Electronics Supplementary Information

δ-MnO_2/holey graphene hybrid fiber for all-solid-state supercapacitor

Jinyang Zhang, Xiaofan Yang, Yibo He, Yonglong Bai, Liping Kang, Hua Xu, Feng Shi, Zhibin Lei, Zong-Huai Liu*

Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, Xi'an 710062, P.R. China, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, P.R. China.

*Corresponding Author: Zong-Huai Liu

E-mail: zhliu@snnu.edu.cn

Experimental Details

Synthesis of δ–MnO_2/HRGO fiber:

20 mg GO was firstly dispersed in 1 mL ultrapure water and treated by ultrasonication for 5 h, the GO homogenous suspension (20 mg/mL) was obtained. By using a wet–spinning method, the GO homogenous suspension (1 mL, 20 mg/mL) was injected into a coagulation bath composed of 5 wt% NaOH/methanol solution using a syringe pump with an injection speed of 100 μL min^{-1}. After immersing for 30 minutes in a coagulation bath, the obtained fiber was transferred into a methanol bath to wash away the residual coagulation solution, GO fiber was obtained and collected onto the bracket. Then GO fiber (20 mg) was soaked in 0.5 M H_3PO_4 solution (50 mL) for 12 h, and calcined at 650 °C for 2 h in N_2, washed with deionized water for 3 times, the hole reduced graphene oxide fiber was fabricated, which was abbreviated as HRGO–650. The HRGO–650 fiber (5 mg) was then

followed by soaking in 4.0 mM $KMnO_4$ solution (100 mL), and stirred at 65 °C for 2 h, δ–MnO_2 was coated on the fiber surface. It was washed with deionized water and dried in the vacuum oven, δ–$MnO_{2(4.0)}$/HRGO fiber electrode was finally prepared. By changing the concentrations of $KMnO_4$ solution, δ–$MnO_{2\ (M)}$/HRGO fiber electrodes with different MnO_2 mass coating were obtained by the similar process, in which M was the concentration of $KMnO_4$ solution. For comparison, GO fiber (20 mg) was also calcined at 650 °C for 2 h under N_2 atmosphere in tube furnace, washed with deionized water for 3 times, the reduced graphene oxide fiber was fabricated, which was abbreviated as RGO.

Characterization

The morphology of the samples were observed on JEM–2100 Transmission electron microscope (TEM), TM–3000 scanning electron microscopy (SEM) and A SU8020 field–emission scanning electron microscopy (FESEM). X–ray diffraction (XRD) patterns were obtained on a D/Max–3c instrument operating at 40 KV and 20 mA, using Cu KR radiation (λ=1.5406 Å). Raman spectra were measured and collected using a Renishaw inVia Raman microscope with an excitation wavelength of 532 nm. X–ray photoelectron spectroscopy (XPS) was performed with the AXIS ULTRA (Kratos Analytical Ltd.) using Kα radiation (1486.6 eV) as an excitation source. To ensure the accuracy of the data measured, all of the binding energies were calibrated relative to the C 1s peak (284.6 eV) from hydrocarbon adsorbed on the surface of the samples. Nitrogen adsorption/desorption isotherms were measured at 77 K on Quantachrome SI-3 analyzer. Samples were degassed at 120 °C for 12 h prior to the measurement. The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) method with the desorption data at the relative pressure (P/P_0) range 0.05-0.35. The total pore volumes were estimated at P/P_0=0.99. The pore size distribution (PSD) curves were calculated from the desorption branch using the nonlocal density functional theory (NLDFT) model. Mechanical property tests were carried on a RGT–10.

Electrochemical measurements:

The cyclic voltammetry (CV) and galvanostatic charge–discharge tests were carried out with a CHI660E electrochemical workstation (CH Instruments Inc. China) in a conventional three–electrode cell which contains the working electrode, counter electrode (Pt foil) and reference electrode (Ag/AgCl electrode) in 1 M Na_2SO_4 aqueous solution. By grid placing δ–MnO_2/HRGO fiber with a length of 1.0 cm into the interlayer between two Ni foam current collectors with a definite of 1.0 cm^2 and followed by uniaxial pressing the electrode adhere to the Ni foam current collectors completely, the working electrode was prepared. The mass loading for working electrode was about 2–3 mg. CV tests and the galvanostatic charge–discharge curves of the electrodes were performed at a potential window of –0.2~0.8 V, and the specific capacitance C (F g^{-1}) was calculated from CV results using the formula: $C = I \times \Delta t/(\Delta V \times m)$. Where ΔV is the voltage change during the discharge process, excluding IR drop in the discharge process, m is the mass of active material for the working electrode (g), I is the applied current density (A), and t is the time of discharge stage (s).

The symmetric δ–$MnO_{2(4.0)}$/HRGO fiber supercapacitor was assembled by using δ–$MnO_{2(4.0)}$/HRGO fibers as both positive and negative electrodes. The δ–$MnO_{2(4.0)}$/HRGO fiber was incorporated with a gel electrolyte of PVA/H_3PO_4 (mass ratio of 1/1) and dried in vacuum, δ–$MnO_{2(4.0)}$/HRGO fiber electrode was firstly obtained. The resulting two fiber electrodes were then twisted together, followed by coat of a second layer of the same gel electrolyte to avoid the short circuit of the wire–shaped supercapacitor. H_3PO_4–PVA gel electrolyte was prepared according to the reported method.[2] By mixing a solution of H_3PO_4 (6 g) and deionized water (60 mL) with PVA powder (6 g), the obtained mixture was heating up steadily to 85 °C under vigorous stirring until the solution became clear and then it was kept at 85 °C for 1 h without stirring. The capacitance C of the supercapacitor was calculated by using the equation: C = I/(dV/dt), where I and dV/dt were the discharge current and the slope of the discharge curve, respectively. The area–specific capacitance C_A

was derived from the equation: C_A=C/A, where A was the surface area of the fiber electrode and was equal to π multiplied by the diameter of the fiber electrode (D) and the device length (L). The mass−specific capacitance C_m was calculated from the equation: C_m=2C/m, where m is the mass of one electrode.

Supplementary Figures and Analysis

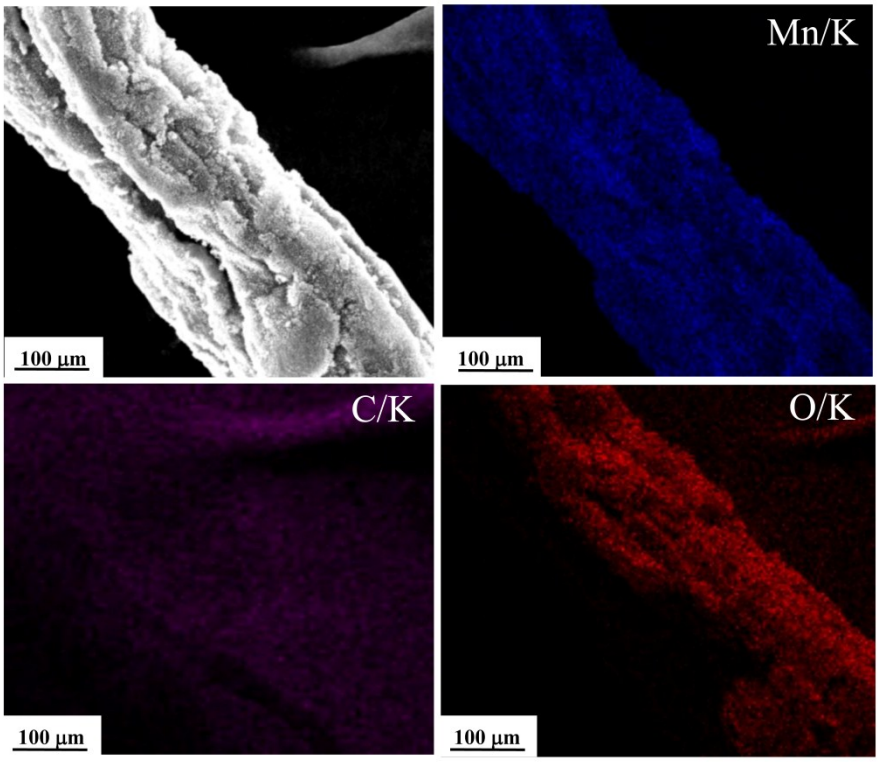

Fig. S1. SEM image of δ−$MnO_{2(4.0)}$/HRGO fiber and Element mappings for Mn, C and O, respectively.

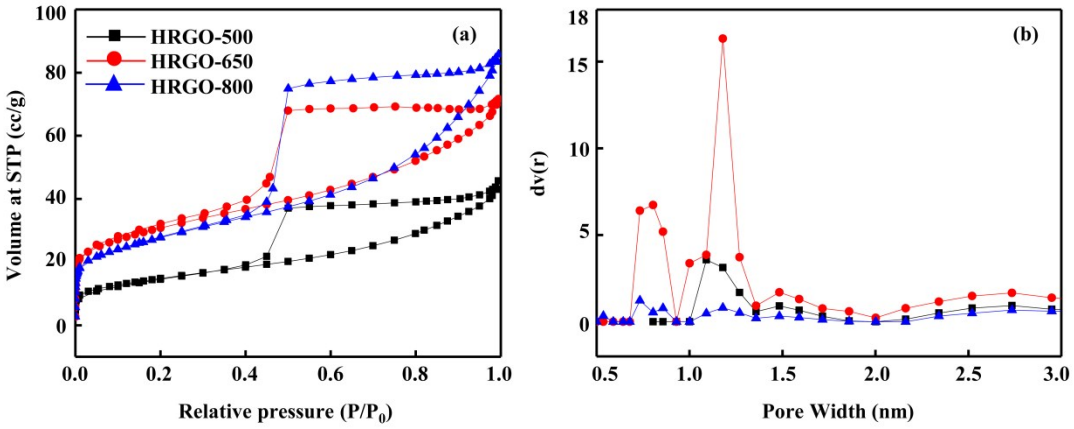

Fig. S2. (a) Nitrogen adsorption and desorption isotherms of HRGO fiber with various calcined temperature. (b) Pore size distributions of HRGO fiber with various calcined temperature.

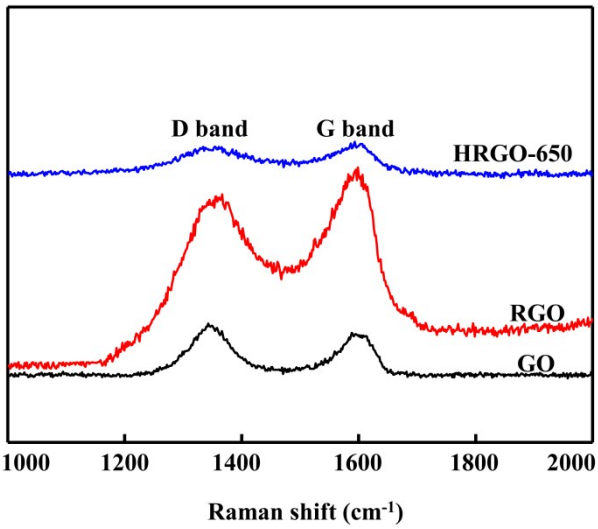

Fig. S3. Raman spectra of GO fiber, RGO fiber and HRGO-650 fiber

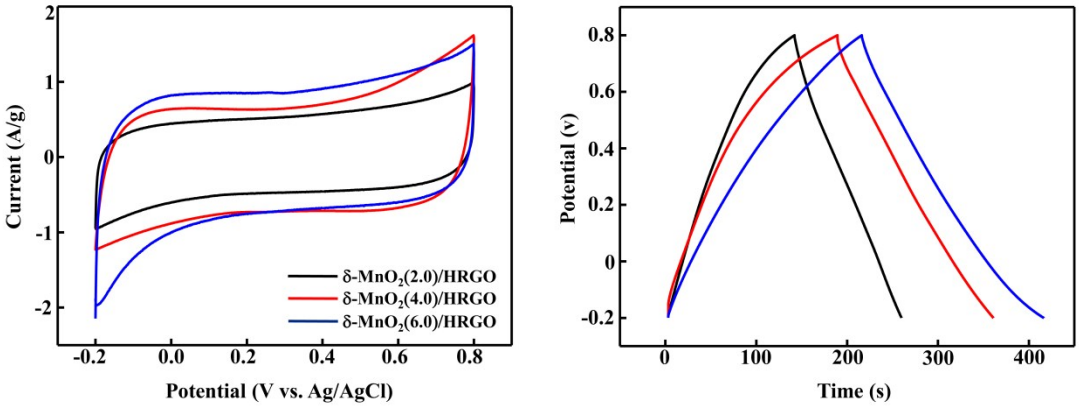

Fig. S4. CV curves (left) and galvanostatic charge-discharge curves (right) of δ-$MnO_{2\ (2.0)}$/HRGO, δ-$MnO_{2\ (4.0)}$/HRGO and δ-$MnO_{2\ (6.0)}$/HRGO in 1M Na_2SO_4 electrolyte.

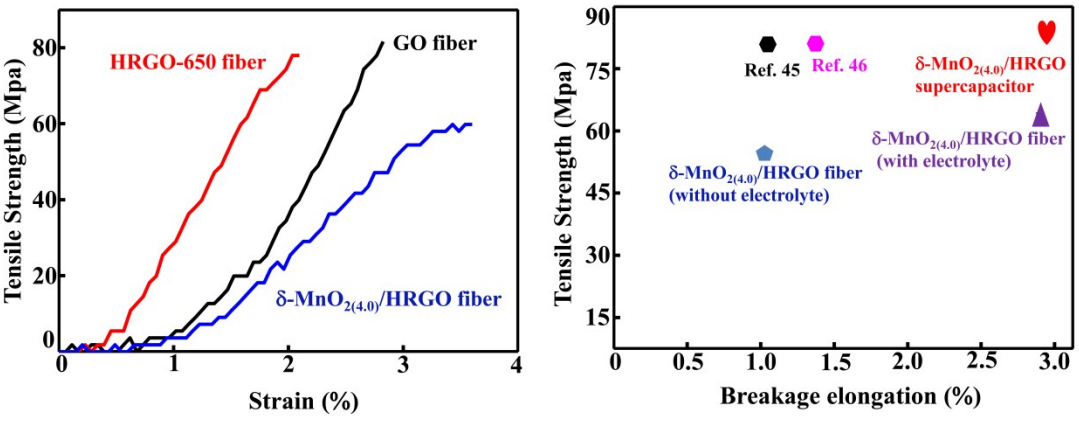

Fig. S5. (a) Typical mechanical measurements under tension for GO fiber, HRGO-650 fiber and δ-$MnO_{2\ (4.0)}$/HRGO fiber and (b) Comparison of mechanical performance for graphene-based fibers/papers.