Polymer based photocathodes for panchromatic tandem dye-sensitized solar cells

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Electronic Supplementary Information



Scheme S1 A schematic idealized energy level diagram of a DSC (left) and a pn-DSC (right).

A schematic idealized energy level diagram of a DSC and a pn-DSC indicating the desired electron transfer processes is shown in Scheme S1. Irradiation takes place from the photoanode side. For traditional DSCs, photons are only absorbed by the photoanode (Scheme S1 left). Dyes commonly used in photoanode can only absorb the visible part of the solar spectrum. For pn-DSC (Scheme S1 right), photoanodes are designed to absorb the visible part of the solar spectrum. Near IR part is transmitted to the photocathode and absorbed by the photocathode. Because the two photoelectrodes are connected in series, the photovoltages of pn-DSCs are sum of the corresponding p and n devices. Therefore, a higher PCE could be expected compared with traditional DSCs.

Experimental

The typical photoanode was constructed as describe elsewhere.¹ A transparent, mesoporous TiO_2 films were prepared by screen printing, then sintering at 510 °C for 30 min. Then the mesoporous TiO_2 films were cooled to 80 °C and immersed into an ethanol solution of a ruthenium-complex (N719 dye) over-nigh, followed by rinsing in ethanol and drying. The thickness of the TiO_2 films is 1.7 µm.

The polymer based photocathode was fabricated as follows: A NiO mesoporous film (1 μm) was fabricated on FTO by spin coating (2000 rpm/30 s), followed by sintering at 510 °C for 30 min under atmospheric conditions. Spin coating paste was produced by mixing a slurry of 10 g of NiO nanopowder (<50 nm, Sigma Aldrich) in ethanol with 30 g of 10 wt% ethanolic ethyl cellulose (Sigma Aldrich) solution, 35 g terpineol and 75 g ethanol. Then spin-cast a blend cholorobenzene solution containing PCPDTBT and PCBM (15 mg mL⁻¹, 35 mg mL⁻¹) on the mesoporous NiO film (1500 rpm/30s), and after that, remove the PCBM by simply soaking this hybrid film in 3-methoxypropionitrile (MePN) over night.

The PSC was assembled by sadwiching a photocathode and a counter electeode with a thermal adhesive film (Surlyn, Dupont). The electrolyte solution was injected into the interspaces between the photocathode and the counterelectrode. The preparation of the DSC and the pn-DSC was similar with that of the PSC. The DSC was assembled with a photoanode and a counter electeode; the pn-DSC was assembled with a photocathode.

Only one type of the electrolyte was used in our study (0.6 M N-methyl-N-butylimidazolium iodide, 0.45 M N-Methyl benzimidazole, 0.1 M LiI and 0.1 M I_2 in 3-Methoxypropionitrile).

The photovoltaic performances of the DSCs were measured by a Keithley 2420 3A source meter controlled by Testpoint software under AM 1.5 solar simulator of 100 mW cm⁻² (solar AAA simulator, oriel USA, calibrated with a standard crystalline silicon solar cell). The active area of

the devices was 0.25 cm² (with a black mask). IPCE measurement was performed on QE/IPCE Measurement Kit (Newport, USA). Under full computer control, light from a 300 W xenon lamp was focused through a monochromator onto the solar cell under test. The UV-visible (UV-vis) absorption spectra were obtained from a UV-vis spectrophotometer (U-3900H, Hitachi, Japan). SEM images were obtained from a field emission scanning electron microscope (SEM, Hitachi S4800, Japan).



Fig. S1. Schematic structure of two different photocathodes (a) photocathode with PCPDTBT porous film; (b) photocathode with mesoporous NiO film covered by pristine PCPDTBT. The PEDOT: PSS layer (60 nm) was fabracated by spin coating (1500 rpm/min 30s) from a aqueous solution (Sigma Aldrich).



Fig. S2. Current density-voltage characteristics and IPCE spectras (insert) of PSCs with different photocathodes (a) photocathode with porous PCPDTBT film (black line); (b) photocathode with mesoporous NiO film covered by pristine PCPDTBT (red line).

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	V _{oc} (mV)	$J_{\rm sc}({\rm mA~cm^{-2}})$	FF(%)	<i>PCE</i> (%)
a	198	0.55	47.2	0.051

Table S1. Photovoltaic parameters of PSCs with different photocathodes.

105

b

(a) photocathode with porous PCPDTBT film; (b) photocathode with mesoporous NiO film covered by pristine PCPDTBT. Photovoltaic parameters of all these cells were taken under AM 1.5 solar simulator of 100 mW cm⁻². Active area=0.25 cm⁻². All cells were illuminated through the photocathode side.

0.04

24.1

0.001



Fig S3. A preliminary aging test for the PSCs. Under indoor conditions at room temperature. Photovoltaic parameters of PSCs were taken under AM 1.5 solar simulator of 100 mW cm⁻². Active area=0.25 cm⁻².

In the first 10 days, dramatic changes occurred in J_{sc} and V_{oc} . Reasons for those changes still need to be further studied. In the next 20 days, the photovoltaic parameters have no obviously change.

H. Linhua, D. Songyuan, W. Jian, X. Shangfeng, S. Yifeng, H. Yang, C. Shuanghong, K. Fantai, P. Xu, L. Linyun and W. Kongjia, *J Phys Chem B*, 2007, 111, 358-362.