

Supporting Information

Synergistic Effects from Graphene and Carbon Nanotubes Enable Flexible and Robust Electrodes for High-Performance Supercapacitors

Yingwen Cheng,^{1,2} Songtao Lu,^{1,2,3} Hongbo Zhang,^{1,2} Chakrapani V. Varanasi,⁴ and
Jie Liu^{1,2,*}

¹ Department of Chemistry, Duke University, Durham, NC, 27705

² Center for the Environmental Implication of NanoTechnology, Duke
University, Durham, NC, 27708

³ Department of Chemistry, Harbin Institute of Technology, Harbin, 150001,
P.R.China

⁴ Army Research Office, Durham, NC 27703

*E-mail: j.liu@duke.edu

1. Materials and Methods:

Synthesis of graphene: The graphene dispersion was made by reducing the graphene oxide synthesized using the modified Hummers method¹. Briefly, the as-synthesized graphene oxide was dispersed in nanopure water and subjected to dialysis to completely remove the residue ions. The suspension was then sonicated for 20 min to ensure complete exfoliation. The reduction of graphene oxide was followed by the method developed by Li et al². 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 then 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 dialysis against a ~0.5% ammonia solution for 24 h to remove the excess ions prior the growth of MnO_2 nanoparticles.

Synthesis of graphene/ MnO_2 composite: The graphene/ MnO_2 composite was prepared by a sonochemical co-precipitation method that is similar as the one that was used to synthesize the f-FWNT/ MnO_2 composites.³ Typically, the graphene dispersion obtained in the previous step was first sonicated for 10min, and then 5ml of KMnO_4 (0.02M) and 5ml of MnSO_4 (0.03M) was slowly added and the mixed solution was sonicated for another 20min. After sonication, the resulting graphene/ MnO_2 composite suspension was filtered through a PTFE membrane (200nm) and washed repeatedly with nanopure water. The filter cake, which is the graphene/ MnO_2 composite, was then dispersed in 60ml water.

Synthesis and functionalization of few-walled carbon nanotubes:

Few-walled carbon nanotubes 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 300sccm of the mixed gas of argon and air (ratio 4:1) at 675°C for 30min 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 solubility⁵. 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 HNO₃ 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 0.2mg/mL dispersion.

Fabrication of the flexible graphene/MnO₂/fFWNTs film: The flexible film was fabricated by the vacuum filtration method. Typically, desired amounts of functionalized fFWNTs dispersion and graphene/MnO₂ suspension were mixed in a glass vial. The amounts varied to control the thickness of the final film (for example, 20 ml of carbon nanotubes dispersion and 33 ml of graphene/MnO₂ suspension were used to make a film with 2.02 mg/cm² areal density). The mixed solution was then sonicated for 20min and filter through a mixed cellulose ester membrane (1.2μm pore size, Millipore). The obtained filter cake was then vacuum dried for 24 hours to get a freestanding film.

2. 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 MnO₂ was estimated by subtracting the contribution of the fFWNTs from the results obtained from the flexible electrodes using the equation below:

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

where the C_{ff} is the C_{sp} of the flexible electrode, C_{CNT} is the C_{sp} of the fFWNTs, $wt\%(CNT)$ is the weight percentage of fFWNTs in the electrode and $wt\%(MnO_2)$ is the weight percentage of MnO₂. 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.

Based on the galvanostatic charge/discharge results, the total capacitance C of the supercapacitor was calculated 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.

3. Characterization of the few-walled carbon nanotubes.

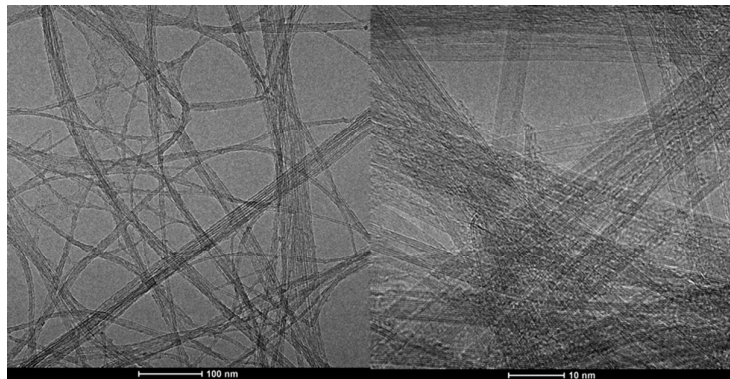


Figure S1: TEM images of the FWNTs. This specific type of carbon nanotubes usually has 3~5 walls.

4. Characterization of the graphene/MnO₂ composite.

This simple chemical co-precipitation process produces uniform MnO₂ coating on the graphene surface, as revealed by the TEM and SEM images (Figure S2a and S2b). The X-ray diffraction pattern acquired from the composite did not show obvious peaks and thus the material is considered to be as amorphous (Figure S2c). The XPS survey scan spectrum (Figure S2d) show only signals from Mn, O and C, free from other contaminates.

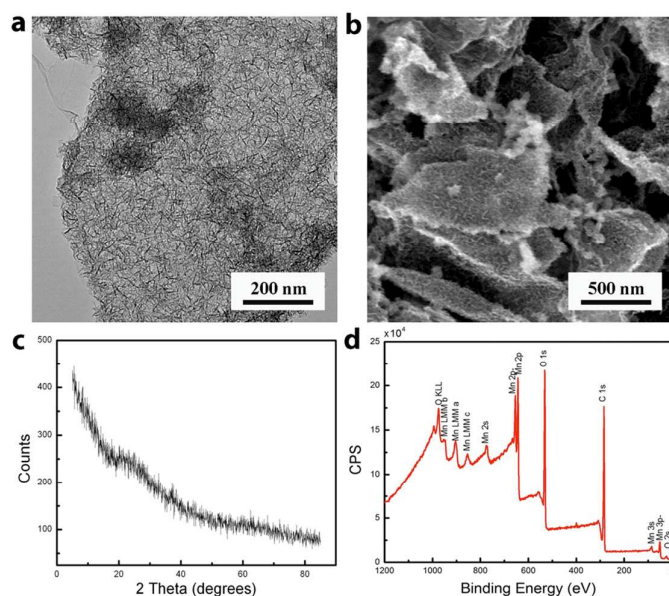


Figure S2. (a) TEM and (b) SEM images; (c) X-ray diffraction pattern and (d) XPS survey scan spectrum of the graphene/MnO₂ composite.

5. Determination of the average oxidation state of Mn in the graphene/MnO₂ composite using XPS measurements.

The average oxidation state of manganese in the graphene/MnO₂ composite was estimated using the core level Mn 3s XPS spectrum.³ This spectrum showed doublet peaks and the separation of these two peaks (ΔE) depends on the Mn oxidation state. Figure S3 presents the variation of ΔE as a function of the manganese oxidation state acquired from standard reference materials. For the synthesized composite, the energy splitting is 4.78 eV (Figure S4) and assuming a linear dependence of ΔE with oxidation state, the average Mn oxidation state in the composite is estimated to be 3.74.

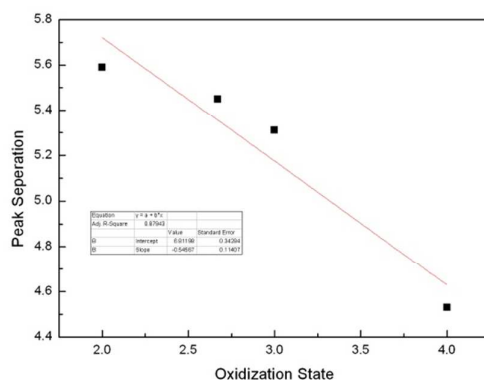


Figure S3: Separation of peak energies ΔE as a function of Mn oxidation state for standard reference material MnO, Mn₂O₃, Mn₃O₄ and MnO₂ (all from sigma-aldrich.)

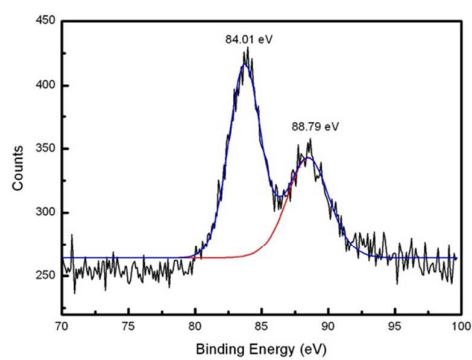


Figure S4: Mn 3s core-level XPS spectrum that used to analysis the average oxidization states.

6. Determination of the weight percentage of MnO₂ in the graphene/MnO₂ composite.

The weight percentage of MnO₂ in the as-synthesized graphene/MnO₂ composite was estimated using a thermogravimetric analysis (TGA) technique at a ramp rate of 5°C/min under airflow. Prior to taking a TGA scan, the composite was heated at 80°C overnight to remove the absorbed water. As can be seen in figure S4, the weight loss is about ~25wt% at temperature up to 800°C, which indicates that the amount of MnO₂ is around 75wt%.

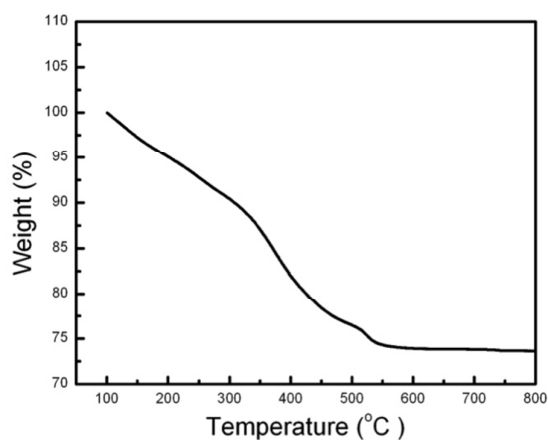


Figure S5: TGA curve of the as-synthesized graphene/MnO₂ composite

7. Digital image of the graphene/MnO₂ composite without carbon nanotubes.

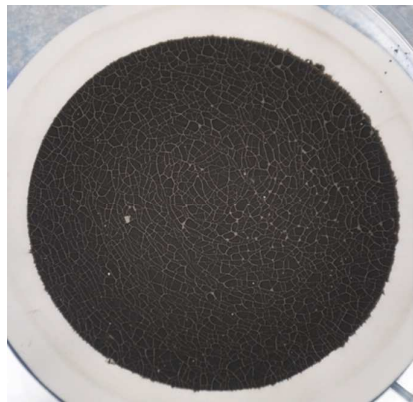


Figure S6: Digital image of the graphene/MnO₂ composite dried on the filter membrane after vacuum filtrating its water dispersion. The composite only form dried powders, no film was observed.

8. Study of the electrochemical properties of the flexible electrode under mechanical deformation.

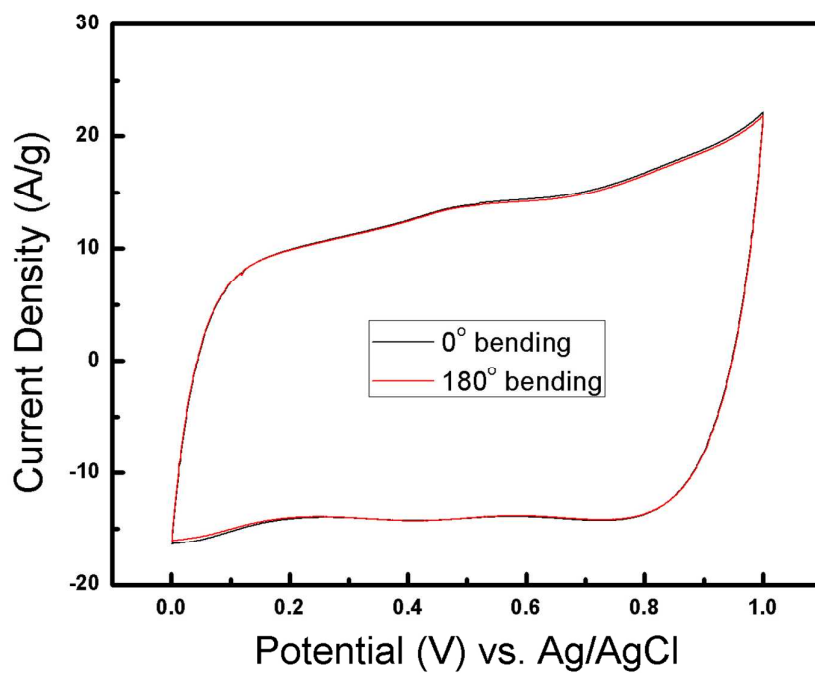


Figure S7: Comparison of the CV curves of the flexible electrode under mechanical deformation acquired at 50 mV/s.

9. Comparison of the electrochemical activity for electrodes made with MnO₂/graphene composite at different areal densities.

The effect of film thickness on the electrochemical performance of the graphene/MnO₂ composite was studied by examining the behavior of electrodes fabricated at different areal densities ($\sim 0.4 \text{ mg/cm}^2$ and $\sim 2 \text{ mg/cm}^2$). Three electrodes were fabricated for each case and the representative results were summarized in Figure S8. As can be seen in this figure, the composite shows nearly ideal supercapacitor behavior at low mass density of 0.4 mg/cm^2 , with all of the CV curves acquired at different scan rates in close to rectangular shape (Fig. S8A). And the specific capacitance drops only by 35% when the scan rate increase from 10 mV/s to 500 mV/s (334 F/g to 216 F/g , Figure S8C). However, at the high areal density of 2.1 mg/cm^2 , the CV curves show significant distortion from ideal rectangular shape when the scan rate is higher than 50 mV/s (Fig. S8B). In the mean time, the specific capacitance of the MnO₂ also fades rapidly at increased scan rates. In fact, MnO₂ lost $\sim 90\%$ of its available capacitance at 500 mV/s , compared with 10 mV/s (from 288 F/g to 30 F/g , Fig. S8C). These results demonstrated that the electrode thickness has a significant effect on the performance of the graphene/MnO₂ composite. We believe that this is because of the limited conductivity in the composite that originates from the isolating MnO₂ coating on graphene. (See main manuscript for detailed discussion)

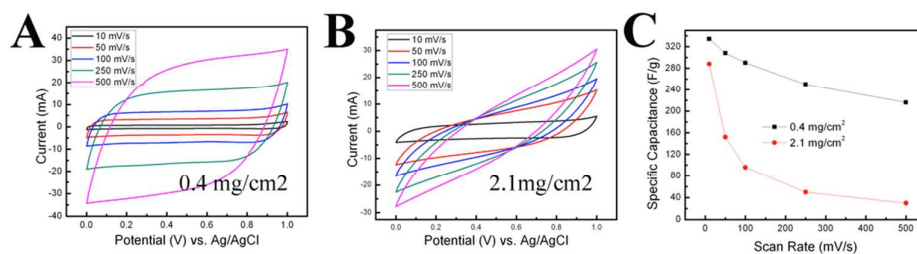


Figure S8: Representative CV curves for the electrodes made with the MnO₂/graphene composite at different areal densities (A) 0.4 and (B) 2.1 mg/cm². (C) Comparison of the specific capacitance of MnO₂ in these two electrodes at different scan rates.

10. Self-discharge of the fabricated full cell.

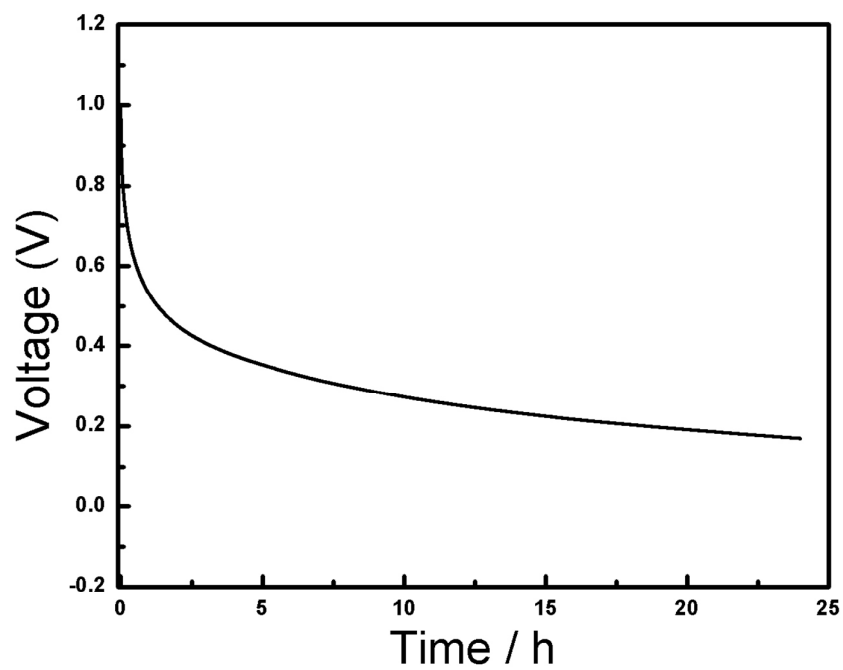


Figure S9: Self-discharge curve for the fabricated flexible symmetrical supercapacitor.

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