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Spectroscopic and electrochemical characteristics of a carboxylated graphene–ZnO composites

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ABSTRACT

Carboxylated graphene–ZnO (G-COOZn) composites were grown as ZnO nanoparticles onto graphene sheets by a one-step thermal method using carboxylated graphene (G-COOH) and $Zn(NO_3)_2$. G-COOH sheets were synthesized from graphene oxide (GO) and chloroacetic acid ($Cl–CH_2–COOH$). GO was used as the starting material, as prepared by the Hummers' method using graphite flakes. GO, G-COOH, and G-COOZn were characterized by XRD, AFM, SEM, TEM, FT-IR, ^{13}C-NMR, and Raman spectroscopy. The electrochemical properties of the G-COOZn supercapacitor were investigated by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge–discharge tests. The results show that the asymmetric supercapacitor has electrochemical capacitance performance within the potential range of 0–1 V. The supercapacitor delivered a specific capacitance of $\sim$238 F g^{-1} at a current density of 50 mA cm^{-2}. This method provides an easy and straightforward approach to deposit ZnO nanoparticles onto graphene sheets, and may be readily extended to the preparation of other classes of hybrids based on GO sheets for specific technological applications.

1. Introduction.

Recent research on graphene has focused on a great diversity of technological applications, including nanoelectronic and optoelectronic devices [1–4] as well as energy-storage materials [5–7]. Graphene sheets have an unrolled 2D structure [8,9] and represent a unique morphology carbon material with potential for electrochemical energy storage device applications due to its superb chemical stability [9], high electrical conductivity [10,11], and large surface area [11,12]. The graphene sheets overlap with each other to afford a three-dimensional conducting network, which facilitates electron transfer between the active materials and the charge collector; thus it is an excellent candidate for use as an electrode material for energy-conversion storage systems. Boosting the capacitive performance of graphene-based energy storage materials by growing redox-active materials on the electrically conducting graphene sheets has thus become a topic of major interest. In most graphene-based composites, prepared by reduction of graphene oxide (GO) followed by the loading of pseudocapacitive nanomaterials, the excellent electric and surface properties of the graphene sheets are not completely revealed due to the formation of agglomerations of graphene during the reaction steps. Thu, the seeking of effective strategies to synthesize well-dispersed graphene-based composites remains an important goal.

The use of GO as a material for the preparation of individual graphene sheets in bulk-quantities, has attracted great attention in recent years [13–15]. In addition, the extremely large specific surface area, the abundant oxygen-containing surface functionalities (including epoxide, hydroxyl, carbonyl, and carboxylic groups) and the high water compatibility, all result in GO sheets being of great promise for future applications [13,14]. For instance, GO sheets modified with polyethylene glycol have been employed as aqueous compatible carriers for water-insoluble drug delivery [16]. The oxygen-containing functional groups on GO sheets have been used as sites for the deposition of metal nanoparticles and organic macromolecules, including porphyrins [17,18]. This has opened up a novel route to a range of multifunctional-nanometer scaled catalytic, magnetic, and optoelectronic materials [19–21]. GO sheets, with their distinctive nanostructure hold great promise for potential applications in many technological fields that include nanoelectronics [22], sensors [23], nanocomposites [24], batteries [25], and capacitors [26].

It is known that the presence of metal oxides such as ZnO, MnO_2, IrO_2, RuO_2 and NiO can improve the capacitance of carbon based supercapacitors, as they can contribute additional pseudo-capacitance to the capacitance due to arising from the carbon materials [27–30]. It is well known that Zinc oxide, has found applications in optics, optoelectronics, sensors, and actuators due to its semiconducting, piezoelectric, and pyroelectric properties [31]. Recently, the suitability of ZnO as a potential candidate for supercapacitor applications has been preliminarily substantiated [32,33]. Attempts to combine ZnO and graphene have been reported in

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efforts to obtain hybrid materials with superior optical or electrical properties [34,35]. Taking into account its eco-friendly nature and the easy growth of wurtzite-structured ZnO on the various substrates, it is meaningful to seek effective preparation strategies and applications of ZnO/GO composites for supercapacitors.

The successful use of –COOH groups combined with Zn (–COOZn) has been previously reported [36–38]. We treated a GO sample with chloroacetic acid under strongly basic conditions in order to activate the epoxide and ester groups, and to convert hydroxyl groups to carboxylic acid (–COOH) moieties [39,40]. The carboxylate groups produced under strongly basic conditions were anticipated to act as a binding site for Zn ion.

In this paper, we report a facile one-pot solvothermal method for the synthesis of a G-COOZn composites using G-COOH and $Zn(NO_3)_2$ as the precursors for forming G-COOZn. The electrochemical properties of G-COOZn were also investigated.

2. Experimental methods

2.1. Preparation of GO

The GO was prepared according to modified Hummers' method [41,42] by reacting commercial flake graphite powder (Aldrich) (5 g) and $NaNO_3$ (3.75 g) with conc. H_2SO_4 (375 mL). This mixture was stirred in an ice-water bath, and 22.5 g of $KMnO_4$ was slowly added over 1 h as stirring was continued for 2 h in an ice-water bath. After the mixture was stirred vigorously for 2 days at room temperature, 700 mL of 5 wt% H_2SO_4 aqueous solution was added over 1 h with stirring, and the temperature was kept at 98 °C. The resultant mixture was further stirred for 2 h at 98 °C. After the temperature was reduced to 60 °C, 15 mL of H_2O_2 (30 wt% aqueous solutions) was added, and the mixture was stirred for 2 h at room temperature. To remove extraneous products from the oxidation (and any other inorganic impurities), the resultant mixture was purified by repeating the following procedure 20 times: centrifugation, removal of the supernatant liquid, then dispersing the solid using vigorous stirring and bath ultrasonication for 1 h at a power of 150 W. The resultant solid was recovered by centrifugation, washed with deionized water and ethanol until H^+ free, and then dried in air at 40 °C.

2.2. Carboxylation of GO

For carboxylation, an aqueous suspension (5 mL) of GO was diluted by a factor of 2 to give a concentration of $\sim$2 mg mL^{-1}, and then bath sonicated for 1 h to give a clear solution. NaOH (1.2 g) and chloroacetic acid ($Cl–CH_2–COOH$) (1.0 g) were added to the GO suspension and bath sonicated for 2 h to convert the –OH groups to –COOH via conjugation of acetic acid moieties giving G-COOH [39,40]. The resulting G-COOH solution was neutralized, and purified by repeated rinsing and filtration.

2.3. Preparation of G-COOZn composites

The G-COOZn composites were synthesized by a hydrothermal process. In a typical synthesis, G-COOH (0.5 g) and $Zn(NO_3)_2$ (1.00 g) were dispersed in deionized water (20 mL) with ultrasonication for 20 min. Subsequently, the mixture was transferred to a polytetrafluoroethylene-lined autoclave and heated at 180 °C for 10 h. After cooling to room temperature, the resulting gray-black suspension was filtered through a 0.22 μm microporous membrane in order to separate the G-COOZn composites.

2.4. Characterization of GO, G-COOH and G-COOZn composites

The powder X-ray diffraction (XRD) pattern measurements of the samples were recorded on a Bruker D8-Advance X-ray powder diffractometer using Cu Kα radiation (λ = 0.1542 nm) with scattering angles (2θ) of 5–80°, operating at 40 keV, and a cathode current of 20 mA. Scanning electron micrographs (SEM) were obtained using a JEOL JSM-840A scanning electron microscope. Transmission electron micrographs (TEM) were obtained with a JEOL JEM-200 CX transmission electron microscope operating at 200 kV. Atomic force microscopy (AFM) images were obtained using an Auto-Probe CP/MT scanning probe microscope (XE-100(PSIA)). Imaging was carried out in non-contact mode using a V-shaped 'Ultralever' probe B (Park Scientific Instruments, boron doped Si with frequency f_c = 78.6 kHz, spring constants k = 2.0–3.8 Nm^{-1}, and nominal tip radius 10 nm). All images were collected under ambient conditions at 50% relative humidity and 23 °C with a scanning raster rate of 1 Hz. Samples for AFM images were prepared by depositing dispersions of GO in ethanol on a freshly cleaved mica surface (Ted Pella Inc. Prod No. 50) and allowing them to dry in air. Raman spectra were obtained using a Jobin Yvon/Horiba LabRAM spectrometer equipped with an integral microscope (Olympus BX 41). A 514.5 nm Ar-laser was used as an excitation source. Samples were sonicated in ethanol and drops were applied to a glass slide for observation. The sample was viewed using a green laser apparatus under a maximum magnification of ×50, and a red laser apparatus under a magnification of ×100. Solid-state ^{13}C-cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (^{13}C-NMR) experiments were performed on a 400 MHz Solid-state Bruker Avance II+ spectrometer (at KBSI Daegu Center, KOREA). The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VERTEX 80v model using the KBr disk method. Steady state photoluminescence (PL) spectra were recorded at room temperature using a Shimadzu RF-5301PC spectrofluorometer.

2.5. Preparation of working electrode and electrochemical tests

The electrochemical measurements were performed in a three-electrode cell system with 1 M Na_2SO_4 aqueous solution as electrolyte. The working electrodes were fabricated by mixing the electroactive materials (G-COOZn), carbon-black, and polytetrafluoroethylene (PTFE) in a mass ratio of 70:20:10 and dispersed in tetrahydrofuran to produce homogeneous slurry. The resulting slurry was coated onto the nickel foam current collector (1 cm × 1 cm) using a blade. And then, the electrodes dried at 70 °C for 12 h. The loading mass of each electrode was about 21.0 mg. Platinum wire and Ag/AgCl (KCl-saturated) electrode were used as counter electrode and reference electrode, respectively. Cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS) were carried out on a PARSTAT 2263 (Princeton Applied Research, USA) instrument. Impedance spectroscopy measurements were performed at a DC bias of 50 mV with sinusoidal signal of 0.1 mV over the frequency range from 10 kHz to 0.1 Hz.

3. Results and discussion

The GO was prepared from flake graphite via a modified Hummers' method [41,42], G-COOH was obtained by reacting GO with chloroacetic acid and the G-COOZn composites were prepared from G-COOH and $Zn(NO_3)_2$. The surface morphology and structure of the as-prepared samples were analyzed by SEM and TEM.

Fig. 1 shows the SEM and TEM results for GO, G-COOH, and G-COOZn. Compared to GO (Fig. 1(a)), the general structure of G-COOH (Fig. 1(b)) is greatly changed. It is found that the jeep-shaped GO