Supporting information

Fe₃O₄ Nanoparticle-Embedded Cellulose Nanofibre/ Graphite Carbon Hybrid Aerogels as Advanced Negative Electrode for Flexible Asymmetric Supercapacitors

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S1. Experimental section

1. Preparation of CNF/RGO-HAs and RGO-HAs substrate material

The typical preparation procedure is as follows: First, 13.125 g of GO solution (0.8 wt%) and 18.3 mL of ultrapure water was weighed and added into a solution containing 21 g of CNFs (0.5 wt%) and ultrasonically dispersed at a power of 650 W and frequency of 20 KHz for 20 min to obtain a uniformly dispersed CNF/GO solution. The aforementioned dispersant was subsequently placed in a mould ($5.4 \times 4.0 \times 3.0$ cm), snap-frozen in liquid nitrogen, and transferred to a freeze dryer and frozen at -45 °C for 24 h. After vacuum drying at 4.5 Pa for 4 days, the preparation of CNF/GO-HAs was complete. The HAs was then placed inside a weighing bottle, transferred to a reactor containing 4 mL of hydrazine hydrate, and heated in an oven at 150 °C for 12 h. After 1 h of annealing in a tube furnace at 220 °C, the CNF/RGO substrate material was formed.

To prepare the RGO-HAs, 13.125 g of GO solution (0.8 wt%) was added to 39.4 mL of ultrapure water and ultrasonically dispersed at a power of 650 W and frequency of 20 KHz for 20 min to obtain a uniformly dispersed GO solution. The aforementioned dispersant was subsequently placed in a mould ($5.4 \times 4.0 \times 3.0$ cm), snap-frozen in liquid nitrogen, and transferred to a freeze drier and frozen at -45 °C for 24 h. After vacuum drying at 4.5 Pa for 4 days, the preparation of GO-HAs was complete. The HAs was then placed inside a weighing bottle, transferred to a reactor

containing 4 mL of hydrazine hydrate, and heated in an oven at 150 °C for 12 h. After 1 h of annealing in a tube furnace at 220 °C, the RGO-HAs substrate material was formed.

2. Preparation of the positive electrode

2.1 Preparation of the CF-CNF/MWCNT-HAs.

The typical procedure was as follows: 72 mg of MWCNTs (TNIM2, d8-15nm) and 14.4 g wooden CNF (0.5 wt.%) were added to 39.5 mL of deionized water. Ultrasonic dispersion (power = 650 W, frequency = 20 kHz) was performed on the mixture for 20 min. High-conductivity chopped CF (18 mg) was next added, followed by another round of ultrasonic dispersion (power = 150 W, frequency = 40 kHz) and high-speed stirring for 15 min to afford a CNF/MWCNT/CF dispersion liquid at 0.3 wt.% (CNF:MWCNT:CF mass ratio = 1:1:0.25). The dispersion liquid was then transferred to a plastic mould (5.4 cm × 4.0 cm × 3.0 cm) and rapidly frozen in liquid nitrogen. It was then placed in a freeze dryer for 24 h at -45 °C, and freeze-dried in a vacuum of 4.5 Pa for 4 days. The afforded CF-CNF/MWCNT-HAs was placed in a vacuum drying box for 24 h at 80 °C.

2.2 Preparation of the CF-CNF/MWCNT/MnO₂ electrode.

The typical procedure was as follows: the CF-CNF/MWCNT-HAs was pretreated at 200 °C in air for 60 min, and subsequently cooled to room temperature (25 °C). It was subsequently immersed in 150 mL of 0.1 mol/L KMnO₄ solution and allowed to react for 3 h at 27 °C [1, 2]. To understand how the reaction time affects the mass specific capacitance of the resulting electrode, the reaction time was varied from 1h to 4 h. The resultant mixture was placed in a 500-mL beaker filled with deionized water and washed for 10-15 times with continuous magnetic stirring, until the solution became colorless. The cleaned HAs was frozen at -45 °C for 24 h, and freeze-dried at 4.5 Pa for 3 days to obtain the CF-CNF/MWCNT/MnO₂-HAs. The freeze-dried HAs was pressed for 10 min at 10 MPa into a thin sheet, which was annealed at 250 °C for 1 h to form the CF-CNF/MWCNT/MnO₂ anode plate.

References

[1] S. W. Lee, J. Kim, S. Chen, P. T. Hammond, Y. Shao-Horn, ACS Nano 2010, 4, 3889.

[2] L. Dong, C. Xu, Y. Li, Z. Pan, G. Liang, E. Zhou, F. Kang, Q. H. Yang, Adv. Mater. 2016, 28, 9313.

S2. Calculations section

1. Determination of the Fe₃O₄ load in the CNF/MWCNT/RGO/Fe₃O₄ electrodes

The typical experimental procedure was as follows. The CNF/MWCNT/RGO/ Fe₃O₄ electrode (1.5 cm × 1 cm) was immersed in 100 mL 1mol/L hydrochloric acid for 12 h, until the Fe₃O₄ was completely dissolved. The mixture was filtered and the resultant filtrate was diluted to 200 mL to prepare Fe³⁺ solutions at different concentrations (3, 6, 9, 12, and 15 mg/L) that were subsequently used to plot a standard curve. The MnO₂ load on the electrode material was then calculated from the atomic absorption spectrum of the sample solution using Equation (1).

$$X_{Fe_3O_4} = \frac{C_1 \times 0.2 \times 231.54}{1.5 \times 55.85} \tag{1}$$

where C₁ is the Fe³⁺ concentration of each test sample, 231.54 is the molecular mass of Fe₃O₄, 55.85 is the atomic mass of iron, $X_{Fe_3O_4}$ and is the load per unit area of the electrode (mg/cm²). All tests were performed in independent triplicates to determine the average value.

2. Determination of the MnO_2 load in the CF-CNF/MWCNT/MnO₂ and CNF/MWCNT/ MnO_2 electrodes

The typical experimental procedure follows. The CFwas as CNF/MWCNT/MnO₂ electrode (1.5 cm \times 1 cm) was immersed in 10 mL concentrated nitric acid for 12 h, until the MnO₂ was completely dissolved. The mixture was filtered and the resultant filtrate was diluted to 200 mL to prepare Mn⁴⁺ solutions at different concentrations (3, 6, 9, 12, and 15 mg/L) that were subsequently used to plot a standard curve. The MnO₂ load on the electrode material was then calculated from the atomic absorption spectrum of the sample solution using Equation (2).

$$X_{MnO_2} = \frac{C_1 \times 0.2 \times 86.94}{1.5 \times 54.94} \tag{2}$$

where C₁ is the Mn⁴⁺ concentration of each test sample, 86.94 is the molecular mass of MnO₂, 54.94 is the atomic mass of manganese, and X_{MnO_2} is the load per unit area of the electrode (mg/cm²). All tests were performed in independent triplicates to determine the average value.

3. Calculation of the areal specific capacitance of the single electrode

(1) The areal specific capacitance of the electrodes was calculated from the CV curves using Equation (3).

$$C_a = \frac{Q}{\Delta U \times S} \tag{3}$$

where C_a (mF/cm²) is the areal specific capacitance, Q is the average charge during electrode charging and discharging, ΔU (V) is the working voltage window of the electrode, and S (cm²) is the test area of the electrodes.

(2) C_a was calculated by galvanostatic charging-discharging using Equation (4).

$$C_a = \frac{I \times \Delta t}{\Delta U \times S} \tag{4}$$

where I is the current during electrode discharging (A), and Δt (s) is the discharge time of the electrode.

(3) The mass specific capacitance with respect to three-electrode configuration is derived from GCD based on Equation (5).

$$C_{s} = \frac{Q(Fe_{3}O_{4} + MWCNT + RGO) - Q(MWCNT + RGO)}{\Delta U \times m}$$
(5)

where C_s is the mass specific capacitance, Q is the charge obtained from the GCD based on CNF/MWCNT/RGO/Fe₃O₄ and CNF/MWCNT/RGO electrodes, ΔU is the voltage range (-1.0V), and m is the mass of Fe₃O₄ on CNF/MWCNT/RGO/Fe₃O₄ electrode.

4. Charge matching between the positive and negative electrodes of the flexible ASC device.

Fig. 6(a) displays the CV plot of the CF-CNF/MWCNT/MnO₂ and CNF/MWCNT/RGO/Fe₃O₄ electrodes in 5 M LiCl solution at a scanning rate of 10 mV/s. The areal specific capacitance of the CF-CNF/MWCNT/MnO₂ electrode was determined as 791.4 mF/cm² and the working potential ranged from 0 to 0.8 V. The

areal specific capacitance of the CNF/MWCNT/RGO/Fe₃O₄ electrode was determined as 666.5 mF/cm² and the working potential ranged from -1 to 0 V. The areal specific capacitance of the CF-CNF/MWCNT/MnO₂ electrode and CNF/MWCNT/RGO/Fe₃O₄ electrodes was determined to be optimal when the amounts of charge stored in the positive and negative electrodes are equal (i.e. q+ = q-), as shown in Equation 6.

$$q = C_a \times \Delta E \times S \tag{6}$$

where Q is the charge on the electrode, and ΔE is the potential during the charging and discharging process. Equal amounts of charge were observed at 10 mV/s.

The face-to-face area of the positive and negative electrodes during device assembly should follow Equation 7:

$$\frac{S_{CF-CNF/MWCNT/MnO_2}}{S_{CNF/MWCNT/RGO/Fe_3O_4}} = \frac{C_{a(CNF/MWCNT/RGO/Fe_3O_4)} \times \Delta E_{(CNF/MWCNT/RGO/Fe_3O_4)}}{C_{a(CF-CNF/MWCNT/MnO_2)} \times \Delta E_{(CF-CNF/MWCNT/MnO_2)}} = 0.95 \approx 1000$$

(7)

5. Calculation of volume specific capacitance, power density, and energy density of the flexible CF-CNF/MWCNT/MnO₂//CNF/MWCNT/RGO/Fe₃O₄ ASC device

(1) The volume specific capacitance of the electrodes was calculated from the CV curves and from Equations 8 and 9.

$$C_{cell} = \frac{Q}{\Delta U}$$
(8)
$$C_{V} = \frac{C_{cell}}{V} = \frac{Q}{V \times \Delta U}$$
(9)

where C_{cell} is the capacitance and C_V are the volume specific capacitance of the device, Q is the average charge during electrode charging and discharging, ΔU (V) is the working voltage window of the device. V (cm³) is the volume of the device, including the volumes of the positive and negative electrode pieces, gel electrolyte, and diaphragm. The area, thickness, and volume of the flexible CF-CNF/MWCNT/MnO₂//CNF/MWCNT/RGO/Fe₃O₄ ASC device were 0.5 cm², 606 μ m (Fig. S15), and 0.303 cm³, respectively.

(2) Equations 10-12 were used to calculate the energy density (E, mWh/cm³), equivalent series resistance (ESR, i.e., the internal resistance of the capacitor, Ω), and power density (P, mW/cm³) of the device, respectively.

$$E = \frac{1}{2 \times 3600} C_{\nu} \Delta U^{2}$$
(10)

$$ESR = \frac{iR_{drop}}{2 \times I}$$
(11)

$$P = \frac{\Delta U^{2}}{4 \times ESR \times V}$$
(12)

where C_v is the volume specific capacitance of the device, ΔU (V) is the working voltage window, and iR_{drop} is the voltage drop.

S3. Various graphs and curves



Fig. S1. the stress-strain curves of CNF/MWCNT/RGO/Fe₃O₄ electrode.



Fig. S2. SEM images of (a) RGO-HAs, (b) CNF/RGO-HAs and (c) CNF/MWCNT/ RGO-HAs

substrate material and their corresponding SEM images.



Fig. S3. (a) Areal capacitance and capacitance retention of the RGO CNF/RGO and CNF/CNT/RGO electrodes calculated from the discharge curves as a function of current density, (b) *iR* drop of the RGO, CNF/RGO and CNF/CNT/RGO electrodes measured at different current densities.



Fig. S4. (a) CV curves of the various Fe³⁺ concentrations CNF/MWCNT/ RGO/Fe₃O₄ electrodes Fe³⁺ collected 25 GCD at mV/s, (b) curves of the various concentrations CNF/MWCNT/RGO/Fe₃O₄ electrodes collected at 20 mA/cm², (c) Area specific capacity of CNF/MWCNT/RGO/Fe₃O₄ electrode and the loading of Fe₃O₄ as a function of the concentration of Fe³⁺, (d) Area specific capacity of CNF/MWCNT/RGO/Fe₃O₄ electrode as a function of CV scan rate, (e) Area specific capacity of CNF/MWCNT/RGO/Fe₃O₄ electrode as a function of d different current density, and (f) Nyquist plots of the various Fe³⁺ concentrations CNF/MWCNT/RGO/Fe₃O₄ electrode.



Fig. S5. The sheet resistance of the CNF/MWCNT/RGO/Fe₃O₄ electrode as a function of Fe^{3+} concentration.



Fig. S6. The full XPS spectra of the CNF/MWCNT/RGO/Fe₃O₄ electrode and its corresponding C

1s.



Fig. S7. TGA curves of the CNF/MWCNT/RGO/Fe₃O₄ electrode under air atmosphere.



Fig. S8. CV curves of the (a) CNF/MWCNT/RGO/Fe₃O₄, (b) CNF/ RGO/Fe₃O₄, and (c) RGO/Fe₃O₄ electrodes; GCD curves of the (d) CNF/MWCNT/RGO/Fe₃O₄, (e) CNF/RGO/Fe₃O₄, and (f) RGO/Fe₃O₄ electrodes.



Fig. S9 The Coulomb efficiency as a function of current density for the CNF/MWCNT/RGO/

 Fe_3O_4 electrode.



Fig. S10. SEM images of (a) RGO/Fe_3O_4 , (b) $CNF/RGO/Fe_3O_4$, and (c)

 $CNF/MWCNT/RGO/Fe_3O_4$ electrode materials.



Fig. S11. Nitrogen adsorption–desorption isotherm and the corresponding pore size distribution (inset) of CNF/MWCNT/RGO/Fe₃O₄ electrode.



Fig. S12. (a) CV curves of CF-CNF/MWCNT/MnO₂ and CF-CNF/MWCNT electrodes collected at 25 mV/s, (b) Nyquist plots of CF-CNF/MWCNT/MnO₂ electrode, (c) CV curves of CF-CNF/MWCNT/MnO₂ electrode collected at various scan rates, (c) the area-specific capacitance and capacitance retention rate as a function of scan rate, (e) CV curves of CF-CNF/MWCNT/MnO₂ electrode collected at different current densities of 1–40 mA/cm², and (f) the area-specific capacitance and capacitance retention rate as a function of current density.

To match the CNF/MWCNT/RGO/Fe₃O₄ electrode, the CF-CNF/MWCNT/ MnO₂ electrode must have a mass area ratio of 9.5 mg/cm², with a loaded MnO_2 amount of 2.6 mg/cm². Fig. S8 illustrate the various electrochemical properties of the CF-CNF/MWCNT/MnO₂ electrode in 5 M LiCl solution. Compared to CF-CNF/MWCNT-HAs substrate, the CF-CNF/MWCNT/MnO₂ electrode has a higher current density (Fig. S8a), indicating that its capacitance is mainly derived from the MnO₂. The AC impedance spectrum (Fig. S8b) indicates that the CF-CNF/MWCNT/MnO₂ electrode also exhibited a very small resistance (~3 Ω). However, the CV curves of this electrode are not symmetrical rectangular when the scan rate increasing from 5 to 100 mV/s (Fig. S8c). This may be attributed to existence of a certain interfacial resistance between MnO₂, CNT and CNF in the electrode. Fig. S8e represents the charge-discharge curves of the CF-CNF/MWCNT/MnO₂ electrode at current densities ranging from 1 to 40 mA/cm². These curves are symmetric and triangular with long discharge times, further indicating the good capacitance of the electrode. Fig. S8f illustrates the change in areal specific capacitance of the electrode with current density, based on the chargedischarge curves. The results indicate that at the current density of 1 mA/cm², the areal specific capacitance of the electrode reached 1223 mF/cm² (mass specific capacitance = 470.4 F/g and remained at 686.9 mF/cm^2 (264.2 F/g) at the current density of 40 mA/cm² with a capacitance retention of 56.2%, suggesting it has a good rate capability.



Fig. S13. (a) CV and (b) GCD curves of the CF-CNF/MWCNT/MnO $_2//CNF/MWCNT/$





Fig. S14. photograph of different color LED indicators (3 V) powered by two units of flexible

ASC device connected in series.



Fig. S15. Cross-sectional SEM image of the flexible CF-CNF/MWCNT/MnO_2//

CNF/MWCNT/RGO/Fe₃O₄ solid-state ASC device.