The Self-Assembly of Shape Controlled Functionalized Graphene/MnO_2 Composites for Supercapacitors

Xiaomiao Feng,*[1] Ningna Chen,[1] Yu Zhang, Zhenzhen Yan, Xingfen Liu, Yanwen Ma,* Qingming Shen, Lianhui Wang, Wei Huang

Key Laboratory for Organic Electronics & Information Displays, Institute of Advanced Materials, School of Materials Science & Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210046, China.

E-mail: iamxmfeng@njupt.edu.cn; iamywma@njupt.edu.cn

1. The dispersibility of graphene and functionalized graphene

Fig.S1 exhibits the digital photograph of graphene (a) and functionalized graphene (b) dissolving in 10 mL of deionized water. As can be seen from the figure, the dispersibility of functionalized graphene is much better than that of graphene without modification under the same condition. The results show that graphene was functionalized by PDDA successfully.

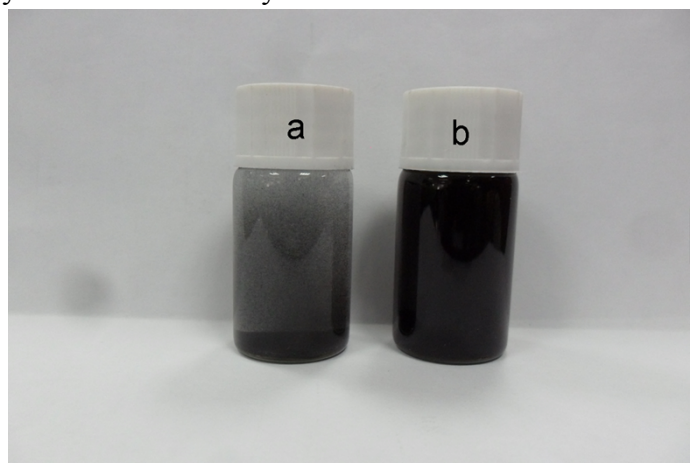


Fig.S1 Photograph of graphene (a) and functionalized graphene (b).

2. The electrochemical performances of different graphene/MnO_2 composites from electrostatic interactions and only mechanical mixture

To evaluate the electrochemical performances of different graphene/MnO_2 composites from electrostatic interactions and only mechanical mixture, cyclic voltammetry (CV) and galvanostatic charge/discharge were employed. As shown in Fig.S2, it can be seen apparently that FG-f-MnO_2 from electrostatic interactions (a) shows larger enclosed area than that of the compsite obtained by mechanical mixture (b) in Fig.S2 (A). The specific capacitances of FG-f-MnO_2 from electrostatic interactions (a) and mechanical mixture (b) are 206 and 25 F g^{-1} at a scan rate of 100 mV s^{-1}, respectively. The galvanostatic charge/discharge curves of at 1.0 A g^{-1} are shown in Fig.S2 (B). The specific capacitances of FG-f-MnO_2 from electrostatic interactions (a) and mechanical mixture (b) are 408 and 33 F g^{-1}, respectively. As shown in Fig.S2 (C) and (D), the specific capacitances of FG-w-MnO_2 from electrostatic interactions (Ca) and mechanical mixture (Cb) are 136 and 16 F g^{-1} at a scan rate of 100 mV s^{-1} and the capacitances of FG-w-MnO_2 from electrostatic

interactions (Da) and mechanical mixture (Db) are 310 and 23 F g^{-1} at 1.0 A g^{-1}, respectively. These results showed that the capacitive properties of different graphene/MnO_2 composites from electrostatic interactions were far superior to that graphene/MnO_2 obtained by only mechanical mixture. From the results, we can see that the specific capacitances from CV data are much smaller than those from GCD data. The possible reasons may be as follows:

Fundamentally, the calculate formulas are different. From the cyclic voltammogram curve, the specific capacitance can be calculated as:

$$C_g = (\int IdV)/(m\ Vv) \qquad (1)$$

Where I represents the response current density (A/g), V is the potential window (V), v is the potential scan rate (mV s^{-1}), and m is the mass of the active material in the electrode (g). From the charge/discharge curve, the specific capacitance can be calculated as: [1]

$$C_{spec} = (I \times t)/(\Delta V \times m) \qquad (2)$$

Where I is the discharge current, m is the electrode mass, t is the discharge time, and ΔV is the voltage range.

The voltage is varied in cyclic voltammetry and the current changes with response to time. However, charge/discharge usually conducted at a constant current, and consequently voltage change. The galvanostatic charge/discharge is more appropriate to reflect the essential characteristics of the active material and present larger capacitance than cyclic voltammetry.

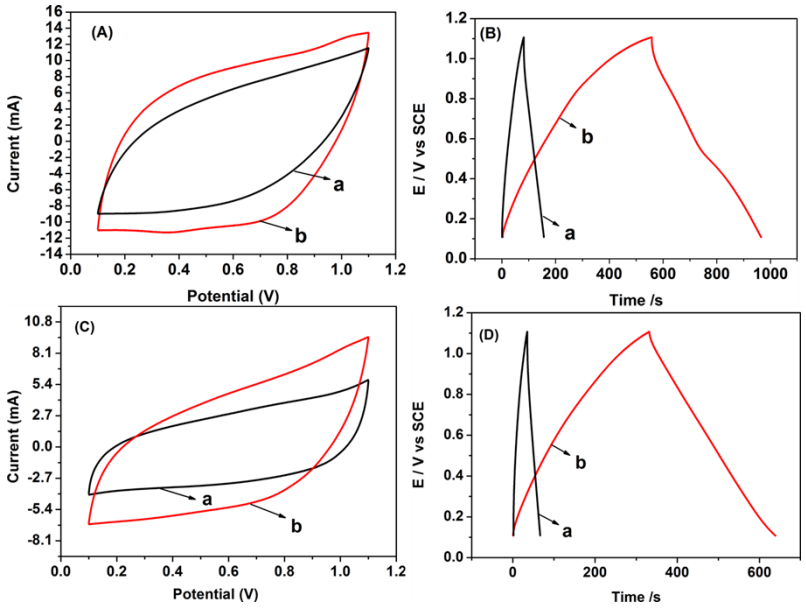


Fig.S2 (A) and (C) Cyclic voltammograms of the graphene/MnO_2 obtained by mechanical mixture (Aa and Ca), electrostatic interactions (Ab) of FG-f-MnO_2 and FG-w-MnO_2 (Cb) at 100 mV s^{-1} scan rate; (B) and (D) Galvanostatic charge/discharge curves of the graphene/MnO_2 obtained by mechanical mixture (Ba and Da), electrostatic interactions (Bb) of FG-f-MnO_2 and FG-w-MnO_2 (Db)at current density of 1.0 A g^{-1} with potential windows of 0.1-1.1 V in 1 M Na_2SO_4.

3. EIS data

An EIS was employed in order to study the conductivities of samples. Fig.S3 depicts the impedance spectra of graphene, MnO_2 nanowire, MnO_2 flowerlike nanosphere, FG-w-MnO_2, and FG-f-MnO_2 electrodes recorded from 0.01 to 100 kHz. The Nyquist plots of MnO_2 nanowire, MnO_2 flower-like nanosphere, FG-w-MnO_2, and FG-f-MnO_2 exhibit a semicircle over the high frequency region. The interfacial charge-transfer resistance was measured by fitting the Nyquist data with an equivalent circuit similar. The interfacial resistance of individual graphene, MnO_2 nanowire, and MnO_2 flowerlike nanosphere was 1.36, 165, and 149 Ω, respectively. After the combination graphene with MnO_2, the resistance of FG-w-MnO_2 and FG-f-MnO_2 was 1.95 and 1.85Ω, respectively, this effectively proved that the conductivities of the both composites were increased.

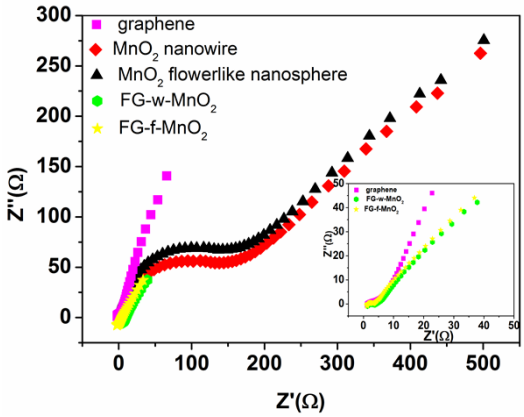


Fig.S3 Nyquist plots of graphene, MnO_2 nanowire, MnO_2 flowerlike nanosphere, FG-w-MnO_2, .and FG-f-MnO_2 electrodes. Insets: the high-frequency parts of graphene, FG-w-MnO_2, and FG-f-MnO_2.

4. Optimal composition of the graphene in the composite materials

The experiments with different ratios of 1:4, 1:3, and 2:3 between graphene and MnO_2 have been studied in the revised manuscript. The specific capacitance was 64, 206 and 91 F g^{-1} at the scan rates of 100 mV s^{-1}, respectively. It is obvious that the ratio of 1:3 exhibited the maximum specific capacitance value indicating that under this condition. The reason might be due to that the high conductivity of graphene and pseudocapacitance of MnO_2 could be achieved the best consequents of synergistic effect at this molar ratio.

5. Ragone chart

In order to compare the performances of FG-f-MnO_2, the Ragone chart, which plots power density versus energy density, is shown in Fig.S3. For high-performance of supercapacitors, the high energy and power densities are expected. Fig.S3 shows Ragone plots of FG-f-MnO_2 at various current densities. The FG-f-MnO_2 delivers a high energy density of 51 Wh/kg at a power density of 500W/kg and a specific capacitance of 408 F/g, demonstrating the excellent capability of synthetic composites as power supply components in supercapacitor.

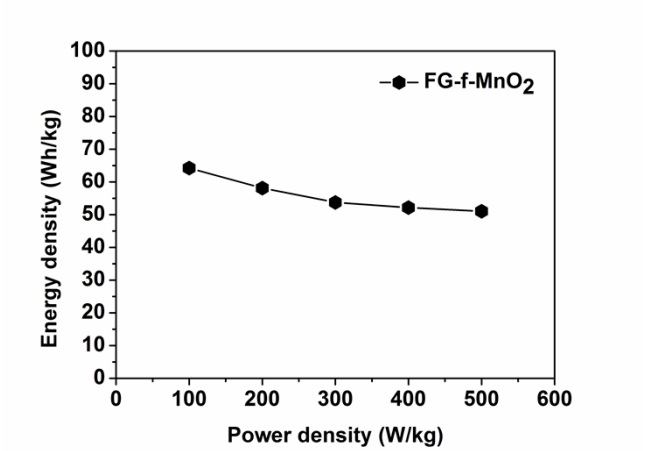
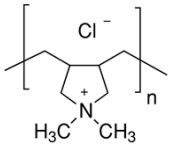


Fig.S4 Ragone plots (energy density vs power density) of FG-f-MnO_2

6. Zeta Potential data

The zeta potential measurement is performed by immersing the two electrodes in a cuvette consisting of the sample. If charged, the particles in the electric field will move with a specific velocity across the field lines toward the oppositely charged electrode. It can be seen from Fig.S4 clearly, PDDA functionalized graphene (a) is positively charged and the MnO_2 (b) is negatively charged which is in agreement with the reported work. [1, 2]

The chemical structure of the PDDA is provided below in structural formula (1):



(1)

wherein n is an integer representing the number of monomer units in the polymer chain. PDDA is a large polycationic homopolymer that exhibits a strong net positive charge. The strong net positive charge on the PDDA molecule is produced by side chain dimethylated ammonium groups on the residues all along the polymer. As mentioned in the literatures,[3, 4] taking advantage of the positively charged of PDDA, it can be modified onto the graphene surface via electrostatic adsorption to form the negative charged functionalized graphene.

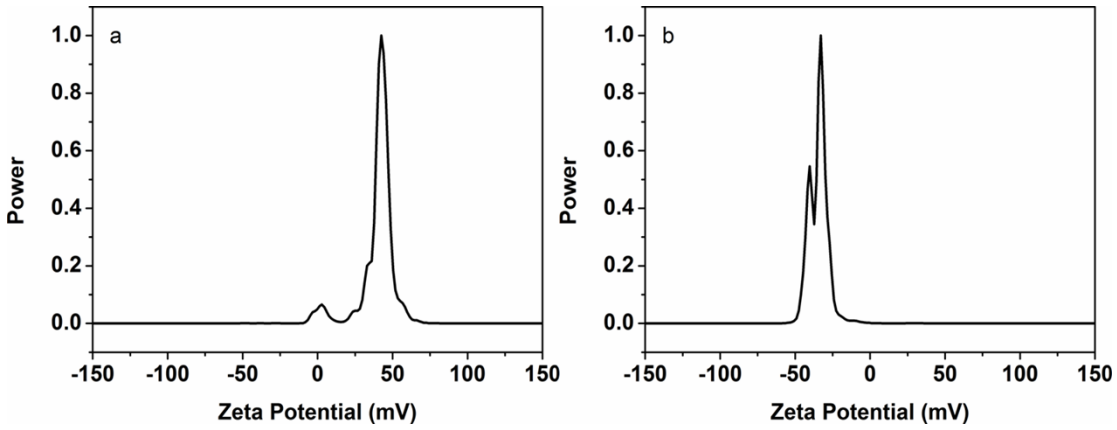


Fig.S5 Zeta Potential Power spectra of PDDA functionalized graphene (a) and MnO_2 flowerlike nanospheres (b)

References

1 J.-L. Zhou, L. Yu, M. Sun, S.-Y. Yang, F. Ye, J. He, and Z.-F Hao, *Ind. Eng. Chem. Res.,* 2013, 52, 9586−9593.

2Y.-X. Yuan, S.-F. Wu, F. Shu, and Z.-H. Liu, *Chem. Commun.,* 2014, 50, 1095.

3 D.-L. Wang, S.-F. Lu, and S.-P. Jiang, *Chem. Commun.,* 2010, 46, 2058–2060

4 Y.-Y. Yin, M. Chen, S.-X. Zhou, and L.-M. Wu, *J. Mater. Chem.*, 2012,22, 11245-11251