The Self-Assembly of Shape Controlled Functionalized Graphene/MnO₂
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).](image)

2. The electrochemical performances of different graphene/MnO₂ composites from electrostatic interactions and only mechanical mixture
To evaluate the electrochemical performances of different graphene/MnO₂ 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-MnO₂ from electrostatic interactions (a) shows larger enclosed area than that of the composite obtained by mechanical mixture (b) in Fig.S2 (A). The specific capacitances of FG-f-MnO₂ 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-MnO₂ 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-MnO₂ 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-MnO₂ 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:

\[
C_g = \frac{\int I dV}{m V v}
\]  
(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:

\[
C_{spec} = \frac{(I \times t)}{(\Delta V \times m)}
\]  
(2)

Where \(I\) is the discharge current, \(m\) is the electrode mass, \(t\) is the discharge time, and \(\Delta V\) 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\(_2\)SO\(_4\).
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 1.85 Ω, respectively, this effectively proved that the conductivities of the both composites were increased.

![Nyquist plot diagram](image)

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.
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):

\[
\text{PDDA} = \overset{\text{N} \text{Cl}^-}{\overset{\text{H}_3\text{C}^- \text{N} \text{CH}_3}{\overset{\text{C}}{\text{C}}}}_n
\]

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