Facile method to functionalize graphene oxide with variable load of magnetite nanoparticles

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Abstract. A facile route for the functionalization in situ of graphene oxide with magnetite nanoparticles (Fe3O4@GO) was developed. We used graphene oxide with different oxidation time (12 and 24 hours) and each one was functionalized with different proportions of Fe3O4 nanoparticles modifying the load of the iron precursor (FeSO4·7H2O). The as-synthesized materials were characterized by multiple spectroscopic techniques (FT-IR, Raman, DRX, XPS) to demonstrate the successful attachment of iron oxide nanoparticle on graphene oxide sheets. Transmission electron microscopy (TEM) revealed that magnetite NPs were firmly decorated on the surfaces of graphene oxides with the mean diameter of about 7 nm. The magnetometry studies showed ferromagnetic behaviour of all composites in the range of 44-66 emu/g at room temperature.

Keywords: Graphene oxide, magnetite nanoparticles, ferromagnetic behaviour, Fe3O4@GO hybrids

1. Introduction

Graphene has stimulated a vast amount of research in recent years owing to its exceptional electrical, thermal, optical, and mechanical properties [1]. Recent research has shown that the graphene-based materials can have a profound impact on electronic devices, chemical sensors, nanocomposites and energy storage [2].

Graphene oxide (GO) is usually considered as an intermediary to produce chemically reduced graphene [3]. It is typically synthesized by reacting graphite powders with strong oxidizing agents in concentrated acids with subsequent dispersion and exfoliation in water or suitable organic solvents [4].

The structure of GO depends on the starting graphite and the synthesis conditions [5-6]. The oxidative process produces carboxylic acid and carbonyl groups at the edges and phenol hydroxyl and epoxide groups mainly at the basal plane of the graphene sheets [7]. These functional groups and the large surface area allow the anchorage of a wide range of metal and inorganic nanoparticles, organic compounds, polymers, and biomaterials [8]. For instance, decorating magnetic iron oxide nanoparticles on GO has promising applications in fields such as biomedicine, catalysis, energy storage and environmental remediation [9-14].

The low toxicity and the exceptional magnetic properties of the magnetite nanoparticles (Fe3O4 NPs) has attracted significant attention in nanomedicine (e.g. drug delivery, magnetic resonance imaging (MRI) and hyperthermia), heavy metal ions removal to water treatment, and fenton-like degradation of organic pollutants [15-17].

In this research, we developed a facile and efficient hydrothermal method to functionalize GO sheets with Fe3O4 NPs. We modified the formulation Fe3O4/GO as well as the oxidation level of graphene oxide to obtain materials with different structural properties and magnetic behavior. At present, we are exploring their possible applications in research areas such as water remediation, specifically for the adsorption of heavy metals and organic dyes in industrial wastewater.
2. Experimental Section

2.1. Reagents and materials
Graphite spectroscopic powder SP1 grade was purchased from Union Carbide Corp. New York, USA. Before GO synthesis, graphite was passed through 400 mesh screen (particle size <37 µm). Phosphoric acid 85 wt% (Duksan, Pure Chemical Co. ltd. South Korean), formic acid 98 wt% (Panreac AppliChem GmbH, Darmstadt, Germany), sulfuric acid 98 wt% (Panreac AppliChem GmbH, Darmstadt, Germany), hydrogen peroxide 30 wt% (Panreac AppliChem GmbH, Darmstadt, Germany), potassium permanganate (Merck KGaA, Darmstadt, Germany), ferrous sulfate heptahydrate (Sigma-Aldrich Co. USA), sodium hydroxide (Sigma-Aldrich Co. USA) and potassium nitrate (Sigma-Aldrich Co. USA) were used directly.

2.2. Pre-oxidative exfoliation of Graphite
The first step of this approach is the mechanical exfoliation of graphite previously meshed to particle size <37 microns in acid media. In detail, 1 g of graphite was put into a beaker, and a 1:1 mixture of concentrated HCOOH/H₃PO₄ (25:25 mL) was added. The dispersion was subjected to conventional sonication by two hours, then filtered and washed with deionized water until pH 7. Finally, exfoliated graphite was dried at 100°C for 5 hours.

2.3. Preparation of Graphene Oxides
GO was synthetized through modified Tour method [18]. In detail, previously exfoliated graphite (2.0 g) was put into a beaker, and a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (240:26.6 mL) was added. The mixture was heated to 50°C for 15 min, and potassium permanganate (12.0 g) was added slowly (0.5 g/10 min) under vigorous stirring. Then, the reaction was carried out for two different times (12 and 24 hours) to obtain the GO12h and GO24h, respectively. Next, each mixture was cooled at room temperature and 10 mL of 30% H₂O₂ was added slowly, leading to bubbling as well as an obvious heating. Immediately after finishing reduction, the dispersion was diluted with cold distilled water (500 mL, 5°C). We observed that the suspension gradually colour change from brown to orange. It was left overnight and then the supernatant was removed. The remaining solid material was repeatedly centrifuged and washed several times with 200 mL of distilled water, 500 mL of aqueous HCl (10 wt%) and, 500 mL of Milli-Q water. This multiple-wash process was repeated until the suspension was neutralized. The purified graphite oxide was dispersed in 500 mL of Milli-Q water and ultrasonicated for two hours to form a homogenous dispersion of graphene oxide.

2.4. Preparation of Fe₃O₄@GO composites
Magnetic nanocomposites with different weight ratios of GO (12 and 24 hours of oxidation) and Fe₃O₄ were prepared in situ by partial oxidation of a Fe⁺² salt solution with KN0₃ under alkaline conditions [19]. The synthetic route is represented in the figure 1. Typically, 500 mL of GO aqueous dispersion (2 mg/mL) was heated to 90°C under stirring in a closed system with nitrogen atmosphere. Following this, a specific quantity of FeSO₄ solution (25 mL) was added to the above solution containing GO, and the agglomeration of the graphene oxide sheets was evident due to iron adsorption. Then, 25 mL of KNO₃ and NaOH aqueous solution was slowly added drop-wise until the pH reached ≈11–12. The reaction was maintained at 90°C for 30 minutes. The obtained black dispersion containing Fe₃O₄@GO materials was centrifuged and washed with ethanol for 15 min at 6000 rpm until neutral pH. Finally, the materials were dispersed in Milli-Q water and dried by lyophilization. A similar procedure was used to prepare Fe₃O₄ nanoparticles. The weights added of FeSO₄, NaOH and KNO₃ are given in the table 1.
2.5. Instrumental

Powder X-ray diffraction (XRD) measurements were recorded on a diffractometer (D8 Advance, Bruker) with CuKα1 radiation (1.54059 Å) at a generator voltage of 40 kV and a 30 mA current. The scan speed was 0.02°/s in the range of 2θ: 3.5-70°. Infrared spectra were obtained using a FTIR spectrometer (Nicolet IS50, Thermo Fischer Scientific) equipped with an attenuated total reflection (ATR) system in the range of 4000-400 cm⁻¹. The Raman spectra were recorded with a Raman microscope-spectrometer (LabRAM HR Evolution, HORIBA), equipped with 532 nm laser as excitation source. The XPS analysis were carried out with the surface characterization platform XPS/ISS/UPS-ACenteno (SPECS, Germany), equipped with a PHOIBOS 150 2D-DLD power analyzer. For the measurements, a monochromatic Al Kα X-ray source (FOCUS 500) operated at 100 W was used. Transmission electron microscopy (120 KV JEM-1210, JEOL) was used to characterize the size, morphology and microstructure of the samples. The magnetization curves at 300 K were measured with a superconducting quantum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design).

| Material          | Label | FeSO₄·7H₂O [g] | NaOH [g] | KNO₃ [g] |
|-------------------|-------|---------------|----------|---------|
| Magnetite NPs     | Fe₂O₃ | 10.8          | 4.32     | 0.873   |
| Fe₃O₄@GO12h       | M1    | 7.2           | 2.88     | 0.582   |
|                   | M2    | 10.8          | 4.32     | 0.873   |
| Fe₃O₄@GO24h       | M3    | 7.2           | 2.88     | 0.582   |
|                   | M4    | 10.8          | 4.32     | 0.873   |

Table 1. Specifications in the synthesis of Fe₃O₄@GO composites and Fe₃O₄ NPs

![Figure 1. Schematic of the fabrication of Fe₃O₄@GO hybrids.](image)

3. Results and Discussion

FTIR-ATR spectra (figure 2) were recorded, and the following functional groups were identified in GO12h and GO24h samples: O-H stretching vibrations (3600-3300 cm⁻¹) are attributed to the hydroxyl and carboxyl groups of GO and residual water, C=O stretching vibration (1720 cm⁻¹), C=C vibrations of unoxidized graphene domains (1626 cm⁻¹), O-H bending (1405 cm⁻¹), C-O-C vibrations from the epoxy groups (1220 cm⁻¹), and C-O stretching vibration from the alkoxy groups (1052 cm⁻¹) [20]. On the other hand, the strong absorption band at about 540 cm⁻¹ (figure 2g) is due to Fe–O stretching vibration for the Fe₃O₄ nanoparticles [21]. Moreover, some characteristic bands of GOs appear in the spectrum of Fe₃O₄@GO hybrids (figure 2c-2f) and the characteristic band for the magnetite NPs was also observed at 540 cm⁻¹, like other works [22-23].
Raman spectrum of magnetite NPs (inset figure 3) present a sharp peak at 665 cm\(^{-1}\) corresponding to \(A_{1g}\) vibrational mode, which is the signature fingerprint for magnetite. Other characteristic peaks appeared at 530 cm\(^{-1}\) and 310 cm\(^{-1}\) associated with the vibrational modes \(T_{2g}\) and \(E_{g}\), respectively [24]. Raman spectra of GOs and magnetic composites (fig. 3) displays the characteristic D band (sp\(^3\) carbon) and G band (sp\(^2\) carbon domains) at 1345 and 1602 cm\(^{-1}\), respectively. If there are some randomly distributed impurities or surface charges in the graphene (or graphene oxide), the G-band can split into two bands, G-band (1602 cm\(^{-1}\)) and D’-band (1860 cm\(^{-1}\)). The main reason is that the localized vibrational modes of the impurities can interact with the extended phonon modes of graphene resulting in the observed splitting. The intensity ratio of the D to G band \((r=I_D/I_G)\) is generally accepted to reflect the graphitization degree of carbonaceous materials and the defect density [25]. The ratio \(I_D/I_G\) for GO12h and GO24h were 1.83 and 2.19 respectively, which is consistent with the oxidation time associated to formation of localized sp\(^3\) defects within the sp\(^2\) carbon network [5]. The ratio \(I_D/I_G\) for M1 (2.04), M2 (2.29), M3 (2.22) and M4 (2.32) magnetic materials shows an increased value compared to that for the GOs, indicating higher structural disorder due to anchorage of the Fe\(_3\)O\(_4\) NPs on graphene oxide sheets [26]. In addition, the Raman spectra of these composites present the characteristic band \(A_{1g}\) for magnetite shifted to 702 cm\(^{-1}\).

Figure 2. FT-IR spectra of GOs, magnetic composites and Fe\(_3\)O\(_4\) NPs.

Figure 3. Raman spectra of GOs, magnetic composites and Fe\(_3\)O\(_4\) NPs (inset).
The XRD patterns of GO12h and GO24h (figure 4) shows a broad peak centered at 2θ= 9.59° and 2θ= 9.42°, corresponding to the (002) interplanar spacing of 0.92 and 0.94 nm. The peak (002) of graphite at 2θ= 26.53° disappears with the oxidation process, suggesting that graphite was successfully converted to graphene oxide by the method used [18]. On the other hand, the diffraction peaks of the as-synthesized Fe$_3$O$_4$@GO hybrid composites (fig. 4e-h) at 18.36°, 30.15°, 35.56°, 37.17°, 43.17°, 53.59°, 57.11°, and 62.70° are associated to the (111), (220), (311), (222), (400), (422), (511), and (440) planes of the magnetite, which are in accord with pure spinel Fe$_3$O$_4$ (JCPDS 89-3854) [27]. Moreover, a very weak diffraction signal appears at 9.84° (suggesting the presence of graphene oxide) presumably because the Fe$_3$O$_4$ NPs generate a more intense diffraction pattern than the disordered few-layers of graphene oxide functionalized [28]. Compare to Fe$_3$O$_4$ NPs, the as-prepared Fe$_3$O$_4$@GO composites presents all diffraction peaks of the magnetite and graphene oxide, indicating that the Fe$_3$O$_4$ NPs are well loaded on the GO sheets.

![XRD profiles](image)

**Figure 4.** XRD profiles of a) graphite and GOs, b) Fe$_3$O$_4$ NPs and magnetic composites, over the range 2θ: 3.5-70°.

The XPS analysis revealed the presence of carbon, oxygen and iron (in magnetic composites) elements. Figure 5a-b show XPS spectra of GOs and it was determined that the C/O atomic ratio for the GO12h and GO24h were 2.18 and 1.76, respectively. As expected, the atomic ratio C/O is greater for the material with less oxidation time. Deconvolution of the C1s peak (figure 5c-d) of graphene oxides shows the different functional groups associated to its structure: C=C (284.5 eV), C-O (286.6 eV), C=O (287.8 eV), and O=C=O (289.4 eV) [29]. With respect to magnetic composites it was found that the elemental composition differs significantly (see %Atomic in the figure 5e-h). The XPS spectra of the Fe$_3$O$_4$@GOs were ordered from the material with the lowest iron content at the highest: M1(7.16%)<M3(11.3%)<M2(14.56%) < M4 (18.61%)).

Finally, the formation of Fe$_3$O$_4$ NPs was confirmed by the high-resolution Fe2p spectra (figure 6). The peaks of Fe2p$_{3/2}$ and Fe2p$_{1/2}$ are located at 711.3 and 724.8 eV, associated to Fe$_3$O$_4$ phase in the magnetic composites, and not at 710.3 and 724.0 eV, which are for $\gamma$-Fe$_2$O$_3$ (maghemite), besides the absence of the satellite peak at 719.0 eV [30].
Figure 5. XPS survey spectra of (a) GO12h, (b) GO24h, C1s for (c-d) GO12h and GO24h, (e) M1, (f) M3, (g) M2, and (h) M4.
Representative TEM images of the obtained Fe$_3$O$_4$@GO composites are showed in the figure 7. Transparent GO sheets with the typical silk veil waves conformation were observed on the grid (figure 7a-b). SAED pattern (figure 7c) shows a hexagonal dots pattern indicating that GO sheets are composed of few stacked layers [31-32].

The Fe$_3$O$_4$ NPs are uniform anchored on the GO sheets and their loading amounts were controlled by changing the mass ratio of the Fe$^{2+}$ to GOs (see table 1). The images on the figure 7d-g are arranged
(left to right) from the material with the highest density of Fe₃O₄ NPs to the smallest (M₄>M₂>M₃>M₁). This is consistent considering that the GO24h has more oxygenated functional groups in its structure that adsorb the Fe²⁺ ions and subsequently work as nucleation points where the magnetite nanoparticles are synthesized and this observation coincides with the elemental composition results explained previously in the XPS analysis. Figure 7h corresponds to a graphene oxide sheet with low particles density on its surface and it was used to has the size distribution of the Fe₃O₄ NPs (figure 7i). The diameter of the nanoparticles is in the range of 3 to 13 nm with an average diameter of 7 nm. Finally, the selected area electron diffraction (SAED, figure 7j) pattern associated to TEM image 7i is in good agreement with the crystal planes found in the previously XRD analysis.

The magnetization hysteresis curves (figure 8) of Fe₃O₄ nanoparticles and Fe₃O₄@GO composites were measured on SQUID at room temperature (see Table 2). The saturation magnetization (Mₛ) values increased with the increment of Fe₃O₄ NPs loaded on the GOs according to the previous analysis by TEM. As it was expected, the Mₛ values of the Fe₃O₄@GO composites were smaller than magnetite NPs (86 emu/g). This value is closer to the reported value of bulk magnetite in other works [33]. On the other hand, obvious hysteresis can be seen in all cases (inset figure 8) and it is clear that all the samples exhibit ferromagnetic behavior with different values of saturation magnetization (Mₛ), remanent magnetization (Mᵣ) and coercitivity (H_c) [34].

![Magnetization hysteresis loops measured at 300K of Fe₃O₄ NPs and magnetic composites. The inset shows the attraction of magnetic composite by a magnet.](image)

| Material         | Label  | Mₛ [emu/g] | Mᵣ [emu/g] | H_c [Oe] |
|------------------|--------|------------|------------|----------|
| Fe₃O₄            |        |            |            |          |
| Fe₃O₄@GO12h      | M₁     | 44         | 0.36       | 5        |
|                  | M₂     | 55         | 1.08       | 4.4      |
| Fe₃O₄@GO24h      | M₃     | 51         | 1.25       | 7.5      |
|                  | M₄     | 66         | 2.4        | 13       |
4. Conclusions
We have demonstrated that graphene oxide can be used as support for the synthesis in situ of magnetite nanoparticles on its surface and that in addition the magnetic properties can be easily modified by varying the Fe$^{2+}$/GO ratio. As for the mechanism, we think that the positive Fe$^{2+}$ ions are coordinated by the oxygen groups via electrostatic attraction and serve as nucleation points for the subsequent formation of the Fe$_3$O$_4$ NPs.

The synthetic route developed is simple, effective and scalable chemical method to deposit Fe$_3$O$_4$ NPs onto GO sheets. The as-prepared materials show ferromagnetic behavior and can be manipulated easily with an external magnetic field, which is very interesting for rapid recovery of the composites in water remediation, for example.

We believe that Fe$_3$O$_4$@GO composites are particularly attractive for the design of novel materials useful for a wide range of potential applications, and its detailed studies on this approach are underway.

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