Surface Modifications of Graphene-based Polymer Nanocomposites by Different Synthesis Techniques

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ABSTRACT

With the appropriate surface treatments, graphene sheets can be separated from graphite material and the layer-to-layer distance can be extended. In the present work, graphene nanosheets (GNS) were separated from graphite by an improved, safer and mild method including the steps of oxidation, thermal expansion, ultrasonic treatment and chemical reduction. For the production of advanced polymer nanocomposites, the distinguished properties of GNS were combined with the structural properties of conducting polypyrrole by the proposed simple and low-cost fabrication technique. The changes in surface morphologies and surface functional groups were estimated by controlling the polymer coating on graphite oxide (GO) sheets, expanded GO and GNS.

INTRODUCTION

Graphene, the world's thinnest sheet – only a single atom thick – has a great potential to provide a new way in energy, computing and medical research [1]. The first graphene sheets were obtained by extracting monolayer sheets from the three-dimensional graphite using a technique called micromechanical cleavage in 2004 [2]. One of the applicable methods is the graphite oxidation in order to reduce the strong bonding between sheets in graphite and to receive monolayer graphene sheet. Potassium chlorate, potassium permanganate, nitric acid, and sulfuric acid are mostly used as oxidizing agents in order to destruct the graphite structure in exfoliation process [3-5]. There have been numerous attempts in the literature to produce graphene sheets by exfoliation or expansion of graphite starting with GO or graphite intercalation compounds. Single graphene sheets are exfoliated from graphite with the thermal expansion and chemical reduction processes [6]. After heat treatment of GO sheets, the crystal lattice planes of graphite flakes are extended and this leads to the formation of expanded graphite called "worm-like" or accordion structure [7].

Graphene sheets have been used as fillers in polymer matrix to improve the characteristic properties of nanocomposites. Researchers have found new methods to enhance the dispersion of graphite nanosheets in a polymer matrix. Chen et. al. demonstrated that sonication process is more applicable to disperse graphite sheets in polymer matrix [8]. This method provides much higher conductive composites than the other composites obtained by conventional methods.

In this work, graphene sheets were separated from graphite flakes with an improved, safer and mild exfoliation technique. GO sheets, expanded GO and GNS, the products obtained after each step in the exfoliation process, were used as filler in conducting polypyrrole matrix in order to fabricate polymer-based nanocomposites. The effect of surface functional groups on

nanocomposite production and the changes in surface morphologies of samples after each treatment were investigated in detail by surface analysis techniques.

EXPERIMENT

Chemical Exfoliation of Graphene Nanosheets from Graphite

Graphene nanosheets (GNS) were exfoliated by following two ways presented in details in our previous publications [7, 9]. 1st way, the shortest exfoliation technique, included graphite oxidation, ultrasonic treatment and chemical reduction. 2nd way, the longest exfoliation technique, contained these steps: graphite oxidation, ultrasonic treatment, thermal exfoliation, ultrasonic treatment and chemical reduction. Both the reaction procedures with thermal expansion and without thermal expansion led to the formation of GNS. Graphite oxide (GO) was prepared by using $K_2Cr_2O_7$ and H_2SO_4 as the oxidizing agents and acetic anhydride as an intercalating agent at 45^oC at different oxidation times changing from 50 min to 10 days [7, 9]. GO sheets were expanded by heating up to 1000^oC rapidly in a tube furnace and kept for 5 min at this temperature under an argon atmosphere to obtain expanded GO samples [10]. Thermal treatment caused the thermal decomposition of acetic anhydride into CO_2 and H_2O gas which swelled the layered graphitic structure and resulted in a high separation of GO sheets [10]. In the proposed two methods, both GO sheets and expanded GO were reduced through refluxing by hydroquinone under N_2 atmosphere for 1 day in order to obtain GNS.

Synthesis of Graphene-based Nanocomposites

Polypyrrole (PPy) was synthesized by using Py (0.0447 mol) as the monomer and $FeCl_3$ (0.107 mol) as the oxidant in the mixture of H_2O and ethanol in 1:1 (v/v) under N_2 atmosphere [11]. PPy was coated on GO sheets, expanded GO and GNS by *in situ* polymerization of pyrrole at room temperature under N_2 atmosphere for 24 h [12]. The precipitated sample was filtered and rinsed several times by ethanol and distilled water to remove excess pyrrole, catalyst and side products. Before polymerization, samples (GO, expanded GO and GNS) and Py monomer in adjusted weight fractions were exposed to ultrasonic vibration for 2 h in order to diffuse Py monomer through the layers. Ultrasonic treatment also provided to break expanded GO apart into thinner graphite nanoplatelets (GNPs) [10].

Characterization

The morphologies of nanocomposites were examined by a Leo Supra 35VP Field Emission Scanning Electron Microscope (SEM). Elemental analyses were performed by Energy-Dispersive X-Ray (EDX) analyzing system. Functional groups on the surface of samples were determined by a Nicolet iS10 Fourier Transform Infrared Spectroscopy (FT-IR). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. This system used a focused monochromatic Al Kα X-rays (1486.7 eV) source and a spherical sector analyzer.

DISCUSSION

SEM images of GO sheets, expanded GO and GNS were shown in Figure 1. Graphite flakes consisted rigid layers [7] but layers were broadened and swollen after oxidation process, Figure 1 a. Heat treatment of GO samples caused the thermal decomposition of acetic anhydride into CO_2 and H_2O vapors which further swelled the layered graphitic structure and thus worm-like structures called expanded GO were obtained, Figure 1 b. After chemical reduction of GO sheets, graphene sheets made of a few graphene layers could be clearly seen in Figure 1 c.
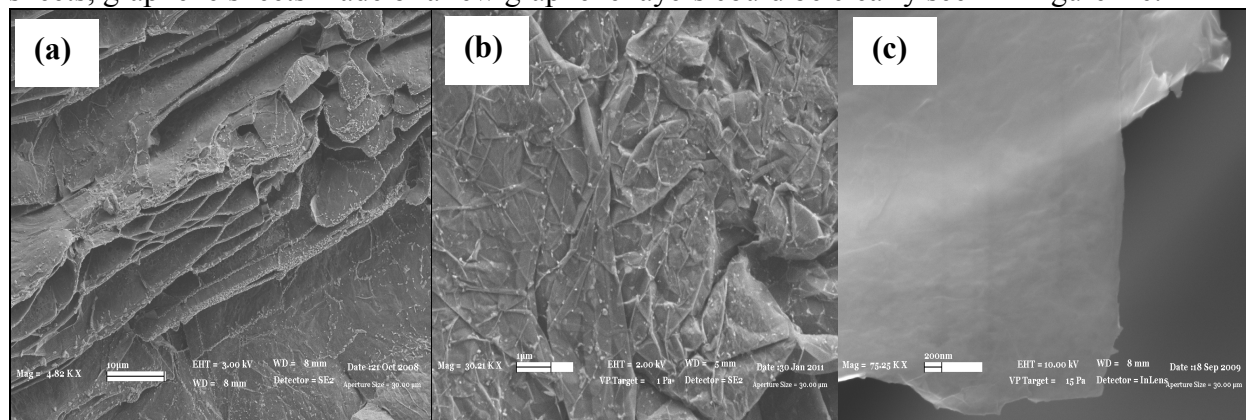
**Figure 1.** SEM images of **(a)** GO sheets, **(b)** expanded GO, and **(c)** GNS.

Polypyrrole (PPy) was synthesized by oxidation of the monomer with $FeCl_3$ had a form of fine black powder and contained irregular sphere-like particles [12]. After PPy coating on GO samples, laminated structure of GO sheets was observed clearly in SEM image, Figure 2 a. PPy was also coated on the surface of expanded GO by *in situ* chemical oxidative polymerization of Py. Polymer coating and irregular sphere-like PPy formation observed clearly in SEM image of expanded GO based nanocomposites, Figure 2 b. This non-uniform polymerization stemmed from the lack of functional groups on the surface of expanded GO since most of oxygen functional groups were eliminated from GO surface during thermal shock. Furthermore, uniformly layer coating of PPy/GNS nanocomposites was observed in Figure 2 c. Pyrrole monomer intercalated into GNS during *in situ* polymerization and polymerized on GNS layer-by-layer.
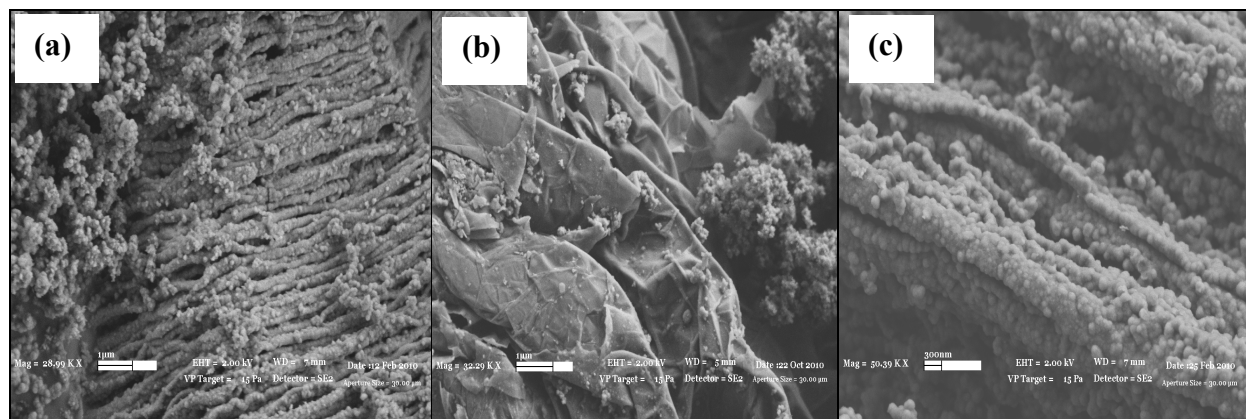
Figure 2. SEM images of **(a)** Py:GO=1:1 nanocomposite, **(b)** Py:expanded GO=1:1 nanocomposite, and **(c)** Py:GNS=1:1 nanocomposite

FTIR, XPS and EDX analyses were used to estimate the amount of surface oxygen functional groups in samples and examine the changes in surface oxygen functional groups after each treatment in exfoliation process.

The characteristic peaks in the FTIR spectrum of GO sheets were two sharp C-H stretching bands at 2850 cm^{-1} and 2916 cm^{-1} and a sharp CH$_2$ bending band near 1480 cm^{-1}, Figure 3. Also, there were a broad band at around 1100 cm^{-1} due to the aromatic C-O stretching and two small peaks due to the C=O stretching. Expanded GO had high carbon content as seen in Figure 3. This indicated that thermal expansion eliminated oxygen functional groups. After the chemical reduction of GO, the intensity of C=O stretching peaks at 1500 cm^{-1} decreased comparably, Figure 3.
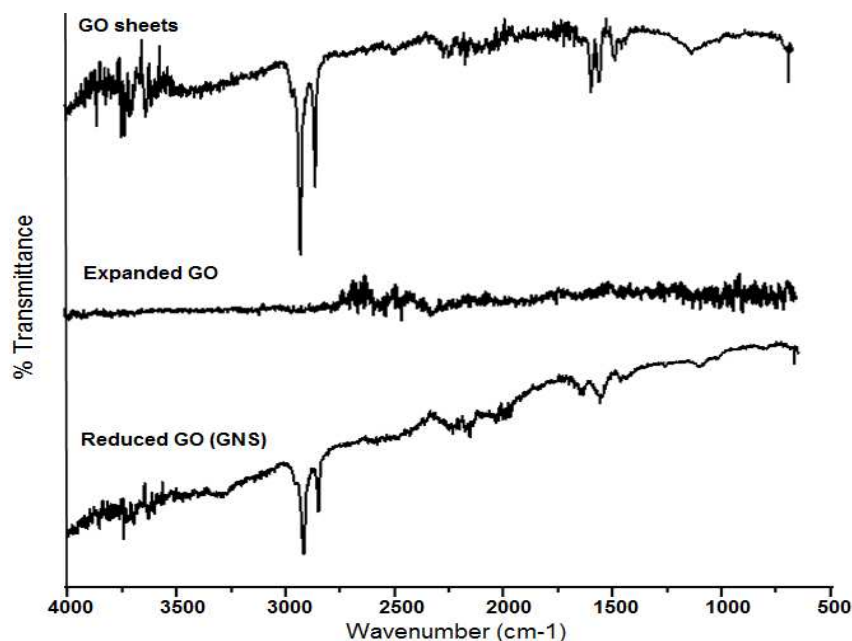
Figure 3. FTIR spectra of GO sheets, expanded GO and reduced GO (GNS).

The atomic ratios and surface functional groups of GO sheets, expanded GO, GNS, and their composites were determined by using the XPS elemental analysis. The intensities of O1s and C1s peaks for GO, expanded GO and GNS were compared in the XPS survey scan spectra, Figure 4. The C/O ratios of GO, expanded GO and GNS were measured as 2.3, 6.0, and 3.2, respectively. These results indicated that thermal expansion led to the removal of oxygen functional groups on the surface of GO samples and thus carbon content increased in the structure of expanded GO. Therefore, PPy was agglomerated on the surface of expanded GO during the production of nanocomposites.
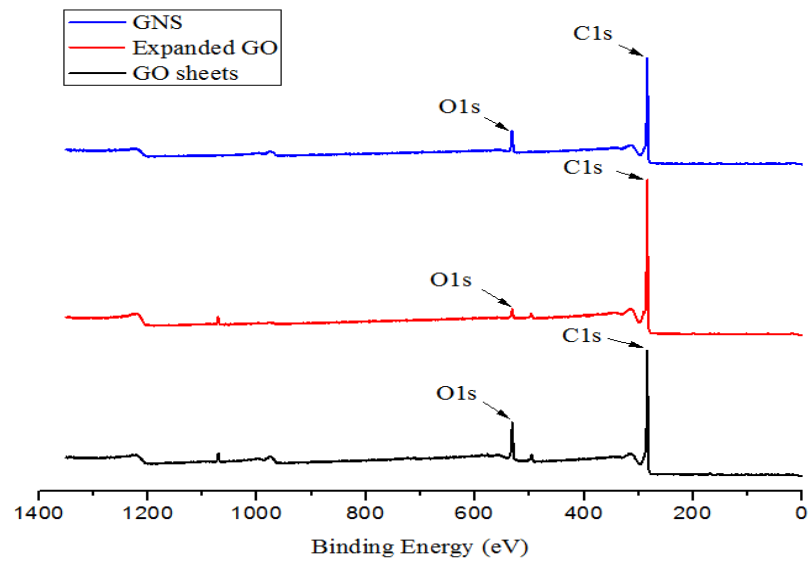
Figure 4. XPS survey scan spectra of GO sheets, expanded GO and GNS.

Table I summarized functional groups, binding energies, FWHM values and atomic percentages which were estimated from the N1s XPS spectra of Py:GO=1:1, Py:Expanded GO=1:1, and Py:GNS=1:1 nanocomposites. Py:GNS=1:1 nanocomposite with the largest FWHM indicated that different types of carbon-oxygen and carbon-nitrogen containing bonds were superimposed [13].

Table I. XPS spectra results for N1s in the samples of Py:GO=1:1, Py:Expanded GO=1:1, and Py:GNS=1:1 composites

Samples	*N1s*			
	Group	**Binding Energy (eV)**	**FWHM**	**At. (%)**
Py:GO=1:1	C-N, N-H	399.9	1.7	12.9
Py:Expanded GO=1:1	C-N, N-H	399.9	1.5	10.1
Py:GNS=1:1	C-N, N-H	399.7	1.9	13.6

Table II showed EDX results of GO sheets, expanded GO, GNS based nanocomposites. The C/O ratios of Py:GO=1:1, Py:Expanded GO=1:1 and Py:GNS=1:1 were calculated as 1.22, 3.55 and 0.95, respectively. The results proved that the higher oxygen amount in GO structure hindered agglomeration and promoted PPy dispersion on the surface of sheets. These observations were consistent with the XPS analysis data and also indicated an increase of carbon content after thermal shock.

Table II. EDX results of GO, expanded GO, GNS based nanocomposites

Samples	Carbon (wt%)	Nitrogen (wt%)	Oxygen (wt%)	Other elements (wt%)
Py:GO=1:1	40.2	16.7	32.9	10.2
Py:Expanded GO=1:1	54.6	23.0	15.4	7.0
Py:GNS=1:1	42.3	7.9	44.3	5.5

CONCLUSIONS

GO sheets, expanded GO and GNS were used as filler in conducting PPy matrix. The change in the amount of surface functional groups of nanocomposites according to filler type and polymer weight was investigated in detail by FTIR, XPS and EDX analyzing system. This comprehensive and quantitative study showed the significant effect of surface oxygen functional groups on nanocomposite production. Since thermal expansion led to the removal of oxygen functional groups on the surface, the C/O ratio increased up to 6.0 in the structure of expanded GO. Therefore, a layer-by-layer polymer coating was achieved on GO sheets and GNS due to the presence of oxygen functional groups. However, non-uniform polymer dispersion on the surface of expanded GO occurred due to the removal of oxygen functional groups on the surface during thermal expansion of GO sheets. Consequently, the relationship between surface functional groups and the chosen polymer carries a significant importance on the fabrication of novel composites.

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