Supporting Information

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Novel Graphene/Carbon Nanotube Composite Fibers for Efficient Wire-Shaped Miniature Energy Devices

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Supporting Information

1. Supporting video

**Video S1.** A commercial red LED lamp was lightened up by a photovoltaic textile composed by 6 photovoltaic wires in series under the illumination of simulated AM1.5 solar light from a solar simulator. The experimental setup is summarized below. The LED was connected to the photovoltaic textile by two metal wires, and they were studied in dark. The solar simulator was then turned on to irradiate the photovoltaic textile that successfully powered the LED. Upon the disconnection of the solar simulator, the LED was turned off.

2. Experimental Section

(1) Synthesis of spinnable CNT arrays

Spinnable CNT arrays were synthesized by chemical vapor deposition in a quartz tube furnace. Fe (1.2 nm)/Al₂O₃ (5 nm) on a silicon wafer was served as the catalyst. Ethylene was used as carbon source with a flowing rate of 90 sccm, and a mixture of Ar (480 sccm) and H₂ (30 sccm) was served as the carrier gas. The growth was conducted at 750 °C, and the resulting spinnable CNT array exhibited a thickness of ~200 μm.

(2) Synthesis of graphene oxide dispersion and graphene fibers

A modified Hummer’s method was used to synthesize graphene oxide. In the preoxidation step, 20 mL concentrated H₂SO₄ was added to a 250 mL round-bottom flask with the temperature slowly increasing to 80 °C, followed by addition of 4.2 g K₂S₂O₈ and 4.2 g P₂O₅. Graphite powder (100 μm, Qingdao Henglide Graphite Co., Ltd.) of 5 g was slowly added to the above flask and kept at 80 °C for 4.5 h, then cooled to room temperature. The mixture was diluted with deionized water and left overnight. The mixture was repeatedly washed with 1 L deionized water by centrifugation at 10000 r.p.m., and the solid at the bottom was dried in air at room temperature. At the second oxidation step, 58 mL H₂SO₄ was added to a 250 mL round-bottom flask at 0 °C by an ice bath. Then 2.5 g preoxidized sample was slowly added to the flask with stirring. 1.25 g KNO₃ and 8 g KMnO₄ were slowly added to the flask at a temperature below 10 °C. The mixture was heated to 35 °C and stirred
for 2 h. The mixture was then diluted with 58 mL deionized water and stirred for 2 h, followed by addition of 350 mL deionized water and dropwise addition of 25 mL 30 % H₂O₂. The resulting mixture was left overnight. The supernatant was decanted and the bottom gel was washed with deionized water, followed by centrifugation with the addition of 1 M HCl solution for at least 5 times to remove the metal oxide and washed with deionized water until the decantate became nearly neutral, followed by ultrasonication for 30 min, and a deep brown gel was obtained. The graphene fibers were fabricated through a wet-spinning method by injecting 2 wt% GO dispersion into a coagulation bath composed of 5 wt% NaOH/methanol solution using a syringe pump. The GO fibers were collected and immersed into methanol to remove the impurities. Graphene fibers were obtained by reducing the GO fibers in aqueous solution of hydroiodic acid (40%) at 80 °C for 8 h, followed by washing with methanol and drying for 12 h in vacuum.

(3) Calculation of electrical conductivities of composite fibers, effective areas of photovoltaic devices and specific capacitances of supercapacitors

The electrical conductivity (σ) with the unit of S/cm was calculated by \( \sigma = \frac{l}{R \cdot S} \), where \( l \), \( R \) and \( S \) correspond to the length, resistance and cross-sectional area of a fiber. As general accepted, the effective area of a photovoltaic wire was calculated by multiplying the length and diameter of the working electrode. The capacitance (C) was derived from the equation: \( C = \frac{l}{dV/dt} \), where \( I \) and \( dV/dt \) correspond to the discharge current and the slope of the discharge curve, respectively. The mass-specific capacitance \( C_m \) was obtained from the equation: \( C_m = 2C/m \), where \( m \) is the mass of one electrode. The area-specific capacitance \( C_S \) was derived from the equation: \( C_S = C/S \), where \( S \) is the surface area of the fiber electrode. The length-specific capacitance \( C_L \) was calculated from the equation: \( C_L = C/L \), where \( L \) is the length of a wire-shaped supercapacitor.

(4) Characterization

The structures were characterized by SEM (Hitachi FE-SEM S-4800 operated at 1 kV), TEM (JEOL JEM-2100F operated at 200 kV) and AFM (SHIMADZU SPM-9500J3), and. Raman measurement was performed on LabRam-1B with excitation wavelength of 632.8 nm and laser power of 4 mW (for Figure S3). Mechanical properties were characterized by a Shimadzu Table-Top Universal Testing Instrument. The electrical conductivity was obtained from a physical property measurement system (KEITHLEY 2182A nanocoltmeter with 6221A DC and AC current source) and VICTOR VC9807A+ digital multimeter. The J-V curves of DSCs were measured by a Keithley 2400 Source Meter under illumination (100 mW/cm²) 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 double potential step method electrochemical deposition and cyclic voltammetry were performed on a CHI 660a electrochemical workstation. The cyclic voltammetry of the DSCs part was performed in an acetonitrile solution containing 5 mM LiI, 0.5 mM I₂ and 0.05 M LiClO₄ with a scan rate of 50 mV s⁻¹ through a three-electrode setup. Galvanostatic charge-discharge characterizations were measured by an Arbin multi-channel electro-chemical testing system (Arbin, MSTAT-5 V/10 mA/16 Ch).
Figure S1. SEM images of a CNT sheet at different magnifications.
Figure S2. Graphene oxide sheets. a, b. Transmission electron microscopy images at low and high magnifications, respectively.
Figure S3. Graphene oxide sheets. a. Atomic force microscopy image. b. The height graph of a sheet at a.
Figure S4. Transmission electron microscopy image of a CNT.
Figure S5. SEM images of a bare CNT fiber at different magnifications.
Figure S6. Optical image of a uniform graphene/CNT composite fiber with the length of 10 cm.
Figure S7. Transmission electron microscopy images of the graphene/CNT composite at low and high magnifications. The red arrows indicate the edges of graphene sheets.
Figure S8. Raman spectra of bare CNT, graphene oxide/CNT and graphene/CNT composite fibers.
**Figure S9.** SEM image of a wire-shaped DSC.
Figure S10. a, b. SEM images of a CNT fiber and graphene/CNT composite fiber after electrodeposition of the same content of platinum. c. Cyclic voltammogram of a CNT/Pt fiber with $V_{pp}$ of 0.45 V. d. Typical J-V curve of the wire-shaped DSC based on the CNT/Pt fiber as the counter electrode. Energy conversion efficiencies were found to be (6.79±0.20)%.
Figure S11. J-V curves of a wire-shaped DSC using graphene/CNT/Pt composite fiber as the counter electrode with and without bending.
**Figure S12.** Schematic illustration to the structure of a wire-shaped micro-capacitor.
Figure S13. a. SEM image of a graphene oxide/CNT composite fiber coated with a gel electrolyte. b. Photograph of a wire-shaped micro-capacitor composed of two twisted fibers as shown in a.
Figure S14. Dependence of specific capacitance on current density for a micro-capacitor based on two bare CNT fiber electrodes.
Figure S15. Nyquist plot of the micro-capacitor composed of two twisted graphene oxide/CNT composite fibers.
Table S1. Average tensile strengths and electrical conductivities of fiber materials. The weight percentages of 0 and 100% correspond to bare CNT and graphene fibers, respectively.

<table>
<thead>
<tr>
<th>Weight percentage of graphene (%)</th>
<th>Strength (MPa)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>500</td>
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<tr>
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Reference for the Supporting Information


