Supporting Information

Realizing both High Energy and High Power Densities by Twisting Three Carbon-Nanotube-Based Hybrid Fibers

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Supporting Information

Experimental section

Preparation of carbon nanotube (CNT) sheets. Spinnable CNT arrays were synthesized by chemical vapor deposition at 740 °C with Fe (1.5 nm)/Al₂O₃ (5 nm) on a silicon substrate as the catalyst. The ethylene with a flowing rate of 90 sccm was used as the carbon precursor and a mixture of Ar (400 sccm) and H₂ (30 sccm) was used as the carrier gases. The growth occurred at 740 °C for 10 min. The CNT sheets with a width of approximately 1 cm were drawn out of the CNT array.

Preparation of CNT/ordered mesoporous carbon (OMC), CNT/Li₄Ti₅O₁₂ (LTO) and CNT/LiMn₂O₄ (LMO) hybrid fibers. The OMC particles (diameters of approximately 1 μm, pore diameter of 3.8-4.0 nm and specific surface area of 900 m² g⁻¹) were obtained from the Nanjing XFNANO Materials Tech Co. Ltd. To prepare the CNT/OMC hybrid fibers, 5 mg OMC and 0.5 mg CNT powders were dispersed in 10 mL N-methyl-2-pyrrolidone. Five stacked CNT sheets with a width of approximately 2 cm were then immersed into the above suspension and rolled into the CNT/OMC hybrid fibers. Prior to preparing the CNT/LTO and CNT/LMO hybrid fibers, LTO and LMO nanoparticles were first synthesized. LTO nanoparticles had been typically synthesized by a solid-state method. TiO₂ and Li₂CO₃ with a molar ratio of 5/2 was mixed and then heated at 800 °C for 24 h. The obtained LTO powder was further treated by a ball-milling machine for 20 h to form LTO nanoparticles. LMO nanoparticles were synthesized through a hydrothermal method. 0.377 g LiOH and 1.37 g γ-MnO₂ were added to 40 mL deionized H₂O to form a black slurry. The slurry was stirred for 0.5 h at room temperature and then added to a mixture of 0.20 g glucose and 40 mL deionized water under stirring. The resulting mixture was reacted at 200 °C for 24 h. The product was filtered and washed with deionized water, followed by drying at 120 °C for 24 h. The LTO and LMO nanoparticles were dispersed in N-methyl-2-pyrrolidone with the same concentration of 5 mg/mL. The resulting dispersions were treated by a probe-sonication using 200 W for 0.5 h. The CNT/LTO and CNT/LMO hybrid fibers were prepared with the same method as CNT/OMC hybrid fibers.

Fabrication of a fiber-shaped energy storage device. To prepare the gel electrolyte, methylene chloride and acetone with a weight ratio of 40/1 were first mixed. Then 0.30 g LiTFSI, 0.35 g SCN and 0.35 g PEO were added to the solution, followed by stirring for 4 h. After coated with a thin layer of gel electrolyte, the three hybrid fibers were placed in parallel with one end fixed on a motor and the other fixed on a paper. The
motor was rotated at a speed of 100 rpm for 1 min to produce the twisting structure. There were typically five twists per centimeter. One end of each electrode was fixed, and the other end was connected to a copper wire by silver glue for the following electrochemical analysis. The three electrodes were sealed in a heat-shrinkable tube which was provided by Suzhou Dasheng Materials Tech Co. Ltd. The resulting tube was treated with a heat gun at 120 °C for 1 min to shrink the diameter from 2 to 1 mm.

Electrochemical measurements. The electrochemical performance of the FESD was characterized by an ARBIN electrochemical station (MSTAT-5 V/10 mA/16Ch). The LIB segment was charged from 0 to 3.3 V at the current densities of 0.5, 1 and 1.5 A/g, and the specific capacity \( (C_L) \) was calculated by \( C_L = (I \times t)/m \), where \( I \), \( t \) and \( m \) represent the discharge current, discharge time and weight of the CNT/LTO fiber electrode, respectively. The CNT/LTO and CNT/LMO fiber electrodes showed linear weight densities of 0.036 and 0.073 mg/cm, respectively. The supercapacitor segment was charged from 0 to 2.8 V at current densities of 1, 1.4, 2 and 4 A/g. The specific capacitance \( (C_S) \) was calculated from the charge and discharge profiles according to \( C_S = I \times t/(m \times u) \), where \( I \), \( t \), \( m \) and \( u \) correspond to the discharge current, discharge time, the mass of the CNT/OMC fiber and the CNT/LTO fiber electrode, potential window, respectively. The CNT/OMC fiber electrode showed a linear weight density of 0.018 mg/cm. The energy density of the FESD was calculated from \( E_v = (I \times U \times t)/v \) or \( E_m = (I \times U \times t)/m \), and the power density \( (P) \) of the FESD was obtained from \( P_v = (I \times U)/v \) or \( P_m = (I \times U)/m \), where \( I \), \( U \), \( t \), \( v \) and \( m \) represent the discharge current, average operating voltage, discharge time, the volume and the mass of the three fiber electrodes, respectively.

Characterization. The structures were characterized by scanning electron microscope (Hitachi FE-SEM S-4800 operated at 1 kV) and X-ray diffraction (XRD, Bruker AXS D8). The charge-discharge tests were carried out in an ARBIN electrochemical station (MSTAT-5 V/10 mA/16Ch). The cyclic voltammetry was conducted by an electrochemical workstation (CHI 660D). The bending measurements were performed at a table-top universal testing instrument (HY-0350). The photographs were taken by a camera (Nikon, J1).
Figure S1. Scanning electron microscopy (SEM) image of the CNT sheet.
Figure S2. a and b) SEM images of OMC nanoparticles at low and high magnifications, respectively.
Figure S3. X-ray diffraction pattern of LTO nanoparticles.
Figure S4. X-ray diffraction pattern of LMO nanoparticles.
Figure S5. SEM image of LTO nanoparticles.
Figure S6. SEM image of LMO nanoparticles.
Figure S7. The size distribution of LTO nanoparticles.
Figure S8. The size distribution of LMO nanoparticles.
Figure S9. SEM image of the CNT/OMC hybrid fiber.
**Figure S10.** SEM image of the CNT/LTO hybrid fiber.
Figure S11. CNT/LTO hybrid fiber. a and b) SEM images by side and cross-sectional views, respectively. c and d) Energy-dispersive X-ray spectroscopy images by side and cross-sectional views, respectively. Here titanium is marked with yellow.
Figure S12. SEM image of the CNT/LMO hybrid fiber.
**Figure S13.** CNT/LMO hybrid fiber. **a** and **b**) SEM images by side and cross-sectional views, respectively. **c** and **d**) Energy-dispersive X-ray spectroscopy images by side and cross-sectional views, respectively. Here manganese is marked with red.
Figure S14. Photograph for the experimental setup to prepare the twisting structure.
Figure S15. Dependence of the specific capacity on the content of LTO in the hybrid fiber at a current density of 0.5 A/g.
Figure S16. Rate capability of the LIB segment.
Figure S17. Dependence of the specific capacitance on the content of OMC in the hybrid fiber at the current density of 1 A/g.
Figure S18. Schematic illustrations to a whole charge-discharge process of the FESD. a) The charge of LIB. b) The self-charge process. c) The discharge of the supercapacitor. d) The discharge of LIB.
**Figure S19.** Cyclic performance of the FESD being alternately operated as a supercapacitor and LIB for continuous 100 cycles.
Figure S20. Energy and power densities of the FESD compared with the previous energy storage systems based on CNT\textsuperscript{[S1]}, polyaniline\textsuperscript{[S2]}, graphene\textsuperscript{[S3]}, V\textsubscript{3}S\textsubscript{4}/MnO\textsubscript{2}\textsuperscript{[S4]}, Ni(OH)\textsubscript{2}/AC\textsuperscript{[S5]} and LTO/AC\textsuperscript{[S6]}. Here AC represents amorphous carbon.
Figure S21. SEM images of an FESD under bending at low and high magnifications.
Figure S22. Dependence of the energy density on the length of the FESD.
References for the Supporting Information


