A new route for the synthesis of polyaniline nanoarrays on graphene oxide for high-performance supercapacitors

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ABSTRACT

A traditional approach is conducted for the preparation of polyaniline/graphene oxide (PANI/GO) nanostructures, where aniline monomer followed by ammonium persulfate (APS) were added to an acidic solution of graphene oxide (GO). Herein, we investigate a condition in which firstly GO is dispersed in acidic media containing APS. The aniline monomer is then added in order to the *in-situ* polymerization of aniline. An investigation is also carried out on the effect of the acid type including sulfuric acid (H_2SO_4), hydrogen chloride (HCl), perchloric acid ($HClO_4$), and *p*-toluenesulfonic acid (PTSA) on the morphology and electrochemical behavior of resultant PANI/GO nanostructures. The characterizations reveal well-defined nanoarrays for PANI/GO-H_2SO_4 electrode with the highest porosity and specific surface area. This electrode exhibits a highest current density in cyclic voltammetry studies and the most specific capacitance (727 F g^{-1}) in charge/discharge studies among other as-prepared electrodes. Utilizing this PANI/GO-H_2SO_4 nanocomposite as the electrodes in a symmetric configuration resulted in the development of devices with remarkable performance including a maximum energy density of 40 Wh kg^{-1} and a power density up to 15.3 kW kg^{-1} with an excellent cycle life (only 4.3% loss after 5000 cycles).

1. Introduction

The depletion of fossil fuel and the increase in environmental pollution caused by the release of CO_2 have triggered an urgent demand for clean and renewable energy sources. Among various energy storage systems, supercapacitors have attracted much more attention for next-generation energy-storage applications because of their higher power density, longer cycling stability, lower cost, and environmental friendliness [1,2]. According to the charge-storage mechanism, supercapacitors can be classified into two types of electrochemical double-layer capacitors (EDLCs, carbonaceous materials) and pseudo-capacitors (mainly transitional metal oxides and conductive polymers) [3–5]. Charge storage in EDLCs is based on a physical charge separation at the interface of electrode and electrolyte, while in pseudo-capacitors it is based on fast and reversible faradaic redox reactions [6,7]. Although EDLCs offer high power density and long cycle life, they suffer from lower capacitance and energy density than that of pseudo-capacitors. Therefore, the combination of carbonaceous materials with metal oxides/conductive polymers is a most promising strategy widely used to simultaneously take both advantages of EDLCs and pseudo-capacitors [8,9]. Among various allotropes of carbon, graphene as a two-dimensional single layer of sp2-hybridized carbon atoms has been the center of a great attention because of its high specific surface area, good mechanical properties and excellent electrical conductivity [10,11]. These outstanding properties make graphene a promising candidate as an EDLC component of hybrid electrodes for supercapacitors [12].

For the pseudo-capacitive component of the hybrid electrode, polyaniline (PANI) is a promising candidate as a low cost, easy synthesis, good environmentally stable, flexible, and high capacitance conductive polymer [13,14]. To date, various nanoarrays of

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PANI such as nanorods [15–19], nanopillars [20] nanocones [21], nanotubes [22], nanofibers [23–25], nanospheres [25] and nanowires [26–31] have been grown on the surface of graphene sheets to attain advanced hybrid electrodes.

In general, there are two approaches to the growth of one-dimensional (1-D) nanoarrays of PANI on the two-dimensional (2-D) sheets of graphene for achieving the three-dimensional (3-D) structures of PANI/graphene composites [32–34]; (I) Non-covalent attachment of in-situ formed PANI nanoarrays on graphene oxide (GO) sheets: In this way, the growth of nanoarrays is started by non-reactive groups or absorbed additives on GO sheets as active sites, followed by conjugation due to van der Waals forces or π-π stacking interactions [28,30,35–37] and (II) Covalent attachment of in-situ formed PANI nanoarrays on functionalized GO sheets [16,18,38–40]. However, the first approach is more interesting because of fewer steps and the lack of pre-modification. Xu et al. [35] reported aligned PANI nanowires produced by a dilute polymerization of aniline monomer in GO aqueous dispersion. They found that GO's oxygen-containing functional groups can act as nucleation sites for PANI nanowire arrays. In addition, they indicated that the adjusting the aniline concentration is a very important task since it allows obtaining sparser and shorter nanowires at lower concentrations, while at high concentrations the self-nucleation of PANI is inevitable. Hao et al. [20] synthesized a reduced cross-linked polyaniline/reduced graphene oxide (r-CPA/rGO) composite in which the CPA nano-pillar arrays are adsorbed on the rGO sheets. They used alkylphenol ethoxylates and citric acid as surfactant and reducing agent, respectively. Gedela et al. reported a solar radiation exfoliated reduced graphene oxide (SrGO)/polyaniline nanofibers composite prepared using chemical oxidative polymerization. They observed that by the implementation of SrGO instead of thermally exfoliated reduced GO, in the processing of PANI composite, the specific gravimetric capacitance values could be almost doubled [41].

However, in all reports on the synthesis of PANI nanostructures on GO sheets by these approaches, researchers have applied conventional route of in-situ chemical oxidation of aniline, through which aniline monomers are dissolved in acidic media containing GO and followed by the addition of APS. In this work, we investigate a situation where, first, GO is dispersed in an acidic medium containing APS and then the aniline monomers are added. Also, we study the possibility of the use of APS as oxidant and surface directing agent. Moreover, we analyze the effect of acid type, as a dopant, on the morphology and the electrochemical behavior of the as-prepared PANI/GO nanostructures. Previous studies have shown the effect of acid type on the morphology and electrochemical behavior of PANI nanostructures alone [42–44], but to the best of our knowledge, there is no report on the effect of the acid type in developing PANI/GO nanostructures. Finally, the electrochemical analysis is carried out to investigate the performance of the as-prepared nanocomposites for supercapacitors applications.

2. Experimental

2.1. Materials

The aniline monomer was purchased from Aldrich and double distilled before use. Pristine graphite, sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrogen chloride (HCl), perchloric acid ($HClO_4$), p-toluenesulfonic acid (PTSA), ammonium persulfate (APS) were all purchased from Merck and used as received.

2.1.1. Preparation of graphene oxide (GO)

GO was synthesized from natural flake graphite using improved Hummers method [45,46]. Briefly, graphite powder (1.0 g) was dispersed in a mixture of concentrated H_2SO_4 and H_3PO_4 (120 and 13.5 mL, respectively) and stirred for 24 h. Then, $KMnO_4$ (6.0 g) was gradually added into above mixture under continuous stirring at a temperature below 30 °C. After stirring the mix at room temperature for 3 days, 400 mL frozen water a 10 mL H_2O_2 were added to it. The resulting suspension was washed under centrifugation with 10% HCl, followed by washing with distilled water to remove residual salts and metal ions. The obtained graphite oxide was sonicated for achieving a stable suspension of GO. Then, the resultant suspension was centrifuged at 5000 rpm for 5 min to remove the un-exfoliated graphite oxide. The purified GO was diluted with distilled water to achieve 1 mg mL^{-1} GO suspension for future use.

2.1.2. Synthesis of PANI/GO nanocomposites

PANI/GO nanocomposites were synthesized by in-situ polymerization in the presence of GO and aniline monomer. In summary, 100 mL of GO suspension was diluted with 40 mL distilled water, and then 1.14 g of APS was added such that the final solution contained 1 M acid. Next, different types of acids were examined, including HCl, $HClO_4$, H_2SO_4, and PTSA. After cooling down to 0−4 °C, 10 mL of ethanol was added to the mixture and stirred thoroughly. Then, 684 μL of aniline was added (the molar ratio of aniline/APS is 3/2) and stirred in ice bath for 24 h. Finally, the product was repeatedly washed with distilled water and methanol to remove any residual oxidant, followed by freeze-drying of collected precipitates.

2.1.3. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics TENSOR 27 spectrometer on KBr pellets. The morphology and microstructure of the as-synthesized samples were characterized by a field-emission scanning electron microscopy (FE-SEM MIRA3 FEG-SEM, Tescan, Czech) and Raman spectroscopy (Bruker, Germany). The XRD patterns of samples were performed on a Siemens D-500 Diffractometer using Cu-K$_\alpha$ radiation (wavelength, $\lambda = 1.5406$ Å) in a 2θ angle range of 10°−80°. The thermogravimetric analysis (TGA) was performed with a thermal analysis system (Linseis L81A1750, German) within a temperature range of 100−800 °C and a heating rate of 10 °C min^{-1} under N_2 atmosphere.

2.1.4. Electrochemical measurements

In order to construct the working electrodes in a three-electrode system, 80 wt% active materials, 10 wt% carbon black, and 10 wt% polyvinylidenefluoride dissolved in N-methylpyrrolidone were mixed to form the slurry. The mixture was kneaded and the resultant pastes were pressed onto carbon paper and dried at 60 °C for 12 h. Platinum wire, saturated calomel electrode (SCE) and 1 M H_2SO_4 were used as the counter electrode, reference electrode, and electrolyte, respectively. Symmetrical supercapacitor devices were assembled using PANI/GO active material on a pair (same size) of Ti foils as the current collectors, 1 M H_2SO_4 aqueous solution as the electrolyte, and the glass microfiber paper as a separator. Cyclic voltammetry (CV), Galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed. EIS was recorded with AC voltage amplitude of 5 mV and frequency range of 100 kHz −0.01 Hz.

3. Results and discussion

A schematic of the synthesis mechanism for the as-prepared PANI nanoarrays on GO sheets is given in Fig. 1. In the first step, the addition of APS and acid to GO suspension leads to the in-site oxidative polymerization of PANI.