



# Synthesis and microwave absorption properties of reduced graphene oxide-magnetic porous nanospheres-polyaniline composites



Juhua Luo<sup>\*</sup>, Yang Xu, Wei Yao, Cuifeng Jiang, Jianguang Xu

School of Material Science and Engineering, Yancheng Institute of Technology, Yancheng, 224051, China

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## ABSTRACT

A ternary composite which was composed of reduced graphene oxide (R-GO), Fe<sub>3</sub>O<sub>4</sub> porous nanospheres (P-Fe<sub>3</sub>O<sub>4</sub>) and polyaniline (PANI) was synthesized by a facile route. The microstructure of the composite was characterized by XRD, FT-IR, FESEM and TEM. The results indicated that the uniform Fe<sub>3</sub>O<sub>4</sub> porous nanospheres with the average size of 250–400 nm were grown on R-GO sheets and the coating layer of PANI covered over the surface of R-GO/P-Fe<sub>3</sub>O<sub>4</sub> composite. With the decreasing content of Fe<sub>3</sub>O<sub>4</sub>, the saturation magnetization of this ternary composite declined while the coercivity showed the opposite trend. The composite showed excellent microwave absorption properties due to the good impedance match characteristic between dielectric loss and magnetic loss. The minimum reflection loss value reached –29.51 dB at 14.69 GHz with thickness of 1.0 mm.

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## 1. Introduction

During the past few decades, electromagnetic (EM) wave absorption materials have attracted much attention due to the rapid development of gigahertz (GHz) telecommunications and electronic systems [1]. The attenuation mechanisms of most EM absorbers are absorbing EM wave by either dissipating EM wave loss or converting EM energy into thermal energy because of their magnetic losses or dielectric losses [2]. However, a new ideal EM wave absorber with strong absorption, wide range of absorption frequency, small thickness and light weight is still pursued desperately.

Compared with traditional microwave absorption materials such as ferrite [3], nickel [4], cobalt [5], and conducting polymers [6,7], reduced graphene oxide (R-GO) has become a promising material in microwave absorption field due to its lightweight, high specific surface area, stable structure and excellent electronic conductivity [8]. Moreover, the residual defects and functional groups present in chemically reduced graphene are helpful in impedance matching, defect polarization relaxation and electronic dipole relaxation, which all serve to improve electromagnetic wave absorption [9]. But the non-magnetic property of R-GO can lead to the unbalance of dielectric permittivity and magnetic permeability

resulting in a bad impedance matching of absorbers. One of the most effective solutions to avoid the dilemma is to couple the graphene materials with magnetic constituents [10–13]. Furthermore, K. Singh et al. reported that the addition of polyaniline could improve the microwave absorption properties of the R-GO/Fe<sub>3</sub>O<sub>4</sub> composites [15]. Also, PANI, as one of most promising conducting polymers, has drawn more attention due to its high electrical conductivity, excellent environmental stability, relatively low density and easy preparation. PANI composites with magnetic nanoparticles have shown enhanced electromagnetic absorption properties. Inspired by these facts, we demonstrated a facile synthesis route to prepare a ternary composite consisting of reduced graphene, Fe<sub>3</sub>O<sub>4</sub> porous nanospheres and polyaniline (R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/PANI), analyzing the formation mechanism and the microwave absorption properties of the ternary composites.

## 2. Experimental

### 2.1. Preparation of the samples

The graphite was synthesized by modified Hummers method [14]. The preparation of Fe<sub>3</sub>O<sub>4</sub> porous nanospheres/graphene composite was based on a facile one-pot solvothermal method. Typically, 0.12 g of graphite oxide powder was dispersed in 60 ml EG (ethylene glycol) and ultra-sonicated for 2 h to obtain a fine dispersion. Then, 1.26 g of FeCl<sub>3</sub>·6H<sub>2</sub>O, 3.59 g of NH<sub>4</sub>AC (ammonium acetate) and 1.87 g of PVP (polyvinylpyrrolidone, Mw:

<sup>\*</sup> Corresponding author.

E-mail address: [luojuhua@163.com](mailto:luojuhua@163.com) (J. Luo).

5800) was added into GO solution with constant stirring to form homogeneous dispersion. The mixture was transferred to a Teflon-lined stainless autoclave and heated at 220 °C for 14 h. The obtained black product was washed by distilled water and ethanol several times and was dried at 60 °C in a vacuum oven to obtain R-GO/P-Fe<sub>3</sub>O<sub>4</sub> powder (m (Fe<sub>3</sub>O<sub>4</sub>):m (GO) = 3:7). Pristine Fe<sub>3</sub>O<sub>4</sub> porous nanospheres were also obtained in a similar manner without the GO solution. P-Fe<sub>3</sub>O<sub>4</sub> powders were introduced to prepare R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/PANI, as described in detail elsewhere [14]. The certain amount of R-GO/P-Fe<sub>3</sub>O<sub>4</sub> powders (R-GO/P-Fe<sub>3</sub>O<sub>4</sub> and aniline in mass ratio of 1:1) were ultra-homogenized in aqueous solution of 10.73 g dodecylbenzenesulfonic acid (DBSA) with an appropriate amount of aniline (1 mL) for 3 h to form a homogeneous dispersion. 2.49 g of ammonium persulfate was dissolved in 50 mL distilled water and then slowly added dropwise to the above mixture solution with vigorous stirring. The polymerization was carried out for 12 h under 5 °C. The composites were obtained by filtering and washing the reaction mixture with distilled water and ethanol and dried under vacuum at 60 °C for 24 h.

## 2.2. Characterization

The resulting powder was characterized by X-ray powder diffraction (XRD) using a diffractometer (RIGAKU, model D/max) with CuK $\alpha$  radiation. The morphologies were studied with a field emission scanning electron microscope (JEOL, model JSM-7001F) and a transmission electron microscope (JEOL, model JEM 2001). Fourier transform infrared spectroscopy (FT-IR) was carried out using the infrared spectrophotometer (NICOLET, model NEXUS 670) in the range from 4000 to 400 cm<sup>-1</sup>. Raman spectra were measured using a Laser Raman spectroscope (Thermo Fisher, model DXR) at a 633 nm wavelength incident laser light. Magnetization measurements were taken at room temperature (293 K) using a vibrating sample magnetometer (LDJ, model 9600-1). The complex permittivity ( $\epsilon_r = \epsilon' - j\epsilon''$ ) and permeability ( $\mu_r = \mu' - j\mu''$ ) of the samples were measured by a microwave vector network analyzer (AGILENT, model N5244A) in the frequency range 2–18 GHz by using coaxial reflection/transmission technique. The samples for vector network analyzer were pressed to be toroidal samples with OD 7 mm, ID 3.04 mm and height about 3 mm according to the mass ration 7:3 of between paraffin and PANI/R-GO/P-Fe<sub>3</sub>O<sub>4</sub>. Microwave absorption properties were evaluated by the reflection loss (RL), which was derived from the following formulas:

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r} \tanh \left[ j \frac{2\pi f d}{c} \sqrt{\mu_r \epsilon_r} \right]} \quad (1)$$

$$RL = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (2)$$

Where  $f$  is the frequency of incident electromagnetic wave,  $d$  is the absorber thickness,  $c$  is the velocity of light,  $Z_0$  is the impedance of free space, and  $Z_{in}$  is the input impedance of absorber.

## 3. Results and discussion

### 3.1. Morphological studies and structural characterization

Fig. 1 shows the XRD patterns of the samples. For GO, a characteristic reflection plan (002) appeared at  $2\theta = 10.96^\circ$ , indicating a highly oxidized GO was synthesized [14]. However, the characteristic peak of GO vanished in R-GO/P-Fe<sub>3</sub>O<sub>4</sub> and R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/PANI composite which demonstrated that GO was reduced mostly by EG in the solvothermal system [12] and indicated the R-GO was

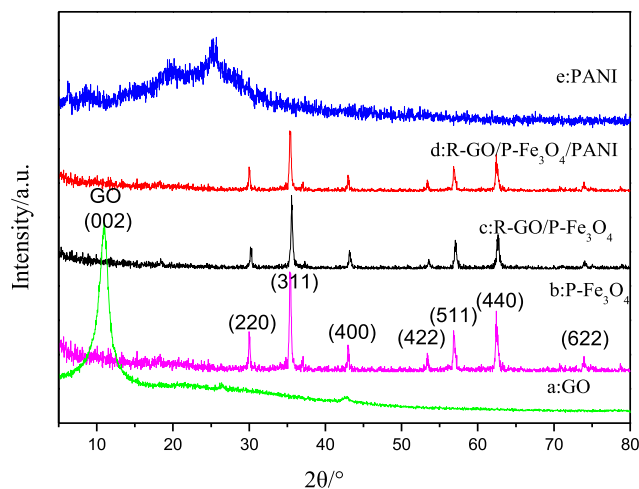


Fig. 1. XRD patterns of (a) GO, (b) Fe<sub>3</sub>O<sub>4</sub> porous nanospheres, (c) R-GO/P-Fe<sub>3</sub>O<sub>4</sub> composite, (d) R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/PANI composite, and (e) PANI.

homogenously dispersed on the surface of porous Fe<sub>3</sub>O<sub>4</sub>. Both of these two composites were identified by the characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> (in Fig. 1b) at  $2\theta = 30.12^\circ, 35.46^\circ, 43.08^\circ, 53.73^\circ, 57.26^\circ, 62.73^\circ$  which were corresponding to the (220), (311), (400), (422), (511), (440) and (622) planes (JCPDS no. 880315) with little shift. These demonstrated the good interfacial interaction between the R-GO and P-Fe<sub>3</sub>O<sub>4</sub> were formed. During the process of preparation of R-GO/P-Fe<sub>3</sub>O<sub>4</sub> composite, PVP plays an important role in controlling the interfacial interactions between R-GO and metal oxide materials. Due to the strong  $\pi$ - $\pi$  interactions between R-GO sheets and PVP molecules, the colloidal suspensions of R-GO decorated by PVP exhibit high stability. Second, the Fe<sub>3</sub>O<sub>4</sub> particles are loaded with PVP-functionalized R-GO sheets, which can be attributed to the absorption interactions between hydrophilic head groups of PVP/residual oxygen containing groups on R-GO, and the metal oxides particles [16]. The formation of R-GO/P-Fe<sub>3</sub>O<sub>4</sub> is illustrated in Fig. 2. Notably, no obvious diffraction peaks for PANI can be observed, which might be due to low content of PANI in the ternary composite, and the result is in agreement with the previous work [17]. The broad peaks of PANI at about  $2\theta = 20.27^\circ$  and  $25.39^\circ$  indicate amorphous nature which is close to the distance of the interplanar aromatic rings and peaks are ascribed to the parallel and perpendicular periodicity of the PANI chains.

In order to confirm the existence of PANI in the ternary composite, FT-IR was used to investigate the composites (shown in Fig. 3). For R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/PANI composite, the characteristic peaks at 1548 and 1459 cm<sup>-1</sup> are attributed to the C=C stretching vibration in quinoid and benzenoid rings of PANI, respectively [18]. The peaks at 1268 and 1207 cm<sup>-1</sup> are assigned to the C-N stretching of the secondary aromatic amine which are characteristic peaks of conducting emeraldine salt form of PANI, and the bands at 1107 cm<sup>-1</sup> can be assigned to an in-plane bending vibration of the C-H (mode of N = Q = N, Q refers to the quinonic-type rings) which is described by Ahmad as the “electronic-like band” formed by protonation [19]. The peak at 792 cm<sup>-1</sup> is attributed to the out-of-plane deformation of C-H in the *p*-disubstituted benzene ring. These results are strong evidences of the existence of PANI in ternary composite. Furthermore, the strong and sharp absorption peak at 609 cm<sup>-1</sup> ascribing to the Fe-O vibration of R-GO/P-Fe<sub>3</sub>O<sub>4</sub> composite disappears in R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/PANI composite indicating the successful coating of PANI on the surface of the binary composite (R-GO/P-Fe<sub>3</sub>O<sub>4</sub>). In further observation, the peak at 1629 cm<sup>-1</sup> both appearing in R-GO/P-Fe<sub>3</sub>O<sub>4</sub> and R-GO/P-Fe<sub>3</sub>O<sub>4</sub>/

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