FABRICATION OF FERRIC OXIDE /CARBON BLACK/CARBON NANOTUBE COMPOSITES FOR PROMTED ELECTROMAGNETIC MICROWAVE PERFORMANCE

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ABSTRACT

Rapid development of electronic technologies brings launch of new kind of electromagnetic interference (EMI) materials to date. Both ferric oxide and carbon-based materials are regarded as ideal microwave absorption materials to be tolerant of matching property. This work, Fe_2O_3/CB, Fe_2O_3/CNT/CB, Fe_2O_3/CNT composites are modified for microwave absorbers with two step routes containing sol-gel and calcination processes. Mixtures of CNT and CB are achieved to improve microwave absorption behaviour, enabling the elongation of bandwidth and stronger RL value of in Fe_2O_3/CNT/CB composite.

1 INTRODUCTION

To date, emerging researches on solution of electromagnetic interference (EMI) have been rapidly developed with boosting popularization of wireless communication technologies such as 3G, 4G and Bluetooth.[1-3] To aim on solving such invisible pollution, numerous efforts has been developed such EMI shielding and absorption technologies to supply efficient protection from EMI affects. For microwave absorber in EMI absorption application, generally, it has been established many system materials like ferromagnetic materials. Iron and its related ferrites, as one important kind of ferromagnetic microwave absorbers, have been raised tremendous research focuses because of cheap resources and strong absorbing ability.[4,5] Ideal microwave absorbers is of characteristics with wider bandwidth and lightweight coating thickness. Recently, many works focus on evolving unique micro-/nanostructures to overcome this issue. Fu et al.[6] has reported hexagonal Fe microflake possessing edge lengths of 5 mm and thicknesses of about 500–1000 nm, presents good electromagnetic wave absorption with the maximum reflection loss is -15.3 dB. A novel nanotube structure of Fe–ferrite composite has been developed from a thermal hydrogen reduction method using a-FeOOH nanowires as precursors and as-obtained Fe–ferrite composite with diameters of 100-200 nm also exhibits good electromagnetic wave absorption with the maximum reflection loss is -18 dB.[7] However, such monophasic ferromagnetic materials fail to meet as-mentioned requirements due to limited absorption frequency and relative mass density, remaining a hotspot to build new ferromagnetic-based composite for EMI absorption research.

Considering a high impedance matching with coordination of electromagnetic constant, one efficient path to improve microwave absorption ability of sole ferrite absorbers is adding carbon-based materials, as like carbon nanotube (CNT) and carbon black (CB), to enlarge the absorption bandwidth.[8,9] It has been evidenced that CNT are charge for producing interfacial polarization to improved attenuation ability to EM waves. Also, being contributed from dielectric polarization and high surface area as features of CB, more multi-scatter and reflection behaviours will occur to improve EM absorption performance. However, augmentations of both dielectric loss mediums need be controlled proper, because too low content and too high content will deteriorate poor impedance matching, combining with ferrite. Hence, it is still a hot issue to rational understand the electromagnetic changes between carbon-based material and ferrite in such composite for enlarging both EM absorption intensity and bandwidth.

This work, being enlightened from previous works, Fe_2O_3/CB, Fe_2O_3/CNT/CB, Fe_2O_3/CNT composites are successfully fabricated for microwave absorbers with using two-step synthesis route containing sol-gel and calcination processes. It shows that rational tuning the composite composition, as obtaining Fe_2O_3/CNT/CB, improves final electromagnetic absorption performance with the broader efficient bandwidth of 3.96 GHz and higher intensity of reflection loss with -22.54 dB.

2 EXPERIMENTAL

2.1 Preparation of Fe_2O_3/CB, Fe_2O_3/CNT and Fe_2O_3/CB/CNT composites

Synthesis route was involved sol-gel process with ferric chloride as iron precursor. A typical synthesis process was followed as below. 0.03 M ferric chloride and 0.08 g CB was dropwised into 0.06 M NaOH with mechanical agitation for 10 min. Then as-obtained solution was heated up to 100 ℃ for acceleration reaction. Then as-obtained products were transferred into muffle furnace to calcine at 200 ℃ for retaining 2 hours and cool down the room temperature subsequently. Preparation of other composites were followed the same processes expect different adding carbon-based materials. In further EM absorption investigation, Fe_2O_3/CB, Fe_2O_3/CNT and Fe_2O_3/CB/CNT composites were firstly dispersed into wax matrix at same weight ratio with 80% for wax. The mass ratio of Fe_2O_3/CB, Fe_2O_3/CB/CNT and Fe_2O_3/CNT composites, labeling as FCC1, FCC2 and FCC3, were 1:1, 2:1:1 and 1:1.

2.2 Characterization

Structures and morphologies of three composites, including Fe_2O_3/CB, Fe_2O_3/CNT and Fe_2O_3/CB/CNT composites, were presented by using a X'PERT PRO MPD spectrometer as a powder X-ray diffraction (XRD) system in the range of 20-80° and a field-emission scanning electron microscope (FESEM) equipped with the type of FEI Quanta 200F. A vibrating sample magnetometer (VSM Lakeshore Model 7400) was used for magnetic properties of three samples under room temperature. Using a vector network analyzer was applied for electromagnetic performance of three composites absorbers with the measured frequency range of 2-18 GHz.

3 RESULTS AND DISCUSSION

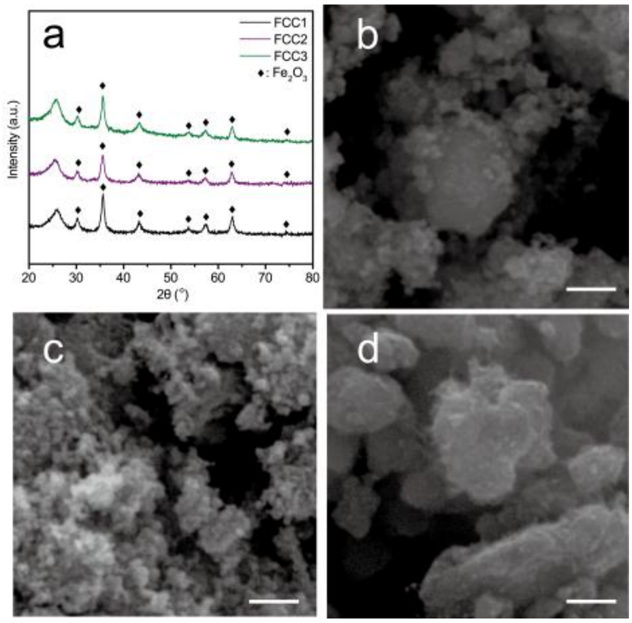

Fig. 1 (a) XRD patterns of three samples (Fe_2O_3/CB, Fe_2O_3/CB/CNT and Fe_2O_3/CNT). (b-d) SEM image of three composites (scale bar: 1 μm).

It depicts XRD patterns of three samples (FCC1, FCC2 and FCC3) in Fig. 1a. Featured peaks are detected as (210), (311), (400), (422), (511), (440) and (533), which are indexed as γ-Fe_2O_3 (NO. 39-1346).[10-12] While the peak around 25 ° belongs to (002) characteristic peak of graphitic carbon, being greatly influenced by combination of CNT and CB microstructures. Fig. 1b shows morphologies of CNT/CB compoiste as the one of three samples with scale bar of 1 μm. γ-Fe_2O_3 microspheres are covered multilayers CB interlink each other, whereas some parts of them are over aggregated. The selected areas are much bushier after CNT adding in FCC2, being found in Fig. 1c. Fig. 1d shows alone CNT adding with remarkable observation of CNT bundles. Since founding of dense FCC2 and over aggregations from FCC1 and FCC3, we infer FCC2 as microwave absorber would present better EM absorption than other two composites with forming efficient conductive loss path.

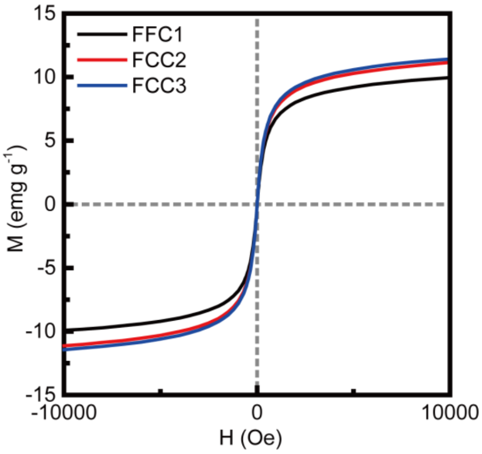

Fig. 2 magnetization curves of three samples at room temperature.

Further magnetization investigation of three composites comes out as displayed in Fig. 2. It can be clearly observed that both three samples show S-shape magnetic hysteresis loops curves, which typically represent ferromagnetic behaviors of three composites. The specific saturation magnetization (M_s) value of FCC3 is 11.42 emu g^{-1}, while ones of FCC2 and FCC1 are 11.15 emu g^{-1} and 9.95 emu g^{-1}, respectively. The phenomenon could be considered that inhomogeneous dispersion and over aggregation of CB, being founding in SEM, covers γ-Fe_2O_3 to reduce these two composites M_s, being founding in SEM. Since larger M_s of FCC3, it might be influence subsequent permeability to effect on electromagnetic absorption. The maximum coactivity (H_c) of 14.20 Oe also be found in FCC3 and that of FCC2 (14.19 Oe) is very close to FCC3, showing advantages of absorption by a high-frequency resonance in these two samples. We infer both FCC2 and FCC3 would behave better microwave absorption performances with fully consideration from M_s and H_c, especially for high frequency bandwidth.

This carbon/ ferrite composite system of microwave absorption concerns electric loss and magnetic loss, being highly relevant to permittivity (ε_γ) and permeability (μ_γ). It is found that changes on the real (a) and imaginary (b) parts of complex permittivity are quite different. (See Fig. 3). $\varepsilon'$of Fe_2O_3/CB composite absorber shrinks fast from 10.35 to 4.13, while those of Fe_2O_3/CB/CNT and Fe_2O_3/CNT absorbers undulate steadily with all data above 8. ε'' shows similar trends which can be observed in Fig. 2b. Since both relatively higher and steady data of ε' and ε'', being derived from Fe_2O_3/CB/CNT and Fe_2O_3/CNT, it might be exhibits better microwave absorption behaviors in Fe_2O_3/CB/CNT and Fe_2O_3/CNT composites absorbers, especially in higher measured frequency. As for permeability, both real and imaginary parts of three samples shows very low values, which means main effects of Fe_2O_3 still working on whole composites with same weight ratio in three samples. However, fluctuation of μ' can clearly found in Fe_2O_3/CB/CNT and Fe_2O_3/CNT absorbers, presenting difference from magnetic storage of CB/CNT and sole CNT. While it is steadily in Fe_2O_3/CB, due to negligible contributions from as-mentioned irregular distribution of CB. Interesting, similar behaviours of μ'' is also found in three samples with obvious fluctuation peak from 12.23 GHz to 15.12 GHz in FCC2. While smaller μ'' changes in FCC3 and that of FCC1 is almost stable. It could be deemed better magnetic loss of FCC3 participates than ones of FCC2 and FCC1 in whole absorption.[13-15] Especially, in frequency range of 12-15 GHz. In conclusion, good balance ε' and ε'' to enhance dielectric loss from Fe_2O_3/CB/CNT than sole CB or CNT adding, being good complementarity from merits of magnetic loss makes Fe_2O_3/CB/CNT is superior to a high impedance matching for absorption.

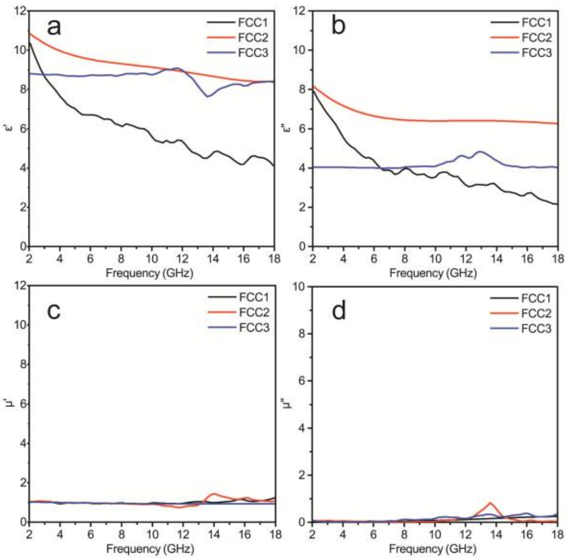

Fig. 3 Frequency dependence of complex permittivity and permeability in three samples. (a,c) Real part of permittivity and permeability. (b,d) Imaginary part of permeability.

Further reflection loss (RL) values of composite specimens can be ascribed to the following equations under a series of thickness layers (1-3 mm)：[1-4]

$$Z_{in} = (\mu_r/\varepsilon_r)^{1/2}\tanh[-j(2\pi f d/c](\mu_r/\varepsilon_r)^{1/2}] \tag{1}$$

$$RL = -20\log|((Z_{in} - Z_0)/(Z_{in} - Z_0)| \tag{2}$$

Fig.4a shows the maximum RL value of Fe_2O_3/CB/CNT is -12.61 dB under 2.5 mm coating thickness, while those of Fe_2O_3/CB and Fe_2O_3/CNT are -11.08 dB and -6.90 dB, being smaller than Fe_2O_3/CB/CNT. Bandwidth below -10 dB of Fe_2O_3/CB/CNT is 5.6 GHz is also larger than those of Fe_2O_3/CB and Fe_2O_3/CNT. RL values under different coating thickness (1-3 mm) can be found in further absorption contour map (Fig 3b-d). Both RL bandwidth and RL value of Fe_2O_3/CB/CNT broaden and strengthen in all range of coating thickness. The maximum RL peak can be found in 17.68 GHz with value of -22.54 dB under 2 mm coating thickness and bandwidth below -10 dB is 3.96 GHz.

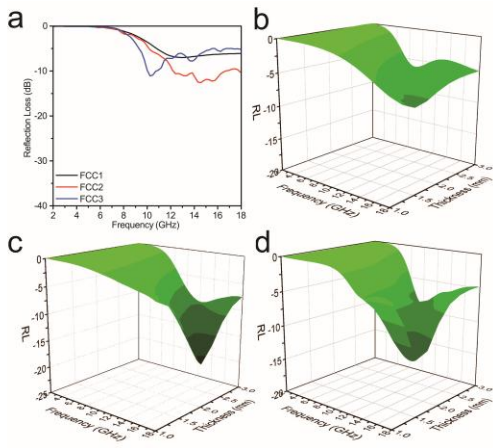

Fig. 3 RL curves at 2.5 mm coating thickness (a) and absorption contour map of three samples under different coating thickness with the range of 1-3 mm (b-d).

3 CONCLUSIONS

In this work, Fe_2O_3/CB, Fe_2O_3/CNT and Fe_2O_3/CB/CNT composites are fabricated with sol-gel method and calcination processes. It is easily to tune magnetization properties such as specific saturation magnetization and coactivity for special absorption demands in three samples by tuning stoichiometric ratio of CB and CNT contents. Optimized Fe_2O_3/CB/CNT composite, as microwave absorber, exhibits prompted absorption behavior with broader bandwidth of 3.96 GHz and stronger RL of -22.54 dB at 2 mm coating thickness, compared with sole CB and CNT-added microwave absorption composites. Such Fe_2O_3/CB/CNT composite paves a better understanding way to rational design of magnetic/electrical loss composite absorbers and can be applied in potential EMI shielding and protection.

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