Synthesis of Graphene Hydrogel and Graphene Oxide/Polyaniline Composites for Asymmetric Supercapacitor

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Abstract. As a kind of new carbon materials, graphene has excellent performances such as superior conductivity, high specific surface area (2675 m$^2$ g$^{-1}$), and high cycle life. But graphene sheets are easily restacked by van der Waals interactions during the processes of preparation, storage, and application of them, which can loss ultrahigh specific surface area. The restacking of graphene sheets could be prevented by constructing graphene hydrogel (GH) or graphene composite. In this work, GH was prepared by a one-step hydrothermal synthesis reaction and glucose is used as a reducing agent, while graphene oxide/polyaniline (GP) composites was prepared by coating polyaniline on GO through in situ chemical polymerization of aniline. Then an asymmetric supercapacitor (GH/GP) was further assembled, where GH and GP are the positive and negative electrodes, respectively. The electrochemical properties of GH, GP, and GH/GP are studied using voltammetry and galvanostatic charge/discharge. The consequences indicate that the energy density of GH/GP reaches 5.6 W h kg$^{-1}$ at power density of 226.5 W kg$^{-1}$ and 3.1 W h kg$^{-1}$ at energy density of 8446.2 W kg$^{-1}$.

1. Introduction

As novel power storage and energy storage device, supercapacitor with long cycle life, high charge and discharge rates, and good operational safety, have recently attracted much attention [1]. The most used materials for supercapacitors include carbon materials, metal oxides/hydroxides, and conductive polymers. Among them, all-carbon materials such as graphene, active carbon, carbon nanotube, and carbon fiber, have high power density and superior cyclic stability, due to rapid ion absorption and desorption, which is called electric double layer capacitor (EDLC). However, this kind of rapid process only occurs at the interface of the materials, so the capacitance of EDLC is very limited (usually below 200 F g$^{-1}$) [2]. In addition, metal oxides/hydroxides, such as RuO$_2$, MnO$_2$, and nickel manganese double hydroxide, and conductive polymers, such as polyaniline, polypyrrole, and polythiophene, usually exhibit higher capacitance than carbon materials, due to redox reactions, which is called faradic pseudocapacitor (PC), but it also limits their charge and discharge efficiency at high rates [3]. Therefore, composite materials such as carbon-metal oxide/hydroxide or carbon-conductive polymer have become the research hotspot, in order to obtain high-performance electrodes with high energy or power density.

In our work, a graphene/polyaniline composite (GP) was composited through in situ polymerization of aniline to polyaniline (PANI) into the graphene oxide (GO). On the other hand, the preparation of 3D graphene hydrogel (GH) by hydrothermal method using glucose as a reducing agent is a simple method. In addition, an asymmetric supercapacitor was also assembled with GH and GP as anode and cathode materials respectively, using a sandwich type construction. This design is considered to be an effective and simple method to improve electrochemical performance, because the
voltage of the supercapacitor can be amplified by combining two different working potential electrode materials. GH and GP composites have excellent electrochemical properties as electrode materials for supercapacitors, which indicated that they have great potential in the field of energy storage.

2. Experimental

2.1. Reagents
Graphite powder (1200 mesh) was purchased from Aladdin. H$_2$SO$_4$ (98%), glucose, hydrochloric acid (HCl), and potassium chloride (KCl) were from Sinopharm Chemical Reagent Co., Ltd. All of these chemicals are analytical grade.

2.2. Sample Preparation
GO was first prepared through a modified Hummer’s method [4], then dispersed in water via sonication for 30 min in order to prepare GO dispersion with a concentration of 2 mg mL$^{-1}$. 30 mL of this GO dispersion was mixed with 60 mg glucose by sonication for 10 min. Then, the mixture was transferred into a Teflon-lined stainless steel reactor and hydrothermally treated at 120 °C for 12 h. Afterwards, the reactor was naturally cooled at room temperature and the cylinder GH was taken out carefully with tweezers, being purified by dialysis in deionized water for 24 h. The dried GH was obtained by freeze-drying for 12 h (20 Pa, -55 °C) in order to calculate the mass fraction of active material ($W_a$) according to Eq. (1):

$$W_a = \frac{W_d}{W_t} \times 100\%$$

Where $W_t$ and $W_d$ are the weight of electrode material. GP composite was synthesized using in situ polymerization of aniline into PANI on GO within an acid condition. Generally, a uniform GO dispersion was prepared with 24 mg GO and 180 mL distilled water through sonication for 10 min. The purified aniline was dissolved in 8.2 mL 1 M HCl and added into the GO dispersion quickly (the mass ratio of aniline to GO is 4.1:1), and then the mixture was stirred for 30 min. Afterward, ammonium persulfate (APS), with a mass ratio to aniline of 3.4:1, was dissolved in 8.2 mL distilled water and added into the above reaction mixture rapidly. The obtained mixture was stirring vigorously within an ice-water bath for 8 h. Finally, the GP composite was collected by filtration and repeatedly washed by water until the filtrate was nearly neutral, followed by re-dispersed in water.

2.3. Characterization
Electrochemical measurements of experiment were performed on a CHI 660c electrochemical workstation. The electrochemical properties of GH and GP were measured by cyclic voltammograms (CV) and galvanostatic charge-discharge (GCD). In a three-electrode system, the working electrode was the samples coated nickel foam, the reference electrode was Hg/HgO electrode, and the counter electrode was a platinum ring. GH and GP were working electrodes fabricated process: a slice of GH was cut and pressed onto a nickel foam sheet at 2 MPa for 30 s. The mass of active material was about 2 mg. CV and GCD were measured in the potential of -1.0 to 0 V at 10, 25, 50, 100, 150, 200, 250, and 300 mV s$^{-1}$ or 0.5, 1, 2, 3, 4, 6, and 10 A g$^{-1}$. 5.0 μL of the GP solution was added dropwise onto a glassy carbon electrode and dried at normal temperature. Then, the dried glassy carbon electrode, Ag/AgCl, and Pt ring were the working electrode, reference electrode, and counter electrode, respectively. And aqueous solution of 2.0 M H$_2$SO$_4$ was used as the electrolyte. The CV test and the GCD curve test were performed between 0 and 0.7 V. In addition, two slices of GH and GP were used as electrodes and a sandwich type construction (glass sheet/Pt foil/GH/separator/GP/FTO) was used to fabricate an asymmetric supercapacitor with filter paper soaked with 5.0 M KOH as the separator in figure 1. CV and GCD curves of the GH/GP were measured in the potential of -1 to 0.7 V at different scan rates or current densities.
The specific capacitance of GH is calculated by the discharge curve of CV \((C_{s1}, \text{F g}^{-1})\) in the two-electrode system according to Eq. (2):

\[
C_{s1} = \frac{4}{mv(V_2 - V_1)} \int_{V_1}^{V_2} I(V) dV
\]

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

The specific capacitance of GH is calculated by the discharge curve of GCD \((C_{s2}, \text{F g}^{-1})\) in the two-electrode system according to Eq. (3):

\[
C_{s2} = \frac{4I\Delta t}{m\Delta V}
\]

where \(I\) is the discharge current, \(\Delta t\) is the discharge time, \(m\) is the total mass of active material of both electrodes, and \(\Delta V\) is the potential window.

The specific capacitance of GH is calculated by the discharge curve of CV \((C_{s3}, \text{F g}^{-1})\) in a three-electrode system according to Eq. (4):

\[
C_{s3} = \frac{1}{mv(E_2 - E_1)} \int_{E_1}^{E_2} I(E) dE
\]

The specific capacitance of GH is calculated by the discharge curve of GCD \((C_{s4}, \text{F g}^{-1})\) in a three-electrode system according to Eq. (5):

\[
C_{s4} = \frac{I\Delta t}{m\Delta E}
\]

The energy density \((E, \text{W h kg}^{-1})\) and power density \((P, \text{W kg}^{-1})\) of a GH//GP asymmetric supercapacitor can be estimated according to Eq. (6) and Eq. (7):

\[
E = \frac{C_{s2}\Delta V^2}{8}
\]

\[
P = \frac{E}{\Delta t}
\]
3. Results and Discussion

3.1. The Morphology of GH and GP
The SEM photos of GH and GP are shown figure 2a and 2b. The SEM image of GH shows a 3D pore structure in figure 2a. The GH structure can hinder restacking of graphene sheets and greatly enhance the rapid diffusion and transport of ions, which increases the specific capacitance of the electrode material. As can be seen from figure 2b, the PANI nanoparticles look like rods and combine well with graphene sheets, indicating that the GP structure stability is better [5].

![SEM of GH (a) and GP (b).](image)

3.2. The Electrochemical Test of GH, GP, and GH//GP
The CV and GCD curves of the GH are shown in figure 3a and 3c. The C_{s1} of the GH only decreases slightly from 548.7 F g^{-1} at 10 mV s^{-1} to 500.0 F g^{-1} at 300 mV s^{-1}, indicating again the superior charge-discharge performance and outstanding specific capacitance. The C_{s2} of GH is 682.3 and 451.7 F g^{-1} at 0.5 and 6 A g^{-1}. As can be seen from the figure, the GCD of GH is close to the isosceles triangle, which implies the EDLC behavior of the electrode material. In 2 M H_2SO_4 solution with three-electrode system, the CV and GCD curves of the GP were tested as shown in figure 4a and 4c. The C_{s1} is 118.9 F g^{-1} at the scan rate of 10 mV s^{-1} and 33.4 F g^{-1} at the scan rate of 300 mV s^{-1}. The C_{s2} of GP is 122.3 and 81.7 F g^{-1} at the current density of 0.5 and 6 A g^{-1}.

To further investigate the electrochemical performance of GH and GP in a two-electrode system, an asymmetric supercapacitor device was constructed using GH and GP for the positive and negative, which is designated as GH//GP. The CV and GCD curves of the GH//GP is shown in figure 5. The C_{s1} is 94.7 and 25.9 F g^{-1} at the scan rate of 10 and 300 mV s^{-1}. The C_{s2} of the GH//GP is 82.3 and 51.4 F g^{-1} at 0.5 and 6 A g^{-1}. The energy and power density of GH // GP is shown in figure 6. The energy density of GH // GP is 5.6 W h kg^{-1} at a power density of 226.5 W kg^{-1} and 3.1 W h kg^{-1} at 8446.2 W kg^{-1}, which is higher than reported in other literature [6].
**Figure 3.** CV (a) and GCD (c) curves of GH; $C_{s-1}$ (b) and $C_{s-2}$ (d) of GH.

**Figure 4.** CV (a) and GCD (c) curves of GP; $C_{s-1}$ (b) and $C_{s-2}$ (d) of GP.
Figure 5. CV (a) and GCD (c) curves of GH//GP; C_{S-1} (b) and C_{S-2} (d) of GH//GP.

Figure 6. Energy and power densities of GH//GP.

4. Conclusions
In conclusion, the GH and GP composites were successfully prepared under simple and environmentally friendly conditions. The assembly of the asymmetric supercapacitor was carried out, and its electrochemical performance was tested by CV and GCD. The results show that the potential window of the asymmetric capacitor reaches 1.3 V, which is larger than the electrode of the bipolar material alone. Energy density of the asymmetrical supercapacitors arrives at 5.6 W h kg^{-1} at a power density of 226.5 W kg^{-1} and remains 3.1 W h kg^{-1} at a power density of 8446.2 W kg^{-1}.

5. Acknowledgments
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6. References

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