Poly(ortho-aminophenol)/graphene nanocomposite as an efficient supercapacitor electrode

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ABSTRACT

Poly(ortho-aminophenol)/graphene nanocomposite was electrochemically synthesized. The nanocomposite represented an excellent supercapacitive behavior resulted from the complementary properties of graphene and the conducting polymer. The nanocomposite was characterized by various methods including scanning electron microscopy, transmission electron microscopy, FT-IR spectroscopy, X-ray diffraction, cyclic voltammetry and electrochemical impedance spectroscopy techniques. As an electrode material, the specific capacitance of the nanocomposite was 281.1 $F\,g^{-1}$ which was about 3 times of the specific capacitance of graphene. This behavior was related to a synergistic effect of the electrical double layer capacitance of graphene and pseudo-capacitance of the conducting polymer. The nanocomposite kept >99% of the initial specific capacitance after 1200 charge/discharge cycles at a current density of $1\,A\,g^{-1}$.

1. Introduction

Growing interest is being focused on supercapacitors as battery-complementary devices which can store and deliver energy at relatively high rates [1]. Because of their long cycle life, rapid charging and discharging at high current densities, wide thermal operating potential range and low maintenance cost, supercapacitors can bridge the gap between traditional capacitors and other power sources, such as batteries and fuel cells [2]. Tow types of supercapacitors are currently under investigation [3]: electrical double-layer capacitors (EDLCs), consisting of high-area carbon materials [4] such as activated carbon [5], carbon black [6], carbon aerogel [7], carbon nanotubes [8], mesoporous carbon [9] and graphene nanosheets (GNS) [10–12], and pseudo-capacitors, consisting of transition metal oxides [13–18], conducting polymers [19–23] and conducting polymer nanocomposites [24–31]. EDLCs store energy via charge separation at the electrode/electrolyte interface while, redox supercapacitors store energy via reversible faradaic processes in the bulk of redox materials through the charge and discharge cycles.

Graphene is a two-dimensional sheet of sp^2-hybridized carbon which firmly packed into a honeycomb lattice. Due to its unique properties, such as large thermal and electrical conductivities, superior mechanical properties, high surface area and chemical stability [32–34], graphene has attracted interest since its isolation from graphite by Geim et al. [35]. It is promising material for application in sensors [36–38], batteries [39], solar cells [40] and supercapacitors [24,41,42] due to the simple synthesis procedure [43]. Specific capacitance up to 135 $F\,g^{-1}$ has been determined for different graphene materials [44]. On the other hand, supporting the high-rate electrochemical redox film on the special two-dimensional structure of graphene can provide both the electrochemical double-layer capacitance and the highly reversible pseudo-capacitance, therefore, remarkably increases the overall capacitance of the composite material and reduces self-discharge [24,28–31,45,46].

Among various materials used to fabricate the supercapacitors, lightweight conducting polymers have been shown to display high capacitances [24,47]. Electronically conducting polymers have good intrinsic conductivity, low band-gap, suitable morphology, fast kinetics of the charge/discharge processes and low cost. The most commonly conducting polymers used in supercapacitor devices are poly(aniline), poly(pyrrole), poly(thiophene) and their derivatives [46].

Aminophenols are interesting electrochemical materials due to presence of two oxidizable functional groups (NH_2 and OH) in these compounds. Oxidative polymerization of ortho-aminophenol

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in acid solutions leads to formation of poly(ortho-aminophenol) with a phenoxazine-like units [48].

Following our recent report on the preliminary results of the supercapacitive behavior of the poly(ortho-aminophenol)/graphene nanocomposite as a communication [47], in this work, a detailed study of this nanocomposite as an efficient supercapacitor electrode is presented.

2. Experimental

2.1. Materials

All chemicals were of analytical grade from Merck and were used without further purification. All solutions were prepared with redistilled water.

2.2. Synthesis of graphene nanosheets

Graphene nanosheets (GNS) were synthesized from graphite powder using a modified Hummer's method [24,36–38,49]. In a typical synthesis process, 2.0 g graphite (Merck, <50 μm) was dispersed into 140 mL concentrated sulfuric acid and 1.0 g sodium nitrate was added to the reaction vessel under an ice bath. Then, 6.0 g potassium permanganate was slowly added to the mixture and was stirred for 2 h to fully oxidize graphite into graphite oxide (GO). Afterwards, the mixture was diluted with redistilled water. After that, a 5% H_2O_2 solution was added to the mixture until the color of the mixture changed to brilliant yellow. The suspension was filtered and the obtained GO was thoroughly washed with redistilled water. Then, GO redispersed in redistilled water and exfoliated to graphene oxide nanosheets using an ultrasonic bath for 3 h. The suspension gradually evolved into a brown solution during the ultrasonication, which GO was transformed into nanosheets. Finally, the exfoliated GO was reduced to GNS by refluxing the GO solution with hydrazine monohydrate at 100 °C for 2 h. In this step, the color of the solution turned to the dark black as the GNS were formed. The final product (the reduced form of graphene) was filtered, washed by redistilled water and ethanol and dried in an oven at 80 °C.

2.3. Electrode preparation

In order to prepare the graphene nanosheets/platinum (Pt/GNS) electrode, GNS (80%) was ground with polyvinylidene difluoride (10%) and acetylene black (10%), and dispersed in N-methyl pyrrolidone by means of an ultrasonic bath to obtain a paste. The paste was supported on a 4.0 mm diameter Pt disk electrode and then heated to 100 °C in an oven for several hours. For preparation of the platinum/poly(ortho-aminophenol) (Pt/POAP) electrode, a Pt electrode was transferred to a 0.1 M ortho-aminophenol + 1.0 M sulfuric acid solution. Potential in the range of −100 to 1000 mV (vs. Ag/AgCl) in a regime of cyclic voltammetry was applied for 100 cycles at a potential sweep rate of 50 mV s^{-1}. A brownish film was deposited on the electrode surface. The platinum/graphene nanosheets/poly(ortho-aminophenol) (Pt/GNS/POAP, the nanocomposite) electrode was similarly fabricated using the Pt/GNS electrode, otherwise the Pt/GNS electrode was employed for the electropolymerization of POAP. The mass of deposited POAP on the Pt/GNS/POAP electrode was calculated from the charge in its characteristic voltammogram based on the Faraday's law and considering a value of 210 g mol^{-1} for POAP oligomer molecular weight and a value of n for the number of exchanged electrons [50].

2.4. Apparatus

Electrochemical measurements were carried out in a conventional three-electrode cell powered by a μ-Autolab potentiostat/galvanostat, type III, FRA2 (The Netherlands). In impedance measurements, a frequency range of 100 kHz to 5 mHz was employed while the a.c. voltage amplitude was 10 mV and the equilibrium time was 5 s. The system was run by a PC through FRA and GPES 4.9 softwares. A Pt disk and an Ag/AgCl, 3 M KCl (from Metrohm) were used as the counter and reference electrodes, respectively. The supporting electrolyte was 1.0 M H_2SO_4.

Scanning and transmission electron microscopies (SEM and TEM) were performed by an X-30 Philips scanning electron microscope and a CEM 902A ZEISS transmission electron microscope, respectively. For TEM, an accelerating voltage of 80 kV was employed and the samples were prepared by placing a drop of the particles, dispersed in acetone, on a carbon-covered copper grid (400 mesh) and evaporating the solvent.

Powder X-ray diffraction (XRD) patterns were measured by a Philips X'Pert (The Netherlands) using Cu Kα radiation at 40 kV and 30 mA in a 2θ degree range 10–60°.

Fourier transform infrared (FT-IR) spectra of KBr powder-pressed pellets having 1 wt% of samples were recorded on an ABB BOMEM model FTLA 2000 instrument.

3. Results and discussion

3.1. XRD patterns

X-ray diffraction patterns of the pristine graphite and the synthesized GNS are depicted in Fig. 1. XRD pattern of the pristine graphite shows two sharp peaks at $2\theta = 26.49°$ and 54.58°, corresponding to the (002) and (004) reflections of graphite respectively, which are assigned to d-spacing of 3.36 and 1.68 Å, respectively. In XRD pattern of the synthesized GNS, however, a broad peak centered at $2\theta = 24.17°$ corresponding to the (002) reflection of graphene with a d-spacing of 3.55 Å is observed. The relatively weak peaks in the 2θ interval of 40–50° are due to (100) and (101) reflections, originated from more common hexagonal and coexisting rhombohedral phases, respectively. The broad reflection peaks of GNS indicates poor ordering of the sheets and hints that the sample is composed of mostly monolayer or few layers agglomerate of GNS [24,51]. This is consistent with the data obtained from electron microscopy (vide infra).
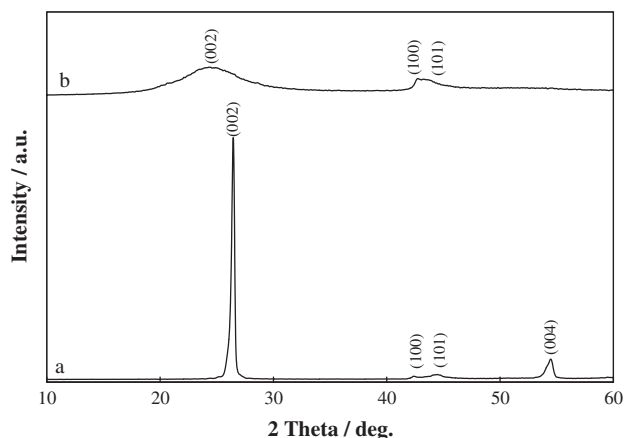

Fig. 1. X-ray diffraction patterns of the pristine graphite (a) and the synthesized GNS (b).