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Polymer nanoparticles as a tool for the exfoliation of graphene sheets

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ABSTRACT

The exfoliation of graphene sheets has been achieved by using commercial graphite in the presence of spherical polymer nanoparticles based on poly(ethylene glycol). The polymer nanoparticles with an average diameter of ~20 nm were prepared by two different methods including the ball milling technique and a magnetic stirring process. These nanoparticles in conjunction with an ultrasonication procedure yielded graphene sheets of about three layers or less. The polymer nanoparticles played a crucial role in the preparation of the graphene sheets through a wrapping process. The number of graphene layers can be tuned by varying the preparation method of the polymer nanoparticles.

1. Introduction

Nanomaterials have attracted much interest and especially carbon-based nanomaterials have been recently in the spotlight of researchers. Among them, graphene plays a dominant role. It is a unique, 2-dimensional carbon allotrope featuring promising electronic and mechanical properties that are relevant for various applications. The remarkable interest in the material graphene is based on its outstanding physical properties such as quantum electronic transport [1,2], high elasticity [3], high mobility [4], and a tunable band-gap [5]. Graphene sheets open up new ways of applications for drug delivery [6], hydrogen storage [7], 8 electric devices [8], ultrasensitive sensors [9], solar cells [10–11], memory cells [12], and ultra-capacitors [13]. There are a number of methods for the preparation of graphene sheets from graphite and the widely used method is the Hummer's method, in which graphene oxide (GO) is formed through an oxidation step followed by chemical reduction of the GO [14–15]. A remarkable feature of this method is the high yield of graphene sheets [16–18]. However, toxic materials are used for the oxidization step, which is forming defects in the graphene sheet structure, thus limiting the application spectrum [19]. In our previous studies, graphene sheets have been exfoliated using ultrasonication in aqueous media containing different types of proteins [20] and DNA [21]. Polymer

nanoparticles with spherical shape are interesting for various applications due to their excellent properties [22]. Recently, polymer nanoparticles were prepared by using the facile magnetic stirring method for the dispersion of nanodiamonds [23]. Our group has been involved in the study of different nanomaterials and polymer nanocomposites [24–26]. In this study, graphene (GRP) sheets have been exfoliated from commercial graphite using an one-step method with the aid of spherical polymer nanoparticles, which were prepared under ultrasonication [23]. The poly(ethylene glycol) nanoparticles (PEG-NPs) with an average diameter of ~20 nm have been prepared by two different techniques, the ball milling and the magnetic stirring process. The effect of the polymer nanoparticles produced by the different methods on the properties of the graphene sheets was investigated. Also, the crucial role of the polymer nanoparticles in the exfoliation process of graphene has been studied.

2. Experimental

2.1. Materials

Graphite was purchased from Aldrich and poly(ethylene glycol) (PEG) from Yakuri Pure Chemicals, Ltd. Deionized water was used throughout.

2.2. Synthesis of PEG-NPs and graphene–PEG-NP

Poly(ethylene glycol)-based nanoparticles (PEG-NPs) were

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prepared according to our previous report [23]. Thus, 25 mg of PEG (0.5 wt%) were dissolved in a glass vial containing 5 ml of deionized water to prepare the solution, and then it was magnetically stirred at room temperature for 24 h to form the solution of the sample PEG-NP-S. On the other hand, a 0.5 wt% PEG solution was prepared in a steel capsule with two balls and milled horizontally to form a homogenous solution of the product PEG-NP-M. For the GRP preparation, 10 mg of graphite were dispersed in 10 ml of an aqueous PEG-NPs solution (0.5 wt%) and the sample obtained was subjected to ultrasonication at three different time intervals (40, 50, and 60 min). Ultrasonication was performed with an ultrasonic processor (Sonics and Materials, Inc., Model VC 750) equipped with a standard probe (diameter: 13 mm). The water-dispersed graphene was collected after centrifugation (2500 rpm, 60 min) and a dark suspension was obtained.

2.3. Characterization

TEM images were obtained using a JEOL JEM-2100 microscope with an accelerating voltage of 200 kV. UV–vis spectra were recorded at room temperature with a UV–vis spectrophotometer (Lambda 750 UV/vis/NIR model) over the range of 200–800 nm in the absorption mode. Raman spectroscopic studies were carried out with a Renishaw in Via Reflex microscope at 632.8 nm (He–Ne laser) and a micro-Raman spectrograph consisting of a Kaiser Optical Systems Nd–YAG laser at 532 nm.

3. Results and discussion

Poly(ethylene glycol) nanoparticles (PEG-NP) were prepared by using the magnetic stirring method (PEG-NP-S) and by the ball milling method (PEG-NP-M). The nanoparticles were used under ultrasonication to exfoliate graphene sheets at different sonication time intervals (40, 50, and 60 min). The exfoliated graphene sheets were characterized using microscopic and spectroscopic techniques, which allow to confirm the exfoliation process. Fig. 1 shows the UV–vis spectra of the samples PEG-NPs, GRP–PEG-NP-S40, GRP–PEG-NP-S50, GRP–PEG-NP-M40, GRP–PEG-NP-M50, and GRP–PEG-NP-M60, where the letters S and M refer to the PEG-NPs preparation method as described above, and the numbers 40, 50, and 60 indicate the sonication time. It can be seen from Fig. 1a that the PEG-NPs have no characteristic absorption peak in the measured range. However, the GRP–PEG-NPs show a characteristic absorption peak at 268 nm, which is related to graphene sheets and corresponds to the excitation of the π-plasmon of the graphitic structure [27–28]. This result confirms the exfoliation of graphene sheets and their dispersion in the solution. It is important to note that the degree of graphene exfoliation is dependent on the nanoparticle preparation technique. From Fig. 1 it can be seen that the concentration of graphene sheets in the samples prepared by ball milling was higher than those obtained by the stirring method under the same conditions. Also, when the sonication time increased, the graphene exfoliation increased, and, in turn, the GRP concentration increased. In addition, the stability of the GRP–PEG-NPs dispersion was confirmed and a stable dispersion observed (Fig. 2).

On the other hand, the morphology of the GRP–PEG-NPs was confirmed using TEM, as shown in Fig. 3. The GRP flakes were on the μm length scale (Fig. 3a). When the ultrasonication time increased, the length of the GRP flakes decreased, as shown in Fig. 3b, in connection with edge defects on the sheets. In addition, the number of layers was 4 or less, as described below in section of the Raman studies.

The GRP sheets obtained by using the PEG-NPs prepared from ball milling show a larger dimension in length and width than
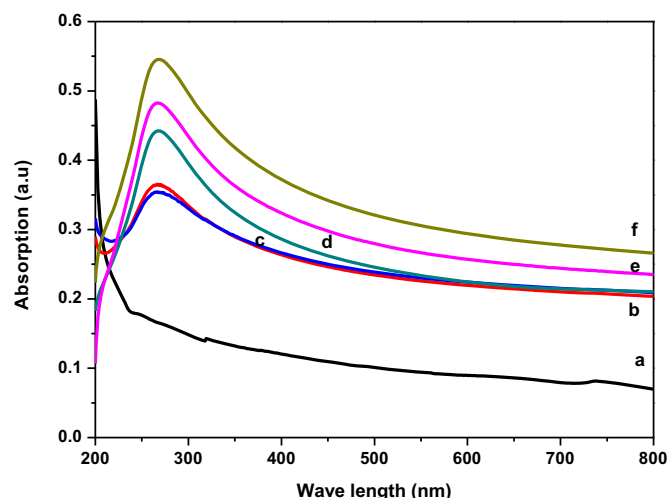

Fig. 1. UV–vis absorption spectra of the samples PEG-NPs (a), GRP–PEG-NP-S40 (b), GRP–PEG-NP-S50 (c), GRP–PEG-NP-M40 (d), GRP–PEG-NP-M50 (e), and GRP–PEG-NP-M60 (f).

Fig. 2. Photographic image of the sample GRP–PEG-NPs, showing the stable dispersion.

those obtained from the stirring method, and the number of layers was 3 or less (Fig. 3c and d). During the GRP exfoliation the cavitation processes originating from the ultrasonication created losses of the graphite, resulting in the exfoliation of the layers. Afterwards, the PEG-NPs existing in the dispersion were incorporated between the layers, and thus decorated the surface of the exfoliated GRP sheets [23,29].

The Raman spectra of the samples GRP–PEG-NP-S50 and GRP–PEG-NP-M50 (Fig. 4) show the most intense peaks at 1354 cm^{-1} for the D band, at 1584 cm^{-1} for the G band, and one observed at