



Preparation and electrochemical capacitive performance of polyaniline nanofiber-graphene oxide hybrids by oil–water interfacial polymerization

Yuhong Jin, Mengqiu Jia*

Laboratory of Electrochemical Process and Technology for Materials, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China



ARTICLE INFO

Article history:

Received 3 November 2013
Received in revised form 7 December 2013
Accepted 18 December 2013
Available online 20 January 2014

Keywords:

Polyaniline nanofiber
Graphene oxide
Interfacial polymerization
Electrochemical capacitive performance

ABSTRACT

Polyaniline nanofiber-graphene oxide (PANIF-GO) hybrids were fabricated by oil–water interfacial polymerization. The structures of PANIF-GO hybrids, pure PANIF and GO were examined by high resolution transmission electron microscopy. It was found that PANIFs were homogeneously inserted between the GO layers or adsorbed on the surface of the GO. Fourier transform infrared spectroscopy and X-ray diffraction showed that PANIFs effectively increased the interlayer distance of GO from 0.83 nm to 1.38 nm. Electrochemical properties for the hybrid electrode were tested by cyclic voltammetry and electrochemical impedance spectroscopy using a three-electrode system. The results indicated that a high specific capacitance of 564.7 F g^{-1} for the hybrids was measured at the current density of 0.5 A g^{-1} in a $1 \text{ M H}_2\text{SO}_4$ aqueous solution compared to 352.8 F g^{-1} for pure PANIF and 30.1 F g^{-1} for GO. Moreover, the PANIF-GO hybrids showed a very long cycle life with only 9.4% specific capacitance loss after 2000 cycles. The as-prepared hybrids are remarkable electrode materials for the supercapacitors.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, growing demands for power sources of transient high-power density have stimulated a great interest in supercapacitor with project applications in digital communications, electric vehicles, burst power generation, memory back-up devices and other related devices which require high-power pulse [1]. Compared with secondary batteries, supercapacitors, also known as electrochemical supercapacitors or ultracapacitors, exhibit faster and higher power capability, long life, wide thermal operating range, and low maintenance cost [2,3].

The main materials studied for the supercapacitor electrode are carbons, metal oxides and conducting polymers. The conducting polymers have received increasing interest as an alternative to carbons and metal oxides in supercapacitor. This is due to low fabrication cost, easy synthesis, flexibility, excellent environmental stability, high conductivity and high pseudo capacitance [4–10]. In particular, polyaniline (PANI) is one of the most promising electrode materials because of its high theoretical pseudo capacitance owing to multiple redox states [11–13]. Moreover, one dimensional nanostructure PANI such as nanotubes, nanofibers and nanowires have received great attention for electrode materials of supercapacitors, because they provide high surface area and high conductivity

leading to high specific capacitance [14,15]. In particular, polyaniline nanofiber (PANIF) had been regarded as ideal supercapacitor electrode materials due to their large specific area and optimized ion diffusion path [16–19], which is necessary for the effective access of electrolyte to the electrode in both electric double layer and redox mechanism. However, PANIF is susceptible to rapid degradation in the charge/discharge process, which is attributed to the swelling and shrinkage of PANIF. In order to alleviate this limitation, the combination of PANI with carbon materials (carbon nanotubes [20,21], porous carbon [22,23], ordered mesoporous carbon [24,25], carbon nanofibers [26], active carbon [27,28] and graphene or graphene oxide [29–31]) has been proved to reinforce the stability of PANI as well as to maximize the capacitance value. Among these carbon materials, graphene and graphene oxide are predicated as an excellent support material due to high surface area, and remarkable mechanical stiffness and excellent conductivity.

Due to the attractive merits of graphene or graphene oxide and the intriguing properties of PANI, composites of these materials should have novel properties as supercapacitors electrode materials. Indeed, previous researches on methods of preparation and performance of graphene or graphene oxide/PANI materials have spotlighted the interesting properties of composites obtained via various approaches. Chen and co-workers [32] studied the effect of carbon particle morphology on the electrochemical properties of nanocarbon/PANI composites. The results showed that graphene/PANI composite exhibits better performance than carbon black/PANI and carbon nanotube (CNT)/PANI. Therefore, compared

* Corresponding author. Tel.: +86 010 64413808; fax: +86 010 64413808.
E-mail address: jjamq@mail.buct.edu.cn (M. Jia).

to CNT, graphene or graphene oxide (GO) is predicated as an excellent support material due to high surface area, and remarkable mechanical stiffness and excellent conductivity. Yan [29] used in situ polymerization to synthesize a graphene nanosheet/PANI composite. Electrochemical test showed a high specific capacitance of 1046 F g^{-1} was obtained at a scan rate 1 mV s^{-1} compared to 115 F g^{-1} for pure PANI. Recently, Zhang [30] has reported PANIF-GO composites prepared by a rapid mixing reaction. The electrochemical tests showed that the introduction of electrical activity PANIF effectively increased the composites electrode capacitance. However, PANIF inserted into GO sheets became scaffolds for secondary growth of PANI and finally turned into irregularly shaped agglomerates containing nanofibers and particulates. It can be explained that PANIFs are formed at an early stage in the polymerization process; as more ammonium peroxydisulfate was fed into the reaction, the PANIFs became scaffolds for secondary growth of PANI, which could affect the properties of the composites.

Interfacial polymerization ion is accepted as a facile approach to make bulk quantities of PANI nanofibers [33]. Wang et al. [34] reported a morphology-controlled strategy to prepare sulfonated graphene/polyaniline composites by a liquid/liquid interfacial method, using sulfonated graphene (SGE) as both a substrate and a macromolecular acid dopant. Composites obtained with two different ratios of SGE to PANI showed higher specific capacitance of 793 F g^{-1} and 931 F g^{-1} , but lower capacity retention after 100 cycles of 77% and 76%, respectively. Herein, we report a simple method to prepare PANIF-GO hybrids by oil-water interfacial polymerization. This method has the advantage of suppressing the secondary growth of PANI. Since the monomer aniline and the initiator are separated by the boundary between the aqueous and the organic phases, polymerization occurs only at this interface where all the components needed for polymerization come together [33,35–37]. PANI is then formed into nanofibers. The two-dimensional planar structure of GO is beneficial to homogeneous nucleation of a large amount of PANI on their surface, giving more active sites for the redox, and the layer-by-layer stacks of crumpled GO sheets and PANI layers prevent the peeling of PANIFs from the GO surface. Consequently, the material can tolerate considerable volume changes, swelling and shrinkage of PANI. PANIF-GO hybrid electrodes conclude two types of capacitive response. The first type is electrical double layer capacitance, which is due to graphene oxide. The second type is pseudo capacitance, which is attributed to PANIF. Interfacial polymerization method was a simple and efficient approach to prepare PANIF-GO hybrids. The electrocapacitive properties of PANIF-GO hybrids in $1 \text{ M H}_2\text{SO}_4$ electrolyte were studied and compared with that of pure PANIF and GO.

2. Experimental

2.1. Preparation of graphite oxide

Graphite oxide was synthesized from natural graphite power (Crystalline, 500 meshes, provided by Qingdao Baichuan Graphite Co. Ltd., Qingdao, China) by a modified Hummers-Offeman method [38]. 1.25 g of Graphite was added into the 65 ml of concentrated sulfuric acid (98 wt%, analytical grade) within an ice bath under violent mechanical agitation and kept for 20 min. Then potassium permanganate (KMnO_4 , analytical grade) was mixed gradually with the aforementioned mixture in order to control the reaction temperature at below 20°C . The reactor was kept in the ice bath for 2 h and the color changed from black to dark-green. Then the reactor was put into the 35°C water bath for 30 min. Distilled water was slowly dropped into the mixture to cause an increase in temperature of up to $95\text{--}100^\circ\text{C}$ with effervescence, and the color changed from dark green to brown. The mixture was stirred at 98°C for 15 min. The water bath was removed, and 25 ml of 30 wt%

H_2O_2 was added into the mixture to remove the excess KMnO_4 . The mixture was rinsed and centrifugated with 5 wt% hydrochloric acid (HCl, analytical grade) and deionized water for several times. The GO dispersion was directly dispersed in the water for next experimental step.

2.2. Preparation of PANIF-GO hybrids

The oil/water interfacial polymerization for PANIF-GO hybrids is illustrated in Fig. 1. The lower layer is the oil phases in which aniline (3.0 g, analytical grade) was dissolved in 100 ml chloroform (CHCl_3 , analytical grade). The upper layer is the water phase in which GO aqueous suspension (6.0 g, 0.5 wt%) and Ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 1.8 g, analytical grade) were added to 100 ml of 1 M HCl aqueous solution after ultrasonication for 2 h. The beaker was kept at room temperature for 24 h. With increasing the reaction time, the product slowly grew on the oil/water interface, and the whole upper layer became dark-green and the lower layer became yellow-brown. Finally, the product was filtered and washed carefully with the deionized water and dried in a vacuum oven at 80°C for 24 h.

3. Characterization methods of PANIF-GO hybrids

The morphology was measured by high resolution transmission electron microscopy (HRTEM JEM-2010). The structure was analyzed by Fourier transform infrared spectroscopy (FT-IR, Bruker Vector 2, using KBr pellets), and X-ray diffraction (XRD, Bruker D8 with $\text{Cu K}\alpha$ radiation).

4. Electrochemical characterization of PANIF-GO hybrids

The electrodes were prepared by mixing 85 wt% as-prepared composite with 10 wt% acetylene black and 5 wt% polytetrafluoroethylene dissolved in ethanol as a binder to form a slurry. The slurry was then pressed onto a stainless steel wire mesh (1 cm^2) at 10 MPa for 1 min in order to ensure a good electrical contact and was dried in vacuum oven at 80°C for 24 h.

All electrochemical experiments were carried out in $1 \text{ M H}_2\text{SO}_4$ aqueous solution using a three-electrode system, which contained a platinum foils as a counter electrode, a saturated calomel electrode (SCE) as reference electrode, the obtained materials loaded on a stainless steel wire mesh as a working electrode. Cyclic voltammetry (CV) measurements were performed in a potential range from -0.2 to $+0.8 \text{ V}$, and the sweep rate range from 2 to 30 mV s^{-1} . For the electrochemical impedance spectroscopy (EIS) measurements were also carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV. Galvanostatic charge/discharge (GCD) curves were measured in a potential range from -0.2 to $+0.8 \text{ V}$, and the current density range from 0.5 to 10 A g^{-1} . All electrochemical data were collected by computer controlled equipment (Corrtest C350, Wuhan China).

5. Results and discussion

5.1. FT-IR characterization

The FT-IR spectra of the GO, PANIF and PANIF-GO hybrids were measured as shown in Fig. 2. For the characteristic peaks of GO, the broad O–H stretching peak at 3410 cm^{-1} , the C=O stretching vibrational band at 1730 cm^{-1} , the C=C band at 1632 cm^{-1} and the C–O stretching vibrations at 1055 cm^{-1} were observed, which was similar with previous reports [39]. For PANIF, the main bands at 3441, 2926, 1575, 1492, 1300, 1138, 803, 579 cm^{-1} for Emeraldine PANIF may be attributed to H–N–H, N–H, C=N, C=C, C–N, C–H

Download English Version:

<https://daneshyari.com/en/article/1441037>

Download Persian Version:

<https://daneshyari.com/article/1441037>

[Daneshyari.com](https://daneshyari.com)