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In-situ polymerization of polyaniline on the surface of graphene oxide for high electrochemical capacitance

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ABSTRACT

Conducting polymer polyaniline (PANI) was in-situ polymerized on the surface of graphene oxide (GO) to form PANI encapsulating GO nanocomposites. The morphology and microstructure were examined by scanning electron microscopy, X-ray diffraction and N_2 absorption/desorption analysis. Electrochemical properties were tested by cyclic voltammetry, galvanostatic charge/discharge cycles and electrochemical impedance spectroscopy. Experimental results showed that ethanol assisted the dispersion of GO in water and facilitated the diffusion of polymer monomers on GO. GO as a support material can provide sufficient reaction sites for the deposition of aniline to form the film-like GO/PANI composites. Capacitive performance illustrated that the in-situ polymerization of PANI on GO was effective in improving the specific capacitance and cycling stability.

1. Introduction

The increasing demand for clean and sustainable energy has driven intensive research efforts on the development of energy storage systems. Supercapacitors, also called electrochemical capacitors or ultracapacitors, are a type of energy storage devices with high power density [1–4]. Recent researches have been focused on the improvement in the energy density of supercapacitors by exploring novel electrode materials, such as carbon nanomaterials [1,5–7], transition metal nanoparticles [8–11] and conducting polymers [3,4,12,13]. Among them, conducting polymers can store charges not only in the electrical double layer capacitor (EDLC), but also by the rapid faradic pseudocapacitance [13,14]. PANI is considered to be one of the most promising conducting polymers for supercapacitors due to its high energy density, facile synthesis, high conductivity and low cost [13–15]. However, there are still some shortcomings of PANI for supercapacitors. Firstly, the practical capacitance is lower than theoretical value because the inner layers of PANI electrodes cannot be fully used. Secondly, the polymers usually showed poor cyclic stability because the polymers are brittle and weak in mechanical strengths [16]. Coupling conducting polymers to a carbon-based material [12,14,17–20] has been shown to be an effective approach to improve the cycling stability. For example, vertically aligned polyaniline nanowhiskers have been successfully synthesized on the external surface of mesoporous carbon through a chemical oxidative polymerization, which delivered a large specific capacitance and good capacitance retention [18].

GO was considered as an excellent carbon substrate due to its unique electronic, thermal, and mechanical properties [6,21,22]. In addition, GO has a number of oxy-functional groups on the surface [23,24] such as –OH, –COOH, –O– and C═O, which make the material hydrophilic and readily dispersible in water as well as in some organic solvents [25]. Due to its oxy-functional groups and good dispersion in water, GO is able to interact closely with the functional groups of aniline via chemical bonding in an aqueous system.

In this work, we report a facile and environmentally friendly in-situ polymerization to prepare GO/PANI nanocomposites. Due to the flexibility of GO and the high energy density of PANI, GO/PANI composites have exhibited the great potential application for supercapacitors. The effects of in-situ polymerization of PANI on the structure and properties were also investigated.

2. Materials and method

2.1. Materials

All the chemicals were of analytical grade. All the aqueous solutions were made up of water purified by AQUELIX pure water system (Millipore, electrical resistivity 13 $M\Omega \cdot cm^{-1}$).

2.2. Preparation of GO

GO was synthesized from natural flake graphite by a modified Hummers method [26]. Graphite (3 g) was mixed with 120 mL of H_2SO_4 (95%) in a 1000 mL flask. The mixture was stirred for 30 min in an ice bath to get a uniform mixture. In the continuous vigorous stirring, potassium permanganate (15 g) was added to the suspension. The addition was carefully controlled to keep the reaction temperature lower than 20 °C. After stirring for 4 h, the ice bath was then removed, and the mixture was stirred for 12 h at room temperature. Then, 400 mL

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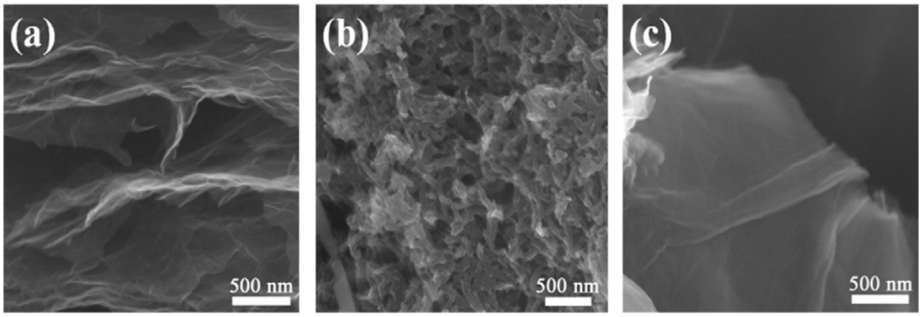

Fig. 1. SEM images of GO (a), pure PANI (b), and GO/PANI (c).

of H_2O was slowly added to the mixture with vigorous agitation. The reaction temperature was rapidly increased to 98 °C with effervescence, and the color changed to brown. The diluted suspension was stirred for another 30 min. Then, 10 mL of 30% H_2O_2 was added to the mixture and the color turned into bright yellow. For purification, the mixture was washed by 5% HCl and then deionized water for several times until the filtration was neutral. In the end, the GO was obtained as gray powders after drying at 120 °C under vacuum.

2.3. Preparation of GO/PANI nanocomposites

GO/PANI nanocomposites were prepared by in-situ polymerization of aniline in the suspension of GO in HCl solution. The purified aniline was dissolved in 1.0 M HCl at a concentration of 0.3 M. GO was dispersed in the above solution by sonicating for 30 min. To avoid aggregation, 5 mL ethanol was added to the solution. In the continuous vigorous stirring in an ice bath, another solution of ammonium peroxydisulfate, with the mole ratio to aniline of 2:3 in 1.0 M HCl, was slowly added to the mixture. The in-situ polymerization of aniline started after about 30 min and the color of the mixture changed to green. The mixture was stirred for 24 h. The composites were washed with water and ethanol repetitively until the filtrate became colorless. GO/PANI composites were collected by filtration and dried at 60 °C for 12 h. For comparison, the pure PANI was synthesized without GO in the same procedure.

2.4. Characterization and testing

Field emission scanning electron microscope (FESEM) observation was performed using a Nova NanoSEM 400 FEI at 15 kV in gentle-beam mode. The structure was analyzed through X-ray diffraction (XRD). The XRD patterns were recorded by DMAX-2500PC with Cu Kα radiation ($\lambda = 1.5406$ Å). The 2-theta angle was from 5° to 90° at the scanning speed of 4° min^{-1}. The specific surface areas were measured by Brunauer–Emmett–Teller (BET) mode according to the N_2 adsorption/desorption isotherms (Micromeritics ASAP 2020).

For the preparation of electrode, GO/PANI powders, carbon conductive additives and the binder polyvinylidene fluoride were dispersed in N-methyl-2-pyrrolidone in the weight ratio of 75:20:5 to make a slurry. Then the slurry was smeared uniformly on a nickel foam current collector ($1.0 * 1.5$ cm^2) and then dried at 120 °C for 12 h in a vacuum furnace. The electrochemical cell is a three-electrode configuration with a Pt plate as the counter electrode, an Ag/AgCl electrode as the reference electrode and 1.0 M Na_2SO_4 aqueous solution as the electrolytes. The electrochemical tests were performed at room temperature. The galvanostatic charge/discharge (GC) performance, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were measured on an electrochemical workstation (Solartron 1287 + 1260 8 w). CV was carried out at different scanning rates from 5 to 100 mV s^{-1} between −0.2 and 0.8 V. EIS measurements were performed over a frequency range from 100 kHz to 0.01 Hz. GC performance was tested between −0.2 to 0.8 V at different rates.

3. Results and discussion

The morphologies of the obtained materials were observed by SEM, as shown in Fig. 1. GO, synthesized from natural flake graphite, looks flexible with full of drapes (Fig. 1a). Pure PANI was very easy to agglomerate as clusters (Fig. 1b). GO/PANI exhibits a film-like morphology and the surface was smooth without any aggregation of polymer clusters (Fig. 1c), which is consist with previous works [14,27,28]. This is mainly

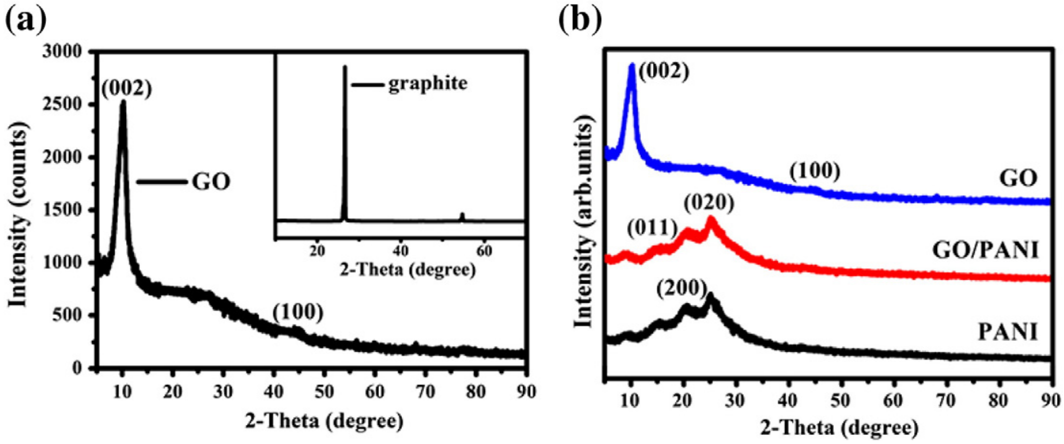

Fig. 2. XRD patterns of pristine graphite and GO (a), pure GO, PANI and GO/PANI composites (b).