

# Supporting Information

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## A Twisted Wire-Shaped Dual-Function Energy Device for Photoelectric Conversion and Electrochemical Storage\*\*

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## **Supporting Information**

#### **Experimental section**

*Preparation of CNT and PANI/CNT composite fibers.* The synthesis of spinnable CNT arrays was previously described<sup>[S1-S3]</sup>, and a height of ~200  $\mu$ m had been mainly used. Highly aligned CNT sheets were drawn out of the spinnable CNT array and stacked along the length direction. Different layers (2, 4, 6, and 8) of CNT sheets with the same width of 0.8 cm were then scrolled into fibers with diameters of 18, 30, 41 and 51  $\mu$ m at the same rotation rate of 1000 rpm, respectively. To prepare PANI/CNT composite fibers, bare CNT fibers were first immersed in the electrolyte containing 0.1 M aniline and 1.0 M H<sub>2</sub>SO<sub>4</sub> for 4 h, and electro-polymerization of aniline was then performed at 0.75 V vs. SCE. The pretreatment in the electrolyte was found to be important for the uniform deposition of the PANI (Figure S18). The pretreatment improves the infiltration of electrolyte into aligned CNTs<sup>[S4]</sup>, so the aniline monomer can be more uniformly dispersed in the fiber. The resulting composite fibers were washed with de-ionized water and dried in air for 8 h.

*Preparation of TiO*<sub>2</sub> *nanotube-modified Ti wires*. Aligned TiO<sub>2</sub> nanaotube arrays were grown on the surface of Ti wire (diameter of 127  $\mu$ m and purity of 99.9%, Alfa Aesar Company) by electrochemical anodization in 0.3 wt% NH<sub>4</sub>F/ethylene glycol solution containing 8 wt% H<sub>2</sub>O at a voltage of 60 V.<sup>[S5,S6]</sup> The anodization was performed in a two-electrode electrochemical cell with Ti wire and Pt sheet as anode and cathode, respectively. The TiO<sub>2</sub> nanotubes with lengths from 11 to 38  $\mu$ m were controlled by increasing the anodization time from 1 to 8 h. The resulting wires were washed with deionized water to remove the electrolyte, followed by heating to 500 °C for 1 h and annealing in air.

Fabrication of the wire-shaped device and resulting powering textile. The  $TiO_2$  nanotube-modified Ti wire was immersed in a 40 mM  $TiCl_4$  aqueous solution at 70 °C for 30 min, followed by rinsing with deionized water and annealing at 450 °C for 30 min. After the temperature was dropped to 120 °C, 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. The resulting fiber electrode was dried in argon and

then twisted with a bare CNT or PANI/CNT composite fiber, followed by insertion into a transparent flexible fluorinated ethylene propylene tube (diameter of 500  $\mu$ m, Shanghai Yi Chuan Shui Plastic Products Co.) The two electrodes were extracted and modified with indium. The 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 introduced to the tube and the two ends were sealed prior to the characterization. To fabricate the powering textile, eight wire-shaped devices prior to introduction of the electrolyte were first woven with each other, followed by connection of the electrodes in series. The electrolyte was then introduced and the tubes were sealed.

*Calculation of the specific capacitance of the energy wires.* The capacitance (C) and specific capacitances ( $C_L$  and  $C_S$ ) of the energy wires were calculated from the CV curves according to the following equations:

$$C = \frac{Q}{\Delta V} = \frac{\int |I| dt}{2\Delta V} = \frac{\int |I| dU}{2\Delta V \times v}$$
(1)  
$$C_L = \frac{C}{L} = \frac{\int |I| dU}{2\Delta V \times v \times L}$$
(2)

$$C_{S} = \frac{c}{s} = \frac{\int |I| dU}{2\Delta V \times \nu \times S}$$
(3)

Where Q (C) is the average charge during the charging and discharging process,  $\Delta V(V)$  is the potential window, I(A) is the current value, t(s) is the sum of charging and discharging time, U(V) is the potential value,  $v(V s^{-1})$  is the scan rate, L is the length of the energy wire and S is the geometric area of the TiO<sub>2</sub> nanotube-modified Ti wire.

*Characterization.* The structures were characterized by SEM (Hitachi FE-SEM S-4800 operated at 1 kV) and TEM (JEOL JEM-2100F operated at 200 kV). Raman measurements were conducted on LabRam-1B with an excitation wavelength of 632.8 nm and laser power of 4 mW. The cyclic voltammetry was performed in an acetonitrile solution containing 5 mM LiI, 0.5 mM I<sub>2</sub> and 0.05 M LiClO<sub>4</sub> with a scan rate of 50 mV s<sup>-1</sup> through a three-electrode setup. J-V curves were recorded by a Keithley 2400 Source Meter under illumination (100 mW/cm<sup>2</sup>) of simulated AM1.5 solar light coming from a solar simulator (Oriel-Sol3A 94023A equipped with a 450 W Xe lamp and an AM1.5 filter). The light intensity was calibrated using a reference Si solar cell (Oriel-91150). The electro-polymerization, cyclic voltammetry and EIS were performed on a CHI 660a electrochemical workstation. The EIS measurement was conducted at the frequency range of 0.1 Hz to 1 MHz. Galvanostatic

charge-discharge and leakage current characterization was measured by an Arbin multi-channel electro-chemical testing system (Arbin, MSTAT-5 V/10 mA/16 Ch). Mechanical measurements were made by a Shimadzu Table-Top Universal Testing Instrument.



*Figure S1.* SEM images of a highly aligned CNT sheet at low (a) and high (b) magnifications.



*Figure S2.* SEM image of a CNT fiber at high magnification. The CNTs remained highly aligned.



*Figure S3.* High-resolution TEM image of a CNT.



*Figure S4.* Electrochemical properties of CNT fibers with increasing diameters from  $18 \text{ to } 51 \text{ }\mu\text{m}$ .



*Figure S5.* SEM images of  $TiO_2$  nanotubes and CNT fibers before and after 5000 charge-discharge cycles.



*Figure S6.* Galvanostatic charge-discharge curves of "energy wires" based on photoanodes with (red color) and without (blue color) adsorption of the dye. The voltage and charge current density were set to be 0.65 V and 1.28 mA cm<sup>-2</sup>, respectively.



*Figure S7.* Raman spectra of the bare CNT fiber and PANI/CNT composite fiber with a weight percentage of 30%.



*Figure S8.* Cyclic voltammograms of the bare CNT fiber and PANI/CNT composite fiber with a weight percentage of 30%.



*Figure S9.* J-V curves of "energy wires" using a bare CNT fiber or PANI/CNT composite fiber (PANI weight percentage of 30%) as one electrode and  $TiO_2$  nanotube-modified Ti wire (length of 28 µm for the  $TiO_2$  nanotubes) as the other electrode.



*Figure S10.* Galvanostatic charge-discharge curves of the wire-shaped device derived from the TiO<sub>2</sub> nanotube with a length of 28  $\mu$ m and the PANI/CNT composite fiber (PANI weight percentage of 30%) at increasing current densities from 0.64 to 2.13 mA cm<sup>-2</sup>.



*Figure S11.* Cyclic voltammetry curves of the wire-shaped capacitor based on bare CNT fiber (black color) or PANI/CNT composite fiber (blue color) at a scan rate of 10 mV/s. The weight percentage of PANI was 30% in the composite fiber.



*Figure S12.* Nyquist plot of the energy wire that was composed of  $TiO_2$  nanotubes with a length of 28 µm and PANI/CNT composite fiber with a diameter of 40 µm and PANI weight percentage of 30%. The inserted graph shows the enlarged part at the high-frequency range.



*Figure S13.* Leakage current curve of the "energy wire" based on  $TiO_2$  nanotubes with a length of 28 µm and PANI/CNT composite fiber with a diameter of 40 µm and PANI weight percentage of 30%. The leakage current was 2.1 µA after 2 h.



*Figure S14.* Stability of wire-shaped energy devices based on the same modified Ti wire (length of 28  $\mu$ m for TiO<sub>2</sub> nanotubes) as one electrode and a bare CNT fiber (**a**) or PANI/CNT composite fiber with the PANI weight percentage of 30% (**b**) as the other. The capacitances were calculated from the galvanostatic charge-discharge curves with a current density of 0.64 mA cm<sup>-2</sup>



*Figure S15.* Mechanical measurements of two types of wire-shaped devices with the same length of 5 mm and other conditions. Blue curve corresponds to the dual-functional "energy wire" that was composed of TiO<sub>2</sub> nanotubes with a length of 28  $\mu$ m and PANI/CNT composite fiber with a diameter of 40  $\mu$ m. Black curve corresponds to a symmetric electrochemical capacitor by twisting two bare CNT fibers.



*Figure S16.* Characterization on the flexibility of the wire-shaped energy device. **a**, **b**. Photographs before and after bending, respectively. **c**. J-V curves before and after bending. **d**. CV curves before and after bending at a scan rate of 50 mV/s.



*Figure S17.* The use of the resulting powering textile woven from eight wire-shaped energy devices. **a**, **b**. Photographs of the powering textile as a solar cell to lighten up a commercial LED under the illumination of simulated AM1.5 solar light. **c**, **d**. Photographs of the powering textile as an electrochemical capacitor to lighten up the LED.



*Figure S18.* SEM images of the PANI/CNT composite fiber (PANI weight percentage of 30%) with (a) and without (b) pretreatment in the electrolyte.

### **Refencences for the Supporting Information**

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