NiO nanowall-assisted growth of thick carbon nanofiber layers on metal wires for fiber supercapacitors

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1. Experimental section

Synthesis of NiO nanowalls on Kovar MWs: Commercial Kovar MWs were sequentially cleaned by sonication in acetone, deionized water, and ethanol for 5 min. NiO nanowalls were deposited using hydrothermal method according to the previous literature \(^1\). Simply, the cleaned Kovar MWs were put into a Teflon-lined stainless autoclave, containing 50 mL homogeneous solution of 1.24 g C\(_4\)H\(_6\)NiO\(_4\)-4H\(_2\)O, 0.37 g NH\(_4\)F and 1.5 g CO(NH\(_2\))\(_2\). Then, the autoclave was sealed and left in an electric oven at the temperature of 130 °C for 5 h. When the equipment cooled down to room temperature naturally, the sample was taken out, washed by distilled water several times and dried in oven at 70 °C for 3 h. Finally, these wires were annealed at 500 °C for 2 h in Ar flow to obtain NiO nanowalls decorated Kovar MWs.

Growing carbon nanofiber (CNF) layers on MWs: CNFs were grown on the NiO nanowall/MW composite wires by chemical vapor deposition method using ethanol as precursor at 600 °C for 40 min.

Preparation of polymer electrolytes: Polyvinyl alcohol (PVA) (molecular weight: 146,000-
186,000; Aladdin Chemicals) and KOH (Lingfeng Chemicals) were used as received. The alkaline PVA/KOH polymer electrolyte was prepared by dissolving 1 g of PVA and 0.56 g of KOH in 10 mL water with continuous stirring for about 3-4 h at 85 °C to form a liquid gel.

**Assembling all-solid fiber supercapacitor:** Two CNF/MW electrodes were immersed into PVA-KOH polymer electrolyte for 12 h. After dried in air for 1 h, these two electrodes were stuck together in parallel on a strip of PET substrate. Here PVA/KOH polymer electrolyte acted as both bonder and separator.

**Characterization**

The products were characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN at 200 kV) with energy-dispersive X-ray spectroscopy (EDS, EDXA, America), X-ray diffraction (XRD, Philips X’pert Pro X-ray diffractmeter with a Cu Kα radiation of 1.5418 Å) and Raman spectroscopy (Renishaw inVia Raman Microscope with an argon-ion laser at an excitation wavelength of 514 nm). Thermo-gravimetry analysis (Netzsch STA-449F3) was performed at a heating rate of 10 °C min⁻¹ in O₂/Ar ambient.

**Electrochemical measurements**

Electrochemical performances of the fiber supercapacitors were studied by cyclic voltammetry (CV), galvanostatic charge–discharge and electrical impedance spectroscopy (EIS) on the VMP3 Electrochemical Workstation (Bio-logic). All electrochemical experiments were carried out using a two-electrode system at ambient temperature. The CV curves of the supercapacitor were measured between 0 and 1 V at different scan rates. EIS was carried out over a frequency range of 100 kHz to 0.01 Hz at open circuit potential with an ac perturbation of 5 mV. The equation, \(C_L = I_D/ (dV/dt)\), was used to calculate the length capacitance from the slope of the charge–discharge curves (dV/dt), where \(I_D\) is the applied current density (μA/cm). Capacitance per unit area, \(C_A\) (mF/cm²), was calculated by the use of following equation: \(C_A = C_L / (\pi d/2)\), where \(d\) is the diameter of the electrode.
Supplementary References

2. Supplementary Figures

**Fig. S1** (a) HRTEM and SAED pattern of NiO nanosheet. Note: The lattice of fringe space of 0.24 nm corresponding to (111) plane of NiO.

**Fig. S2** (a) SEM image of the whole CNF/MW composites and (b) enlarged top-view image.
Fig. S3 (a) HRTEM image of CNF; (b) SEM image of large particles that are derived from NiO nanowalls after CNF growth.

Fig. S4 shows the high-angle annular dark-field scanning TEM (HAADF-STEM) image of CNF/nanoparticle composites. It can be clearly seen that nanoparticles were coated by carbon shells and they catalyzed CNF growth. The EDS elemental mapping images (Fig. S4b-d) confirm the core-shell structure and also indicate that the nanoparticles is mainly composed of metallic Ni since little O signal was detected.

Fig. S4 (a) HAADF-STEM image of the CNF/MW and (b-d) EDS elemental mapping images of C, Ni and O.
Fig. S5 TG and DTG curve of CNF/Ni. TG analysis were carried out in 8% O$_2$/Ar at a heating rate of 10 °C/min. The contents of CNFs and Ni metal in the composite are calculated to be 80.6 and 19.4% respectively.

As shown in Fig. S6a, the leakage current reduced quickly in the beginning and then gradually became smaller and more stable (finally to ~4.18 μA after 2 h). The low leakage current means less shuttle reactions caused by the impurities in the electrode materials. Fig. S6b further shows a stable output circuit voltage of 0.2 V after 8 h, indicating the excellent capacitor performance.

Fig. S6 (a) Leakage current curve and (b) self-discharge curve of the fiber supercapacitor.
To understand the capacitive contribution of Ni particles in the final CNF/MW composites, we measured the CV curves (Fig. S7) of bare Kovar, reduced Ni/MW and CNF/MW on three-electrode system—a more sensitive manner to measure the electrochemical reaction involved in electrode’s surface than two-electrode system. The recued Ni/MW was prepared by reducing NiO/MW with H$_2$ gas at 600 °C, the same temperature as CNF growth. The morphology of reduced Ni on Kovar MW is shown in Fig. S7c-d. As shown in Fig. S7a, all curves have redox peaks, indicating the pseudocapacitive property of these fiber electrodes. Fig. S7b gives the calculated $C_A$ for each electrode at different scanning rates. The capacitance of Ni/MW is about 30-40% to that of CNF/MW electrode depending on the different scan rates. In CNF/MW composite, a part of Ni particles were coated by carbon. If this part is neglected, the capacitance given by Ni particles in CNF/MW composite should be 30-40%. In other word, the portion of capacitance of CNFs in CNF/MW electrode is 60-70%.

Fig. S7 (a) The CV curves of pure Kovar MWs substrate, r-Ni, and CNF/MW in 3M KOH solution at a scan rate of 200 mV/s. (b) $C_A$ of these fibers at different scan rate. (c and d) SEM images of Ni particles on Kovar MW that reduced from NiO/MW by H$_2$. 
Fig. S8 (a) Cycle performance with the different current density and (b) Nyquist plot of fiber supercapacitors, inset shows the data in high frequency range.

Fig. S9. SEM image of CNF/MW electrode charged/discharged for 3000 cycles in 3M KOH aqueous solution under 3-electrode system.
Fig. S10 (a) Schematic of two fiber supercapacitors connected in series. (b) Galvanostatic charge/discharge curves of single and two series-connected devices.