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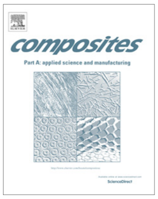

Graphene-enhanced microwave absorption properties of Fe_3O_4/SiO_2 nanorods

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ABSTRACT

Fe_3O_4/SiO_2/graphene composite composed of Fe_3O_4/SiO_2 core–shell nanorods and graphene nanosheets were synthesized by a facile wet chemical method. Structure and morphology studies reveal that the Fe_3O_4/SiO_2 nanorods with porous structure and large aspect ratio are densely wrapped by the graphene nanosheets. By changing the graphene content, the electromagnetic properties of the Fe_3O_4/SiO_2/graphene composite can be well tuned. When the weight ratio of Fe_3O_4/SiO_2 to graphene reaches an appropriate value, excellent microwave absorption performance is achieved due to the large electromagnetic losses and good impedance matching. The Fe_3O_4/SiO_2/graphene composite with graphene content of 5 wt.% shows the minimum reflection loss of −27.1 dB at 12.2 GHz when the coating layer thickness is only 1.5 mm.

1. Introduction

High-performance microwave absorption materials which convert electromagnetic (EM) energy to thermal energy or other forms of energy have become a hot topic in solving serious EM pollution problems caused by wide applications of electromagnetic wave devices, such as wireless networks, communication equipments, and personal digital devices [1,2]. The ideal EM wave absorbing material is required to have strong EM wave absorption, wide absorption frequency range, low density, high thermal stability and antioxidation capability, which facilitate its practical applications in civil and military fields [3]. Inverse spinel type Fe_3O_4 is a conventional EM wave absorbing material because of its low cost, easy fabrication, and excellent magnetic properties which produce large magnetic loss in alternating electromagnetic field. However, it is difficult for individual Fe_3O_4 material to fulfil the requirements for high-performance EM wave absorbers in gigahertz frequency range due to the shortcomings of permeability reduction caused by Snoek's limit at high frequency, narrow absorption frequency range, high density and ease of oxidation [4]. To improve the absorbing properties of Fe_3O_4 in high frequency region, extensive studies have been made to develop Fe_3O_4 composite absorbers which combine magnetic loss and electric loss, such as Fe_3O_4/TiO_2 [3], Fe_3O_4/ZnO [5], Fe_3O_4/carbon nanotubes [6], and Fe_3O_4/SnO_2 [7].

Among various electric loss type materials, carbonaceous materials are considered as promising candidates for achieving lightweight and high-efficiency characteristics [8–11]. Particularly, two-dimensional graphene sheets have attracted much attention owing to the superior electronic, mechanical and chemical properties [12,13]. Moreover, the large specific surface and layered structure endow graphene a potential nanoscale building block for new hybrid materials. Recent research shows that Fe_3O_4 nanoparticle-functionalized graphene sheets have better EM wave absorption properties than individual Fe_3O_4 particles. For example, Sun et al. prepared Fe_3O_4 nanoparticle-graphene composite and obtained a minimum reflection loss (RL) of −15.38 dB with a layer thickness of 2.0 mm [14]. Xu et al. reported a hollow Fe_3O_4/graphene composite which exhibited a minimum RL of −24 dB at 12.9 GHz with a layer thickness of 2.0 mm [15]. Zong and co-workers loaded Fe_3O_4 nanoparticles on graphene by a co-precipitation route. Such composite displayed strong EM wave attention with minimum RL of −44.6 dB when the thickness was 3.9 mm [16]. In previous studies, however, most Fe_3O_4–graphene composite absorbers are based on Fe_3O_4 spheres in nanoscale or submicron-scale. It is known that one dimensional (1D) Fe_3O_4 nanostructures could overcome the Snoek's limit and have large magnetic loss in gigahertz frequency region due to the large shape anisotropy field. Nevertheless, 1D Fe_3O_4–graphene composite absorbers, which are expected to possess excellent microwave absorbing performance, are seldom reported. To the best of our knowledge, only in Ren's study, the Fe_3O_4 nanorods with the aspect ratio (length/diameter) of about

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4 were perpendicularly grown on graphene sheets. Such three-dimensional composite absorbers exhibited minimum RL of −31.9 dB as the thickness is 2.5 mm.

In the present work, we synthesized the Fe_3O_4 nanorods with much larger aspect ratio (15–22) and fabricated Fe_3O_4/SiO_2 core–shell nanorods–graphene composite absorber. The large aspect ratio of the Fe_3O_4 nanorods produces large shape anisotropy field and results in large permeability in high frequency range, which benefit the improvement of high-frequency absorbing properties. The formation of SiO_2 shell on Fe_3O_4 can effectively prevent the oxidation and improve the stability of Fe_3O_4 nanorods. Such composite absorbers combine the advantages of 1D Fe_3O_4/SiO_2 nanorods and graphene, making the best of the contributions from magnetic loss and electric loss. Meanwhile, we investigated the effects of graphene on tuning the EM properties by changing the graphene content. With an appropriate amount of graphene, the Fe_3O_4/SiO_2/graphene composite achieves an enhanced dielectric properties and improved impedance matching, which lead to an excellent microwave absorption performance at very thin layer thickness.

2. Experimental section

2.1. Sample preparation

2.1.1. Synthesis of FeOOH/SiO_2 nanorods

The synthesis of FeOOH/SiO_2 nanorods was carried out as previously reported [17]. Briefly, 0.6 M of $FeCl_3·6H_2O$ and 0.07 M of 37% HCl were added to a 500 mL Schott bottle and aged in an oven at 98 °C for 24 h. Subsequently, the obtained precipitates were collected, washed with water for several times, and then redispersed in 200 mL of water. 10 mL of polyacrylic acid (0.1 M) solution was added to the suspension for the surface modification of FeOOH nanorods. After overnight stirring, the FeOOH nanorods were collected and were redispersed in 180 mL of water, followed by addition of 6 mL of ammonia solution, 160 mL of ethanol, and a certain amount of tetraethyl orthosilicate (TEOS). After stirring for 1 h, the FeOOH/SiO_2 nanorods were collected and washed with water.

2.1.2. Preparation of FeOOH/SiO_2/graphene composite

Graphite oxide (GO) was synthesized by a modified Hummers method [18]. To obtain FeOOH/SiO_2/graphene composite, a certain amount of FeOOH/SiO_2 nanorods was added to GO suspension with the mass percentage of GO of 5 and 10 wt.%. Corresponding FeOOH/SiO_2/GO composites were marked as FSG-1 and FSG-2. After being sonicated for 0.5 h, the black precipitates were collected, washed, and finally dried.

2.1.3. Conversion from FeOOH/SiO_2/GO to Fe_3O_4/SiO_2/graphene composite

The Fe_3O_4/SiO_2/graphene composite were produced by annealing the FeOOH/SiO_2/GO composite at 400 °C for 1 h under a continuous H_2/N_2 gas flow.

2.2. Characterization

The phase composition and crystal structure of the samples were measured by X-ray diffractometer (XRD, D/MAX-1200, Rigaku Denki Co., Ltd., Japan) with Cu Kα irradiation. Transmission electron microscopy (TEM, JEOL-2100F) and field emission scanning electron microscopy (JSM-7500F) were used to observe the morphology and microstructure of the samples. The Raman spectra of the samples were obtained by using an in Via Laser Raman spectrometer (LabRAm HR Evolution). X-ray photoelectron spectroscopy (XPS) measurement was performed on a spectrometer with Mg Kα radiation (ESCALAB 250, Thermofisher Co.). Room-temperature magnetic properties of the samples were measured by a Lakeshore vibrating sample magnetometer (VSM).

To test the EM parameters of the Fe_3O_4/SiO_2 nanorods and Fe_3O_4/SiO_2/graphene composites, the powders were mixed with paraffin and pressed into toroidal shape with outer diameter of 7.00 mm and inner diameter of 3.04 mm by pressing. The complex permittivity and permeability values were measured in the 2–18 GHz frequency range by an Agilent N5230C network analyzer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Fe_3O_4/SiO_2 core–shell nanorods and Fe_3O_4/SiO_2/graphene composites with different amount of graphene. Clearly, the introduction of graphene did not change the structure and composition of the Fe_3O_4/SiO_2 nanorods. All the XRD curves of the samples display characteristic diffraction peaks of Fe_3O_4 which correspond to the (220), (311), (222), (400), (422), (511), (440), and (533) planes according to JCPDS No. 87-0245. Except for the peaks of Fe_3O_4, no other diffraction peaks from SiO_2, GO or graphene can be found. It implies that the SiO_2 is amorphous structure and the GO is effectively reduced into graphene without self-restacking of the graphene sheets [19]. Raman spectroscopy was used to further investigate the structure of the Fe_3O_4/SiO_2/graphene composites. Fig. 2 shows the representative Raman spectra of GO and Fe_3O_4/SiO_2/graphene composite (FSG-2). The GO spectrum exhibits two peaks at 1348 and 1588 cm^{-1}, which are assigned to the D-band and G-band, respectively [20]. The D band is a first-order zone boundary phonon mode associated with defects, while the G band is a radial C—C stretching mode of sp^2 bonded carbon [21]. The intensity ratio of D band to G band (I_D/I_G) is commonly used to reflect the degree of the defects in the graphene or the edges. Compared with GO, the I_D/I_G value of the Fe_3O_4/SiO_2/graphene composite shows a slight increase, and meanwhile the G band of the composite becomes weaker and broader. These phenomena were generally observed in many graphene–nanoparticle composites, and were regarded as a higher degree of defects in the graphene and a decrease in the average size of sp^2 carbon domains, which derive from the reduction of GO as well as the interaction between nanoparticles and graphene sheets [16,22,23].

XPS measurements were carried out to determine the chemical composition of the Fe_3O_4/SiO_2/graphene composite (FSG-1). The Fe 2*p* XPS spectrum in Fig. 3(a) shows two peaks at 710.7 and

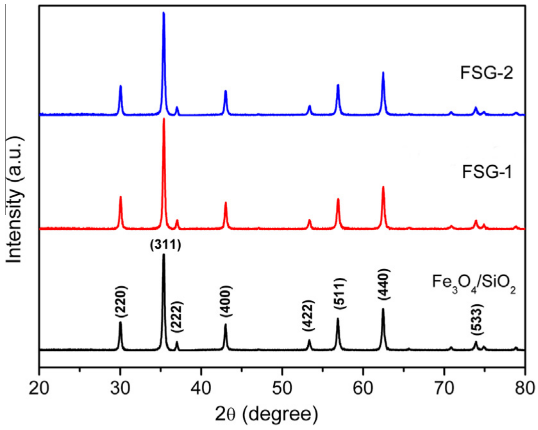

Fig. 1. XRD patterns of Fe_3O_4/SiO_2 core–shell nanorods and Fe_3O_4/SiO_2/graphene composites with different amount of graphene (FSG-1 and FSG-2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)