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Supporting Information

for Adv. Mater., DOI: 10.1002/adma. 201302951

Integrated Polymer Solar Cell and Electrochemical Supercapacitor in a Flexible and Stable Fiber Format

Zhitao Zhang, Xuli Chen, Peining Chen, Guozhen Guan, Longbin Qiu, Huijuan Lin, Zhibin Yang, Wenyu Bai, Yongfeng Luo, and Huisheng Peng*



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Experimental section

The fabrication of the integrated "energy fiber" based on dye-sensitized solar cell and supercapacitor was summarized below. For the PC part, the aligned TiO₂ nanaotube arrays grown on the surface of Ti wire were realized by an electrochemical anodization in 0.3 wt% NH₄F/ethylene glycol solution containing 8 wt % H₂O at 60 V for 6 h. The modified wire was washed with deionized water to remove the electrolyte, followed by heating to 500 °C for 1 h and annealed in air. It was then immersed in a 100 mM TiCl₄ aqueous solution at 70 °C for 30 min, and then rinsed with deionized water, followed by annealing at 450 °C for 30 min. After the temperature was cooled to room temperature, it was immersed into 0.3 mM N719 solution in a mixture solvent of dehydrated acetonitrile and tert-butanol (volume ratio of 1/1) for 16 h. Finally, MWCNT sheet was wound around the dye-absorbed working electrode. For the ES part, the gel electrolyte was coated on the titania nanotube-modified Ti wire, followed by the

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attachment of the MWCNT sheet. The wrapped fiber was sealed in a glass capillary tube. The three electrodes were extracted and modified by indium. The electrolyte was infiltrated into the cell by a capillary force. The redox electrolyte (containing 0.1 M lithium iodide, 0.05 M iodine, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide, and 0.5 M 4-tert butyl-pyridine in dehydrated acetonitrile) was also injected into the cell by the capillary force.

Optical micrograph was obtained from Olympus BX51. The structural characterizations were made by scanning electron microscopy (Hitachi FE-SEM S-4800 operated at 1 kV). The electrochemical measurements were made through a CHI 660D electrochemical work station at room temperature. The photoelectric conversion was characterized by recording J–V curves with a Keithley 2400 Source Meter under illumination (100 mW/cm²) of simulated AM 1.5 solar light coming from a solar simulator (Oriel-Sol3A 94023 A equipped with a 450W Xe lamp and an AM1.5 filter).



Figure S1. Sealed integrated devices based on the dye-sensitized solar cell before and after bending for five cycles. a. Photographs before and after bending. b. J-V curves of the PC part before and after bending. c. Charge-discharge curves of the ES part before and after bending at a current of 1 μ A. d. Photocharge-discharge curves before and after bending with the discharging current of 1 μ A. The entire photoelectric conversion and storage efficiency was calculated as 0.66%.



Figure S2. Schematic illustration to the fabrication of the all-solid-state, coaxial and integrated "energy fiber" to simultaneously realize the photoelectric conversion (PC) and energy storage (ES). For the PC part, perpendicularly aligned titania nanotubes are grown on a Ti wire by electrochemical anodization, followed by coating of P3HT:PCBM and PEDOT:PSS layers. A multi-walled carbon nanotube (MWCNT) sheet is finally wrapped onto the modified Ti wire to produce the PC part. For the ES part, the electrolyte is coated on the titania nanotube-modified Ti wire, and MWCNT sheets are attached to the ES part.



Figure S3. Structure characterization of the "energy fiber". a) and b) Scanning electron microscopy (SEM) image of a bare Ti wire at low and high magnifications, respectively. c) SEM image of P3HT:PCBM layer. d) SEM image of PEDOT:PSS layer. e) and f) MWCNT sheet at low and high magnifications in the ES part, respectively.



Figure S4. P3HT:PCBM layer coated on the modified Ti wire surface by top (a) and side (b) views.





Figure S5. Photograph of an integrated "energy fiber".





Figure S6. Schematic illustration to the mechanism of the PC part.





Figure S7. SEM images of TiO_2 nanotube arrays grown with the increasing time by a side view. a) 1 min. b) 5 min. c) 10 min. d) 15 min. e) 20 min. f) 30 min.





Figure S8. a) and b) Dependence of the photoelectric conversion efficiency of the PC part on the time in argon and air for a period of ten days, respectively.



Figure S9. The changes of voltages and entire photoelectric conversion and storage efficiencies of the integrated "energy fiber" during the photocharging and galvanostatic discharging process. The red line corresponds to the charging and discharging curve, and the blue line shows the change of entire efficiencies. Every dot in the blue line is calculated by the different voltage which corresponds to the dot in the red line.





Figure S10. a) SEM image of a bent "energy fiber" at low magnification. b) MWCNT sheet at a) being stably attached on the surface during the bending. c) SEM image of a bent "energy wire" by twisting two electrodes of modified Ti wire and aligned MWCNT fiber. d) MWCNT fiber being separated from the modified Ti wire during the bending.





Figure S11. Photograph of the "energy fiber" before and after bending.



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Figure S12. Dependence of the entire photoelectric conversion and storage efficiency of the "energy fiber" on the time in argon.