



# Preparation of reduced graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite and its microwave electromagnetic properties

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## ABSTRACT

The reduced graphene oxide (r-GO) coated with Fe<sub>3</sub>O<sub>4</sub> composite was synthesized through a facile method involving decomposition of Fe(OH)<sub>3</sub> in argon atmosphere and reduction in hydrogen and argon mixture atmosphere. The Fe<sub>3</sub>O<sub>4</sub> particles evenly distributed on r-GO, with the diameters from 10 nm to 40 nm, are monocrystalline. The composite demonstrates a reflection loss below –10 dB in 14.3–18 GHz range, and the maximum absorption of –22.2 dB at 17.3 GHz. The microwave absorption of r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites is attributed to relaxation and polarization of the residual groups and defect of graphene and polarization attributed to the presence of Fe<sup>2+</sup> ions in Fe<sub>3</sub>O<sub>4</sub>.

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## 1. Introduction

As a unique two dimensional carbon material, graphene has been attracting more and more attention from both experimental and theoretical scientific communities, since it was discovered in 2004 [1]. Due to its special surface properties and layered structure, graphene becomes potential nanoscale building blocks for new hybrid materials. Recent research showed that metallic nanoparticles or inorganic nanoparticles, such as Au, and Mn<sub>3</sub>O<sub>4</sub>, could be attached to graphene or graphene oxide (GO) to form hybrid materials [2], which have potential applications in magnetic resonance imaging (MRI) contrast agent, lithium ion batteries, hydrogen storage, and electromagnetic wave absorption, etc. [3–6].

In recent years, magnetic nanoparticles are of great interests for their unique magnetic and electric properties. In the previous researches, the main methods for synthesizing r-GO/Fe<sub>3</sub>O<sub>4</sub> composites included the solvothermal method and the co-precipitation method. Zhan and co-workers [7] synthesized the composites through solvothermal synthesis and used the hybrid materials as electromagnetic wave absorber. Zhou et al. [8] and Shen et al. [9] adopted solvothermal synthesis for loading of doxorubicin hydrochloride and provided an opportunity for the applications in the fields of biomedicine, biomaterials separation and biodiagnostics. Tung et al. [10] prepared hybrid material of Fe<sub>3</sub>O<sub>4</sub>-functionalized graphene and its composites with polymer through co-precipitation method as electromagnetic shielding materials. He et al. [11] and

Narayanan et al. [12] synthesized reduced graphite oxide–Fe<sub>3</sub>O<sub>4</sub> composites used for biosensor by co-precipitation method, exhibiting a variety of good electrochemical characteristics. Their work showed the unique properties of graphene/Fe<sub>3</sub>O<sub>4</sub> hybrid materials, which provided reasons for exploring additional novel synthetic routs for preparing these materials.

Herein, in order to synthesize the composite with better microwave electromagnetic properties, we reported a facile method involving decomposition and reduction of Fe(OH)<sub>3</sub> to prepare the r-GO/Fe<sub>3</sub>O<sub>4</sub> composite. The morphology, particles size, structure and microwave electromagnetic properties of composite were investigated.

## 2. Experimental

GO was prepared by the modified Hummers method as reported in Ref. [13]. The r-GO was prepared by reduction of GO with mixed gas of hydrogen and argon at 450 °C for 1 h. The composite of r-GO/Fe<sub>3</sub>O<sub>4</sub> was prepared by decomposition and reduction of hydroxide in tubular furnace. In a typical process, 50 mg Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 50 mg r-GO were first sonicated in 40 ml ethyl alcohol for 10 min. After adding sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) into the mixed solution, the mixture was vigorously stirred at 60 °C for 1 h. Then 7.5 mg NaOH was dissolved in 10 ml distilled water to prepare NaOH solution, and the solution was dropped into above mixture. The mixture was stirred at room temperature for 2 h. Then the mixture was washed with distilled water, until the pH reached 7 and dried at 60 °C for 12 h. The obtained powder was heated slowly to 450 °C in argon atmosphere and calcined at this

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temperature for 2 h. Then decreasing the temperature to 350 °C, the reduction was carried out at this temperature for 30 min under a 5% hydrogen/95% argon mixture atmosphere in tubular furnace.

The synthesized product was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Electromagnetic parameters (the complex permeability ( $\mu_r$ ) and permittivity ( $\epsilon_r$ ))

were measured by a vector network analyzer (HP8722ES) over the frequency range of 1–18 GHz, in which the r-GO/Fe<sub>3</sub>O<sub>4</sub> composites were mixed with paraffin at certain mass filling ratio (10 wt%) and compressed to standard ring shapes (outer diameter: 7 mm, inner diameter: 3 mm, and thickness: 2 mm) and the reflection loss was calculated using the measured  $\epsilon_r$  and  $\mu_r$ .

### 3. Results and discussion

XRD measurements were utilized to investigate the phase composition and the crystalline structure of the synthesized samples. As shown in Fig. 1, the XRD pattern of graphite oxide (pattern a) has a sharp peak at  $2\theta=11.1^\circ$ , corresponding to the (001) reflection of graphite oxide [14], and the interplanar spacing of GO is larger than that of graphite due to the introduction of oxygen-containing functional groups on the graphene sheets of GO during the oxidation process. From pattern b, disappearance of the peak at  $2\theta=11.1^\circ$  provides the evidence for reduction of GO. The (002) diffraction peak at  $26.4^\circ$  of graphite structure can be seen obviously. These data suggest that graphene was successfully prepared by reduction of GO with hydrogen. The XRD pattern of r-GO coated with Fe<sub>3</sub>O<sub>4</sub> material is shown in Fig. 1 (pattern c), it could be seen that all of the peaks of Fe<sub>3</sub>O<sub>4</sub> are conspicuous, indicating r-GO/Fe<sub>3</sub>O<sub>4</sub> nanocomposites were obtained.

The morphologies and structure of r-GO and r-GO/Fe<sub>3</sub>O<sub>4</sub> were investigated by TEM. Fig. 2a shows low magnification TEM image of r-GO, which presents a typical wrinkled morphology. The HRTEM image in Fig. 2b shows the thickness of r-GO sheets is less than 10 nm. From Fig. 2c it is found that the carbon sheets were decorated by nanoparticles with diameters from 10 nm to

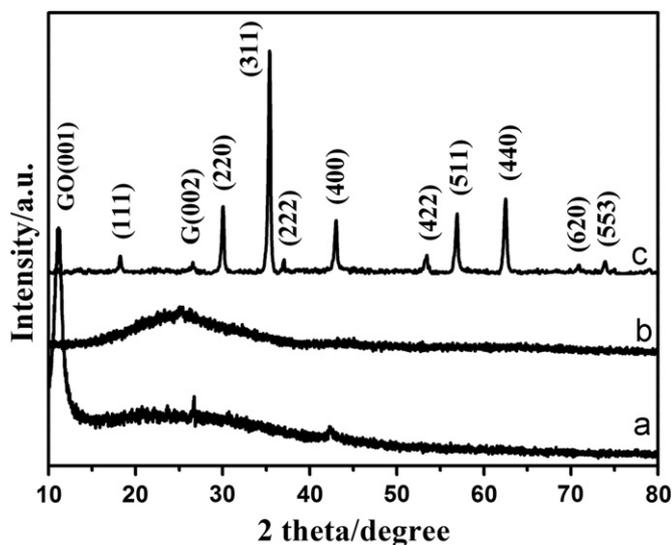


Fig. 1. XRD patterns of (a) GO, (b) r-GO and (c) r-GO/Fe<sub>3</sub>O<sub>4</sub> composites.

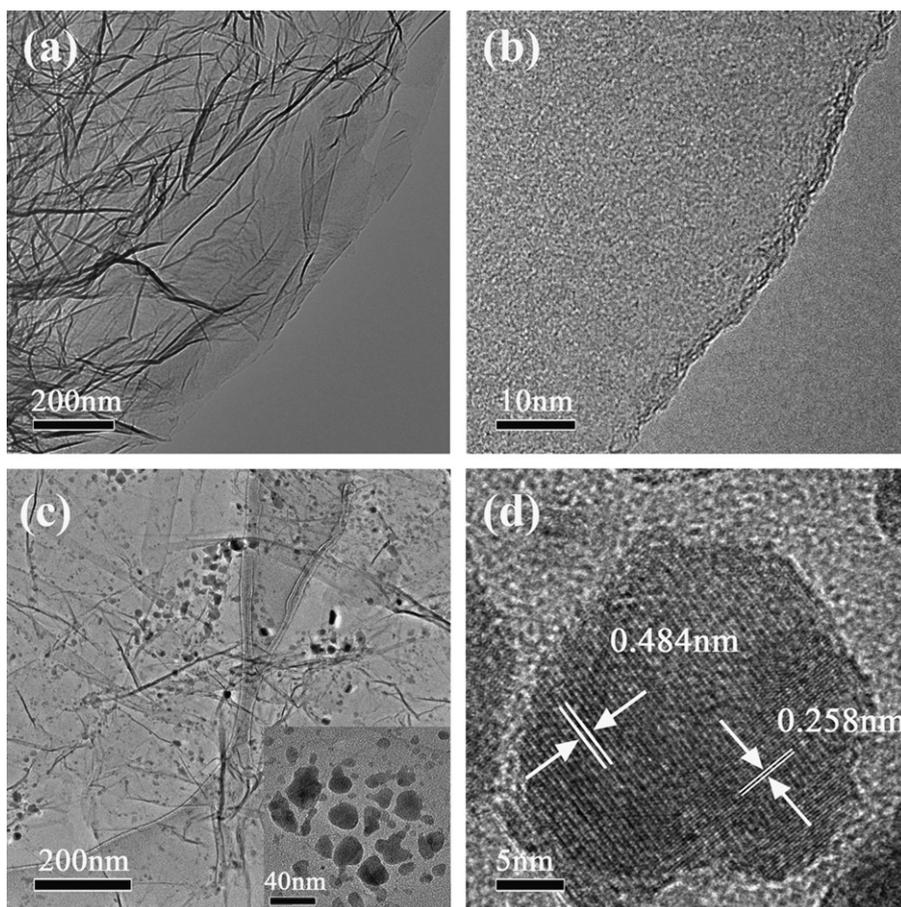


Fig. 2. (a) TEM and (b) HRTEM images of r-GO, and (c) TEM and (d) HRTEM images of r-GO/Fe<sub>3</sub>O<sub>4</sub>.

40 nm. The inset in Fig. 2c is a high magnification image of nanoparticle concentrated area, in which we can see that nanoparticles with different diameters are evenly distributed. HRTEM image of particles reveals that  $\text{Fe}_3\text{O}_4$  nanoparticles are monocrystalline and indicates that the lattice fringes with interplanar-spacings distances are 0.484 nm (111) and 0.258 nm (311). All the results demonstrate that  $\text{Fe}_3\text{O}_4$  nanoparticles were coated on the surface of graphene and the nanoparticles exhibited even distribution.

Fig. 3(a and b) shows the real ( $\epsilon'$ ) and the imaginary parts ( $\epsilon''$ ) of relative complex permittivity and the real ( $\mu'$ ) and the imaginary parts ( $\mu''$ ) of relative complex permeability of the composite, respectively. It is found that the  $\epsilon'$ ,  $\epsilon''$  decrease with increasing the frequency in 1–18 GHz, demonstrating a frequency-dependent dielectric response. The  $\mu'$  and  $\mu''$  maintain around 1 and 0 in the whole frequency range, respectively. This result is different from that of the  $\text{Fe}_3\text{O}_4$ /ferrocenyl–CuPc nanospheres reported by Wei et al., which shows resonant peaks in permittivity and permeability curves [15]. The reason may be attributed to the low loading and the small size of  $\text{Fe}_3\text{O}_4$  particles in the present study. Fig. 3(c) shows frequency dependence of the dielectric loss tangent ( $\epsilon''/\epsilon'$ ) and the magnetic loss tangent ( $\mu''/\mu'$ ) of the composite. It is observed that the variation tendency of dielectric loss and magnetic loss was similar and the value of dielectric loss was much higher than that of magnetic loss in frequencies ranging from 1 to 18 GHz, suggesting that microwave absorption enhancement of the composite results mainly from dielectric loss rather than magnetic loss.

The reflection loss (RL) of the composites can be evaluated by

$$RL = 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right| \quad (1)$$

$$Z_{in} = \sqrt{\mu_r/\epsilon_r} \tan h[j(2\pi f d/c) \sqrt{\epsilon_r \mu_r}] \quad (2)$$

where  $Z_{in}$  is the normalized input impedance when the electromagnetic wave incidence is normal to the absorber,  $f$  is the frequency of the electromagnetic wave,  $d$  is the thickness of the absorber, and  $c$  is the velocity of electromagnetic waves in free space. The calculated RL for r-GO and composite with thickness of 2 mm are shown in Fig. 3(d). It was clearly seen that although the maximum absorption of r-GO was lower than  $-10$  dB, the composite exhibited a maximum absorption of  $-22.2$  dB at 17.3 GHz, and the bandwidth corresponding to reflection loss at  $-10$  dB can reach 3.7 GHz (from 14.3 to 18 GHz).

We can infer that the main contributors for RL are relaxation and polarization of the defects and residual groups of r-GO's surface. The defects and residual group could be the polarization centers [16], which would generate polarization and relaxation under the altering electromagnetic field, to attenuate electromagnetic wave. The polarization attributed to the presence of  $\text{Fe}^{2+}$  ions in  $\text{Fe}_3\text{O}_4$  also enhance the dielectric loss [17]. Due to low loading and small size of the  $\text{Fe}_3\text{O}_4$  particles, the natural resonance of the  $\text{Fe}_3\text{O}_4$  presents little effect on the absorption of the composite. In addition, coating of  $\text{Fe}_3\text{O}_4$  particles on graphene may improve the impedance match characteristics, decreasing

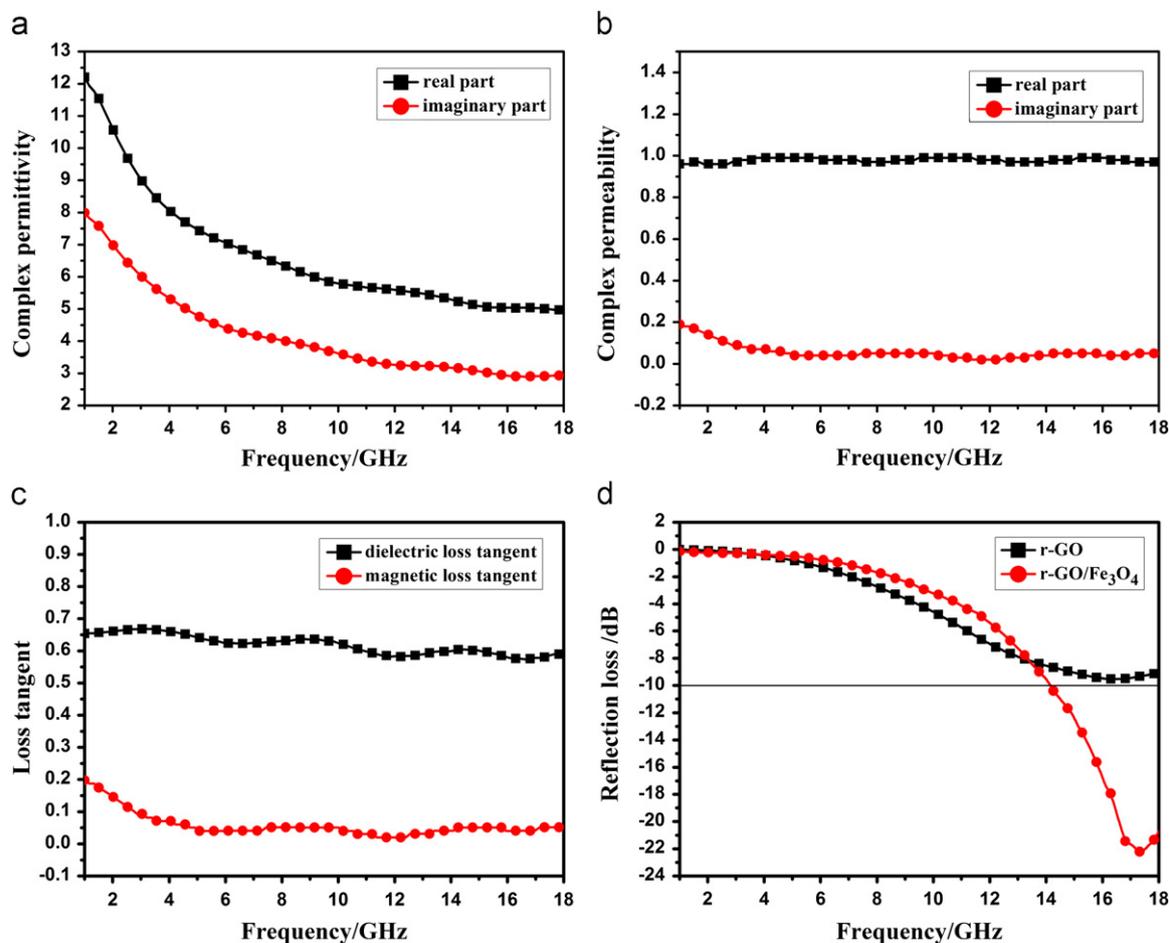


Fig. 3. Frequency dependence of (a) the complex relative dielectric permittivity, (b) the complex relative magnetic permeability, (c) the loss tangent of dielectric/magnetic of composite and (d) the reflection loss for r-GO and r-GO/ $\text{Fe}_3\text{O}_4$  composite.

the surface reflection and benefitting the absorption. For the sake of synergistic effect of graphene and  $\text{Fe}_3\text{O}_4$ , it can be believed that the r-GO/ $\text{Fe}_3\text{O}_4$  composite can obtain better microwave absorption properties in high frequency bands.

### Conclusion

In summary, we reported a facile method for preparing the r-GO/ $\text{Fe}_3\text{O}_4$  composite, in which the  $\text{Fe}_3\text{O}_4$  particles were crystallized well. As a result of relaxation and polarization of groups of graphene surface and  $\text{Fe}_3\text{O}_4$  particles, the r-GO/ $\text{Fe}_3\text{O}_4$  composite demonstrates a maximum absorption of  $-22.2$  dB. It is believed that such composite can find its applications in microwave absorbing area.

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