Electronic Supplementary Information (ESI)

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 [S1]. Simply, the cleaned Kovar MWs were put into a Teflon-lined stainless autoclave, containing 50 mL homogeneous solution of 1.24 g $C_4H_6NiO_4{\cdot}4H_2O$, 0.37 g NH_4F and 1.5 g $CO(NH_2)_2$. Then, the autoclave was sealed and left in an electric oven at the temperature of 130℃ 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℃ for 3 h. Finally, these wires were annealed at 500 ℃ 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 ℃ 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 O_2/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/cm^2), 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

S1 J. H. Zhu, J. Jiang, J. P. Liu, R. M. Ding, H. Ding, Y. M. Feng, G. M. Wei and X. T. Huang, *J. Solid State Chem.*, 2011, **184**, 578.

2. Supplementary Figures

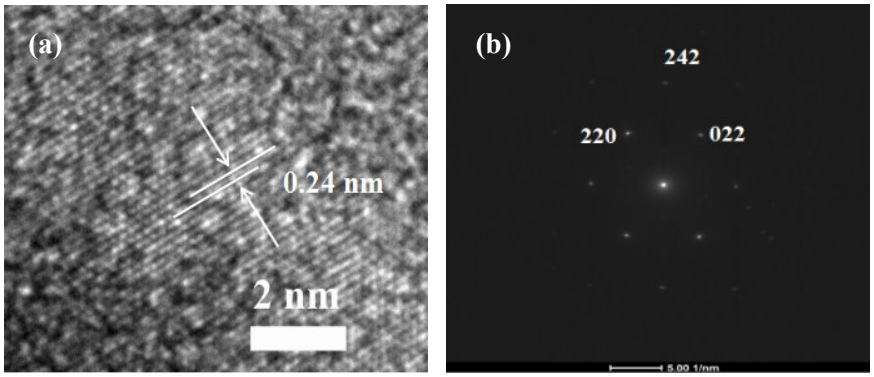

Fig. S1 (a) HRTEM and SAED pattern of NiO nanosheet. Note: The lattice of fringe space of 0.24 nm corresponding to (111) plane of NiO.

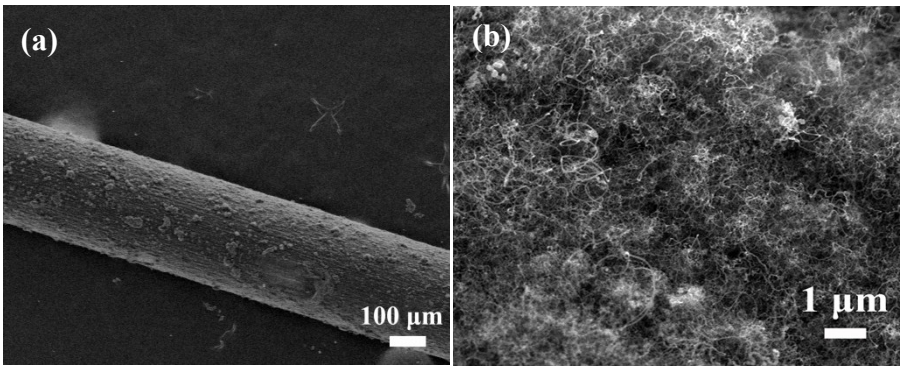

Fig. S2 (a) SEM image of the whole CNF/MW composites and (b) enlarged top-view image.

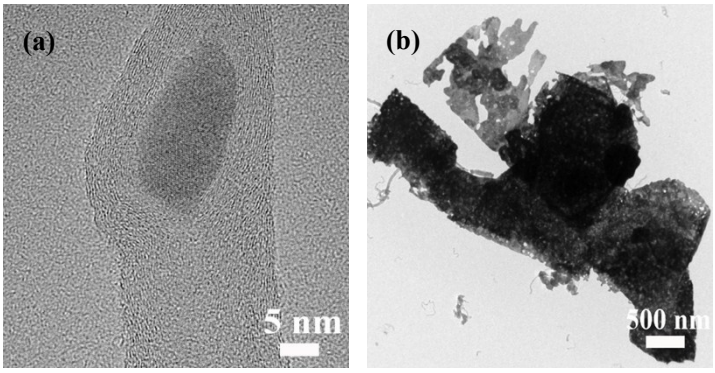

Fig. S3 (a) HRTEM image of CNF; (b) SEM iamge of large particles that are derived from NiO nanowalls after CNF growth.

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.

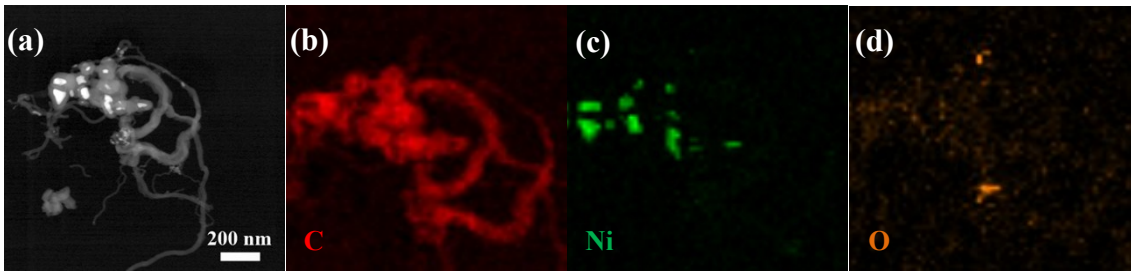

Fig. S4 (a) HAADF-STEM image of the CNF/MW and (b-d) EDS elemental mapping images of C, Ni and O.

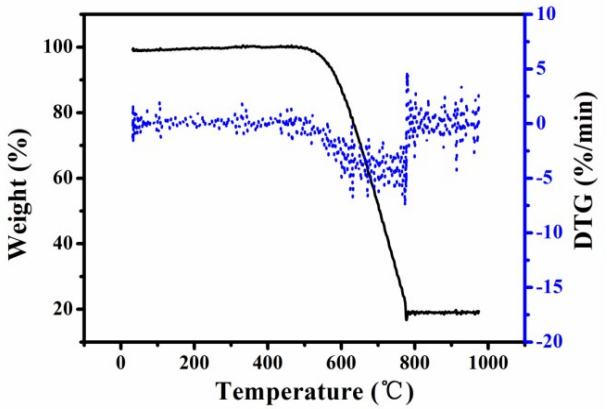

Fig. S5 TG and DTG curve of CNF/Ni. TG analysis were carried out in 8% O_2/Ar at a heating rate of 10 ℃/min. The contents of CNFs and Ni metal in the composite are calculated to be 80.6 and 19.4% respectively.

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.

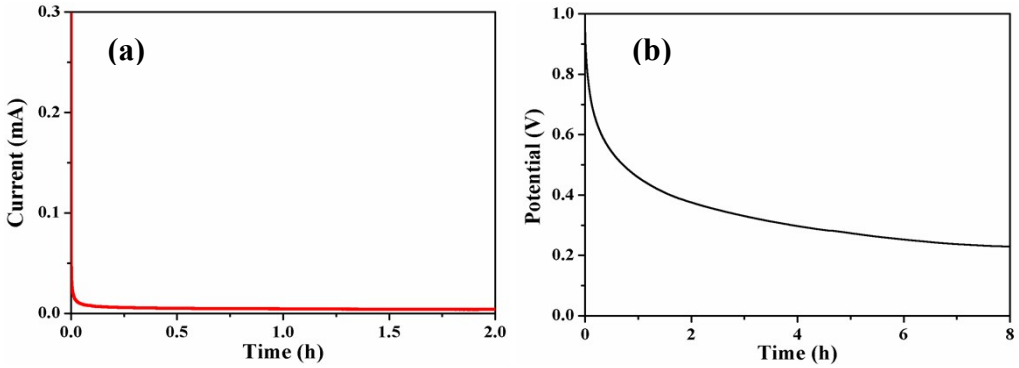

Fig. S6 (a) Leakage current curve and (b) self-discharge curve of the fiber supercapacitor.

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%.

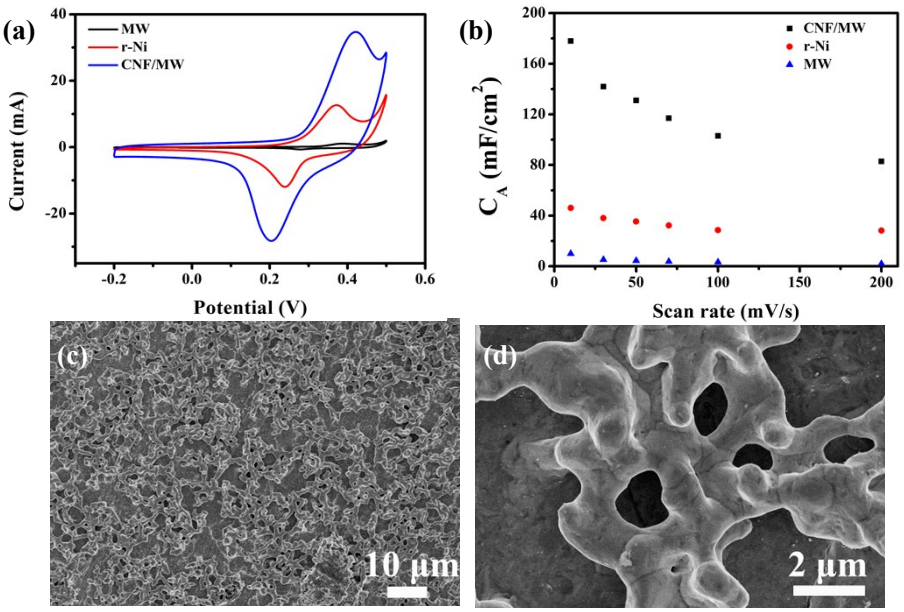

Fig. S7 (a) The CV curves of pure Kovar MWs substrate, r-Ni, and CNF/MW in 3M KOH solution at a scan rate of 200 mV/s. (b) C_A of these fibers at different scan rate. (c and d) SEM images of Ni particles on Kovar MW that reduced from NiO/MW by H_2.

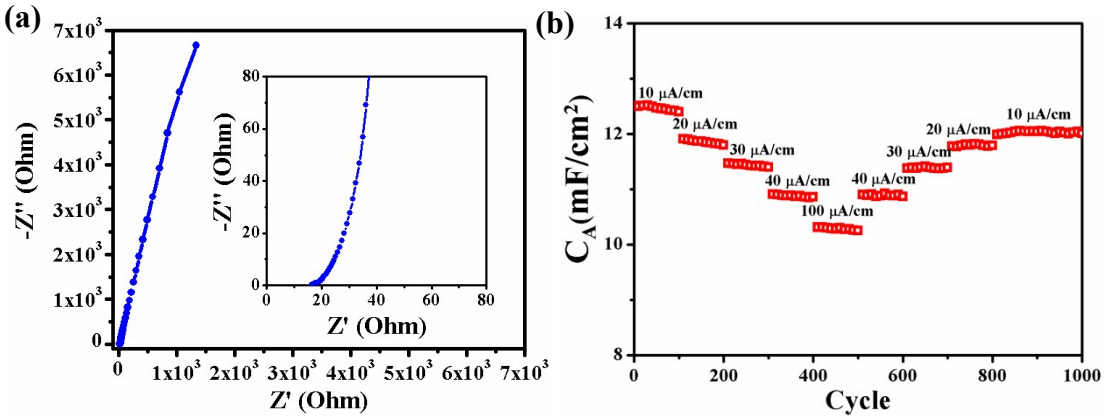

Fig. S8 (a) Cycle performance with the different current density and (b) Nyquist plot of fiber supercapacitors, inset shows the data in high frequency range.

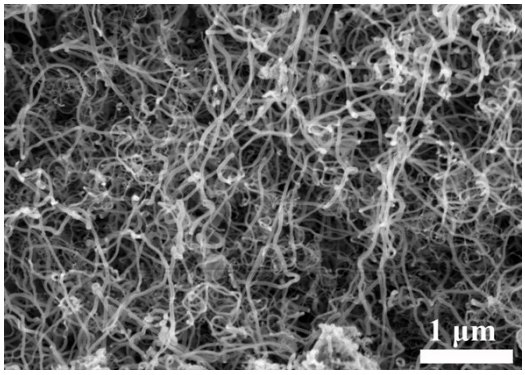

Fig. S9. SEM image of CNF/MW electrode charged/discharged for 3000 cycles in 3M KOH aqueous solution under 3-electrode system.

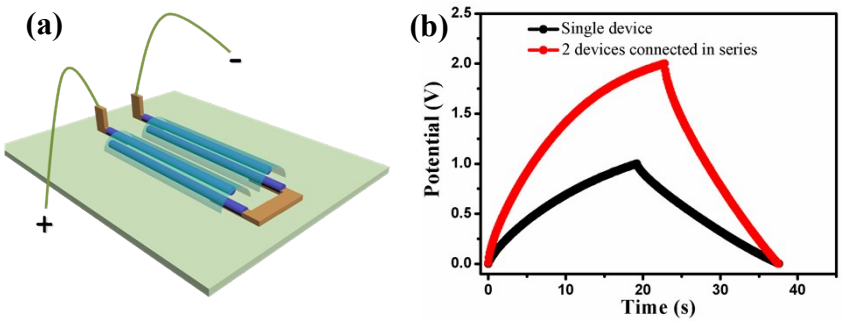

Fig. S10 (a) Schematic of two fiber supercapacitors connected in series. (b) Galvanostatic charge/discharge curves of single and two series-connected devices.