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Cubic $NiFe_2O_4$ particles on graphene–polyaniline and their enhanced microwave absorption properties

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ABSTRACT

The geometrical morphology of magnetic particles has an important influence on microwave absorption properties, but seldom researches have been focused on this issue. In this paper, cubic $NiFe_2O_4$ particles on graphene–polyaniline hybrid material were synthesized by a two-step method. TEM results show that most of $NiFe_2O_4$ particles have a cubic geometrical morphology. The investigation of the microwave absorbability reveals that the composites exhibit enhanced microwave absorption properties and wide absorption bandwidth. The maximum reflection loss is up to −50.5 dB at 12.5 GHz and the absorption bandwidths exceeding −10 dB are 5.3 GHz (from 11.0 to 16.3 GHz) with a thickness of 2.5 mm. The Cole–Cole plots demonstrate that there are multi-dielectric relaxation processes and the values of C_0 indicate that the magnetic loss of the composites is mainly caused by natural resonance and eddy-current effects. Furthermore, our development strategies confirm that the surface modification of polyaniline and cubic $NiFe_2O_4$ particles on graphene makes the composites have a promising future in microwave absorption materials.

1. Introduction

Microwave absorption material can absorb electromagnetic (EM) waves effectively and convert EM energy into thermal energy by interference. Graphene (GN), a two-dimensional (2D) single layer of carbon atoms patterned in a hexagonal lattice, has attracted increasing attention for its potential applications due to its outstanding properties [1,2]. The high dielectric loss and low density enable it to be used as microwave absorbing material. Nevertheless, GN is found to be non-magnetic and the microwave absorption mostly contributes to its dielectric loss and electromagnetic parameter [3]. According to EM energy conversion principle, apart from dielectric loss and magnetic loss, the proper matching between dielectric loss and magnetic loss also determines the attenuation characteristics of EM absorption material. Therefore, one of the effective ways to reduce the problem is to couple GN with magnetic particles [4–9]. For example, Ren investigated the electromagnetic absorption properties of graphene/Fe_3O_4@Fe/ZnO nanocomposites and the results showed that the maximum R_L values were lower than −30 dB with a thickness of 2.5–5 mm [4]. Hu and co-workers fabricated 3D Fe_3O_4-graphene nanocomposites, the maximum reflection loss was −27 dB with a thickness of 4 mm and the absorption bandwidths with reflection loss less than −10 dB ranged from 6.5–10.3 GHz [6]. Zong coupled graphene with $CoFe_2O_4$ [8] or $NiFe_2O_4$ [9] particles to enhance the microwave absorption properties. $NiFe_2O_4$ a typical magnetic-media material, the high magnetic loss factors and attenuated EM waves enable it to be used as a microwave absorption material [10]. The microwave absorption properties of graphene with $NiFe_2O_4$ nanorods also have been reported [11].

Polyaniline (PANI) is one of the most promising conducting polymers with excellent physical and chemical properties. Its microwave absorption properties are closely related to its structure [12]. Over the past decade, much attention has been paid to the EM absorption properties of PANI/$BaTiO_3$ [13], PANI/$CoFe_2O_4$ [14], PANI/Fe_3O_4 [15] and PANI/Carbon Nanotube [16], but these reports are confined to study the binary composites. Recently, the ternary composites such as EG/PANI/CF [17], EG/PANI/CF [18] and PANI-RGO-Co_3O_4 [19] have been synthesized due to their multi-functional electrical and magnetic properties, but the microwave absorption properties and the absorption bandwidth are not satisfactory, and the focus are mainly on the magnetic particles. Except for multi-interfacial polarization and impedance matching, the geometrical morphology of magnetic particles also has an important influence on microwave absorption properties. However, until now, seldom researches have been focused on this issue.

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Herein, cubic $NiFe_2O_4$ particles on graphene–polyaniline (c-$NiFe_2O_4$/GN-PANI) were synthesized by a two-step method and the microwave absorption properties of the composites were investigated. The results indicate that the composites exhibit excellent microwave absorption properties and wide absorption bandwidth. The maximum reflection loss is up to −50.5 dB at the frequency of 12.5 GHz and the absorption bandwidths with the reflection loss below −10 dB are 5.3 GHz with a thickness of 2.5 mm, which are significantly higher than the previous composites.

2. Experimental section

2.1. Synthesis

Graphene oxide (GO) was synthesized by Hummers method [20]. The composites were prepared as follows: Firstly, 50 mg of GO was dissolved in 1 mol/L aqueous concentrated H_2SO_4 solution and then the mixture cooled down to 0–5 °C under stirring. Then 0.1 mL of aniline monomer was added into the above solution and stirred for 30 min. $(NH_4)_2S_2O_8$ (APS) dissolved in 5 mL concentrated H_2SO_4 solution (aniline/APS = 1.5) was added. The mixture was stirred for 24 h and the resulting precipitates were washed with deionic water and ethanol. Secondly, 0.6 g of $Ni(NO_3)_26H_2O$ and 1.6 g of $Fe(NO_3)_39H_2O$ were added to the precipitates and stirred at room temperature for a period time, then NH_3H_2O was added to the solution slowly until pH = 11. The mixture was transferred to a Teflon-lined autoclave and maintained at 180 °C for 12 h, the reduction of GO and the crystallization of cubic $NiFe_2O_4$ particles happen in a one step process by the hydrothermal method. In our work, NH_3H_2O is selected to accomplish two functions. In the first place, NH_3H_2O plays an important role in the formation of cubic $NiFe_2O_4$ particles. In the second place, NH_3H_2O is a reducing agent, promoting the reduction reaction of GO. The composites were washed with deionized water several times and dried at 60 °C for 12 h.

2.2. Measurements

The X-ray powder diffraction (XRD) analyses of the resulting samples were characterized using an X-ray diffractometer (Philips-PW3040/60). The morphology of the products was investigated using a field emission transmission electron microscope (FETEM) on a Tecnai F30 G^2. The X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer. The Fourier transform infrared (FTIR) spectra were recorded on a NICOLET iS10. The Raman spectroscopy was carried out on a Jobin-Yvon HR800 Raman spectrometer. The thermal gravimetric (TG) analysis was performed on a Q2000 thermogravimetric analyzer. The magnetic property of the product was measured by a vibrating sample magnetometer (VSM). The relative complex permittivity (ε' and ε'') and permeability (μ' and μ'') were carried out by the HP8753D vector network analyzer at the frequency range of 2–18 GHz.

3. Results and discussions

To investigate the formation of $NiFe_2O_4$ particles on GN-PANI, XRD patterns of GN-PANI and c-$NiFe_2O_4$/GN-PANI in Fig. 1. For GN-PANI in Fig. 1a, the diffraction peaks appear at $2\theta = 14.9°$, 20.1° and 25.2° are corresponding to the (011), (020) and (200) planes of PANI, respectively, indicating that GN is fully interacted with PANI molecules. As previously reported [21], XRD patterns of PANI powder exhibit a broad amorphous peak at $2\theta = 19°$ and two weak crystalline peaks at $2\theta = 15°$and 24°. In our experiment, the crystalline peak is more prominent than the amorphous peak,

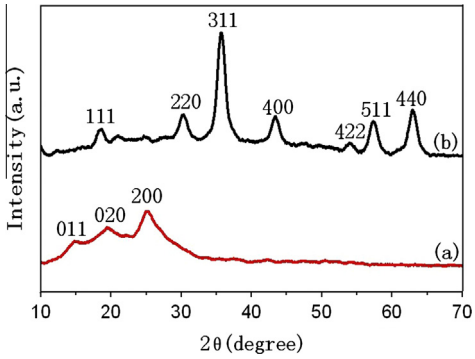

Fig. 1. XRD patterns of GN-PANI (a) and c-$NiFe_2O_4$/GN-PANI (b).

suggesting that PANI powder has a crystalline character. Fig. 1b shows the XRD patterns of c-$NiFe_2O_4$/GN-PANI. In Fig. 1b, it can be observed that seven diffraction peaks at $2\theta = 18.5°$, 30.2°, 35.7°, 43.4°, 54.0°, 57.3°and 62.9° are assigned to reflections of (111), (220), (311), (400), (422), (511) and (440) planes of $NiFe_2O_4$ (JCPDS card no. 10-0325) respectively, confirming $NiFe_2O_4$ particles are formed in the composites.

To investigate the morphology and structure of the products, TEM images are taken for GN-PANI and c-$NiFe_2O_4$/GN-PANI and the corresponding results are presented in Fig. 2. Fig. 2a shows that GN-PANI exhibits some wrinkled forms, which is attributed to PANI. It is well known that GN sheets with chemical groups are easily coated with PANI by an in situ polymerization. As shown in Fig. 2b, large-scale $NiFe_2O_4$ particles with a relatively uniform size are obtained, as indicated by the red arrows. It is evident that GN-PANI, as indicated by the green arrows, is well decorated by a large quantity of $NiFe_2O_4$ particles. The outline of both GN-PANI and $NiFe_2O_4$ particles is clearly observable. Fig. 2c further demonstrated that most of $NiFe_2O_4$ particles covered on GN-PANI. Besides, these $NiFe_2O_4$ particles are firmly attached on the surface of GN-PANI, even sonication is used during the preparation of TEM specimens, indicating that the excellent adhesion between GN-PANI and $NiFe_2O_4$ particles is formed. HRTEM image of a typical $NiFe_2O_4$ particle (inset in Fig. 2c) clearly demonstrates that the morphology of $NiFe_2O_4$ particle is cubic. Fig. 2d also shows that most of $NiFe_2O_4$ particles have a cubic geometrical morphology, as indicated by the arrows. To further determine the distribution of the elements of $NiFe_2O_4$ particles, the composites are examined with the annular dark-field scanning transmission electron (ADF-STEM). Fig. 2e gives the ADF-STEM image of the composites taken at this region. The image analysis indicates that the particles covered on GN-PANI are $NiFe_2O_4$. The SAED patterns in Fig. 2f shows the correspondence of (220), (311), (400), (422), (511) and (440) to the cubic spinel structure [22], indicating that $NiFe_2O_4$ particles have high crystallinity. In order to verify the crystalline structure of $NiFe_2O_4$ particles, we present the HRTEM image of c-$NiFe_2O_4$/GN-PANI in Fig. 2g, which shows that the majority of $NiFe_2O_4$ particles are cubic and that the minority of $NiFe_2O_4$ particles are spherical, as indicated by the blue arrows. Furthermore, all the $NiFe_2O_4$ particles show a well-defined lattice plane with perfect crystallinity, the crystal lattice fringe with a spacing of 0.25 nm can be assigned to the (311) plane of $NiFe_2O_4$, which is consistent with the XRD results. The analysis of EDS shown in Fig. 2h confirms the existence of C, N, O, Ni and Fe elements in the composites (Cu peak forms Cu grid). The atomic ratio of Ni and Fe (inset in Fig. 2h) is approximate 1:2, which is consistent with the stoichiometry of $NiFe_2O_4$. The above analysis helps us draw the conclusion that the particles grown on the surface of GN-PANI are cubic $NiFe_2O_4$ particles.