}$ $cm^2V^{-1}s^{-1}$]
ITO/PEDOT-PSS	3.54
PH1000-EG-H_2SO_4	3.88
neat PH1000	1.13

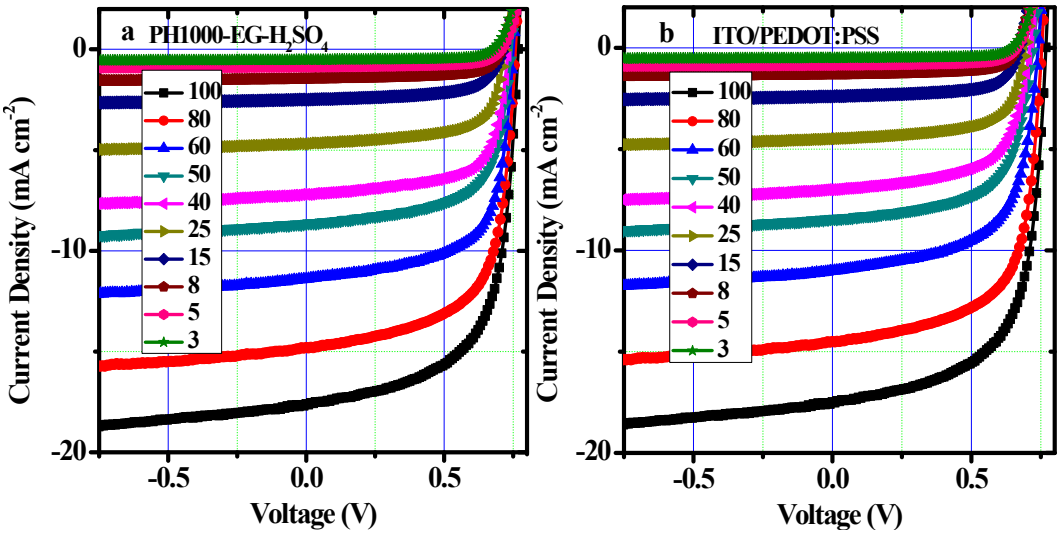

Figure S5. *J-V* curves of PSCs with PH1000-EG-H_2SO_4 as the transparent electrode

(a) and ITO/PEDOT:PSS as the transparent electrode (b) under different illumination intensities, as obtained from standard AM 1.5G illumination.

Reference:

1. W. Yu, L. Huang, D. Yang, P. Fu, L. Zhou, J. Zhang and C. Li, *Journal of Materials Chemistry A*, 2015, **3**, 10660-10665.
2. J. Ye, L. Zhu, L. Zhou, X. Liu, X. Zhang, H. Zheng, G. Liu, Z. Shao, X. Pan and S. Dai, *Solar Energy*, 2016, **136**, 505-514.