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Fe_3O_4@LAS/RGO composites with a multiple transmission-absorption mechanism and enhanced electromagnetic wave absorption performance

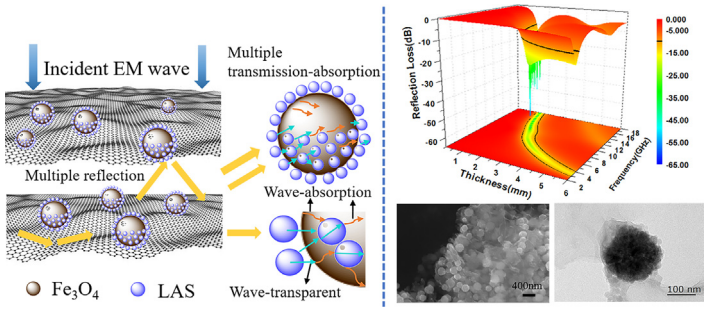
Yanan Yang[a], Long Xia[a,*], Tao Zhang[a], Bin Shi[a], Longnan Huang[a], Bo Zhong[a], Xinyu Zhang[a], Huatao Wang[a], Jian Zhang[a], Guangwu Wen[b]

[a] School of Materials Science and Engineering, Harbin Institute of Technology (Weihai), Weihai 264209, PR China
[b] School of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, PR China

HIGHLIGHTS

- Fe_3O_4@LAS/RGO composites with uniform size were successfully synthesized.
- Fe_3O_4@LAS/RGO composites have excellent microwave absorption performance and broad bandwidth.
- The addition of lithium aluminum silicate glass-ceramic contributes to the synergy of dielectric loss and magnetic loss.
- A multiple transmission-absorption mechanism was introduced for the material to effectively improve impedance matching.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, Fe_3O_4@LAS/RGO composites with uniform size and extraordinary electromagnetic wave absorption properties were successfully synthesized by a simple three-step method. The Fe_3O_4 nanospheres with a diameter of about 200 nm are tightly attached by the lithium aluminum silicate (LAS) glass-ceramic particles with a diameter of about 20 nm and evenly distributed among the graphene sheets. The method of coating a microwave absorber with a wave-transparent material introduces a multiple transmission-absorption mechanism for the material to effectively improve impedance matching. The input impedance Z_{in} value (~1.0) of Fe_3O_4@LAS/RGO is better and more stable than the Z_{in} value (~1.2) of Fe_3O_4/RGO. The RL values of Fe_3O_4@LAS/RGO could reach −65 dB at 12.4 GHz with a thickness of only 2.1 mm and the absorption bandwidth with RL values less than −10 dB (over 90% electromagnetic wave absorption) is up to 4 GHz at the corresponding thickness. The intrinsic properties of the component of Fe_3O_4@LAS/RGO composites and the composite structure of the material lead to a variety of microwave absorption mechanisms acting together to improve the microwave absorption properties of the composites.

1. Introduction

In recent years, with the rapid development of modern science and technology, a large number of electronic communication devices have been extensively used. While science and technology facilitate human life, many electromagnetic (EM) radiations are generated during the operation of electronic devices and endanger production and life, resulting in EM pollution [1–4]. It would not only affect the normal

* Corresponding author.
E-mail address: xialonghit@gmail.com (L. Xia).

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operation of various electronic devices, but also cause long-term damage to human health. Therefore, researchers have been active in exploring high-performance, lightweight, broadband microwave absorbers to attenuate EM wave. Fe_3O_4 is a traditional absorbing material and absorbs EM wave mainly through natural resonance [5–8]. It has been extensively studied because of its excellent microwave absorbing properties and low cost. However, the impedance matching of pure Fe_3O_4 is poor. At the same time, the Fe_3O_4 has such disadvantages as high density, poor high-temperature characteristics, and narrow absorption band, which makes it difficult to meet the high demands of thin thickness, bandwidth, lightweight and high absorption for the current absorbing material [9–13]. Therefore, recent researchers have improved EM wave absorption properties by compounding Fe_3O_4 with other absorbing material. Some Fe_3O_4-based composites, such as Fe_3O_4/conductive polymers [14–16], and Fe_3O_4/dielectric materials [17–19], Fe_3O_4/carbon [20–23], have been studied and analysed.

Graphene has a certain dielectric loss performance [24,25]. When graphene and traditional microwave absorbing materials are compounded, it not only overcomes the disadvantages of high density of traditional microwave absorbing materials, but also broadens the microwave absorbing band to achieve lightweight, high strength, broadband absorption [19,26,27]. Sun et al. [28]. employed the successful preparation of mesoporous Fe_3O_4@ZnO sphere decorated graphene (GN-pFe_3O_4@ZnO) composites, and they found that the minimal RL of epoxy containing 30 wt% GN-pFe_3O_4@ZnO is almost −40 dB. Ren et al. [29]. prepared quaternary nanocomposites consisting of graphene, Fe_3O_4@Fe Core@Shell and ZnO nanoparticles, and the absorption bandwidth with RL less than −20 dB is up to 7.3 GHz. Wang and coworkers [30] investigated the electromagnetic absorption properties of graphene-Fe_3O_4 nanohybrids; the results showed that the maximum reflection loss of the nanohybrids was up to −40.36 dB with a thickness of 5.0 mm at 7.04 GHz and the absorption bandwidth with reflection loss less than −10 dB was about 2 GHz. It can be concluded that graphene-Fe_3O_4 composite is an admirable electromagnetic wave absorber. However, graphene-Fe_3O_4 composites usually have only a certain large thickness (about 4–5 mm) to achieve the best reflection loss [30–32]. As we all know, the ideal absorbing material should have a loss mechanism in which the dielectric loss and the magnetic loss act together, and it is also necessary to satisfy the impedance matching as much as possible [33]. In recent studies, the addition of oxide ceramic material has introduced multiple interfacial polarizations to improve impedance matching and to overcome the shortcomings of the narrow absorption band and high density of iron oxide absorbers [34,35]. Chen et al. [36]. reported that the porous Fe_3O_4/Fe/SiO_2 core/shell nanorods were fabricated and the bandwidth with the reflection loss below −10 dB is up to 6.96 GHz, with 2 mm in thickness of the absorbers. Che et al. [37]. prepared CoNi@SiO_2@TiO_2 core-shell-shell microspheres and the RL value of CoNi@SiO_2@TiO_2 absorber reaches as high as −58.2 dB with a thickness of only 2.1 mm. It can be seen that the extraordinary wave-transparent properties of ceramic silicate materials can significantly improve the lightness and thinness of the wave absorbing composites.

LAS glass-ceramic is an important role of glass-ceramics systems and famous for its high temperature stability, thermal shock resistance and ultra-low or even negative thermal expansion coefficient [38]. At the same time, LAS exhibits high transmittance to EM wave. The LAS is coated on the iron oxide to ensure that the EM wave enters the iron oxide more and is further lost. Herein, we design a transmission-absorption mechanism by combining the wave-transparent material with the microwave absorbing material and demonstrate the successful preparation of Fe_3O_4@LAS/RGO through a three-step process. With an absorber thickness of only 2.1 mm, the minimum reflection loss is −65 dB at 12.4 GHz and the absorption bandwidth with RL values less than −10 dB is in the range of 10.7–14.7 GHz. It can be noted that the addition of LAS contributes to the synergy of dielectric loss and magnetic loss and better satisfies impedance matching. We believe that the fabrication of the material will bring fresh ideas to the design of new high-performance microwave absorbers.

2. Experimental section

2.1. Synthesis of Fe_3O_4 nanospheres

Fe_3O_4 nanospheres were prepared by solvothermal method according to the reported method [39]. Typically, 0.27 g $FeCl_3{\cdot}6H_2O$ and 1 g CH_3COONa were added to 75 mL of ethylene glycol and stirred for 60 min to dissolve and mix the reactants. The solution was then transferred to a Teflon-lined stainless-steel autoclave and heated at 200 °C for 10 h. The product was washed three times with ethanol and deionized water, and the Fe_3O_4 black precipitate was separated by using a magnet.

2.2. Synthesis of Fe_3O_4@LAS nanospheres

The preparation of LAS sol was based on our previous report [40]. The as-prepared Fe_3O_4 black precipitate was added to the LAS sol with molar ratios of Fe_3O_4/LAS of 1:0.1, 1:0.2, 1:0.3, 1:0.4, 1:0.5 and 1:1, respectively. The mixture was stirred for 60 min to thoroughly mix and vacuum dried at 40 °C and further sintered in a tube furnace under a nitrogen atmosphere at 500 °C for 1 h. The binary composites prepared by the above method are described as FL-1, FL-2, FL-3, FL-4, FL-5 and FL-10, respectively.

2.3. Synthesis of Fe_3O_4@LAS/RGO composite material

After cooling down to room temperature, the sintered samples with different ratios were ground and added to ethanol dispersions containing 40 mg of oxidized graphite and 1 g of polyethylene glycol, and continuously stirred for 12 h, and then transferred to autoclaves for reaction at 200 °C for 10 h. The Fe_3O_4@LAS/RGO composites were vacuum dried at 40 °C. The as-obtained composites are described as FLR-1, FLR-2, FLR-3, FLR-4, FLR-5 and FLR-10, respectively. The preparation process is shown in Fig. 1.

2.4. Synthesis of Fe_3O_4/RGO composite material

To compare the performance differences of Fe_3O_4@LAS/RGO and Fe_3O_4/RGO, Fe_3O_4/RGO was prepared by solvothermal method. In a typical recipe, 40 mg of graphite oxide (GO) and 1 g of polyethylene glycol were added to 75 mL of ethylene glycol and stirred for 30 min to dissolve and mix the reactants. 0.27 g $FeCl_3{\cdot}6H_2O$ and 1 g CH_3COONa were then added to the solution and stirring was continued for 30 min. The mixture was then transferred to autoclave and reacted at 200 °C for 10 h. After cooling down to room temperature, the resultant was washed three times with ethanol and deionized water and dried in vacuum at 40 °C.

2.5. Characterization

The structures of as-obtained Fe_3O_4 and Fe_3O_4@LAS/RGO were investigated by X-ray diffraction (XRD) on a Rigaku D/Max 2000 VPC with monochromatic Cu Kα radiation. Raman spectra (Renishaw, RM-1000) were used to characterize the structure of Fe_3O_4@LAS/RGO using a 532 nm laser. The morphologies of Fe_3O_4, Fe_3O_4@LAS and Fe_3O_4@LAS/RGO were observed by a MX2600FE field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS) and high resolution transmission electron microscopy (HRTEM, Tecnai F30 FEG). The magnetic properties were measured by a vibration sample magnetometer (VSM, LakeShore 7307). The complex permittivity and complex permeability values in the frequency range of 2–18 GHz were measured by using a vector network analyzer (Agilent N5245A). A sample containing 50 wt% of composites was pressed into a ring with an outer diameter of 7 mm, an inner