

# Fabrication, Characterization and Properties of Superparamagnetic Reduced Graphene Oxide/Fe<sub>3</sub>O<sub>4</sub> Hollow Sphere Nanocomposites

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**Abstract:** The reduced graphene oxide wrapped Fe<sub>3</sub>O<sub>4</sub> hollow nanospheres have been synthesized by a simple self-assembly process driven by electrostatic interaction. The structure, the chemical component and the morphology were characterized by XRD, SEM, TEM, FTIR, and Raman spectroscopy. Result show that the fabricated nanocomposites exhibit superparamagnetic property with the saturation magnetization of 70.2 A m<sup>2</sup> kg<sup>-1</sup> at room temperature and allow rapid separation in water solution under an external magnetic field. The high magnetism and excellent water dispersibility make the nanocomposites ideal candidates for various important applications such as magnetic resonance imaging, biosensors, communication, and microwave absorption.

**Key words:** Fe<sub>3</sub>O<sub>4</sub>; graphene; nanocomposites; superparamagnetic

Owing to its superior electronic, thermal and mechanical properties as well as chemical stability, graphene as a well defined two dimensional honeycomb structure of carbon materials has been attracting more and more attention from both experimental and theoretical scientific communities<sup>[1-4]</sup>. Graphene and graphene oxide (GO) are potential nanoscale building blocks for new hybrid materials because of their layered structure and special surface properties<sup>[5,6]</sup>. It is believed that the composites of metal oxides and graphene would have better functionalities and performances in their applications<sup>[7]</sup>. Among those hybride materials, the ones with the magnetic nanoparticles (e.g. Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>) are an important class of materials due to their numerous applications in various technological fields<sup>[8,9]</sup>.

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticle (NPs) have attracted world-wide research attention not only because of their unique size- and morphology-dependent physical and chemical properties, but also for their potential applications in many fields, including magnetic storage, biosensors, communication materials, magnetic resonance imaging and as materials for microwave absorbing and shielding research<sup>[10-12]</sup>. The

controlled synthesis processes of Fe<sub>3</sub>O<sub>4</sub> NPs to deliver a desired structure, composition, and shape control made them be used in various promising applications. There are many reports of the GO/Fe<sub>3</sub>O<sub>4</sub> composites that are synthesized by the chemical methods including the in-situ reduction of iron precursors into GO sheets<sup>[13-16]</sup>. However, these strategies lack the control of morphology, loading ratio and the size of the Fe<sub>3</sub>O<sub>4</sub> NPs over GO, which restricts their practical use. In this regard, the synthesis of GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites via a method involving the ex-situ controlled synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs and their controlled assembly on GO sheets is a promising way to develop highly efficient materials for technological applications<sup>[17,18]</sup>.

In the present paper, a simple self-assembly process driven by electrostatic interaction was used to produce reduced graphene oxide/magnetite (r-GO/Fe<sub>3</sub>O<sub>4</sub>) nanocomposites. A typical procedure is present in Fig.1. The process is driven by the mutual electrostatic interaction between negatively charged GO and positively charged 3-aminopropyltriethoxysilane (KH540) modified Fe<sub>3</sub>O<sub>4</sub> hollow nanospheres, resulting in a flexible and ultrathin r-GO coating enwrapping

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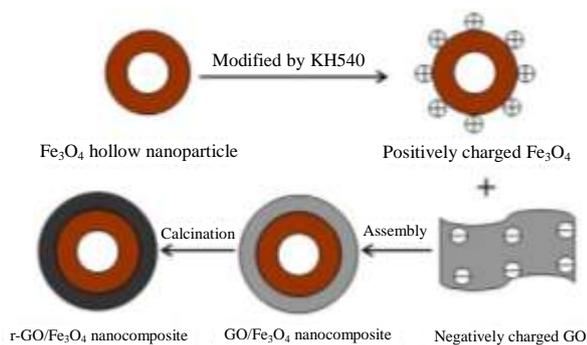


Fig.1 Synthetic route to r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites

the Fe<sub>3</sub>O<sub>4</sub> NPs. The method demonstrated in this paper is a viable and facile approach and can be extended to fabricate other graphene-based nanocomposites.

## 1 Experiment

### 1.1 Synthesis of r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites

The preparation of GO was carried out by a modified Hummers method<sup>[19]</sup>. Fe<sub>3</sub>O<sub>4</sub> hollow nanospheres were fabricated according to the literature with minor modification<sup>[20]</sup>. The as-prepared Fe<sub>3</sub>O<sub>4</sub> hollow nanospheres were first surface modified with amino groups as follows: 2 mL of KH540 was added dropwise to the Fe<sub>3</sub>O<sub>4</sub> NPs solution (1 g dispersed in 45 mL ethanol and 5 mL distilled water). The solution was adjusted to pH=10 by ammonia and stirred for 24 h. The resulting aminated Fe<sub>3</sub>O<sub>4</sub> and GO (200 mg) were separately dispersed in hydrochloric acid aqueous solution (600 mL, pH=3.0) by sonication. The zeta potentials of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and GO solutions at pH=3.0 were about +42 mV and -25 mV, respectively. The above two solutions were then mixed under mild stirring. GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites were formed by the electrostatic interaction between the two oppositely charged nanomaterials. Finally the resulting production was recovered by centrifugation and rinsed with ethanol and H<sub>2</sub>O several times, and then dried under vacuum at 60 °C to obtain GO/Fe<sub>3</sub>O<sub>4</sub> composite. After calcination at 450 °C for 3 h under nitrogen, black r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites were obtained.

### 1.2 Characterization

The FTIR spectra were recorded on a MAGNA-IR 750 FTIR spectrometer. The crystal structures and microstructures of the nanocomposites were characterized by XRD (Ri-gaku/Max-3A, Cu K $\alpha$ ,  $\lambda$ =0.15406 nm), SEM (JEOL JSM-6330F) and TEM (JEOL 2010, 200 kV). Raman spectra were recorded on a LabRAM HR UVNIR multichannel confocal microspectrometer (HORIBA Jobin Yvon, France) with 635 nm laser excitation. Magnetic properties of Fe<sub>3</sub>O<sub>4</sub> and r-GO/Fe<sub>3</sub>O<sub>4</sub> were investigated with a MPMS-XL-7 superconducting quantum interference device (SQUID) magnetometer (Quantum Design, USA) at room temperature.

## 2 Results and Discussion

In the present work, Fe<sub>3</sub>O<sub>4</sub> NPs were firstly modified by surface grafting of KH540 to render the oxide surface to be charged positively. Fig.2 shows FTIR spectra of Fe<sub>3</sub>O<sub>4</sub> NPs, KH540 and the KH540-Fe<sub>3</sub>O<sub>4</sub>. Compared with Fe<sub>3</sub>O<sub>4</sub> NPs, KH540-Fe<sub>3</sub>O<sub>4</sub> presents absorption bands at 2975 and 2858 cm<sup>-1</sup> assigned to stretching vibration of C-H bond of the propyl amine group. The silica network adheres to the particle surface via Fe-O-Si bond. The corresponding adsorption bands appearing at around 550 and 635 cm<sup>-1</sup> overlap the Fe-O vibration of Fe<sub>3</sub>O<sub>4</sub>. However, the silane polymer over the surface of KH540-Fe<sub>3</sub>O<sub>4</sub> can be confirmed with the bands at around 1110, 1045 and 980 cm<sup>-1</sup> from the SiO-H and Si-O-Si groups. The two broad bands at 3410 and 1630 cm<sup>-1</sup> are attributed to the N-H stretching vibrations and NH<sub>2</sub> bending mode of free NH<sub>2</sub> group, respectively. Furthermore, hydrogen-bonded silanols also absorb at around 3410 cm<sup>-1</sup><sup>[21,22]</sup>. Then the modified Fe<sub>3</sub>O<sub>4</sub> NPs are assembled with negative GO by electro-static interactions. Finally, the precipitations are reduced to r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites by calcination.

The crystal structures of as-synthesized GO, Fe<sub>3</sub>O<sub>4</sub> NPs and r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites were studied by XRD (Fig.3). All the diffraction peaks and positions of Fe<sub>3</sub>O<sub>4</sub> NPs and r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites can be indexed to the cubic

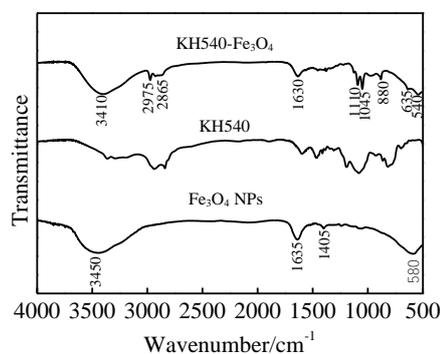


Fig.2 FTIR spectra of Fe<sub>3</sub>O<sub>4</sub> NPs, KH540 and KH540-Fe<sub>3</sub>O<sub>4</sub>

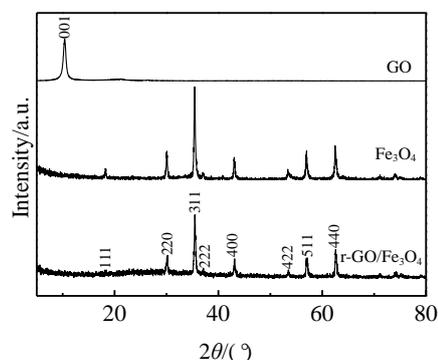


Fig.3 XRD patterns of GO, Fe<sub>3</sub>O<sub>4</sub> hollow spheres and r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites

$\text{Fe}_3\text{O}_4$  (JCPDS 86-1354). The characteristic diffraction peak of GO is observed at  $2\theta=10.5^\circ$  corresponding to the (001) reflection<sup>[8]</sup>. This sharp peak disappears at the XRD pattern of r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites compared with the pristine GO, indicating that oxygen intercalated into the interlayer spacing of graphite is largely removed by reduction.

The morphology of the as-prepared  $\text{Fe}_3\text{O}_4$  NPs was investigated by SEM and TEM. As shown in Fig.4a, the products consist of a large quantity of spheres with average diameter of ca. 250 nm. Moreover, the void in nanoparticle packing gives rise to the porosity in the overall assembled structure. The contrast of TEM image (Fig.4b) has confirmed the hollow sphere structure of the products.

The microstructure and the size of r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites were characterized by TEM. As shown in Fig.5a and 5b, the r-GO successfully wraps around the surfaces of  $\text{Fe}_3\text{O}_4$  hollow nanospheres and shows crinkled and rough textures that are associated with the presence of flexible and ultrathin r-GO sheets. The SAED pattern (inset in Fig.5b) exhibits a remarkable single-crystal feature, in which the spots are assigned to (220) and (311) of cubic  $\text{Fe}_3\text{O}_4$ .

Raman spectroscopy is a powerful tool to characterize carbonaceous materials because of its high Raman intensities. As shown in Fig.6, the Raman spectra of GO and r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites exhibit a D-band peak at about  $1350\text{ cm}^{-1}$  attributed to the breathing mode of k-point phonons of  $A_{1g}$  symmetry and a G-band peak at  $1580\text{ cm}^{-1}$  due to the Brillouin-zone-centered LO-phonon<sup>[23]</sup>. The intensity ratio of the D and G band ( $I_D/I_G$ ) is a useful indicator to evaluate the ordered and disordered crystal structures of carbon<sup>[24]</sup>. The  $I_D/I_G$  of r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposite increases to 1.20 compared with that of GO (0.90). The higher  $I_D/I_G$  value of nanocomposite is attributed to many carbon cavities and the

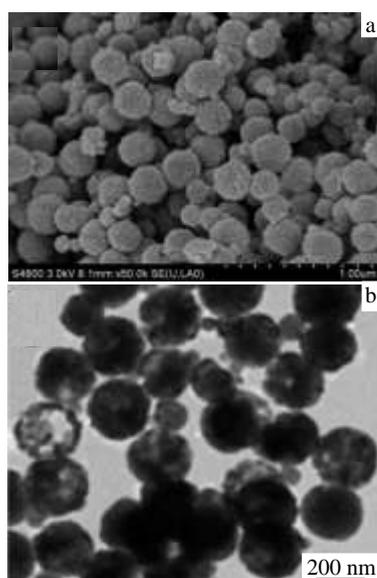


Fig.4 SEM image (a) and TEM image (b) of  $\text{Fe}_3\text{O}_4$  hollow NPs

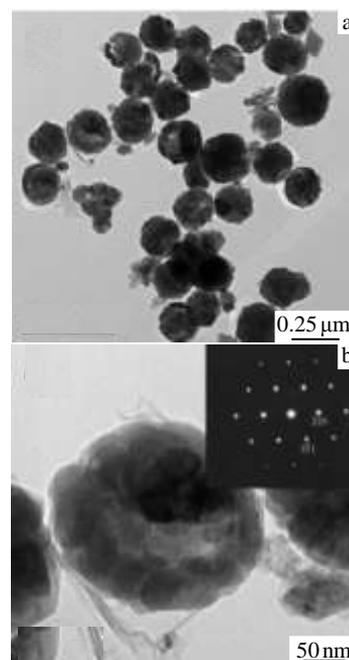


Fig.5 TEM image (a) and corresponding magnified image-SAED pattern (b) of r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites

increased disordered degree resulting from the emission of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which is in good agreement with previous report<sup>[25]</sup>.

The magnetic properties of r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites and  $\text{Fe}_3\text{O}_4$  NPs were investigated by SQUID at room temperature. For both profiles of the magnetization curves of  $\text{Fe}_3\text{O}_4$  NPs and r-GO/ $\text{Fe}_3\text{O}_4$  (Fig.7), the magnetization curves show S-like curves and the magnetic remanences are nearly zero. This result indicates that there is almost no remaining magnetization when the external magnetic field is removed, which is characteristic of superparamagnetic behavior. The  $M_s$  value of r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites ( $70.2\text{ A m}^2\text{ kg}^{-1}$ ) is bigger than the reported values of other  $\text{Fe}_3\text{O}_4$ -based nanocomposites<sup>[8,26]</sup>. The r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites show a decrease in saturation magnetization ( $M_s$ ) compared to the  $\text{Fe}_3\text{O}_4$  NPs ( $70.2\text{ A m}^2\text{ kg}^{-1}$  vs  $74.9\text{ A m}^2\text{ kg}^{-1}$ ), which is in good agreement with the results previously reported by other groups<sup>[27-30]</sup>. According to these reports, the value of  $M_s$  of  $\text{Fe}_3\text{O}_4$ -based nanocomposites is mainly attributed to the  $\text{Fe}_3\text{O}_4$  NPs size and the amount of magnetic component. Because the size of naked  $\text{Fe}_3\text{O}_4$  NPs is similar to that of enwrapped in r-GO sheets (Fig.4), and the effect of NPs size on  $M_s$  can be neglected. Taking into account the non-magnetism of r-GO, the value of  $M_s$  for r-GO/ $\text{Fe}_3\text{O}_4$  nanocomposites greatly depends on the amount of magnetic component. Therefore, the content of  $\text{Fe}_3\text{O}_4$  nanospheres in the nanocomposites estimated from the  $M_s$  is to be 93.7 wt%. Superparamagnetism can make magnetic NPs easily disperse in the solution with magnetic interactions between each other and avoid magnetic clustering.

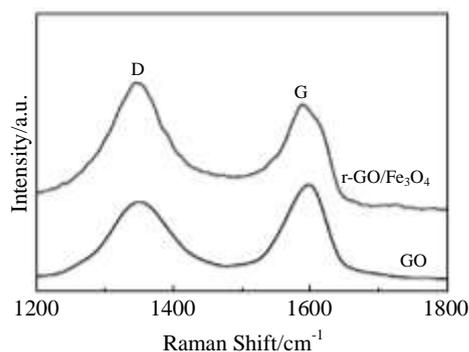


Fig.6 Raman spectroscopy of GO and r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites

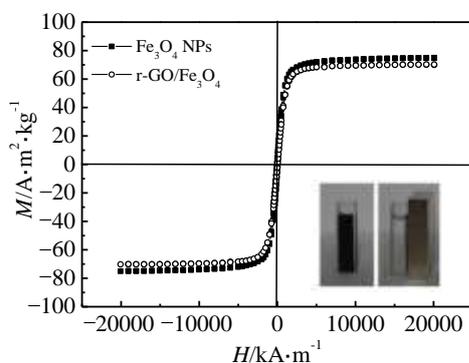


Fig.7 Magnetization curves of Fe<sub>3</sub>O<sub>4</sub> and r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites. The inset shows the dispersion and separation process of the aqueous solution of r-GO/Fe<sub>3</sub>O<sub>4</sub> in the absence (left) and presence (right) of an external magnetic field

Furthermore, it is possible to manipulate superparamagnetic NPs by an applied magnetic field. As shown in the inset of Fig.7, r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites can be well dispersed in the deionized water. When an external magnetic field is applied for a while, the as-prepared r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites are attracted to the wall in a short time, and a nearly colorless solution is obtained. Therefore, the attraction and the redispersion processes can be readily controlled by switching an external magnetic field, showing good dispersion and magnetic separation characteristics in aqueous solution. Due to the superparamagnetic behavior, the high saturation magnetization and the good dispersibility in aqueous solution, the obtained r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites are promising multifunctional candidates in many fields.

### 3 Conclusions

1) The r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites can be synthesized by a simple self-assembly route and subsequent annealing process.

2) The r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites combine the unique and attractive behavior of r-GO nanosheets with excellent superparamagnetic properties of Fe<sub>3</sub>O<sub>4</sub> NPs. The high

magnetism and the excellent dispersibility make these nanocomposites attractive lightweight candidates for technological application.

3) The novel and effective self-assembly process driven by electrostatic interaction can be extended to fabricate other graphene-based composites.

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## 超顺磁性还原氧化石墨烯/Fe<sub>3</sub>O<sub>4</sub>空心球纳米复合材料的合成、表征及性能研究

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**摘 要:** 采用一种简单有效的静电自组装的方法成功合成出还原氧化石墨烯包覆 Fe<sub>3</sub>O<sub>4</sub> 空心球纳米复合材料 (r-GO/Fe<sub>3</sub>O<sub>4</sub>)。运用 X 射线粉末衍射(XRD)、扫描电子显微镜 (SEM)、透射电子显微镜(TEM)、高分辨透射电镜(HRTEM)、红外-可见光谱 (FT-IR) 以及拉曼光谱等手段对合成出的产物进行了系统的表征。r-GO/Fe<sub>3</sub>O<sub>4</sub> 纳米复合材料表现出优良的超顺磁性, 室温下的饱和磁化强度高达 70.2 A m<sup>2</sup> kg<sup>-1</sup>, 并且在外加磁场下可以快速在水溶液中实现分散和分离。较高的饱和磁化强度和优良的水分散性使得这种新型的 r-GO/Fe<sub>3</sub>O<sub>4</sub> 纳米复合材料在包括磁共振成像、生物传感器、通信以及微波吸收等领域具有一定的应用价值。

**关键词:** Fe<sub>3</sub>O<sub>4</sub>; 石墨烯; 纳米复合材料; 超顺磁性

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