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Fabrication of reduced graphene oxide/multi-walled carbon nanotubes/zinc ferrite hybrid composites as high-performance microwave absorbers

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ABSTRACT

Reduced graphene oxide/multi-walled carbon nanotubes/zinc ferrite (RGO/MWCNTs/$ZnFe_2O_4$) hybrid composite was fabricated by a facile solvothermal route. The structure, morphology and magnetic properties of the as-prepared composite have been investigated. It was found that the MWCNTs twisted around $ZnFe_2O_4$ microspheres and interlinked with RGO, which resulting in the highly connected three-dimensional conductive networks were observed in the ternary composite. Moreover, the ternary composite exhibited excellent microwave absorption performance with the minimum reflection loss of −22.2 dB and maximum absorption bandwidth (less than −10 dB) of 2.3 GHz for a thickness of only 1.0 mm. Besides, the microwave absorption mechanism of the composite was also explored. These results indicated that the RGO/MWCNTs/$ZnFe_2O_4$ composite was an ideal candidate to be used as microwave absorbers with lightweight, high-efficient performance and thin thickness.

1. Introduction

With the rapid development of electronic devices and wireless communication, the problem of electromagnetic pollution has become increasingly serious, which not only affects the operation of variously commercial or industrial equipment but also has harmful effects on the human health [1–5]. Therefore, the design and development of novel microwave absorption materials have become a research focus in materials science field [6–11].

Carbon-based materials have become the current focus for microwave absorption application due to their outstanding properties, such as low density, thin matching thickness and high complex permittivity [12–14]. Among them, reduced graphene oxide (RGO), a two-dimensional (2D) single-atomic layer graphite, which has been reported as a promising candidate as microwave absorbers owing to its low density, high specific surface areas, residual defects and high dielectric loss [2,3,7,11,14–20]. However, the microwave absorption performance of sole RGO is very weak due to its bad impedance matching characteristic as well as single dielectric loss mechanism [14,16,18,20–22]. Therefore, it still remains a challenge to design and fabricate high-performance microwave absorber based on RGO.

As we all known, a good microwave absorbent needs to meet two requirements: well impedance matching and strong electromagnetic attenuation. Therefore, a feasible route to enhance the microwave absorption ability of RGO could be to fabricate the hybrid composites by incorporating semiconductor compounds [23–25] or magnetic loss materials (ferrite, magnetic metals and alloys, etc) [3,15,26–30] into RGO. For example, Chen et al. fabricated the RGO–hematite nanocomposites by in situ one-pot synthesis using a surfactant-governed approach in the presence of polyvinylpyrrolidone (PVP). The hybrid composites exhibited excellent microwave absorption properties with the minimum reflection loss (RL_{min}) of −90.2 dB at 6.1 GHz at a thickness of 4.5 mm and effective absorption bandwidth ($RL < -10$ dB) of 9.3 GHz (from 8.7 to 18.0 GHz) at a thickness of 2.5 mm. Especially, the microwave absorption properties of RGO/spinel ferrites (MFe_2O_4, M = Fe, Co, Ni, Zn, Mn, etc) composites have been intensively studied in the past few decades [3,16,22,26,27,31–37]. Among them, $ZnFe_2O_4$ is a kind of important spinel ferrites, which has remarkable properties, such as a moderate saturation magnetization, excellent chemical stability and soft magnetic

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characteristic [9,36,38]. Moreover, it can produce magnetic loss for a microwave absorber. Generally, the excellent microwave absorption performance is primarily due to efficient complementarity of complex permittivity and permeability, so single magnetic loss or dielectric loss in absorbers could only produce a weak impedance matching. Therefore, numerous studies on $ZnFe_2O_4$ and $ZnFe_2O_4$-related composites as microwave absorbers have been reported in the literature [7,36,38–42]. For example, Yan et al. fabricated two kinds of $ZnFe_2O_4$ nanomaterials (hollow nanospheres and nanosheets) via a facile solvothermal method and found that the $ZnFe_2O_4$ hollow nanospheres exhibited much better microwave absorption performance than that of $ZnFe_2O_4$ nanosheets [40]. Li et al. fabricated the $ZnFe_2O_4$/polypyrrole core-shell nanoparticles by using solvothermal method in combination with in-situ chemical oxidative polymerization. The core-shell nanoparticles exhibited enhanced microwave absorption than pure $ZnFe_2O_4$ nanoparticles and the RL_{min} reached −28.9 dB [39]. Yang et al. synthesized the $ZnFe_2O_4$/RGO nanohybrids by a facile one-step hydrothermal strategy and demonstrated the microwave absorption properties of the $ZnFe_2O_4$/RGO nanohybrids were much better than those of the RGO. The RL_{min} of the nanohybrids reached −29.3 dB at 16.7 GHz and effective absorption bandwidth was 2.6 GHz (15.4–18.0 GHz) with a thickness of only 1.6 mm [36]. Zhang et al. successfully synthesized the core-shell $ZnFe_2O_4$@SiO_2 hollow microspheres/RGO composite by a three-step method. The RL_{min} was −45.8 dB at 7.6 GHz with a thickness of 3.7 mm and the bandwidth reached 4.0 GHz (from 7.7 to 11.7 GHz) with a thickness of 3.0 mm [42]. Feng et al. fabricated yolk–shell $ZnFe_2O_4$@RGO@-TiO_2 microspheres by combining a layer-by-layer coating process with chemical etching route and found the RL_{min} reached −44.3 dB at 15.92 GHz and the effective absorption bandwidth was 4.1 GHz with a thickness of 2.6 mm [38]. However, to the best of our knowledge, there have been rare reports on the hybrid composites of RGO with multi-walled carbon nanotubes (MWCNTs) and $ZnFe_2O_4$ microspheres as microwave absorption materials.

Herein, we reported a facile one-pot solvothermal route to fabricate hybrid composite of RGO/MWCNTs/$ZnFe_2O_4$ as lightweight and high-performance microwave absorbers. Results demonstrated that the ternary composite presented obviously enhanced microwave absorption properties in terms of both the minimum reflection loss and absorption bandwidth compared with pure $ZnFe_2O_4$ microspheres. This work aimed to explore a facile method to fabricate RGO-based magnetic hybrid composite as high-performance microwave absorbers and clarify the possible microwave absorption mechanism.

2. Experimental section

2.1. Materials

Natural graphite flakes (purity degree > 99%, Qingdao Huatai Lubricant Sealing S&T Co. Ltd., Qingdao, China) were used after dried at 60 °C in vacuum for 12 h. Commercially carboxylic MWCNTs of 10–20 nm in outer diameter and 10–30 μm in length were provided by Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China). Ethylene glycol (EG), polyethylene glycol (PEG, M_w = 6000 g mol^{-1}), sodium acetate (NaAc), ferric chloride ($FeCl_3 \cdot 6H_2O$), Zinc chloride ($ZnCl_2$), $KMnO_4$, glucose, anhydrous ethanol, H_2O_2 (30 wt%), $NH_3 \cdot H_2O$ (25–28 wt%), concentrated H_2SO_4 (98 wt%), H_3PO_4 (85 wt%), HNO_3 (65–68 wt%) and HCl (36–38 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemical reagents were analytical grade and used without further purification. Water was purified by deionization and filtration with a Millipore purification apparatus (18.2 MΩ cm).

2.2. Preparation of samples

Graphite oxide (GP) was prepared by the improved Hummers' method as described in our previous work [43]. Pristine MWCNTs (1 g) were purified by refluxing in concentrated HNO_3 solution at 120 °C for 6 h. The acid-treated MWCNTs (denoted as MWCNTs) were washed several times with deionized water until pH became neutral and then freeze-dried for 24 h.

RGO was obtained by the exfoliation and reduction of graphene oxide (GO). In a typical process, the aqueous dispersion of GO (5 mg/mL) was first achieved by dispersing 0.5 g of GP into 100 mL of deionized water using an ultrasonicator (180 W) for 1.5 h. Then, 0.2 g glucose was fully dissolved in the GO dispersion under vigorous stirring for 30 min at room temperature. Next, 1 mL $NH_3 \cdot H_2O$ was added drop-wise into the above dispersion and then reacted at 95 °C for 1 h under vigorous stirring. Lastly, after the reaction mixture was cooled to room temperature, the products were collected by centrifuging and washed with deionized water and anhydrous ethanol for several times and dried in a vacuum oven at 60 °C for 24 h.

A facile one-pot solvothermal method was used to fabricate the RGO/MWCNTs/$ZnFe_2O_4$ hybrid composite. In a typical procedure, RGO (17 mg) was dispersed into EG (40 mL) by ultrasound treatment for about 1.5 h to produce a homogeneous dispersion. Then, the acid-treated MWCNTs (17 mg) were fully dispersed into the RGO/EG dispersion by ultrasound treatment for 40 min. Next, a mixture of $ZnCl_2$ (0.34 g, 2.5 mmol) and $FeCl_3 \cdot 6H_2O$ (1.35 g, 5.0 mmol) were dissolved in the above-mentioned RGO/MWCNTs/EG dispersion to form a clear mixture dispersion, followed by the addition of NaAc (3.6 g) and PEG (1.0 g) under vigorous stirring. The reaction mixtures were vigorously stirring for 1.0 h at 50 °C and then sealed in a Teflon-lined stainless-steel autoclave. After that, the autoclave was heated to and maintained at 200 °C for 8 h. After the reaction was finished, the autoclave was cooled to room temperature. Lastly, the black products were collected by magnetic separation, and then washed with deionized water and anhydrous ethanol for several times and dried in a vacuum oven at 60 °C for 24 h. For comparison purposes, pure $ZnFe_2O_4$ microspheres were also synthesized by the same procedures without adding RGO and MWCNTs.

2.3. Characterization

The crystalline structure of the samples was characterized by X-ray diffraction (XRD) using a LabX XRD-6000 (Shimadzu, Japan) with Cu-Kα radiation ($\lambda = 0.154$ nm) in the scattering range (2θ) of 10–80° with a scanning rate of 2°/min. The morphology analysis was performed by a field emission scanning electron microscopy (FESEM) (Hitachi-Su8020, Japan) and field emission transmission electron microscopy (FETEM, FEI-TF20, USA). Raman spectra were acquired at room temperature by using a laser confocal Raman spectrometer (Renishaw-2000, UK) in the range of 100–3000 cm^{-1}. The magnetic properties measurements were carried out at room temperature on a vibrating sample magnetometer (VSM, Nanjing NanDa Instrument Plant HH-20, China). Electromagnetic parameters (relative complex permittivity and permeability) were measured on a vector network analyzer (VNA, the 41st institute of CETC, AV3629D, China) in the frequency range of 2.0–18.0 GHz by using the transmission/reflection coaxial line method. The measured specimens were prepared by uniformly mixing the as-prepared powders with different weight percentages (25 wt%, 50 wt% and 75 wt%, respectively) into paraffin matrix with a thickness of 2.0 mm, and then pressed the mixture into a toroidal shape with outer diameter of 7.0 mm and inner diameter of 3.04 mm. It should be mentioned that the actual power level in