Graphene oxide/Fe$_3$O$_4$ nanorods composite: structural and Raman investigation

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Abstract. The emerging field of organic/inorganic nanocomposites has become the focus of considerable research in recent years. In particular, graphene coated with iron oxide nanostructures are widely required for various applications. In this work, we report the preparation of graphene oxide/magnetite GO/Fe$_3$O$_4$ nanocomposite via a simple hydrothermal method. Our experimental results obtained by transmission electron microscopy (TEM) reveal that well-defined Fe$_3$O$_4$ nanorods (NRs), about 8-11 nm in diameter and 50-60 nm in length, were uniformly anchored on graphene oxide nanosheets. X-ray diffraction (XRD) confirms the successful assembly of Fe$_3$O$_4$ on to GO nanosheets. Thermo gravimetric analysis results (TGA) show a good thermal stability for the nanocomposite. Raman laser studies carried out at various laser powers and acquisition times show that all the samples undergo changes in intensities and peak positions which reflect the modification of the electronic structure and electron-phonon interactions.

1. Introduction
The scientific interest in graphene, a new crystalline form of carbon consisting of a two dimensional sp$^2$ bonded sheet, has generated thousands of publications and an accelerating pace of research owing to its exceptional physical properties, chemical tunability, and potential for various applications [1]. Graphene can generally be produced by several disruptive technologies and each strategy has its own advantages and disadvantages; nevertheless, the production of large-area and free-standing graphene-based hybrid with high flexibility and multifunctional features is still a challenge [2]. On the other hand, graphene oxide, an atomically thin and semi-aromatic network of sp$^2$/sp$^3$ bonded carbon atoms intermittently decorated with oxygen-containing functionalities on its basal planes and in edges, is currently the ideal precursor for cost-effective and scalable production of graphene via a simple chemical method [3]. The polar lamellar surface of GO allows developing various graphene-based hybrid materials via easy chemical modification by the incorporation of various types of nanoparticles such as metal [4,5], metal oxide [6], and quantum dots [7]. Among those hybrid materials, the ones
with the magnetic nanoparticles constitute an important class of materials due to their numerous applications in different technological field as energy storage, enhanced optical limiting, magnetic resonance imaging (MRI), drug delivery and environmental remediation [8]. Our previous work reports the synthesis of graphene derivatives decorated with Fe$_3$O$_4$, one of the most attractive supraramagnetic materials due to its remarkable properties [9]. As results, we reveal a charge transfer and donor-acceptor interaction between the Fe$_3$O$_4$ nanostructures and the graphene derivatives which can be supported by the fact that graphene oxide is an excellent electron acceptor. Recently, significant importance has been given to develop these phenomena in graphene-based nanocomposites through functionalization and chemical doping [10].

In the present investigation, our goal is to prepare graphene coated with Fe$_3$O$_4$ nanoparticles and to further elucidate the effect of the laser power beam on our elaborated samples using Raman spectroscopy with an excitation wavelength of 785 nm and different parameters (power and acquisition time). The structural and thermal properties are provided by TEM, XRD and TGA.

2. Experimental details

2.1. Synthesis of Graphene oxide

GO nanosheets are synthesized from natural graphite powders using a modified Hummers method as shown in Figure 1. Briefly, 2 g graphite powder was added to 46 ml concentrated sulphuric acid at 0 °C, and then 6g of potassium permanganate was added gradually under magnetic stirring. The mixture was then stirred at 35 °C for 40 min, followed by slowly increase in temperature until 98 °C. Simultaneously, 92 ml of distilled water was slowly added and the mixture was maintained at that temperature for 20 min under reflux condition. At the end of the reaction, 280 ml of distilled water followed by 20 ml of 30% H$_2$O$_2$ solution was added. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution and then washed several times with acetone and water. After this, the sample was dried in a vacuum oven at 60 °C overnight [11].

![Figure 1: TEM image of GO/Fe$_3$O$_4$ nanocomposite](image)

2.2. Synthesis of GO/Fe$_3$O$_4$ nanocomposite

Graphene oxide/Fe$_3$O$_4$ nanocomposites were synthesized through a facile chemical process as reported in our previous work [12]. For the mixture of GO with FeSO$_4$.7H$_2$O and FeCl$_3$ solution, the molar ratio Fe$^{3+}$ and Fe$^{2+}$ was adjusted to 1.5:1. Under ultrasonic agitation, black precipitate was produced immediately by adding sodium hydroxide (NaOH). The Obtained Fe$_3$O$_4$ precipitate was stirred at 65 °C for 30 min in water bath. To purify the prepared Fe$_3$O$_4$ particles, the samples were washed...
repeatedly with deionized water and ethanol until pH level of 7 was reached. Particles were then dried in vacuum.

3. Results and discussion

3.1. Transmission electron microscopy (TEM)
As shown in Figure 1, the morphology of magnetite-graphene oxide was observed by TEM. Generally, controlling the size and the shape of these magnetic nanostructures is still a great challenge in research field. TEM image clearly reveals that the iron oxide nanostructures in the nanocomposite are well-defined as one dimensional (1D) nanorods with about 8-11 nm in diameter and 50-60 nm in length. The Fe\textsubscript{3}O\textsubscript{4} nanorods are uniformly dispersed on the surface of graphene oxide nanosheets. No serious aggregation of Fe\textsubscript{3}O\textsubscript{4} nanorods is observed due to the enormous surface area of GO which provide numerous active sites for deposition of the nanorods, thus it can effectively hinder their agglomeration [13].

3.2. X-ray diffraction (XRD)
Structural properties of GO, Fe\textsubscript{3}O\textsubscript{4} NRs and GO-Fe\textsubscript{3}O\textsubscript{4} nanocomposites were investigated as shown in Figure 2. XRD pattern of GO has a strong diffraction peak at 2\theta=11.64° which originated from the diffraction on its (001) layer planes. The basal spacing (d\textsubscript{basal}) is greatly expanded to 0.75 nm for GO compared to the interlayer distance of graphite 3.35 Å as reported in the literature [14]. This broadness is attributed to the introduction of various oxygen-containing functionalities and intercalated water molecules between graphite layers. For Fe\textsubscript{3}O\textsubscript{4} nanorods, all diffraction peaks in the XRD pattern, at 2\theta= 30.34°, 35.79°, 43.26°, 53.84°, 56.81°, 63.01° and 75.32° corresponding to the reflections from the (220), (311), (400), (422), (511), (440) and (533), can be easily indexed to the pure cubic inverse spinel structure of magnetite, which matches well with the reported data (JCPDS: 63-3107) [15]. The peaks are intense and well defined which suggests a good degree of structural order at long range. As a result of combination between the two components, GO/Fe\textsubscript{3}O\textsubscript{4} spectrum presents a broad peak around 25° corresponding to the layer exfoliation and partial reduction of GO which confirm the dispersion of Fe\textsubscript{3}O\textsubscript{4} onto graphene layers. This broadness overlapsthe majority of Fe\textsubscript{3}O\textsubscript{4} peaks due to the low concentration of Fe\textsubscript{3}O\textsubscript{4} in the composite.

**Figure 2:** X-ray diffraction of GO, Fe\textsubscript{3}O\textsubscript{4} and GO/Fe\textsubscript{3}O\textsubscript{4} nanocomposite
3.3 Thermogravimetric analysis (TGA)
Thermogravimetric analysis is also performed on GO, Fe$_3$O$_4$ NRs and GO-Fe$_3$O$_4$ nanocomposite to distinguish the thermal stability and confirm the attachment of Fe$_3$O$_4$ nanoparticles on the surface of graphene. Figure 3 shows TGA curve of GO, two stages appeared for mass loss with increasing temperature. The first mass loss at around 100 °C can be ascribed to the removal of the adsorbed water. The second main mass loss at around 200 °C is attributed to the decomposition of labile oxygen functional groups [16]. However, there was no significant weight loss in the TGA curve of Fe$_3$O$_4$ NRs. For the nanocomposite, there isa slow mass loss observed between room temperature and 360°C. This could be attributed to the removal of the remaining water in the composite. Interestingly, the thermogravimetric profile shows a much better thermal stability for the GO/Fe$_3$O$_4$ nanocomposite [17].

![Figure 3: TG curves of GO, Fe$_3$O$_4$ and GO/Fe$_3$O$_4$](image)

3.4. Raman spectroscopy

3.4.1 Raman spectra of GO
Raman spectroscopy affords a non-destructive technique in the study of the bonding nature of carbonaceous materials. Graphene oxide spectra exhibit two main characteristic peaks of carbon networking structures commonly known as G-band and D-band as shown in Figure 4. The G-band corresponds to the first-order scattering of the E$_{2g}$ mode observed for sp$^2$ carbon domains, whereas the D-band is due to phonon branches around the K point and caused by structural effects or edges that can break the symmetry and selection rule [18]. Generally, position and relative intensity of these two bands are very sensitive to structural changes and there are several factors that can affect them, such as doping, layer numbers, exfoliation, and defects on the surface or in the edges [13]. Figure 4a depicts the Raman spectra of GO under different laser power and acquisition time. The change of these two parameters have a clear effect on the sample, by increasing the laser power D band is become larger which can be explained by the creation of more defects as well as the two bands are red-shifted as shown in the table below, provide reliable evidence for the modification in the electronic properties of graphene due to the laser-induced electron-phonon interaction.

Moreover, It can be seen from Figure 4b that I$_D$/I$_G$ increases with increasing the laser power confirming a remarkable increase in the size of the defect domains in GO.
Table 1: G and D position under different laser power and acquisition time

| Samples(Power, time) | 1mW.60s | 1mW.120s | 10mW.60s | 10mW.120s | 25mW.60s | 25mW.120s |
|----------------------|---------|----------|----------|----------|----------|----------|
| G band position      | 1620    | 1614     | 1587     | 1580     | 1569     | 1564     |
| D band Position      | 1372    | 1356     | 1314     | 1295     | 1268     | 1265     |

3.4.2. Raman spectra of Fe3O4 nanorods

The same analysis is applied on the magnetite avoiding the high laser power (25mW) because Fe3O4 is a material for which special care has to be taken during the measurement of Raman spectra due to the transition metal inside its structure is divalent: ferrous/ferric (Fe2+/Fe3+). The high laser power focused on a small area increases the local temperature to hundreds of degrees which may causes thermal transformation, oxidation, phase transition or decomposition of the sample [19].

The theoretical analysis based on the factor-group approach predicts five Raman active bands A1g, Eg and three T2g, however earlier studies are reported that only four bands around 190-700 cm⁻¹ are observed [20]. In Figure 5, Raman spectra of magnetite are affected by the laser power. The peaks in Raman spectrum of magnetite under 10mW and 60s are well defined and located at 290, 360, 501 and 670 cm⁻¹, respectively. The feature at 1306 cm⁻¹ is assigned to a two-magnon scattering which arises from the interaction of two magnons created on anti-parallel close spin sites.
3.4.3. Raman spectrum of GO/Fe₃O₄ nanocomposite

As a result of the Raman study above, GO/Fe₃O₄ nanocomposite is acquired under 10 mW as power laser and 60s as acquisition time in Figure 6. Consequently, the GO/Fe₃O₄ spectrum presents the trace of the two components which confirm the functionalization of graphene oxide sheets by the magnetite nanoparticles. Obviously, magnetite peaks are in the low frequency region as well as the graphene bands are blue-shifted after incorporation with Fe₃O₄ nanoparticles. Singh K et al. attributed this blue-shifted to the charge transfer from the iron oxide to the graphene oxide [21].

After chemical functionalization of GO with Fe₃O₄ nanorods, the ratio of the intensities of the D and G bands increases from 1.10 to 1.22, which is attributed to the decrease in the mean crystallite size of graphene network by the creation of new graphitic domains that are smaller than those present in the GO. On the other hand, the FWHM of D band corresponding to the nanocomposite is less than that of GO which can be explained by the order between GO nanosheets after incorporation with Fe₃O₄ nanoparticles.

4. Conclusion

In summary, we have successfully prepared GO/Fe₃O₄ nanocomposite via a simple chemical synthesis method. The characterization techniques were carried out using: TEM, XRD, TGA and Raman
spectroscopy. Our experimental results realized by TEM and XRD confirm the functionalization of graphene oxide nanosheets with Fe₃O₄ nanorods. The thermal stability of the nanocomposite is confirmed by TGA. Moreover, the detailed Raman studies show the influence of the laser power on the samples. The D and G bands show a sensitive response, which reveal an electron-phonon interaction caused by laser irradiation. Raman spectrum of magnetite shows four Raman activate modes in the low wave number region which confirm that Raman spectroscopy is a useful technique to identify the spinel phase of iron oxide, thus can provide us more information about interactions in graphene based materials.

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