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Controlled synthesis of porous Fe_3O_4-decorated graphene with extraordinary electromagnetic wave absorption properties

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Abstract

Porous Fe_3O_4-decorated graphene (GN–Fe_3O_4) composites with different microstructures were successfully synthesized by a modified two-step method. The microstructure and morphology were confirmed by X-ray diffraction (XRD), transmission electron microscopy and scanning electron microscopy. XRD studies show that the products consist of highly crystallized Fe_3O_4 but disorderedly stacked GN sheets. Electron microscopy images reveal that Fe_3O_4 nanoparticles with different sizes and microstructures are uniformly coated on both sides of GN sheets, without large vacancies or apparent aggregation. Electromagnetic wave absorption properties of epoxy containing 30 wt.% GN–Fe_3O_4 composites were investigated at room temperature in the frequency range of 0.5–18 GHz. In particular, the porous, flower-like Fe_3O_4-decorated GN sample exhibits an enhanced dielectric loss due to the porous microstructure of Fe_3O_4. The multiple absorbing mechanisms attribute to the improved impedance matching which indicates the as-prepared porous GN–Fe_3O_4 composites could be a potential candidate for lightweight electromagnetic wave absorption materials.

Keywords: Fe_3O_4; Composites; Microstructure; Electromagnetic wave absorption

1. Introduction

The high density of electromagnetic (EM) radiation due to the rapid development of wireless communication has resulted in a new kind of pollution in our surroundings. This unnoticed health hazard has been confirmed as having a great effect on the health and safety of humans, especially for children and patients. Various research reports have shown that, even after short-term radiation, people could have sleep disturbance, headache, nausea, visual disorders, respiratory problems, and nervous excitation. Symptoms after long-term exposure without any protection may include brain tumors, cancer and DNA damage [1]. This increasing radiation problem has therefore attracted much attention in different countries, and great efforts have been made to remove these harmful effects of EM waves. Efficient detection systems for measuring the power density of radiation have been proposed so that hazardous regions can be avoided. However, the use of EM wave absorption material is a more active and thorough method to eliminate EM wave pollution [2–5].

Excellent EM wave absorption materials are required to be lightweight, with strong absorption and high thermal stability, with a broad absorption frequency bandwidth. Fe_3O_4 is a very popular EM absorber because of its strong absorption property and low cost [6]. Importantly, its magnetic properties can be tuned through its size and shape [7]. However, the high density of Fe_3O_4 has limited its use in industrial applications. Recently, there has been growing and widespread interest in the synthesis of porous Fe_3O_4 nanoparticles for different applications [8–13], including the attenuation of EM waves [14,15]. The porous structure of Fe_3O_4 nanoparticles with lighter weight increases the

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number of surface atoms with unsaturated bonds, which in turn increases the number of dipoles. Accordingly, the effect of the dipole polarizations is improved, which is helpful in the enhancement of dielectric loss [14]. Various Fe_3O_4-based composites have also been fabricated, such as Fe_3O_4-decorated graphene (GN) [15–18] or core–shell structures [7,19,20], which take an advantage of the superior properties of the two components. The high specific surface area, prominent thermal stability, low weight and remarkable structure flexibility of GN [21,22] suggest that GN would be an ideal matrix for assembling Fe_3O_4 nanoparticles.

Although a variety of Fe_3O_4 nanoparticle-assembling materials with different EM wave absorption properties have been successfully synthesized, to the best of our knowledge there are few reports on the controlled synthesis of porous Fe_3O_4-decorated graphene (GN–Fe_3O_4) composites. In the present work we provide a controllable two-step method for synthesizing the porous GN–Fe_3O_4 composites, schematically illustrated in Fig. 1. As shown in the figure, porous Fe_3O_4 nanoparticles were prepared by a simple hydrothermal route using a complex polyol system as the solvent, and modified GN dispersion was obtained by the exfoliation and reduction of graphite oxide (GO) in the presence of sodium dodecylbenzenesulfonate (SDBS). Electropositive Fe_3O_4 nanoparticles were then attached to the negatively charged coated GN sheets through electrostatic interaction. Unlike the reported in situ synthesis [23–25], the preparation of Fe_3O_4 nanoparticles does not occur simultaneously with the deposition process, thus making the coverage more controllable. Moreover, we obtain for the first time highly porous and monodispersed Fe_3O_4 nanoparticles using a complex polyol system without any hard or soft template, which is both simple and environmentally friendly [9]. Finally, the EM wave absorption properties of the prepared GN–Fe_3O_4 composites are investigated and found to have extraordinary EM attenuation characteristics.

2. Experimental

2.1. Materials and characterization

All chemicals in this experiment were analytical grade and used without further purification. The GO used in this work was prepared from natural graphite powder (Nanjing JCNO Tech Co., Ltd.) according to the method of William et al. [26].

The structural characterization of GN–Fe_3O_4 was carried out by powder X-ray diffraction (XRD) performed on a Bruker D8 Advance system by using Cu K_α radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB 250 photoelectron spectrometer. Transmission electron microscopic (TEM) images were obtained using a Tecnai 12 transmission electron microscope. Field-emission scanning electron microscopy (SEM) images were carried out with a Hitachi S-4800 microscope. The composites samples used for EM absorption measurement were prepared by mixing the epoxy with 30 wt.% GN–Fe_3O_4. The mixtures were then pressed into toroidal samples. The complex permittivity and permeability of the composites were measured using an Agilent E8363A vector network analyzer in the frequency range of 0.5–18 GHz.

2.2. Preparation of GN dispersion and Fe_3O_4

For the exfoliation of GO, sonication by a bath sonicator was carried out for 0.5 h to yield a GO aqueous dispersion (1.25 mg ml^{-1}). The homogeneous GO dispersion (140 ml) was mixed with hydrazine solution (0.5 ml, 80 wt.%) and SDBS (140 mg). The mixture was stirred at 80 °C for 24 h to obtain the modified GN dispersion, which was directly used for the following assembly process.

The Fe_3O_4 nanoparticles were synthesised through a simple hydrothermal route [27] in the presence of polyethylene glycol (PEG, $M_w = 4000$). In a typical synthesis, 1.35 g (5 mmol) of $FeCl_3{\cdot}6H_2O$, 3.60 g of NaAc and a

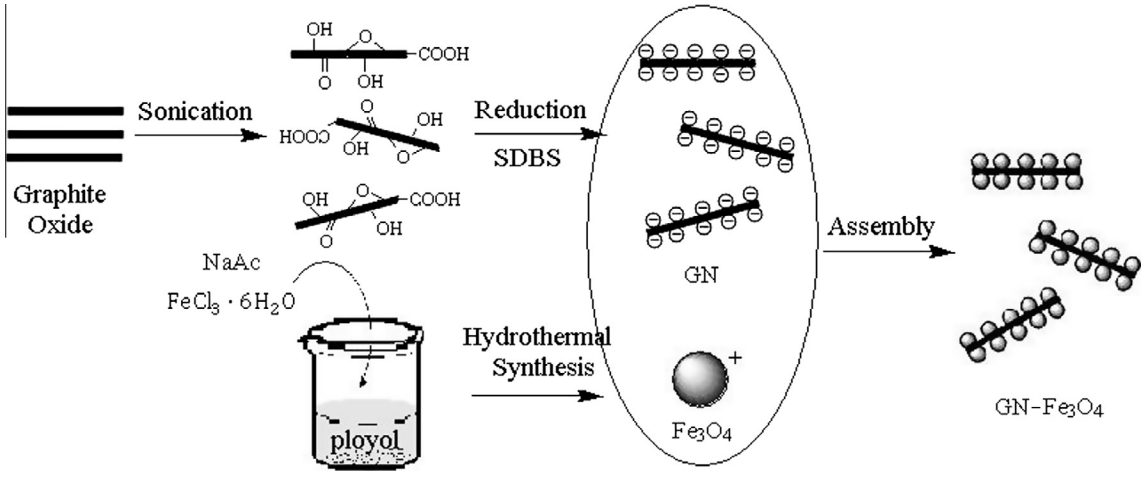

Fig. 1. Illustration of the two-step synthesis of GN–Fe_3O_4.