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Synthesis and characterization of covalently-grafted graphene–polyaniline nanocomposites and its use in a supercapacitor

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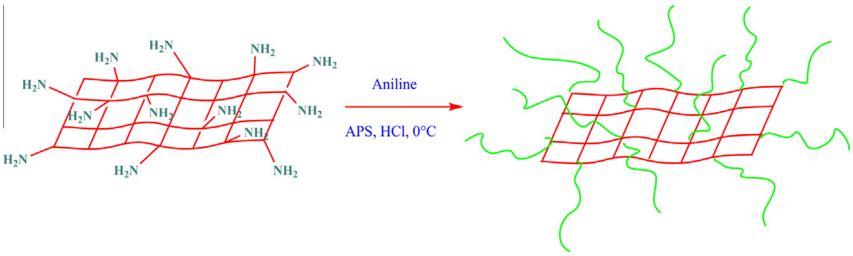
HIGHLIGHTS

- Covalently-grafted graphene–polyaniline nanocomposites were synthesized.
- Diazotization followed by amination of GO was used during the fabrication.
- Uniform fibrous polyaniline was grafted to the graphene layers.
- The resulting nanocomposites showed highly enhanced electrochemical performances.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis and characterization of three dimensional, covalently-grafted graphene–polyaniline nanocomposites have been reported. To enhance the grafting of polyaniline and prevent the aggregation and damage of the sp^2 network of the graphene sheet, numerous nucleation sites are introduced by diazotization with *p*-aminobenzoic acid followed by amination using the Schmidt reaction. The covalent functionalization and reduction was confirmed by FT-IR, Raman, XRD, XPS and UV–vis spectroscopy. *In situ* oxidative polymerization of aniline was performed using enhanced amino-functionalized graphene in the presence of ammonium peroxide as an oxidizing agent. SEM results show that uniform fibrous polyaniline was grafted to the graphene layers. The resulting nanocomposites showed enhanced electrochemical performances when compared to pristine polyaniline and aminized graphene.

1. Introduction

Graphene, the thinnest sp^2-hybridized single layer of carbon atoms, has drawn much attention since its discovery by Geim [1] in 2004 due to its unique nature, including high conductivity, good thermal stability and excellent mechanical properties [2–4]. A high surface-to-volume ratio makes graphene applicable in various applications, including energy storage materials [5], polymer nanocomposites [6], and electrocatalysis [7–9]. The key aspect to explore graphene properties is to control its thin sheet size and homogeneous dispersion, which is necessary for improving its electrochemical properties [10]. Recent studies have shown enhanced electrochemical properties of graphene by functionalization in supercapacitor applications [11,12].

Conducting polymers and high surface area carbon materials have been extensively used for high performance energy devices [13]. Conducting polymers, such as polyaniline (PANI), are promising materials for high performance energy devices because of high electrical conductivity, high electrochemical activity, high reversible pseudocapacitance, good biocompatibility and simple cost effective synthetic route [14]. Electrochemical double layer

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capacitance (EDLC) of graphene and redox capacitance of PANI are prime candidates for energy storage applications. Functionalization of graphene increases the interfacial interactions between the graphene layer and polymer matrix and imparts a good synergetic effect for energy storage applications, such as supercapacitors [15].

Extensive efforts have been made to prepare PANI-graphene nanocomposites for electrochemical applications including electrochemical synthesis [16] and *in situ* polymerization methods [17]. The combination of PANI and graphene decreases the graphene aggregation and enhances the electrochemical properties of the resulting nanocomposites. The properties of graphene-PANI nanocomposites are highly related to the interfacial interactions between graphene and PANI. To enhance the interfacial interactions and improve the electrochemical properties, direct exfoliation through *in situ* polymerization of aniline from the carboxylic functionality of graphene oxide (GO) [17] or a *in situ* polymerization-reduction/dedoping-redoping process [18] are used. Alternatively, Baek et al. [19] reported the synthesis of PANI-rGO nanocomposites using functionalized graphene, and Liu Jianhua et al. [15] and Zexiang Shen [5,20] grafted PANI to a graphene sheet. The drawbacks of both cases is that the conjugated system in graphene is destroyed through the ester and amide link formation, and highly corrosive thionyl chloride have been used for the preparation. Recently, researchers have reported that graphene can be chemically functionalized through diazotization where the sp^2 carbon of graphene is covalently bound with sp^3 carbon of the grafted compounds [21,22]. The reduction of diazonium salt leads to covalent functionalization of the epitaxial and edge sides to the surface of graphene [23,24]. When diazonium ion is heated, nitrogen is split off and an aryl radical formation occurs, which can be covalently bound to the graphene [25,26].

In this study, GO was diazotized with *p*-aminobenzoic acid and consequently, carboxylic groups were converted to amino groups using an acid-catalyzed Schmidt reaction. The reaction of carboxylic acid with hydrazoic acid leads to the formation of amine with the loss of CO_2 and N_2. Three dimensional, amino functionalizationis supposed to provide effective nucleation sites for PANI grafting on the graphene sheet and helps to avoid the dangling π-conjugative structure. The conjugative structures improve the charge transfer between the graphene sheet and PANI, which may lead to improved electrochemical properties. Amino-functionalized graphene, followed by *in situ* oxidative polymerization of aniline was performed to produce graphene-PANI nanocomposites. The electrochemical properties of fabricated composites were measured using cyclic voltammetry (CV) and a galvanostatic charge–discharge (CD) system.

2. Experimental

2.1. Materials

Acid-treated, natural expandable graphite (Grade 1721) was purchased from Asbury Carbon. Concentrated sulfuric acid (conc. H_2SO_4), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2, 30 wt%), *N,N′*-dimethylformamide (DMF), sodium nitrite ($NaNO_2$), *p*-aminobenzoic acid and ammonium persulfate (APS) were purchased from Daejung Reagents & Chemicals (Korea) and used as received without further purification. Aniline monomer was purchased from Yakuri Pure Chemicals Co., Ltd. (Kyoto, Japan) and vacuum distilled before use to remove impurities.

2.2. Preparation of graphene oxide (GO)

GO was prepared by expanding acid-treated graphite in a microwave oven for 10 s, followed by further oxidation using the Hummer's and Offeman method [27]. In brief, 7 g of expanded graphite was dispersed in 500 mL conc. H_2SO_4 and the mixture was cooled to 0 °C followed by the addition of 7 g $NaNO_3$. The reaction mixture was stirred for 30 min at the same temperature using a chilled ice bath and 42 g of $KMnO_4$ was slowly added in a small lots over 30 min to maintain the temperature below 15 °C. After incubating at 35 °C for 3 h, the solution was diluted with 300 mL DI water and the oxidation reaction was performed for 1 h at 95 °C with vigorous stirring. The resulting slurry was cooled and diluted with 2 L of deionized water followed by the addition of 60 mL H_2O_2. During the addition of H_2O_2, vigorous bubbles were observed and the color changed to golden yellow, which was further stirred for 1 h. The resulting GO suspension was centrifuged and washed with 1 M HCl to remove metallic impurities and then diluted with deionized water until the pH reached 7. The concentration of the GO slurry was set to 10 mg/100 mL for further diazotization reaction.

2.3. Preparation of diazotized graphene oxide (DGO-COOH)

To make epitaxial and edge functionalization, diazotization of GO was performed with *p*-amino benzoic acid as shown in Scheme 1, following previously reported procedures.[21,28] First, 5 g (0.0364 mol) of *p*-aminobenzoic acid was dissolved in 200 mL conc. HCl, resulting in a white suspension that was cooled to 0 °C. An ice cold aqueous solution of 2.51 g (0.0364 mol) $NaNO_2$ was added drop-wise to the above solution, resulting in a clear yellowish solution of *p*-aminobenzoic acid diazonium salt. After 30 min, 5 g of GO suspension (1 g/100 mL) in deionized water was added slowly to the mixture of diazonium salt solution. The solution was stirred for 3 h at 0 °C to get a homogenous dispersion and then the reaction temperature was increased to 25 °C followed by 6 h stirring. The temperature was then increased to 60 °C and the reaction mixture was stirred for 12 h. Vigorous evolution of nitrogen gas was observed as bubbles during the stirring. The resulting DGO-COOH was centrifuged and washed with copious amounts of methanol and water, and dried in a vacuum oven at 65 °C for 12 h.

2.4. Preparation of DGO-NH_2

The DGO-COOH was converted to the amino groups according to the modified Schmidt reaction as shown in Scheme 1. Briefly, 3 g of DGO-COOH was dispersed in toluene using ultrasonication for 30 min under nitrogen atmosphere. The resulting dispersion was cooled to 5 °C and 3 mL conc. H_2SO_4 was added drop-wise with continuous stirring. After 30 min, the ice bath was removed and 3 g of NaN_3 was added to the above mixture in small amounts over 30 min and stirred for 30 min at the same temperature. The temperature of the reaction was increased to 60 °C and the mixture was stirred for another 12 h. The resulting mixture was cooled and diluted with distilled water followed by filtering and drying under vacuum at 65 °C for 12 h. The final DGO-NH_2 product was a black powder.

2.5. Preparation of RDG-NH_2

Reduction of DGO-NH_2 with hydrazine was performed in DMF for the preparation of RDG-NH_2, as shown in Scheme 1. In brief, 2 g DGO-NH_2 was dispersed in DMF using ultrasonication and 50 mL hydrazine (aqueous 30% solution) was added to the dispersion. The reaction mixture was heated to 70 °C for 12 h resulting in a black dispersion of the reduced RDG-NH_2. The solution was filtered and washed with copious amounts of DI water and dried in a vacuum oven at 65 °C for 12 h.