



Tremella-like graphene/polyaniline spherical electrode material for supercapacitors



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ABSTRACT

A novel tremella-like graphene/polyaniline composite was achieved from self-assembly of graphene nanosheets during polymerization of aniline in H₂O/N, *N*-dimethylformamide solution, and was further employed as an electrode for supercapacitors. This graphene/polyaniline composite demonstrates a spherical tremella-like structure and a large specific capacity of 497 F g⁻¹ at a current density of 0.5 A g⁻¹. Particularly, an outstanding rate capability of 456 F g⁻¹ under 5 A g⁻¹ after 1000 cycles was obtained. Scanning electron microscopy showed that polyaniline nanoparticles were uniformly deposited on free-standing graphene nanosheets, and self-assembled to a spherical tremella-like structure. Therefore, this unique nanostructure is promising for high-performance electrochemical applications.

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1. Introduction

Supercapacitors or electrochemical capacitors are considered as very promising candidates for future power storage devices due to their high power density and outstanding cycling performance [1,2]. There are two energy storage mechanisms for supercapacitors: the electric double-layer (EDL) capacitance and the pseudo-capacitance [3]. The EDL capacitance arises from the charge separation at the electrode/electrolyte interface, but the energy densities of EDL capacitors are too low for many important applications [4]. The high capacitances of pseudocapacitors are derived from fast, reversible redox reactions on the surfaces or in the bulk phase of active materials [5]. Polymers are usually used as pseudocapacitor active materials [6].

Among all of the developed materials, electronically conducting polymers such as polypyrrole, polythiophene and especially polyaniline (PANI), are widely investigated because of their easy synthesis, relative high specific capacitance and low fabrication cost than many other electrode materials [7]. However, severe volume swelling and shrinkage during charge-discharge processes lead to the mechanical degradation of these conductive polymers, which causes the obvious capacity fading [8,9]. In addition, low electrical conductivity can also influence the pseudocapacitive

performance of PANI when structured as electrode material of supercapacitors [10].

Graphene, a two-dimensional all-sp²-hybridized carbon, which was first obtained in 2004 by Geim [11], has attracted a great attention due to its extraordinary electric, mechanical properties and thermal properties [12–16]. These properties suggest wide applications, such as fabricating electronic devices, lithium-ion batteries and supercapacitors [12,17,18]. The combination of PANI with graphene has been proved to be attractive to reinforce the stability and the electrical conductivity of PANI as well as maximize the capacitance value [19,20]. Therefore, high dispersion of PANI on a support material with excellent conductivity and high surface area should be a promising way to improve the capacitive properties of PANI. Recently, many attempts have been devoted to the use of graphene/PANI as electrode materials in supercapacitors [21–30]. Xu et al. [31] constructed a hierarchical nanocomposite containing PANI nanowires and graphene oxide (GO) nanosheets by dilute polymerization, and found that this architecture material showed a capacitance of 227 F g⁻¹ at the current of 2 A g⁻¹. Covalently-grafted graphene/PANI nanocomposites with capacitance of 338 F g⁻¹ at the scan of 5 mV s⁻¹ were synthesized by diazotization chemistry to enhance the three dimensional functionalization of graphene with *p*-aminobenzoic acid [32]. Kumar et al. [20] synthesized polyaniline-grafted reduced graphene oxide composites with capacitance of 250 F g⁻¹ by functionalizing graphite oxide with 4-aminophenol via acyl chemistry, where a concomitant reduction of GO takes place.

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However, up to now, much attention has been paid on the preparation method of PANI/graphene materials; few researches investigated the influence of the constructed architecture by graphene nanosheets (GNS) on the electrochemical performance for supercapacitors. In addition, graphene/PANI composites with a sheet-like morphology have a strong tendency to restack during solvent evaporation, which may hinder the diffusion of electrolytes [33]. Therefore, designing a three-dimensional structure which is conducive to charge transfer and diffusion of electrolyte can improve the electrochemical properties of composites effectively.

In this paper, a novel tremella-like graphene/polyaniline (TGP) composite was achieved from self-assembly of GNS during polymerization of aniline in H₂O/N, *N*-dimethylformamide (DMF) solution. The composites have a three-dimensional porous structure which is conducive to electron transfer and diffusion of electrolyte. An excellent specific capacitance as high as 456 F g⁻¹ at a current density of 5 A g⁻¹ was obtained in the TGP electrode; good rate performance and cyclic stability were also exhibited in this electrode. The results demonstrate that the synergistic effects between PANI and GNS significantly affect the electrochemical performance of supercapacitor electrodes.

2. Experimental

2.1. Preparation of graphite oxide

GO was prepared by a modified Staudenmaier's method [34]. KClO₃ was employed as the oxidants to obtain GO. Firstly, 87.5 ml sulfuric acid (98%), 45.0 ml nitric acid (68%, all analytical pure grade) and 5 g natural graphite (47 mm, provided by Jing Yuan Co. Ltd. Baotou, China) were mixed together in an ice-water bath. After 15 min, certain amounts of KClO₃ (analytical pure, 99.5%) were gradually added into the obtained hydrated colloid, and the mixture was laid at room temperature for 96 h. Then the GO obtained by filtration was washed with deionized water until neutralization, and dried at 40 °C for 24 h. Finally, GNS were obtained after the treated GO was put into a muffle oven preheated to 1050 °C for 30 s.

2.2. Preparation of TGP composites

The TGP composite was synthesized via an in situ polymerization. First, 0.01 g GNS powders obtained above were dispersed in 10 ml DMF solution by sonication for 20 minutes, and 0.2 g aniline was added into the above suspension with sonication for another 1 h. The temperature was then cooled to 5 °C. Ammonium persulfate (0.4 g) in 100 ml deionized water was added into the as-prepared mixture and kept at 5 °C for 10 h. After the reaction the composite washed with deionized water and ethanol, respectively, and dried in an oven at 40 °C for 24 h. Finally, the resulting product was collected by washing and drying, and labeled as TGP (the weight ratio of PANI in the TGP composite is calculated to be 44%). For comparison, pure PANI was also prepared with the same chemical process.

2.3. Characterization

The microstructures of the samples were observed by scanning electron microscope (SEM, ZEISS SUPRA 55) and high resolution transmission electron microscope (HRTEM, JEOL 3010). X-ray diffraction (XRD, Rigaku D/max-2500B2+/PCX system) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the range of 5–90° (2 θ) at room temperature. The functional groups were measured by Fourier transform infrared spectroscopy instrument (FTIR, Nicolet Nexus 670).

2.4. Electrochemical measurements

The TGP material, carbon black, and polyvinylidene fluoride (PVDF) as binder, were mixed in a mass ratio of 80:10:10 and dispersed into a certain volume in NMP. Then the resulting mixture was coated onto the nickel foam substrate, which was followed by drying at 120 °C for 12 h in a vacuum oven. The mass of each electrode is about 3 mg, including conducting agent and binder. The surface area of each electrode is 100 mm².

All electrochemical measurements were done in a standard three-electrode system: nickel foil electrode with the active material as the working electrode, nickel hydroxide electrode as a counter electrode, and an Hg/HgO as a reference electrode. The measurements were carried out in a KOH aqueous solution (30 wt. %). Galvanostatic charge/discharge test was taken by CT2001A Battery Program Controlling Test System (China-Land Comp. Ltd.) within the voltage range of -0.8–0 V. The cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out on a CHI 660B electrochemical working station. For the cyclic voltammetric measurements, the sweep rate ranged from 1 to 50 mV s⁻¹ within a potential range of -0.8 to 0 V. For the EIS measurements, the frequency range was from 1 Hz to 10 kHz.

3. Results and discussion

3.1. Morphology and structure of PANI, GNS and TGP

The morphologies of the obtained GNS were observed by TEM and HRTEM and their images are shown in Fig. 1(a) and (b). Fig. 1(a) exhibits the TEM image of GNS with thin wrinkled structure that graphene owns intrinsically [35]. As is shown in Fig. 1(b), the thickness of the GNS is approximately 3–6 nm and is composed of approximately 5–10 wrinkled individual monoatomic graphene layers. Fig. 1(c) shows that the PANI fiber woven into pieces looks like weaving seats. As for the TGP composites in Fig. 1(d), a spherical morphology is observed instead of the sheet morphology of PANI or GNS. The diameter of the sphere assembled by nanosheets is about 10 μm from Fig. 1(e). The nanosheets with the thickness of about 50 nm are perpendicular to the centre of sphere. High magnification SEM images shown in Fig. 1(f) reveal that PANI attached on graphene sheets exhibits a granulated morphology. That could be ascribed to the affinity between two components both having conjugated structures. Plenty of holes have been formed between nanosheets, which are not only beneficial to the electrolyte infiltration but also good for the ion transmission.

On the basis of the above experimental results, formation mechanisms of PANI and TGP are illustrated in Fig. 2. In the chemical oxidation polymerization process of aniline, two possible nucleation sites, bulky solution and solid substrates [31], compete with each other. GNS bring negative charges due to their residual carboxylic groups, [36] Therefore, aniline monomer can be adsorbed on the surface of GNS under ultrasonication. Under this condition of the reaction, most active nucleation sites were generated on the graphene nanosheet surface at the beginning of the polymerization by heterogeneous nucleation. These active sites would minimize the interfacial energy barrier between the solid surface and bulk solution, which is beneficial to the subsequent growth of PANI on the solid substrates [31,37]. PANI nanoparticles would further grow along the initial nuclei, and therefore, layered PANI nanoparticles on the graphene nanosheets were produced. After that, the soft nanosheets will self-assemble in the principle of minimizing surface energy, and finally form a spherical morphology with holes, like tremellas (Fig. 1c,d). In the process of the preparation of pure PANI, nucleation will take place after the initial nucleation on the solid surface [38]. Consequently, the nucleation will result connected PANI nanowires by using

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