Preparation of Graphene Oxide/Pristine Graphene/Polyaniline Ternary Composites through a Simple Method and Application to Supercapacitor

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Abstract. A new graphene oxide/pristine graphene/polyaniline (GPP) composite is successfully prepared. Transmission electron microscope, Scanning electron microscope, Raman spectroscopy and X-ray photoelectron spectroscopy were used to characterize the electronic structure and morphology of GPP composites. The specific capacitance of GPP is 1231.8 F g\(^{-1}\) and 598.1 F g\(^{-1}\) in a three-electrode system and a symmetric supercapacitor at 1.0 A g\(^{-1}\). The specific capacitance of GPP maintains about 71.2% and 55.1% after 10000 cycles in the three-electrode and two-electrode systems, respectively.

1. Introduction
The composite materials of supercapacitor such as carbon-conductive polymer or carbon-metal oxide start a new upsurge. Previously, we studied the synthesis of composed of graphene oxide (GO) and pristine graphene (PG) by a co-exfoliation method. However, compared with the performance of pseudocapacitive materials, the binary composite material still have comparatively low specific capacitance and energy density. Found polyaniline (PANI) is particularly valuable due to its outstanding performance, for instance, high electrochemical performance, low cost, and good stability [1-3].

In this paper, a graphite oxide/pristine graphene/polyaniline (GPP) was manufactured by in situ polymerization of aniline to polyaniline upon the PG/GO (GP) composite. Here, a sandwich type construction was also used to assemble the GPP into symmetric supercapacitor. This assembly method can be considered as an efficient method of increasing the specific capacitance.

2. Experimental
2.1. Sample Preparation
12 mg GP mixed with 90 mL water and sonicated using an ultrasonic cell disruptor at 300 W and 20 kHz. 49.2 mg of aniline and 4 mL of 1 M HCl aqueous solution were quickly mixed, and it was mixed with the prepared GP [4]. For comparison, the reaction time of GPP varied as 1, 2, 4, 6, and 8 h, the resulting composites were designated as GPP1, GPP2, GPP4, GPP6, and GPP8, respectively.

2.2. Characterization
Through calculation, the mass of the GPP film is 0.01 mg on the glassy carbon electrode. The dried glassy carbon electrode, Pt ring, and Ag/AgCl were connected to the working electrode, the counter electrode, and the reference electrode. Cyclic voltammograms (CV) tests and galvanostatic charge/discharge (GCD) curves were tested within 0.0 to 0.7 V. The GPP composite material is applied
to two FTO electrodes to assemble a two-electrode system as shown in Figure 1. The specific capacitances of the GPP composites were calculated from CV \( (C_{s-1}, \text{ F g}^{-1}) \), as shown in the Eq. (1):

\[
C_{s-1} = \frac{1}{m v(E_2 - E_1)} \int_{E_1}^{E_2} I(E)dE
\]  

(1)

The current at a given potential \( V \) is named \( I \), the potential window is named \( E_2-E_1 \), the scan rate is named \( v \), and the total mass is named \( m \).

The specific capacitances of the GPP composites were calculated from GCD \( (C_{s-2}, \text{ F g}^{-1}) \), as shown in the Eq. (2):

\[
C_{s-2} = \frac{I \Delta t}{m \Delta E}
\]  

(2)

The discharge current is named \( I \), the total mass is named \( m \), the discharge time is named \( \Delta t \), and the potential window is named \( \Delta E \).

In a symmetric supercapacitor, the specific capacitances of the GPP composites were calculated from CV \( (C_{s-3}, \text{ F g}^{-1}) \), as shown in the Eq. (3):

\[
C_{s-3} = \frac{4}{m v (V_2-V_1)} \int_{V_1}^{V_2} I(V)dV
\]  

(3)

The current at a given potential \( V \) is named \( I \), the potential window is named \( V_2-V_1 \), the scan rate is named \( v \), and the total mass is named \( m \).

The specific capacitances of the GPP composites were calculated from GCD \( (C_{s-4}, \text{ F g}^{-1}) \), as shown in the Eq. (4):

\[
C_{s-4} = \frac{4I \Delta t}{m \Delta V}
\]  

(4)

The discharge current is named \( I \), the total mass is named \( m \), the discharge time is named \( \Delta t \), and the potential window is named \( \Delta V \).

The energy density \( (E, \text{ W h kg}^{-1}) \) and power density \( (P, \text{ W kg}^{-1}) \) of symmetric supercapacitor was calculated from Eq. (5) and Eq. (6):

\[
E = \frac{C_{s-4} \Delta V^2}{8 \times 3.6}
\]  

(5)

\[
P = \frac{3600E}{\Delta t}
\]  

(6)

3. Results and Discussion

Figure 2 displays the TEM of GP and GPP composites under different reaction time. The image shows that PANI has been evenly distributed on the GP, which diameter is about 50 nm (Figure 2b-f). But unlike the image in Figure 2a, the GPP image shows a small PG pasted on a large-sized GO sheet and indicates PANI nanoparticle array upon the GP sheet.

Figure 3 exhibits the SEM images of GP and GPP composites. Figure 3a displays the SEM image of GP evidences that the smaller PG sheets repaired the larger wrinkled GO sheets. The SEM image of GPP1 in Figure 3c exhibits morphology of the GO. As shown in the images of GPP2, GPP4, GPP6 and GPP8 in Figures 3c-f, the folds of GO got into unclear as the dose of PANI components increases. Surprisingly, without separate PANI were discovered in GPP’s TEM or SEM, indicating that a good structure stability of GPP.
Figure 1. Schematic diagram of preparation process of the GPP composite.

Figure 2. The TEM of (a) GP, (b) GPP1, (c) GPP2, (d) GPP4, (e) GPP6, and (f) GPP8 composites.

Figure 3. The SEM of (a) GP, (b) GPP1, (c) GPP2, (d) GPP4, (e) GPP6, and (f) GPP8 composites.

Figure 4. (a) Raman spectra of PANI, GP, and GPP1 to GPP8 composites. (b) XPS spectra of GPP8 and GP composites.
The Raman spectra of PANI, GP and different GPP composites are shown in Figure 4a. The Raman spectrum of PANI shows the obvious peaks in the figure, which indicates the characteristic peak of PANI. The Raman spectrum of GP is shown that D and G bands are affected by sp²-hybridized carbon and disordered graphite structure [5]. The characteristic peaks of GP and PANI are included in all GPP composites. It shows that the ternary compound has been successfully prepared. The XPS of GP and GPP8 is exhibited in Figure 4b. It can be seen from the figure that the C/O ratio of GPP8 is lower than that of GP, which is attributed to PANI and GP being successfully combined together.

Figure 5 displays CV (a), GCD (b), $C_{s1}$ (c), and $C_{s2}$ (d) of the GPP1 to GPP8 composites under the various reaction time. The $C_{s1}$ and $C_{s2}$ calculated based on Figure 5a and 5b are shown in Figure 5c and 5d, respectively. Both $C_{s1}$ and $C_{s2}$ of the GPP composites increase with the increase of reaction time. Figure 6 depicts CV (a) and GCD (b) of the GPP8 composite, and $C_{s1}$ and $C_{s2}$ (d) of the GPP1 to GPP8 composites. Based on the results shown in Figure 5c, the $C_{s1}$ of GPP8 is still 1156.7 and 903.3 F g⁻¹ at a scan rate of 10 and 300 mV s⁻¹, respectively. The $C_{s2}$ of GPP8 composite is 1311.6 and 976.9 F g⁻¹ at 0.5 A g⁻¹ and 10 A g⁻¹, which are more excellent than those of GPP composites in Figure 5d.

The CV and GCD curves of GPP8 composite are exhibited in Figure 7a and 7b. The $C_{s3}$ and $C_{s4}$ of this symmetric supercapacitor were 582.1 and 635.3 F g⁻¹, respectively. The specific capacitance of a symmetric supercapacitor was lower than that in a three-electrode system, and with the increase in current density or scan rate, the specific capacitance decreases faster, which is the influence of the capacitor configuration and electrodes.

The cycling stability of GPP8 is also tested. As shown in Figure 8, the $C_{s1}$ of GPP8 composites remain 71% and 55% after 10000 cycles in the three electrode system and symmetric supercapacitor. Figure 9 shows the power and energy densities of GPP8. The energy density of the PG/GO₁₀:₁ reaches 10.8 and 14.1 W h kg⁻¹ at a power density of 841.3 and 52.4 W kg⁻¹.
Figure 6. CV (a) and GCD (b) of GPP8, $C_{s1}$ (c), and $C_{s2}$ (d) of the GPP1 to GPP8 composites in the three-electrode system.

4. Conclusions
In summary, a facile way has been designed to synthesize GPP. Through electrochemical tests, it was found that GPP composites exhibit excellent electrochemical performance. GPP composite exhibit the specific capacitance of 1156.7 and 1311.6 F g$^{-1}$ at 10 mV s$^{-1}$ and 0.5 A g$^{-1}$, respectively. The specific capacitance still remains 903.3 and 976.9 F g$^{-1}$ at 300 mV s$^{-1}$ and 10 A g$^{-1}$.

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6. References
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