

Preparation and characterization of conducting polymer nanocomposite with partially reduced graphene oxide



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ABSTRACT

We report here a synthetic route to producing electro-conductive graphene/polymer nanocomposite (GP) based on poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) and partially reduced graphene oxide (pRGO). GP was prepared by *in situ* oxidative polymerization of EDOT using PSS as a template in the presence of graphene oxide (GO). During the polymerization, GO was partially reduced, while the resulting nanocomposite (GP) displayed a stable aqueous suspension. Compared with a simple mixture of GO and pre-prepared PEDOT:PSS, GP showed an enhanced electrical conductivity of 9.2 S cm^{-1} .

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1. Introduction

Graphene, one-atom layer of graphite, has attracted enormous attention in a recent decade due to its outstanding thermal, optical, mechanical, and electrical properties [1–3]. Due to these unique properties, graphene has been explored for application in various areas such as transparent electrodes, electronic and energy storage devices, and nanocomposites. For the fabrication of graphene nanocomposites, various materials, such as small organic molecules like surfactants, polymers, carbon nanotubes, and metallic nanoparticles, have been used [4]. Particularly, composites of graphene with conducting polymers are of scientific and industrial interest because of their synergetic properties arising from the high conductivity. Among conducting polymers, PEDOT:PSS is the most promising material because it exhibits good conductivity, water-solubility, outstanding transparency, and excellent processability [5–7]. PEDOT:PSS is primarily made by aqueous oxidative polymerization of EDOT monomer in the presence of the template polymer PSS. The features of PSS in this complex are well discussed in previous reports [5,8].

Several methods were reported for the preparation of graphene and PEDOT:PSS nanocomposite, such as mixing of preformed PEDOT:PSS with graphene [9], *in situ* chemical polymerization of EDOT monomer in the presence of PSS and graphene [10], and *in situ* polymerization of EDOT with sulfonated graphene [11,12] or

PSS-wrapped graphene [13], and chemical reduction of GO in the presence of the PEDOT:PSS.

Reduced graphene oxide (RGO), which is prepared through chemical reduction of GO [14], possesses good electrical conductivity and high surface area. However, extremely low water-dispersibility of RGO has limited its application for the nanocomposite with PEDOT:PSS. On the other hand, nanocomposite of PEDOT:PSS with water-dispersible GO can be easily accomplished. However, because of poor conductivity of GO, the reduction of GO is an unavoidable process using a strong reductant, which is usually treated as toxic chemicals. Furthermore, PEDOT:PSS could be dedoped by a strong reductant, which leads to a decrease in conductivity [10]. Therefore, it is highly desirable to hybridize PEDOT:PSS with graphene without reduction process of GO mediated by a strong reductant.

Highly electron-rich EDOT has been investigated as a reductant since the oxidation potential of EDOT was found close to that of terthiophene which was used as the reductant in the preparation of Au nanoparticles [15]. Recently it was reported that EDOT reduced AgNO_3 into Ag nanoparticles [16], and HAuCl_4 into Au nanospheres [17]. Furthermore, EDOT also promoted the reduction of a highly oxidized graphite and a mechanically strong hydrogel composed of graphene and PEDOT was synthesized [18]. In this paper, polymerization of EDOT was carried out in the presence of GO, using PSS as a template. The resulting nanocomposite (GP) of PEDOT:PSS with GO was characterized by XPS, FT-IR, Raman spectroscopies, and its morphological and electrical properties were investigated. Discussions were made by comparing GP with the simple mixture (G + P) of GO and pre-prepared PEDOT:PSS.

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2. Experimental

2.1. Materials

For the preparation of GO, graphite, KMnO_4 (99.0%), and NaNO_3 (99.0%) were purchased from Sigma–Aldrich, and H_2SO_4 (95.0%), HCl (34–37%), H_2O_2 (34.5%) from Samchun Chemicals. For the hybridization of graphene and PEDOT/PSS, EDOT monomer, PSS (70,000 g/mol, 30 wt% aqueous solution), sodium persulfate (SPS), iron(III) sulfate (IS) were purchased from Sigma–Aldrich. EDOT was purified by distillation under reduced pressure and stored in a refrigerator prior to use. All other reagents were of analytical grade and used as supplied without further purification.

2.2. Preparation of GP

Graphene oxide (GO) was synthesized from graphite powder by a modified Hummers method [19]. 0.8 g GO was dispersed in 150 mL distilled water and ultrasonicated for 2 h. GO dispersant was added into the mixture of 1.87 g of EDOT and 16.13 g of 30% PSS solution, and agitated with 600 rpm at 10 °C. 4.7 g of SPS and 0.026 g of IS in 10 mL of water was added and the oxidative polymerization of EDOT was carried out with 600 rpm at 10 °C for 28 h. The reaction mixture was filtered using nylon membrane filter (0.2 μm) and carefully washed with water. The 2.3 g of dark blue GP was obtained after drying at 50 °C in vacuum for 24 h. 0.45 g of GP was dispersed in 30 mL of water and ultrasonicated for 2 h. Graphene paper was made by vacuum filtration of aqueous dispersion of GP using a Anodisc membrane filter (47 mm in diameter, 0.22 μm pore size), and then dried at 50 °C for 48 h [20,21]. Theoretically, the content of GO in GP is 11.9 wt%.

For comparison, pristine PEDOT:PSS was prepared without the addition of GO according to the same synthetic procedure as that for GP. 0.45 g of as-prepared PEDOT:PSS was dispersed in 30 mL of water and 0.05 g of GO was added. The dispersion was ultrasonicated for 2 h, and graphene paper was also prepared separately under the same conditions, and the resulting paper was labeled as G + P.

2.3. Characterization

The structural and morphological characterization of GP nanocomposite was conducted by FT-IR, XRD, Raman, SEM and AFM. XPS and FT-IR spectra were recorded on a K-Alpha of Thermo Scientific, and from KBr pellets on PerkinElmer, respectively. The Raman shift spectra were obtained with an inVia Raman microscopes (Renishaw) at an excitation wavelength of 514 nm. SEM and

Atomic force microscopy (AFM) images were taken by FE-SEM (JSM 6700F, JEOL) and XE-100 of Park Systems, respectively. Elemental analysis was conducted with Flash EA1112. The electrical conductivity measurements were made by the conventional four-probe technique at the room temperature.

3. Results and discussion

3.1. Chemical structure characterization

XPS was employed to analyze the structure of the resulting nanocomposite compound (GP). The formation of PEDOT:PSS in GP was confirmed using the S_{2p} spectrum, as shown in Fig. 2a. GP exhibited two major peaks contributed from sulfur atom in PEDOT and PSS, and each peak can also be de-convoluted into two components; spin-split doublet S_{2p} at 163.6 ($\text{S}_{2p_{3/2}}$) and 164.8 eV ($\text{S}_{2p_{1/2}}$), which correspond to thiophene of PEDOT, and the peak at 168.6 eV and at 169.8 eV originates from the sulfonate (SO_3^-) and sulfonic acid groups (SO_3H) of PSS, respectively [13,22,23]. The formation of PEDOT:PSS in GP was also confirmed by the similarity of both S_{2p} spectra of GP and the mixture (G + P) of GO and PEDOT:PSS, as illustrated in Fig. 2b.

The structural transition of GO in GP nanocomposite was investigated by C_{1s} of XPS (Fig. 2c). There are three main peaks with binding energies at about 284.7, 286.0, and 287.9 eV, which are attributed to C–C/C=C, C–O–C, and C=O species, respectively [24,25]. G + P also showed the same profile as illustrated in Fig. 2d. The peak corresponding to C=O for GP is extremely small and the area relative to that of C–C/C=C peak is 0.14 whereas the area of C=O relative to that of C–C/C=C peak is 0.25 for G + P. It is well known that C=O peak of GO diminishes progressively during the reduction reaction and finally disappears when GO was transformed into perfectly reduced GO. In this study, it is considered that GO in GP was partially reduced during the polymerization of EDOT.

In C_{1s} spectrum of XPS, C–O–C peak of GO is also indicative of de-oxygenation of RGO platelets after chemical reduction. We, however, were not able to evaluate the extent of reduction in GP since C–O–C of PEDOT in GP also exhibited a strong peak at the same binding energy.

Reduction of GO in GP was further investigated using FT-IR. As described in Fig. 3a, GO showed three characteristic bands at about 1720, 1640, and 1056 cm^{-1} , which can be assigned to C=O, C=C, and C–O–C bonds, respectively. The spectrum of GP showed a decrease in the C=O peak which confirms the partial reduction of GO, on the other hand, the peak due to C–O–C shifted to 1034 cm^{-1} . C–O–C in PEDOT:PSS was known to appear at around

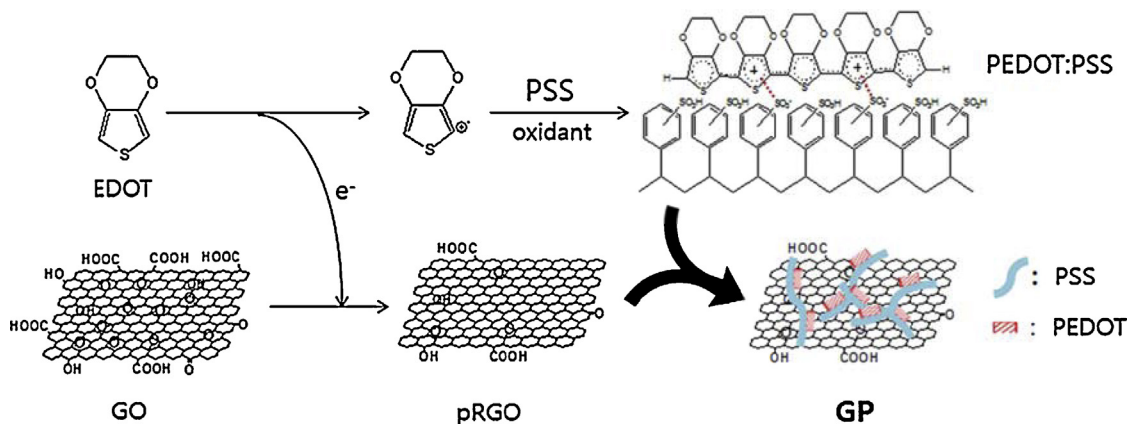


Fig.1. Schematic diagram of the synthesis of the GP nanocomposite.

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