The Preparation of Composite Material of Graphene Oxide–Polystyrene

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Abstract. The graphite was exfoliated using the high intensity ultrasound. From the delaminated nanosheets graphene oxide was prepared. Graphene oxide–polystyrene (GO–PS) composite was synthesized using direct emulsion polymerization of styrene in the presence of graphene oxide. The as-prepared samples were characterized by X-ray diffraction (XRD), Raman spectroscopy and infrared spectroscopy. The morphology of prepared composite was characterized using high resolution scanning electron microscopy (HRSEM).

Keywords: graphene oxide, polystyrene, composite materials

1. Introduction

The graphene oxide has proven to be soluble in water, is amphiphilic, non-toxic and biodegradable and form stable colloids. The surface of graphene oxide contains epoxy, hydroxyl, and carboxyl groups, which can interact with cations and anions.

GO–polymer composites have attracted much attention due to their unique organic–inorganic hybrid structure and exceptional properties. Core–shell structured polystyrene-magnetite-graphene oxide composite nanoparticles were synthesised by sequentially depositing Fe_3O_4 nanoparticles and GO sheets onto the carboxyl functionalized PS template nanoparticles through electrostatic interactions [1]. Core–shell structured polystyrene microspherical particles were synthesised by adsorbing the GO sheets on the PS surface through a strong π–π stacking interaction [2]. Wu [3] report the synthesis of polystyrene reduced graphene oxide composites by a two-step in situ reduction technique, which consisted of a hydrazine hydrate reduction and a subsequent thermal reduction at 200 ℃ for 12 h. A simple method was used to synthesize the polyaniline nanofiber-coated polystyrene/graphene oxide (PANI-PS/GO) core shell composite using a solution mixing process. GO could be easily coated on PANI-coated PS to form core shell structure through the ring-opening reaction of the epoxide groups in the GO sheets with amine groups in the PANI nanofibers [4]. Polystyrene particles covered with GO sheets of nanoscale size have been successfully prepared by aqueous mini-emulsion polymerization of styrene using GO as the sole surfactant based on a novel procedure entailing ox-idation and chemical exfoliation of graphite nano fibres [5]. Polystyrene-intercalated GO has been prepared by emulsion polymerization with the aid of sodium laurel sulfate and polystyrene has been intercalated into the interlayers of GO [6]. Graphene oxide–polystyrene composite foaming was prepared by blending of solution polystyrene dissolved in dimethylformamide followed by CO_2 supercritical drying [7]. Graphene nanosheets–polystyrene nanocomposites were prepared by in situ emulsion polymerization and reduction of graphene oxide using hydrazine hydrate. PS microspheres covalently linked to the edges of graphene nanosheets [8]. Yu at all present the first successful application of p-phenylenediamine-4vinylbenzen-polystyrene modified graphene oxide for application in corrosion protection [9].

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In this paper, we report on the synthesis of graphene oxide–polystyrene (GO–PS) composites prepared by a one-step in situ direct emulsion polymerization of styrene in the presence of GO which leads to a new class of GO based materials and their use in a variety of applications.

2. Experimental

2.1. Preparation of graphene
The graphene was synthesized from the natural graphite (Koh-i-noor Grafite Ltd., Czech Republic) by unique method reported elsewhere [10] using a high intensity cavitation field in an ultrasonic pressurized batch reactor (UIP1000hd, 20kHz, 2000W, Hielscher Ultrasonics GmbH, 14513 Teltow, Germany).

2.2. Preparaton of grapheme oxide
The graphene oxide (GO) was prepared from graphene using the modified Hummers method [11]. In a typical experiment, H_2SO_4 (60 ml), H_3PO_4 (10 ml), graphene (1 g), and $KMnO_4$ (3 g) were mixed in a round-bottom flask. The mixture was then heated to 40 ℃ and stirred for 6 h, affording a pink, dense suspension. The suspension was then poured onto a mixture of ice and 30% H_2O_2 (200 ml), and the color turned to bright yellow. The product was purified by dialysis (Spectra/Por 3 dialysis membrane) and centrifuged. Purified GO product was obtained as a brown, honey-like suspension.

2.3. Preparation of grapheme oxide polystyrene composite
GO–PS was prepared by direct emulsion polymerization of styrene [12] in the presence of GO. In a typical experiment, 0.3 g of GO was dispersed in 75 ml of distilled water in a 4-neck round-bottom flask fitted with mechanical stirrer, condenser, thermometer and nitrogen inlet. The suspension of graphene oxide was purged by inert gas (nitrogen or argon) for 10 minutes due to the removal of oxygen, beacuse it inhibits free radical polymerization. Then, a mixture of 5 ml of styrene and 0.1 ml divinylbenzene was added and reaction mixture was heated. When the reaction mixture warmed to 91 ℃, 2 mL solution of sodium 4-styrenesulfonate is added (4.00 g of sodium 4-styrenesulfonate in 100.0 mL water) and then, after 3 minutes the 4 mL of the solution of potassium persulfate and sodium bicarbonate (1g $K_2S_2O_8$ and 3.5 g $NaHCO_3$ in 100 ml water) was added. The reaction mixture is continuously stirred and heated. After 85 min a mixture of 1 ml styrene, 0.05 ml divinylbenzene, 4 ml of water, 4 ml solution of sodium 4-styrenesulfonate, and 0.5 mL of the solution of potassium persulfate and sodium bicarbonate were added; heating and stirring continuos next hour. After cooling of mixture, it was filtered and purged with ethanol. Thereafter the composite material was dried at 85 ℃.

2.4. Characterisation methods
Diffraction patterns were collected with diffractometer Bruker D2 equipped with conventional X-ray tube (Cu Kα radiation, 30 kV, 10 mA). The primary divergence slit module width 0.6 mm, Soller Module 2.5, Airscatter screen module 2 mm, Ni Kbeta-filter 0.5 mm, step 0.00405 °, a counting time per a step 1 s and the LYNXEYE 1-dimensional detector were used.

High resolution scanning electron microscopy (HRSEM) analysis was conducted on a FEI Nova NanoSEM scanning electron microscope equipped with an Everhart-Thornley detector (ETD), Through Lens detector (TLD), Low Vacuum detection (LVD) HELIX and sample plasma cleaner using accelerating voltage 4-30 kV. Samples on the carbon holder were coated with a thin gold layer using vacuum sputtering.

The Raman spectra were acquired with DXR Raman microscope (Thermo Scientific) with 532 nm (6 mW) laser, 32 two-second scans under 10x objective of an Olympus microscope.

Infrared spectra were recorded using Nicolet Impact 400D spectrometer approximately in 4000-500 cm^{-1} range with accessories for diffuse reflectance measurement.

3. Results and Discussion

The scheme of GO–PS composite preparation method is outlined Figure 1a. The XRD pattern of GO and GO–PS composite is displayed in Figure 1b. The GO pattern showed a characteristic peak at 9.35 ° corresponding to an interlayer spacing of 0.945 nm, indicating the presence of oxygen and oxygen containing

functional groups (-COOH, -OH, C-O-C) after oxidation [13]. Very strong peak at 3.17 °, indicated preferred orientation of GO [14]. The XRD pattern of GO–PS composite showed two main broadening peaks. The first at 11.55 ° is the polymerization peak and was attributed to the intermolecular backbone–backbone correlation and the size of the side group, which corresponds to an approximately hexagonal ordering of the molecular chains; the latter peak at 18.7 ° was amorphous halo and corresponds to the van der Waals distance [15].
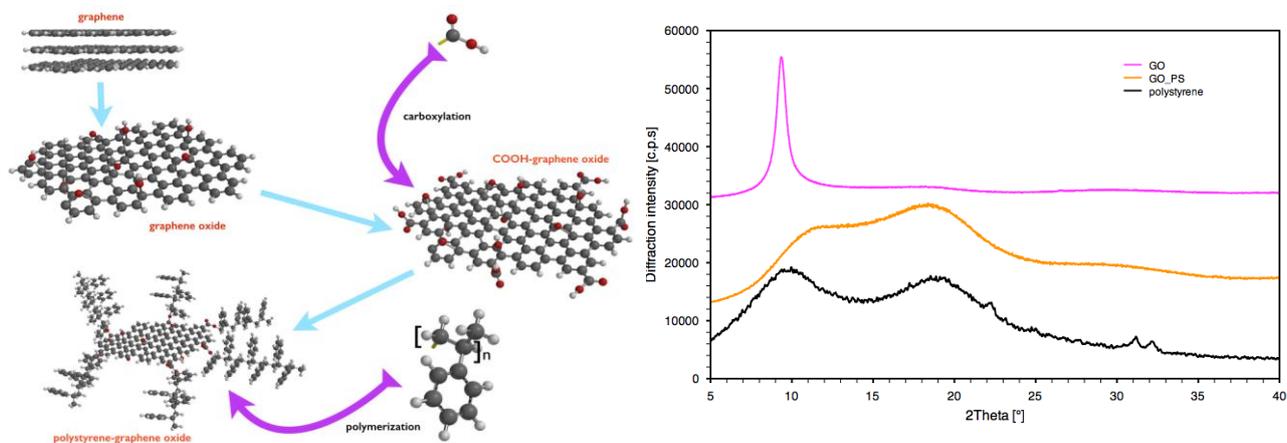

Fig. 1: a) Scheme of preparation of graphene oxide-polystyrene composite and
b) XRD pattern of grapene oxide and graphene oxide-polystyrene composite

The DRIFT spectrum of GO is shown in the Figure 2a. The broad, intense band centered at 3450 cm^{-1} was assigned to O-H stretching vibrations of the C-OH groups and the bands at 1737 cm^{-1} were assigned to C=O stretching vibrations of the carbonyl and carboxylic groups. The band at 1630 cm^{-1} was due to skeletal vibrations from unoxidised graphitic domains, the peak at 1224 cm^{-1} was expression of C-OH stretching while the peak at 1050 cm^{-1} was assigned to C-O stretching vibrations. The main vibration modes of polystyrene, out-of-plane bending of the CH groups in the aromatic ring were located at 699 cm^{-1}, deformation vibrations of the CH groups in the aromatic ring at 754 cm^{-1}, v(C=C) vibration in vinyl groups at 1447 and 1490 cm^{-1}, stretching vibrations of the carbons in the aromatic ring at 1601 cm^{-1}, vibration of PS units at 1942 cm^{-1}, symmetrical and asymmetrical stretching vibrations of the CH$_2$ groups at 2848 and 2921 cm^{-1} and stretching vibrations of the CH groups in the aromatic ring at 3024 and 3062 cm^{-1}.
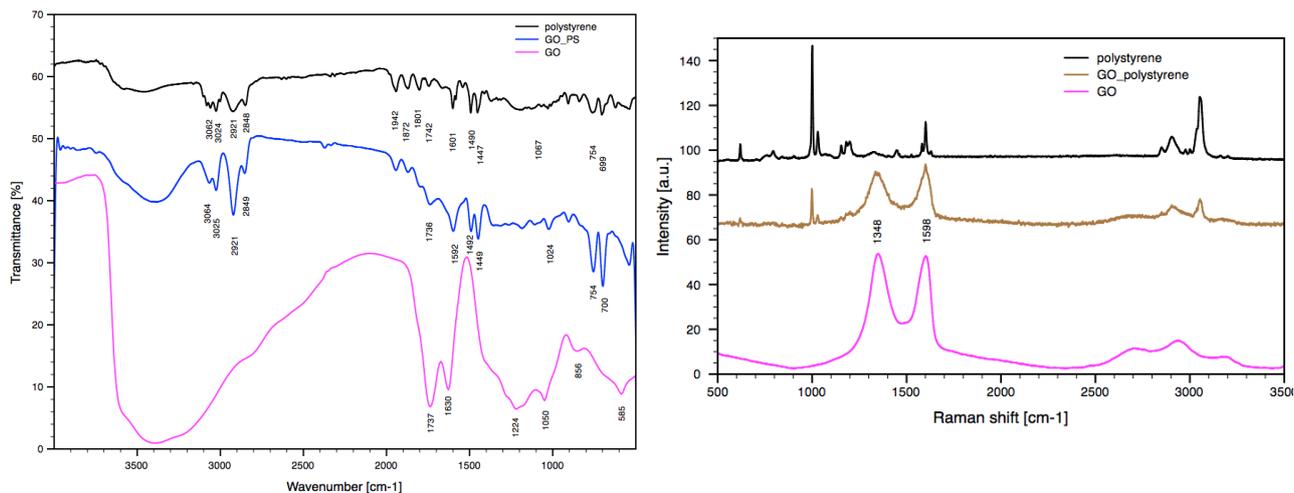

Fig. 2: a) Infrared spectra of graphene oxide–polystyrene composite and its components
b) Raman spectrum of grapene oxide, polystyrene and graphene oxide–polystyrene composite

The Raman spectrum of GO, PS and GO–PS composite is presented in Figure 2b. In the Raman spectrum of the GO, the G band is broadened and shifted slightly to 1605 cm^{-1}, whereas the intensity of the D band at 1347 cm^{-1} increases substantially. The G band is common to all sp^2 carbon forms and provides

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information on the in-plane vibration of sp^2 bonded carbon atoms and the D band suggests the presence of sp^3 defects [16]. In the Raman spectrum of GO–PS, the C-H stretch mode in the vinyl group at 3054 cm^{-1} and C-C stretch vibration in benzene at 995 cm^{-1} was detected [17].

Figure 3a shows the SEM images of the GO–PS composite, which clearly displays the bulk of small balls in composite. The polymer and GO form an interconnected bulk network and the GO is uniformly dispersed in the polystyrene matrix. The small balls of polystyrene whose surface are covered by GO are clearly seen in Figure 3b at a higher magnification.
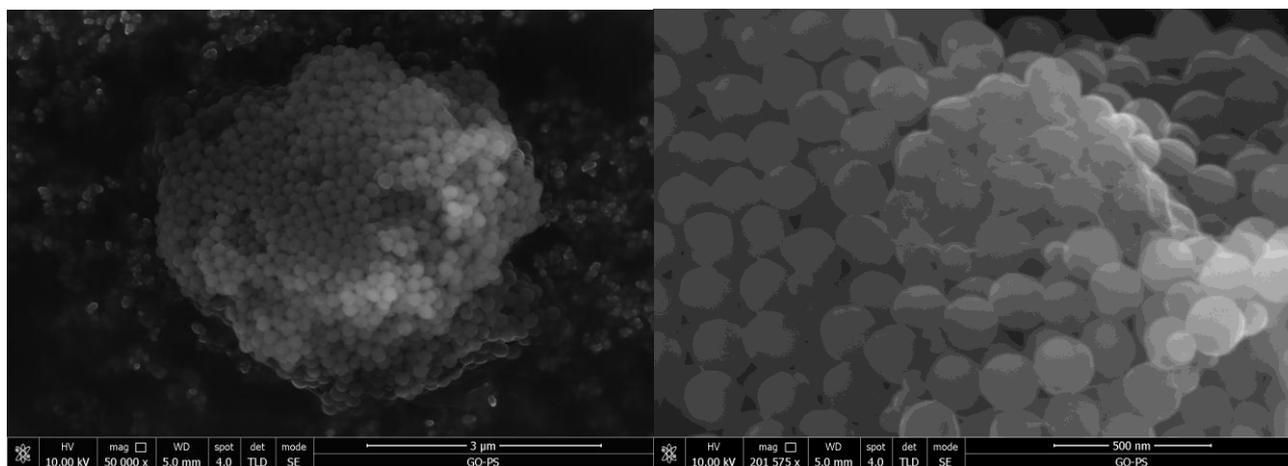

Fig. 3: SEM images of graphene oxide–polystyrene composite a) scale 3 μm, b) scale 500 nm.

4. Conclusions

The composite material of graphene oxide–polystyrene was prepared by directly synthesis at the laboratory scale. The composite is relatively stable and synthesis is quite well reproducible, which the X-ray and Raman measurements confirmed. However, the distribution of individual composite parts is located randomly. Potential applications of this composite material GO-PS lies primarily in the possibility of use as a sorbent for heavy metals, radionuclides, and other trace elements. These abilities, however, must be validated by long-term tests.

5. Acknowledgements
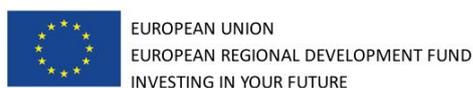
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