

Graphene oxide/polyaniline nanotube composites synthesized in alkaline aqueous solution



Qiguan Wang^a, Shenbao Qiu^a, Sumin Wang^{a,*}, Jiayin Shang^a, Rongna Zhao^a,
Xinming Wu^a, Weixing Chen^a, Hongwei Zhou^a, Xinhai Wang^{b,*}

^a Scientific Research Innovation Team of Solidification Theory and Functional Materials, Shaanxi Key Laboratory of Photoelectric Functional Materials and Devices, School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710021, People's Republic of China

^b School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People's Republic of China

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ABSTRACT

We report a facile strategy to synthesize graphene oxide/polyaniline (GO/PANI) nanotube composites by using in situ polymerization in an alkaline solution. Because the carboxyl groups on GO surface possess reactivity with both aniline and alkali, which can stabilize the aniline droplets, the size of obtained GO/PANI nanotube aggregates were reduced compared to that of pure PANI. The doping effect between PANI nanotube and GO is characterized by Fourier transform infrared spectroscopy and X-ray photoelectron spectra, and the electrochemical performances of the nanotube composites are evaluated by galvanostatic charge–discharge. As the oxygen-containing groups on the edge of GO can serve as an excellent electrolytic accessible surface for redox-active PANI nanotubes, the maximum specific capacitance of 277 F g^{-1} at 1.0 A g^{-1} is observed at the GO/PANI electrodes. Moreover, the GO/PANI nanotube composite shows excellent long-term cyclic stability (less than 6% decrease in specific capacitance after 1000 cycles at a current density of 1.0 A g^{-1}), because the swelling and shrinkage of PANI during doping–dedoping processes can be efficiently restrained by the high flexible GO sheets intercalated within the system. In addition, the GO/PANI nanotube composites possessed a catalytic activity toward the redox reaction of H_2O_2 with a detection limit of $8.6 \mu\text{M}$, indicating a positive synergistic effect for the improvement of electrochemical performance.

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1. Introduction

Polyaniline (PANI) is regarded as one of the most promising electrode materials because it possesses a high electrical conductivity and superior redox properties in addition to its easy synthesis and good environmental stability [1–3]. Especially, the nanostructured PANI such as PANI nanotubes or nanofibers, which provides a high specific surface area, excellent electrical and electrochemical performances, has attracted widespread attention [4,5]. However, PANI often exhibits a poor life and fast decayed performance in usage due to chain breaking [6], which has limited its extended applications.

Graphene and graphene oxide, composed of two-dimensional monolayer of carbon atoms, have attracted much attention because of their outstanding thermal, mechanical, and electrical properties [7,8]. To stabilize and improve the electrochemical

properties, extensive efforts and many approaches have been developed to combine graphene and its derivatives with nanostructured PANI. Mao et al. [9] and Zhang et al. [10] prepared graphene/PANI nanofiber composites by in situ polymerization method with or without the presence of surfactants, and the specific capacitance of 526 F g^{-1} and 480 F g^{-1} was achieved respectively. By using in situ polymerization of aniline monomer in HClO_4 solution, Li et al. [11] prepared graphene nanosheet/polyaniline nanofiber composites, with a remarkable specific capacitance of 1130 F g^{-1} at a scan rate of 5 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ solution. Moreover, the composites present excellent long cycle life with 87% specific capacitance retained after 1000 charge/discharge processes. Liu et al. [12] reported a flexible graphene sheet/polyaniline nanofibers composite paper, which showed a specific capacitance of 301 F g^{-1} . It can be 67% specific capacitance retained after 400 charge/discharge cycles. Wang et al. [13] prepared GO/PANI nanofiber composites by in situ polymerization. The highest initial specific capacitance reaches 627 F g^{-1} , and the capacitance retention of 73% after 500 cycles is obtained. In those preparations, in situ polymerization of aniline monomer and GO generally occurs

* Corresponding author. Fax: +86 29 86173324.

E-mail addresses: suminwang@163.com (Q. Wang), xinhaiwanghenu@163.com (X. Wang).

under high acidic conditions. At the initial stage of polymerization process, aniline monomers were preferentially reacted with inorganic strong acids to form anilinium cations, which makes the interactions between GO and the resulting PANI relatively weak due to the low ionization of carboxyl on GO in acidic conditions. If the polymerization happens in alkaline environment, the high-grade ionization of carboxyl on GO can make the interactions between GO and the formed anilinium cations enhanced.

In fact, PANI nanotubes have been successfully synthesized guided by alkali via good control of the molar ratio of aniline and the alkali (sodium hydroxide) [14], in addition to the template-free acidic polymerization method [15–18]. During the polymerization process, aniline monomers were dispersed as small droplets suspended in alkaline aqueous solution and the sulfate ions generated from the oxidant ammonium persulfate actually role as the dopant inducing the growth of anilinium cations. Because GO possesses carboxyl groups that can be interacted with both alkali and aniline, addition of GO in alkali/aniline system should improve the stability of aniline droplets. Moreover, the high-grade ionization of carboxyl on GO in alkaline environment can enhance the interactions between GO and the formed anilinium cations as a dopant (Fig. 1), favoring the formation of nanostructured products. Based on above considerations, we herein prepared GO/PANI nanotube composites in alkaline media, which showed improved electrochemical performances.

2. Experimental

2.1. Materials

Aniline, graphite powder, ammonium persulfate (APS), and H_2O_2 were purchased from Shanghai Chemical Reagent Company. Aniline was used after distillation. All other reagents and chemicals were used as received unless otherwise noted.

2.2. Synthesis of GO/PANI nanotube composites

GO was prepared by oxidation of natural graphite powder by using the modified Hummers method [19]. GO/polyaniline nanotubes were synthesized based on a reported reaction [14]. 0.08 g NaOH and 4 mmol of aniline monomer (An) were mixed in 40 mL of deionized water by ultrasonic stirring at room temperature for 2 h. After that, various weight ratios of dried GO was added into aniline dispersion with further sonication for 30 min. The mixture was placed in refrigerator ($5^\circ C$) for another 2 h. APS with molar ratio An/APS = 1:1 was dissolved in 10 mL deionized water and was cold at the same condition. Then it was added to the above mixture and placed in refrigerator for 24 h. Finally, the resulting precipitate was filtered, washed with deionized water and methanol several times, and then dried in a dynamic vacuum at $50^\circ C$ for 24 h. According to the mass feed ratios of the GO to the aniline monomer (1:250, 1:200, 1:150, 1:100, 1:50, and 1:10), the obtained composites are

designed as GOPA1:250, GOPA1:200, GOPA1:150, GOPA1:100, GOPA1:50 and GOPA1:10, respectively.

2.3. Capacitor assembly and measurements

To analyze the capacitance of obtained composites, sandwich-type cells were assembled with two symmetric electrodes, prepared by pressing GO/PANI powder with 10 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) binder onto a stainless steel mesh with diameter 16 mm. The electrolyte used in the cell was 1.0 M H_2SO_4 with a microporous polyethylene-polypropylene separator. The electrodes and separator were soaked in the electrolyte before cell assembly. The symmetrical cell was enclosed in a coin-type test cell (CR2032) and sealed. Constant-current charge-discharge cycling of the cell was conducted over voltage ranges of 0.1–0.8 V at a current loading of $1.0 A g^{-1}$ with Neware battery test equipment (CT3008W, China) at room temperature.

2.4. Characterization

The GO/PANI nanotube composites were monitored by using a Fourier transform infrared (FT-IR) spectrometer (Nicolet Magna-IR 750) employing the KBr disk method. The surface chemistry of GO/PANI nanotubes was analyzed using a Kratos AXIS 165 X-ray photoelectron spectrometer. All spectra were calibrated with the C 1s photoemission peak for sp^2 hybridized carbons at 284.5 eV. Curve fitting of the photoemission spectra was done after a Shirley type background subtraction. The room temperature resistance of the samples in compressed pellet form was measured by using a standard four-point probe configuration. Morphology and interior structure of GO/PANI were investigated using a scanning electron microscope (Hitachi S-3400N, SEM) and a transmission electron microscope (JEOL JEM-2010, TEM). For the TEM experiments, an appropriate amount of the dilute GO/PANI aqueous dispersion was poured onto carbon-coated copper TEM grids. Cyclic voltammetric and amperometric experiments were conducted with a CHI660 workstation (Shanghai Chenhua, Shanghai). All experiments were carried out using a conventional three electrode system in 0.1 M phosphate buffer solution (PBS), where a platinum wire was used as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was prepared by solution casting of 50 μL of nanomaterial/DMF dispersion (1 mg/mL) on ITO plates and dried. EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

The morphology and structure of the PANI and GO/PANI composites were characterized by using SEM and TEM. From SEM images shown in Fig. 2, the pure PANI prepared (Fig. 2a) shows large aggregated particles composed of tubular structures of

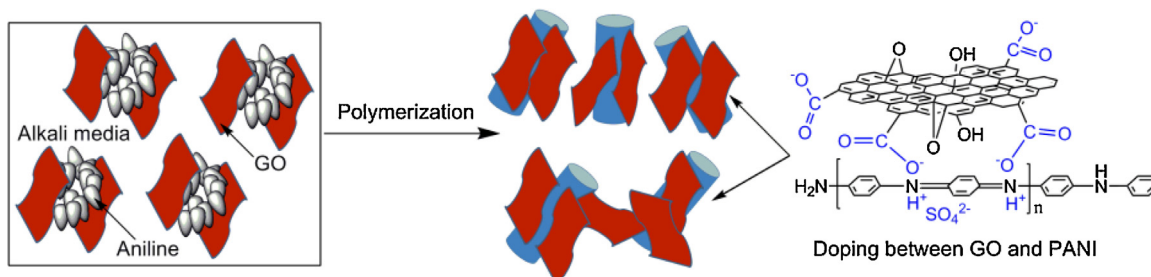


Fig. 1. Illustration of stabilization of aniline droplets by GO in alkaline aqueous solution and doping reaction between GO and PANI.

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