The structure characteristic and electrochemical performance of graphene/polyaniline composites

Ling Liu, Jie Yang, Yunpeng Jiang, Yan Huang, Qinghan Meng*

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

ABSTRACT

In this paper, polyaniline–graphene (PANI–G) composites were obtained through in situ polymerization of aniline in a suspension of graphite oxide, followed by reduction of hydrazine. The structure characteristic of the composites was characterized by fourier-transform infrared spectroscopy, ultraviolet–visible spectroscopy, X-ray diffraction and scanning electron microscopy. Electrochemical performance of the composites as electrode materials was studied by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The results showed that the redox state of PANI was emeraldine base in hydrazine treated composites and the PANI–G composites exhibited a layered structure with increasing graphene ratio in composites. The PANI–G composites had good electrochemical performance in acid electrolyte, indicating the emeraldine base form of PANI can be doped into the conductive emeraldine salt form. The specific capacitance of the PANI–G composites increased and charge-transfer resistance decreased with increasing graphene ratio in composites.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Polyaniline (PANI) is one of the most promising conductive polymers because of its environmental stability, low cost, controllable electrical conductivity, and interesting redox properties [1]. PANI has four redox states, which are leucoemeraldine base (LB), emeraldine salt (ES), emeraldine base (EB) and pernigraniline base (PB). The EB form of PANI can be conveniently doped into the conductive and electrochemically active ES form with positive charges at low pH values (pH < 3) [2,3]. However, PANI is susceptible to rapid degradation in performance upon repetitive cycles (charge/discharge process) because of its swelling and shrinkage. In order to alleviate this limitation, the combination of PANI with carbon materials [4–10] such as carbon nanotube, mesoporous carbon and carbon nanofiber has been proved to reinforce the stability of PANI as well as maximize the capacitance value [11,12].

Graphene is a two-dimensional form of graphite that has attracted great interest [13,14] because of its high surface area, excellent mechanical properties, and conductivity [15,16]. Thus, the combination of graphene with PANI remarkably enhances the conductivity and mechanical strength, which exhibits excellent performance as electrode material for supercapacitors. Many researches on the preparation of polyaniline–graphene (PANI–G) composites by in situ polymerization of aniline in the presence

of graphene or graphene oxide [17–28] have been reported. The pure graphene cannot be dissolved or dispersed even after the lasting ultrasonic treatment [29,30], so graphene oxide (GO) has been widely used in material chemistry and basic research. GO is a functionalized graphene, which is a one-atom planar crystal with aromatic regions and aliphatic regions. There are a large number of hydrophilic functional groups on the surface of GO, which makes it accessible to combine with PANI. The oxygen atoms in GO destruct its conjugate structure and decrease largely its conductivity, therefore it is necessary to convert GO to conductive graphene by a reduction reaction. Hydrazine is generally used as a reducing agent. However, Zhang [27] pointed out previously that hydrazine reduction procedure of polyaniline–graphene oxide (PANI–GO) composites can reduce not only GO but partially PANI as well, which would lead to decrement in the level of crystallinity of associated PANI. So the composites after hydrazine reduction were reoxidized or even reprotonated to bring back the PANI crystallinity. Goswami [28] reported no definite well resolved peak was registered, instead a very broad peak appeared which can be assigned to PANI with low level of crystallinity in this hydrazine treated sample. But the redox state of PANI was not deeply studied.

The redox state of PANI in hydrazine treated composites and electrochemical performance of PANI–G composites were investigated in this paper. The PANI–G composites were prepared through in situ polymerization of aniline in a suspension of GO, followed by hydrazine reduction. The structure characteristic of composites was analyzed by fourier-transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV-vis) spectroscopy, X-ray diffraction (XRD)

---

* Corresponding author. Tel.: +86 1064436876; fax: +86 1064436876.
E-mail address: qhmeng@mail.buct.edu.cn (Q. Meng).

and scanning electron microscopy (SEM). Electrochemical performance of composites was characterized by cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) test.

2. Experimental

2.1. Preparation of GO

GO was synthesized using a modified Hummers method. Graphite powder was mixed with H_2SO_4, $K_2S_2O_8$, and P_2O_5. The mixture was kept at 80 °C for 4.5 h. Distilled water was added for dilution which was followed by filtration, washing, and drying. H_2SO_4 and $KMnO_4$ were slowly added to the pretreated graphite in an ice bath. The mixture was reacted at 35 °C for 2 h, and distilled water was added for hydrolysis. After 2 h, 30% H_2O_2 was added to the mixture. The mixture was allowed to stand for at least 12 h, after which the clear supernatant was decanted. The remaining precipitate was washed with 5% HCl solution and washed again with distilled water. The final solution was centrifuged and ultrasonicated for 4 h. The concentration of the obtained GO was 2.4%.

2.2. Preparation of polyaniline–graphene oxide (PANI–GO) composites

Homogenous composites of GO and PANI were prepared by in situ polymerization of aniline in a suspension of GO in acidic solution. The weight ratio of aniline to GO was varied as 90:10, 80:20, 70:30 and 60:40, and the resulting composites were named as PANI–GO10, PANI–GO20, PANI–GO30 and PANI–GO40, respectively. Typically, the purified aniline was dissolved in 1.2 M HCl at a concentration of 0.5 M. GO was dispersed in the resulting solution by bath-sonicating for 1 h. While maintaining vigorous stirring in ice bath, another solution of ammonium peroxydisulfate, with a mole ratio to aniline of 1:1, was slowly dropped to the mixture. The mixture was allowed to stir in ice bath for 3 h. The composites were collected by filtration and repetitively washed with acetone, ethanol, and water until the filtrate become colorless. The resulting materials were dried at 60 °C in an oven.

2.3. Preparation of the PANI–G composites

The PANI–GO composites (PANI–GO10, PANI–GO20, PANI–GO30 and PANI–GO40) were reduced by hydrazine. Typically, 0.1 g of composite was heated with 0.1 mL of hydrazine in 50 mL of water at 95 °C for 1 h. The reduced composite was filtered and repetitively washed with deionized water to remove excess hydrazine. The resulting materials were dried at 60 °C in an oven, and the dry samples were named as PANI–G10, PANI–G20, PANI–G30 and PANI–G40, respectively.

2.4. Characterization

Functional groups of composites were characterized by American NEXUS FTIR spectroscopy. XRD patterns were obtained using Japanese D/Max 2500 diffractometer (40 kV and 200 mA) using Cu Kα radiation, performed in the 2θ range of 5° to 90° at a scan rate of 10° min^{-1}. Surface morphology of composites was observed using Japanese Hitachi S-4700 SEM under operating voltage of 200 keV.

All electrochemical experiments were carried out in 1 M sulfuric acid aqueous solution at room temperature. Galvanostatic charge/discharge experiments were conducted using an Arbin battery tester (BT-4, USA) in a two-electrode system which can measure their characterizations more accurately. CV and EIS measurements were performed using an electrochemical station (Zahner-Electrik, Germany) in a three electrode system, in which
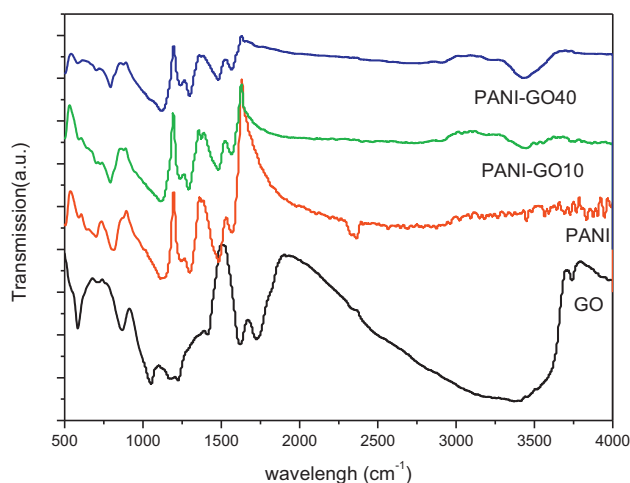
(a) GO, PANI and their composites
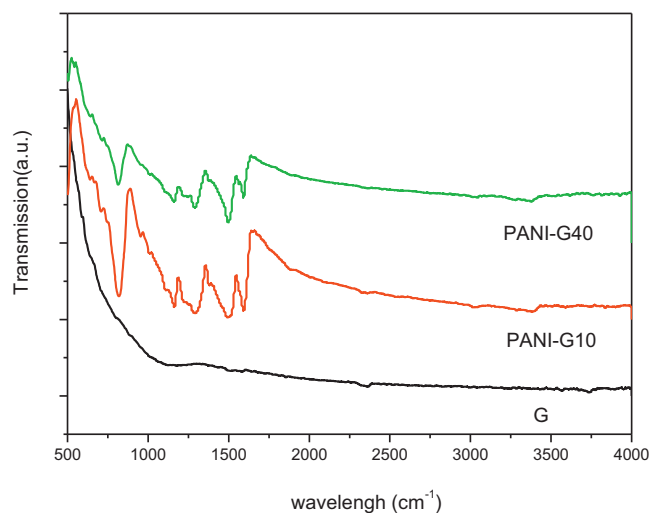
(b) graphene and PAN-G composites

Fig. 1. FTIR spectra of GO, graphene and the composites.

platinum foils and saturated calomelelectrode were used as counter and reference electrodes.

3. Results and discussion

3.1. FTIR spectrum analysis

Fig. 1(a) shows the FTIR spectra of GO, PANI and their composites before reduction. It can be seen from the spectrum of GO that, a broad and intense absorption peak emerges at 3000–3700 cm^{-1}, attributed to the -OH stretching vibration in COOH and intercalated water. Besides, absorption peaks emerge at 1726 cm^{-1}, 1620 cm^{-1}, 1225 cm^{-1} and 1051 cm^{-1}, attributed to C=O characteristic absorption, O—H flexural vibration, C—OH stretching vibration and C—O stretching vibration, respectively, which were consistent with previous reports [31]. According to the spectrum of GO, there are at least some functional groups (e.g. —OH, —COOH, —C=O) in GO synthesized by modified Hummers' method, so the GO is easy to form hydrogen bonds with water, which leads to good hydrophilicity. The spectrum of PANI shown in Fig. 1(a), absorption peaks centering at 813 cm^{-1}, 1122 cm^{-1}, 1299 cm^{-1}, 1483 cm^{-1} and 1567 cm^{-1} are attributed to the flexural vibration inside and outside aromatic C—H plane, C—N in PANI, the aromatic C=C stretching vibration of