Supporting Information

Flexible Asymmetric Supercapacitors with High Energy and High Power Density in Aqueous Electrolytes

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I. Materials and Methods:

Preparation of RGO/MnO$_2$ binary composite:

Prior to the synthesis of the composite, reduced graphene oxide (RGO) was first prepared by reducing the graphene oxide (synthesized using the modified Hummers method[1]) following the method developed by Li et al.[2] Typically, 18.0 µL of hydrazine (35% in water) and 126 µL of ammonia solution (28% in water) were added to 30 mL of graphene oxide dispersion (at 0.25 mg/mL) in a flask. After vigorous shaking for a few minutes, the flask was put in an oil bath and was kept at 90°C for 1 h. After the solution cooled down to room temperature, the as-synthesized dispersion was subjected to a dialysis process against a ~0.5% ammonia solution for 24 hrs to remove the excess ions prior the growth of MnO$_2$ nanoparticles on RGO.

The RGO/MnO$_2$ binary composite was prepared by a sonochemical co-precipitation method that is similar as used in the synthesis of the fFWNTs (functionalized few-walled carbon nanotubes)/MnO$_2$ composites.[3] Typically, the RGO dispersion obtained in the previous step was first sonicated for 10 min, and then 5 ml of KMnO$_4$ (0.02M) and 5 ml of MnSO$_4$ (0.03M) was added subsequently and the mixed solution was continuously sonicated for 20min. After sonication, the resulting RGO/MnO$_2$ composite suspension was filtered through a filtration membrane (1.2 µm pore size) and washed repeatedly with nanopure water. The filter cake, which is the RGO/MnO$_2$ composite, was then dispersed in 60 ml water.

Synthesis and functionalization of few-walled carbon nanotubes:

Few-walled carbon nanotubes (FWNTs) were prepared by a bimetallic catalysts Co/Mo supported on MgO using the chemical vapor deposition (CVD) method.[4] In the process, methane was used as the carbon source and hydrogen was added with certain ratio to control the methane decomposition rate. In a typical growth experiment, Co/Mo supported MgO catalyst was put into a quartz tube and was flushed with hydrogen while the catalyst was heated to growth temperature. Methane was then introduced. After reacting for desired time (10–30 min), methane flow was turned off and hydrogen flow was turned on while the system is being cooled down.

The as-synthesized FWNTs were first purified with a two-steps process to remove the impurities of amorphous carbon and metallic species. Briefly, the raw materials were put in a tube furnace and then heated up under 300 sccm of the mixed gas of argon and air (ratio 4:1) at 675°C for 30 min to burn away the poorly crystallized carbon. Then the material is refluxed in 6M HCl for 30min to dissolve the catalysts and catalyst support. The FWNTs was collected by vacuum filtration and then dried using the freeze-drying process.

After purification, the FWNTs were functionalized to ensure water solubility [5]. Typically, 10mg of purified FWNT was dispersed in 15ml oleum and the solution was stirred continuously at room temperature for 48 hours. The solution was then heated to 70°C and 5ml of concentrated HNO_3 was slowly added at the rate of 0.3ml/min. The final mixture was kept at 70°C for 2 hours, after which the solution was cooled. The solution was then slowly added to 250ml of nanopure water to dilute the acids and then

filtered, freeze-dried and weighted. Finally, the nanotubes was dispersed in nanopure water to create 0.2 mg/mL dispersion.

Fabrication of the flexible RGO/MnO$_2$/fFWNTs film as the positive electrode: The flexible film was fabricated by the vacuum filtration method. Typically, 20 ml of fFWNTs dispersion and 33 ml of RGO/MnO$_2$ suspension were mixed in a glass vial. The mixed solution was then sonicated for 20min and filtered through a mixed cellulose ester membrane (1.2µm pore size, Millipore). The obtained filter cake was then vacuum dried for 24 hours and a freestanding film will form.

Fabrication of the flexible AC/fFWNTs film as the negative electrode: The flexible film was also fabricated by the vacuum filtration method. Typically, 24 mg of activated carbon (MTI Incorporation, CA) and 30 ml of fFWNTs dispersion were mixed in ethanol. The mixed dispersion was then sonicated for 20 min to ensure close interaction between nanotubes and activated carbon. After soncation, the mixture was filtered through a filtration membrane and the filter cake was also dried under vacuum for 24 hours to form a freestanding film.

Assembly of the asymmetric supercapacitor: The asymmetric supercapacitors were fabricated using the roll-up approach in this study. A schematic illustration of the device is shown in Figure 3a of the main manuscript. To fabricate such devices, the films were first stacked together in the order of separator (Celgard, 2501), flexible AC/CNTs film, another separator and flexible graphene/MnO$_2$/CNTs film. Two platinum wires were used to connect the flexible electrodes to the external circuit. The stacked films were then rolled up around the Pt wires and afterwards a

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narrow piece of carbon tape was used to wrap around the device to hold the rolled

structure. The device was then immersed to 1M Na_2SO_4 for the electrochemical

measurements.

II. Data Analysis

Using the cyclic voltammetry testing data, the specific capacitance was calculated

according to the equation of $C = (\int IdV)/vmV$, where C is the specific capacitance

(F/g), I is the response current, V is the potential window, v is the CV scan rate (mV/s),

and m is the mass of the electrode material.

The specific capacitance of MnO_2 was estimated by subtracting the contribution of

the fFWNTs from the results obtained from our flexible electrode using the equation

below:

$$C_{sp} = \frac{C_{ff} - C_{CNT} * wt\%(CNT)}{wt\%(MnO_2)} \qquad \text{(Equation 1)}$$

where the C_{ff} is the specific capacitance of the flexible electrode, C_{CNT} is the C_{sp} of the

fFWNTs and wt% is the weight percentage of fFWNTs in the electrode. Based on our

measurements, the C_{CNT} at different scan rates of 10, 50, 100, 250 and 500 mV/s are 67,

64, 61, 56 and 48 F/g, respectively.

The specific capacitance of activated carbon was calculated similarly using

Equation 1. In this case the C_{ff} is the capacitance of the flexible AC/fFWNTs film and

the wt% of MnO_2 was replaced by the weight percentage of AC, which is 80%.

Energy density and power density of the assembled asymmetrical supercapacitor

Based on the galvanostatic charge/discharge data, the total capacitance C of the asymmetric supercapacitor was calculated by using

$$C = i/-[\Delta V/\Delta t]$$

where i is the current applied, and $\Delta V/\Delta t$ is the slope of the discharge curve after the iR drop.

Based on the capacitance calculated, the energy density and power density were calculated using equation:

$$E = \frac{CV^2}{2m}$$

where C is the capacitance of the full cell and V is the voltage difference between the voltage after the iR drop at the beginning of discharging and the voltage at the end of discharge, m is the total mass of the electrode material from both electrodes. The power density was calculated using:

$$P = \frac{E}{t}$$

where E is the energy density and t is the corresponding discharge time in hour.

III. Optimization of the positive and negative electrodes for the asymmetric supercapacitor.

As for a full supercapacitor, the balance of the charge flow between the positive electrode and the negative electrode is critical for optimum performance (i.e. $q_+ = q_-$). The charge stored by each electrode depends on its specific capacitance (C_{sp}), the

potential range of the charge/discharge process (ΔE) and the mass of the electrode (m)

following the Equation:

$$q = C_{sp} * \Delta E * m$$

and in order to get equal charge flow ($q_+ = q_-$), the mass ratio between the positive and

negative electrodes need to follow:

$$\frac{m_+}{m_-} = \frac{C_- * \Delta E_-}{C_+ * \Delta E_+}$$

on the basis of the specific capacitance values and potential windows found for the

flexible graphene/MnO2/CNTs electrode and the AC/CNTs, the optimal mass ratio

between these two electrodes was determined to be as 0.65 for the flexible asymmetric

supercapacitor. Prior testing, both electrodes were polarized to 0.0 V vs. the Ag/AgCl

(4M KCl) reference electrode for 30 min.

Supporting Figures
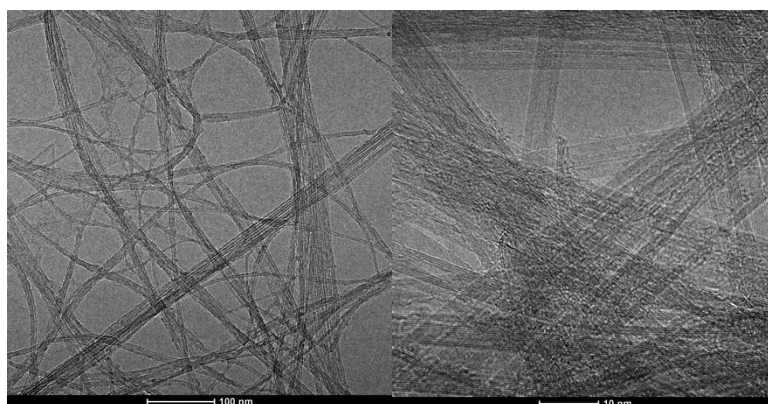
Figure S1: TEM images of the FWNTs. This specific type of carbon nanotubes
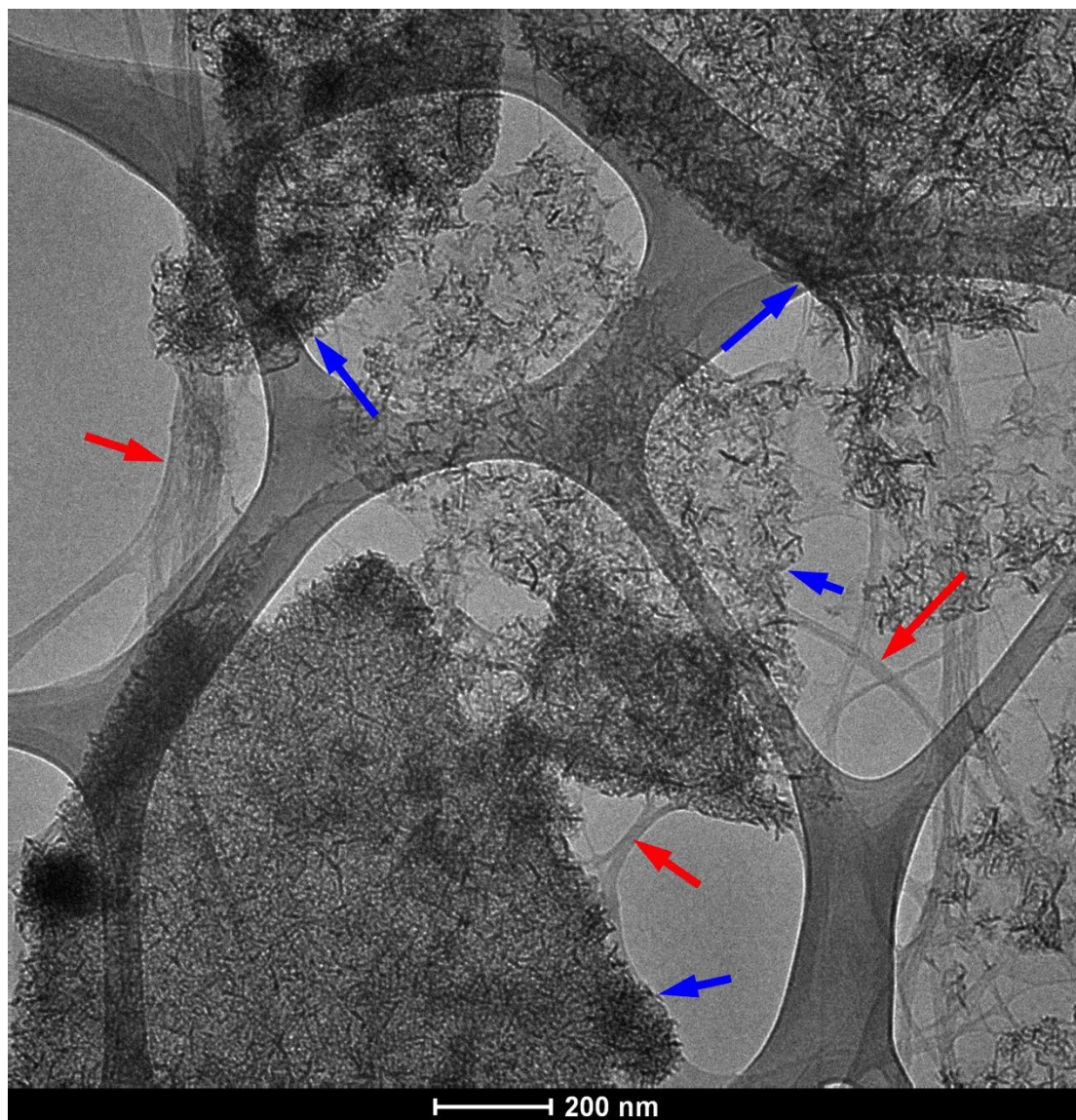
usually has 3~5 walls.

Figure S2: TEM image of the ternary composite formed by mixing graphene/MnO_2 and
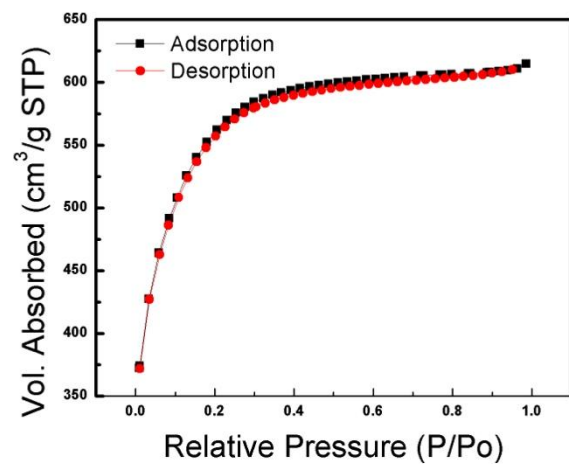
fFWNTs via 20 min sonication.

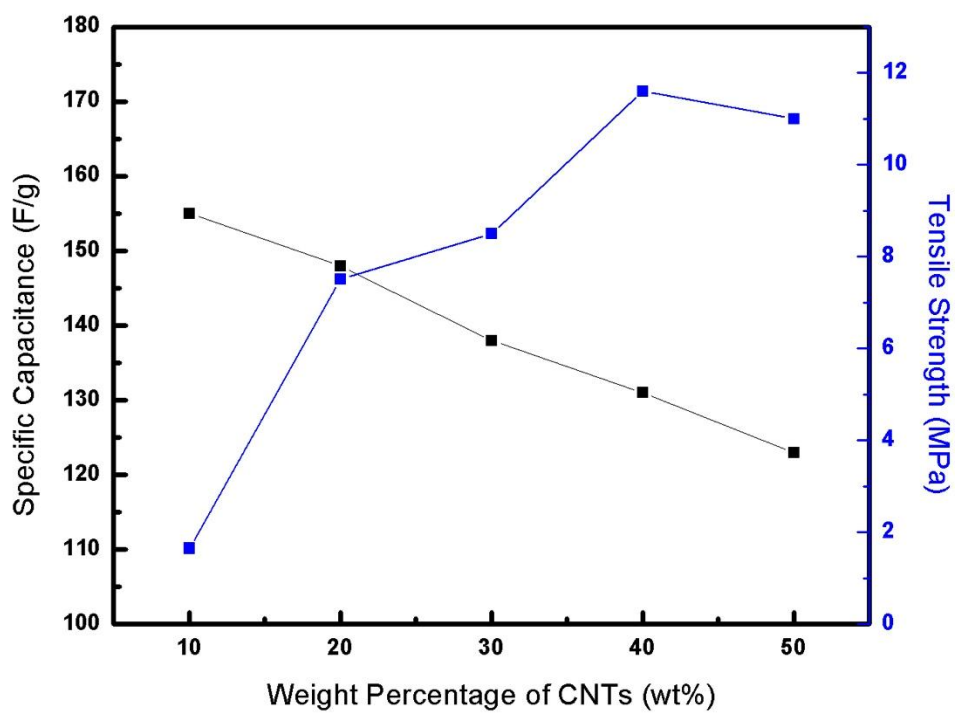Figure S3: Nitrogen adsorption-desorption isotherm for the activated carbon material

measured at 77K.

Figure S4: Compare of the specific capacitance and tensile strength of the flexible

film made with different weight percentage of carbon nanotubes.
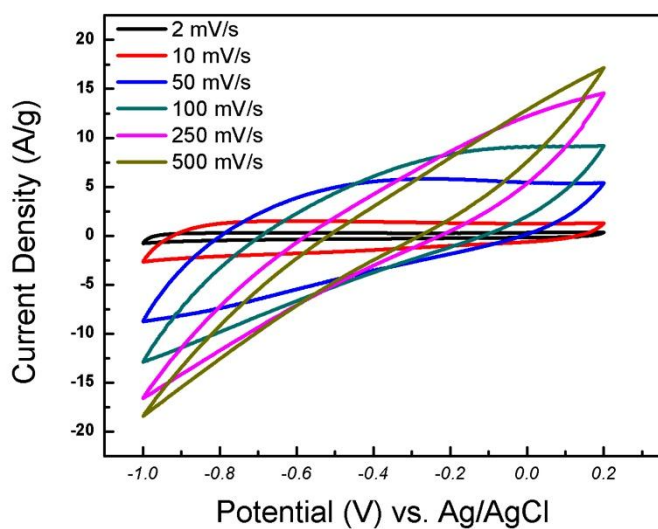
Figure S5: CV curves of the activated carbon electrode fabricated by the conventional

method of mixing AC (70 wt%), carbon black (20 wt%) and PVDF (10 wt%) in NMP

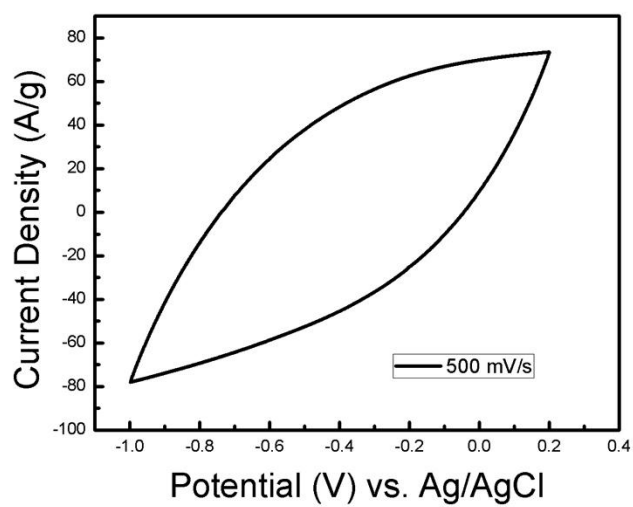and casting the slurry in Ni foam.

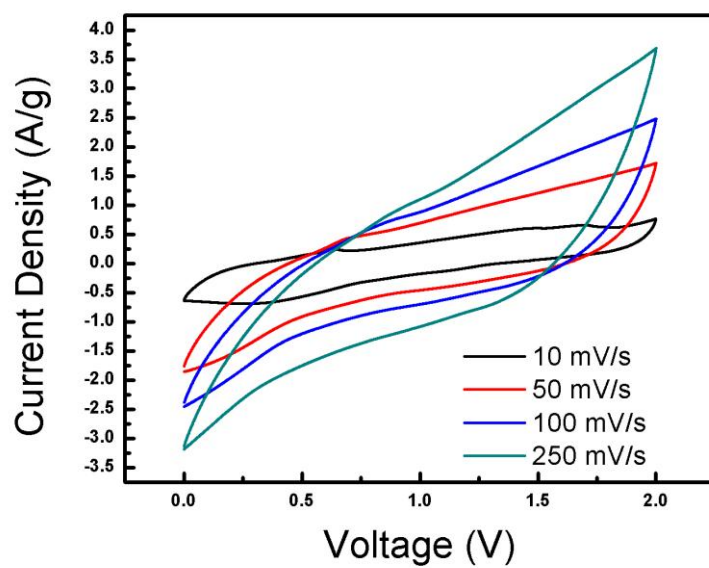Figure S6: CV curve of the flexible AC/CNTs film acquired at 500 mV/s.

Figure S7: Characterization of the asymmetric supercapacitor using electrodes

fabricated by the conventional method. The negative electrode was fabricated as

described in Figure S6 and the positive electrode was fabricated by casting the slurry of

graphene/MnO_2 (70 wt%), carbon black (20 wt%) and PVDF (10 wt%) in Ni foam.

References:

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2. Li, D., Muller, M.B., Gilje, S., Kaner, R.B. & Wallace, G.G. Processable aqueous dispersions of graphene nanosheets. *Nat Nanotechnol* **3**, 101-105 (2008).

3. Hou, Y., Cheng, Y.W., Hobson, T. & Liu, J. Design and Synthesis of Hierarchical MnO(2) Nanospheres/Carbon Nanotubes/Conducting Polymer Ternary Composite for High Performance Electrochemical Electrodes. *Nano Lett* **10**, 2727-2733 (2010).

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5. Brozena, A.H. et al. Outer Wall Selectively Oxidized, Water-Soluble Double-Walled Carbon Nanotubes. *J Am Chem Soc* **132**, 3932-3938 (2010).