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ARTICLE

A novel Fe_3C/graphitic carbon composite for electromagnetic wave absorption properties in C-band

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Electromagnetic (EM) wave absorber with the characteristic absorption in the millimeter wave range is very important for the EM industry. Especially, the absorption properties in microwave frequency range C-band (4-8 GHz) are necessary in the field of military aircraft. Herein, Fe_3C/graphitic carbon (Fe_3C/GC) composite has been synthesized through a low-cost and facile ion-exchanged route. The Fe_3C/GC could exhibit excellent EM wave absorption properties in C-band with the frequency range of 4-8 GHz and also exhibits good dielectric loss, which could be attributed to the existence of lightweight GC in the composite. The reflection loss value of Fe_3C/GC composite exceeds –10 dB in the frequency range of 4-8 GHz with a absorber thickness of 2-4 mm, implying its potential application of lightweight EM wave absorber in C-band. Moreover, the Fe_3C/GC shows better electromagnetic wave absorption properties that other iron compound GC-based composites, such as Fe_2N/GC and Fe/GC.

Introduction

Electromagnetic (EM) absorbing materials have attracted interesting attention because of its potential applications in the EM industry, such as military aircraft, radar and wireless communications.[1,2] Considerable investigations have been focused on the effective EM wave absorption materials with the properties of wide frequency range, strong absorption, low density and high resistivity.[3] Metal oxides, such as Fe_3O_4,[1] ZnO,[4] MnO_2,[5] $BaTiO_3$ [6] and TiO_2,[7] have been widely used in EM wave absorbing area. Although they have the advantages of low cost, easily preparation and non-toxicity, the nature of low efficient EM wave absorption properties would restrain their further applications.[8] In addition, magnetic particles and the magnetic particles coated with a nonmagnetic insulator have attracted particular interest, such as Fe/Ni,[9] carbonyl iron,[10] FeCuNbSiB,[11] hybrid structure of SiC/Co,[12] Fe/Y_2O_3[13] and Fe/ZnO.[14] However, the high density and matching thick thickness of these materials would limit their applications in practice.

Recently, lightweight carbon-based materials have exhibited significant value in the EM wave absorbing material due to their good conductive, chemical inertness and high temperature resistance.[15,16] Among these, carbon-coated Ni or Fe nanocapsules are promising in the field of EM wave absorption.[17] Moreover, carbon nanotubes (CNTs)-Fe (Co, Ni) composites have also been widely applied in EM wave-absorption area.[18-20] However, most of the research works are focused on the frequency range of Ku-band (12.4–18 GHz) and S-band (2.0–4.0 GHz).[21] It is still a challenge to obtain the materials which could exhibit good reflection loss with small matching thickness in C-band (4.0–8.0GHz). The absorption properties in microwave frequency C-band are essential in many fields, including satellite, aerospace and civil use. Hence, it is necessary to exploit new lightweight materials with excellent EM wave absorption properties in the C - band.

In this work, the Fe_3C/graphitic carbon (Fe_3C/GC) composite has been synthesized by our previous large-scale and facile ion-exchanged route.[22] The Fe_3C/GC composite is investigated in terms of complex permittivity and permeability. Herein, it's the first time of the Fe_3C/GC composite applied in EM wave absorption area, and the corresponding reflection loss value of the composite could exceed -10 dB in 4-8 GHz frequency range with the absorber thickness of 2-4 mm. We also compared the EM wave absorption properties of Fe_3C/GC composite with other composites, including Fe_2N/GC and Fe/GC.

Experimental

Synthesis

The Fe_3C/GC composite was synthesized by our previous ion-exchanged route.[22] In a typical synthesis, 0.12 mol/L $FeCl_2$ solution was exchanged with 9 g polyacrylic weak-acid cation-exchanged resin (AC) under stirring at room temperature for 16 h. After centrifugation, washing and drying, the AC-Fe^{2+} precursor were formed. Finally, the precursor was heated at 800 °C for 1 h under nitrogen atmosphere with a heating rate of 5 °C/min to prepare Fe_3C/GC composite. To investigate the wave-absorption

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performance of different iron-crystal, the Fe/GC composite was synthesized by carbonizing AC-Fe^{2+} precursor at 1100 °C under nitrogen ambitent. Also, the Fe_2N/GC composite was synthesized by pyrolysis the AC-Fe^{2+} precursor at 800 °C under the mixture of nitrogen and ammonia for comparison.

Characterizations

X-ray powder diffraction (XRD) patterns were obtained by a Rigaku D/max-IIIB diffractometer using Cu Ka radiation (λ= 1.5406 Å). The transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon coated copper grids were used as the sample holders. Thermogravimetric analysis was performed on a TG (TA, Q600) thermal analyzer under air with a heating rate of 10 $°C·min^{-1}$. Fourier-transform infrared spectra (FTIR) of the samples were acquired with a PE Spectrum One BIR spectrometer. Magnetization was measured at 300 K in a physical properties measurement system (PPMS, Quantum Design Inc.) up to a field of (20 kOe).

The composite samples used for the measurement of relative permittivity ($\varepsilon_r = \varepsilon' + j\varepsilon''$) and permeability ($\mu_r = \mu' + j\mu''$) were prepared by mixing the products and paraffin wax in a mass ratio of 7:3. The complex permittivity and permeability of the mixtures in a frequency range of 2 to 18 GHz were evaluated using an Agilent N5244A vector network analyzer. The reflection loss (RL) was calculated according to the following equations.

$$\varepsilon_r = \varepsilon' + j\varepsilon'' \quad (1)$$

$$\mu_r = \mu' + j\mu'' \quad (2)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left[j \frac{2\pi f d \sqrt{\mu_r \varepsilon_r}}{c} \right] \quad (3)$$

$$RL = 20\log\left| \frac{Z_{in} - 1}{Z_{in} + 1} \right| \quad (4)$$

Where f is the frequency of the EM wave, d is the thickness of the absorber, c is the velocity of light; Z_{in} is the input impedance of the absorber.

Results and discussion

The synthetic process of the Fe_3C/graphitic carbon (Fe_3C/GC) composite is shown in Fig. 1. Firstly, the AC resin exchanged with Fe^{2+} ions to form AC-Fe^{2+} precursor. After carbonization, the Fe_3C/GC could be obtained. TEM is a useful tool to characterize the morphology of nanostructures. As shown in Fig. 2a, the synthetic Fe_3C/GC composite is composed of Fe_3C nanoparticles with the diameter between 50 and 200 nm dispersed on graphitic carbon surface. The dark spherical particles are attributed to the Fe_3C phase. The magnified image in Fig. 2b further indicates the graphitic carbon in the composite existed in the form of nanosheets and

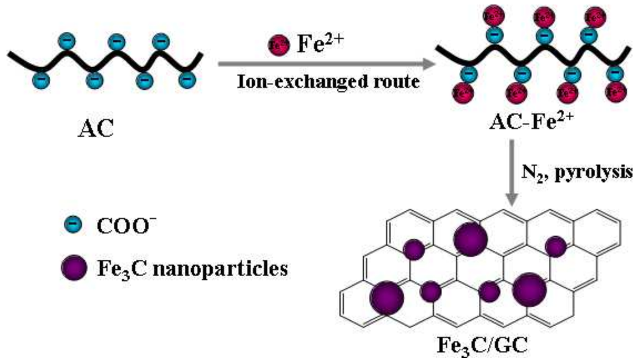

Fig. 1. The synthetic process of Fe_3C/GC composite

nanobelts. It is better to observe the structure on a high resolution and Fourier transform (FT) images (Fig. 2c and 2d). The interlayer spacings of 0.21 and 0.34 nm are ascribed to the planes of Fe_3C(211) and C(002), respectively.

The XRD pattern of the Fe_3C/GC composite shows in Fig. 3a. The obvious diffraction peak at 2θ=26.4° is assigned to the (002) plane of graphitic carbon (JCPDS No. 41−1487). The other diffraction peaks at around 2θ = 37.8°, 39.9°, 40.7°, 42.9°, 43.7°, 44.6°, 45.1°, 46.0°, 48.7° and 49.1° are attributed to the (210), (002), (201), (211), (102), (220), (031), (112), (131), and (221) planes of Fe_3C phase (JCPDS No.89−2867), respectively. As compared, the composite with different iron phase was also synthesized, namely Fe/GC and Fe_2N/GC composites (see experiment section). As shown in Fig. 3b and 3c, it can be seen that the Fe/GC and Fe_2N/GC are composed of α-Fe and graphitic carbon, Fe_2N and graphitic carbon, respectively. Raman was used to further investigate the carbon phase in composite (Fig. S1, ESI). The Raman spectra of all the composites are characterized by three main featured peaks, namely 1366 (D-band), 1580 (G-band) and 2730 cm^{-1} (2D-band). The D-band is ascribed to the vibrations of carbon atoms with dangling bonds in

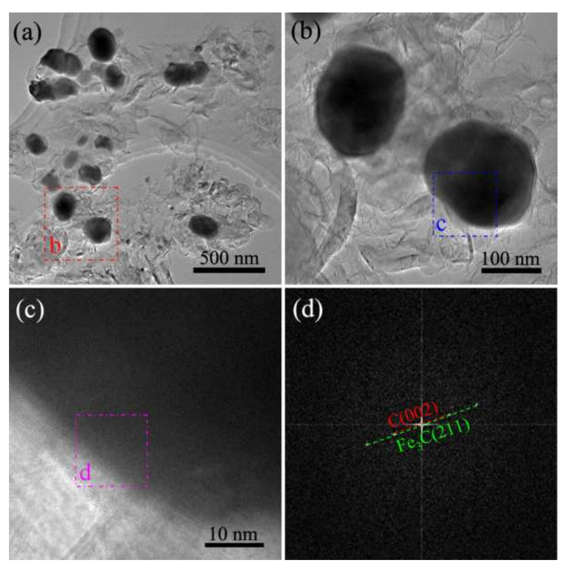

Fig. 2 (a-b) TEM and (c) HRTEM images of Fe_3C/GC composite. (d) The Fourier transform (FT) image of (c).

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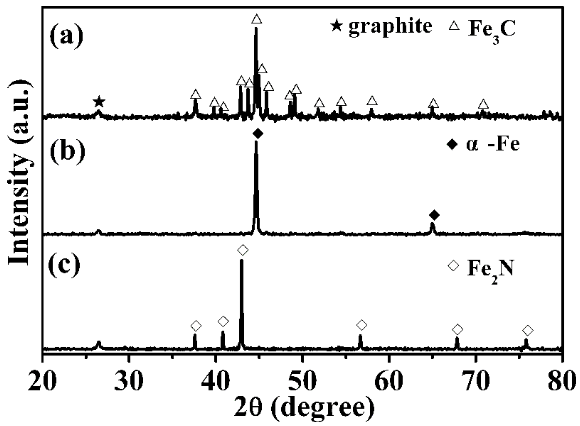

Fig. 3 XRD patterns of (a) Fe_3C/GC, (b) Fe/GC and (c) Fe_2N/GC composites.

disordered graphite planes and the defects incorporated into pentagon and heptagon graphite-like structures, while the G-band is attributed to the stretching modes of carbon sp^2 bonds of the graphite (E_{2g} mode). The G peak is much higher in intensity and narrower in width compared to the D peak, implying the well crystalline of the graphitic carbon in the composites. The second-order 2D-band is typical of graphitic carbon. Moreover, the intensity ratio between G-band and D band (I_G/I_D) is proportional to the graphitization degree of carbon. I_G/I_D values for Fe_3C/GC, Fe/GC and Fe_2N/GC are about 3.52, 3.61 and 4.01, respectively, also indicating the well crystalline of the graphitic carbon in the synthetic composites.

The magnetization curves of the synthetic composites were investigated at 300 K and 20 kOe (Fig. S2, ESI). The saturation magnetization and coercivity of the Fe_3C/GC composite are about 17.72 and 0.5 emu/g, respectively. The Fe_3C/GC composite displays a very low coercivity of 100 Oe at room temperature and 20 kOe. The negligible coercivity and remanence demonstrate a superparamagnetic behavior of the Fe_3C/GC composite. The hysteresis loops for Fe/GC and Fe_2N/GC composites display zero coercivity with no remanence, indicating the superparamagnetic behaviour of the samples. The saturation magnetization of Fe_3C/GC, Fe_2N/GC and Fe/GC composites are about 17.72, 40.30 and 54.19 emu/g, respectively.

To calculate the GC content of the three composites, TGA analyses under air have been performed in the revised manuscript (Fig. S3 and Table S1). The GC content in Fe3C/GC, Fe2N/GC and Fe/GC composites are about 40.3 wt%, 38.1 wt% and 44.1 wt%, respectively, indicating the similar GC content in the three composites.

Graphitic carbon (GC) is a typical microwave absorbing material for dielectric loss, so the magnetic nanoparticles/GC composite has dual-loss characteristics. Moreover, the existence of GC in the magnetic composite greatly effect on the electronic and magnetic properties of materials. Therefore, the magnetic nanoparticles/GC composite may exhibit good EM absorption properties. To understand the possible microwave absorption mechanism, the real (ε') and imaginary part (ε'') of the relative permittivity for the composites were investigated in the frequency range of 2~18 GHz. As shown in Fig. 4a and 4b, the real (ε') and imaginary (ε'') part of the relative permittivity of the Fe_3C/GC composite exhibits a decrease tendency in the frequency range of 2–18 GHz with a small fluctuation. However, the ε' value of Fe_2N/GC composite is increase in the frequency range of 3–6.5 GHz, the ε'' value of Fe_2N/GC and Fe_3C/GC composite exhibits an increase tendency in

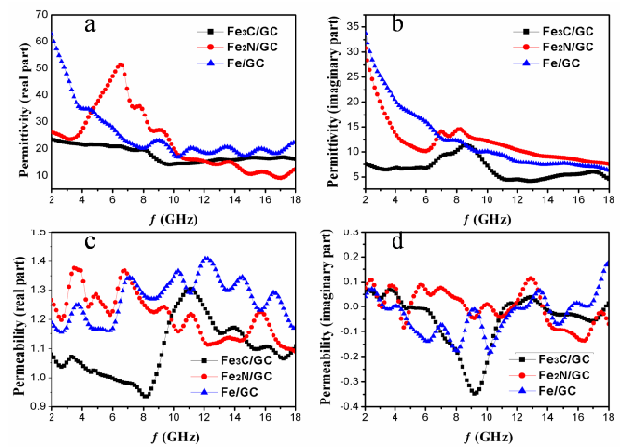

Fig. 4 (a) Real and (b) imaginary parts of relative permittivity; (c) Real and (d) imaginary parts of relative permeability for mixed paraffin wax with composite (weight fraction of 70%).

the frequency range of 3–6.5 GHz. According to the free electron theory,[23] $\varepsilon'' = 1/2\pi\varepsilon_0\rho f$, where ρ is the resistivity. The low ε'' value indicates a higher electric resistivity, which is attributed to the magnetic Fe_3C nanoparticles coated by GC in the composite. The ε'' value of the Fe_3C/GC composite in the range of 2 to 18 GHz is close to the reported carbon/ferrite composites[24] and (Fe, Ni)/C nanocapsules,[25] suggesting that the synthetic Fe_3C/GC composite exhibits strong dielectric loss against EM wave. Although the resistivity of the bulk graphite is about 7.5×10^{-6} Ω·m, which is close to that of metallic magnets (10^{-6}–10^{-8} Ω·m),[26] it is expected that the electrical resistivity may increase owing to the curving graphite shells with a thickness of several nanometers exhibits the special microstructure and defect properties.[27] Different magnetic materials may exhibit different dielectric loss performances. The magnetic Fe_3C nanoparticles in the cavities of GC may increase the electric resistivity, and the protective graphite shell plays a role as

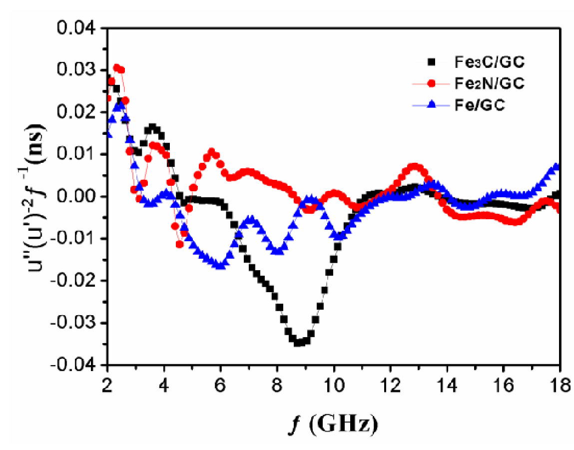

Fig. 5 Values of $\mu''(\mu')^{-2}f^{-1}$ for the composites vs frequency.

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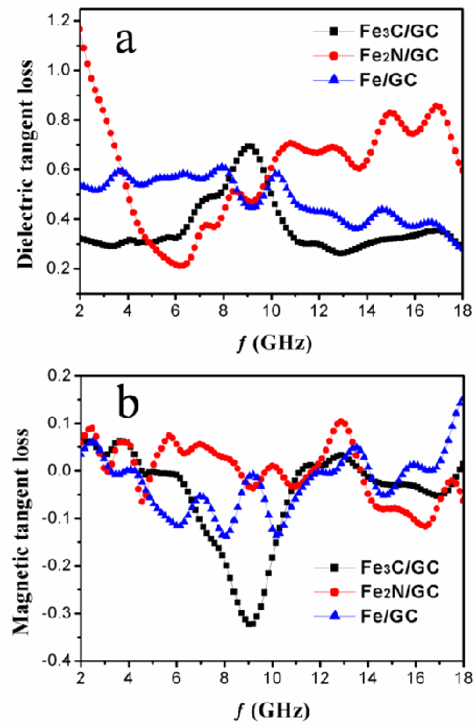

Fig. 6 (a) dielectric loss tangents and (b) Magnetic loss tangents of mixed paraffin wax with composite for weight fraction of 70 %.

an insulator in the composite. Compared with Fe_2N/GC and Fe/GC composites, the relatively lower ε'' values of the Fe_3C/GC is attributed to the performance of Fe_3C is different from that of Fe_2N and Fe.

The frequency dependence of the real part (μ') and imaginary part (μ'') of relative permeability of the composites are shown in Fig. 4c and 4d. It can be seen that the μ' value of Fe_2N/GC and Fe/GC composites exhibit a decrease tendency in the frequency of 2–18 GHz with a small fluctuation. Only the μ' value of the Fe_3C/GC composite is significantly increase in the range of 8–11 GHz. The μ'' values of the Fe_2N/GC and Fe/GC composites are fluctuates around zero, whereas the minimum μ'' value of Fe_3C/GC composite appears at 9.2 GHz. The maximum value of μ'' appeared at 3.6 GHz, implying the natural resonance occurred in the Fe_3C/GC composite. It has been shown that the electromagnetic transformation is associated with the energy transfer between vectors of electric and magnetic fields, and further gives rise to the resonance behavior when their energy states satisfy the matching with the frequency of the electromagnetic wave. The negative values of the imaginary part indicate that the loss associated with the magnetic vector is even smaller than those needed for the permeability in medium, probably aroused by the radiation and/or transfer of energy.[28] The natural resonance equation is as followed: $2\pi f_r = \gamma H_a$,[29] where γ is the gyromagnetic ratio, H_a is the anisotropy field, and f is the resonance frequency. Therefore, the decrease of the relative permeability of Fe_3C/GC composite is attributed to the lower magnetization value of Fe_3C than that of Fe and the magnetic dilution of GC. In fact, the anisotropic energy of small-sized particles, especially in the nano-scale, could remarkably increase because of the surface anisotropic field affected by the small size effect.[9]

The eddy current loss phenomenon is related to thickness (d) and the electric conductivity (σ) of the composites, which can be expressed by the followed equation:[30]

$$\mu''(\mu')^{-2} f^{-1} = 2\pi\mu_0 d^2 \sigma$$

where μ_0 is the vacuum permeability. Fig. 5 shows the calculated values of $\mu''(\mu')^{-2} f^{-1}$ changed with the frequency. Generally, the magnetic loss of material mainly originates from natural resonance, exchange resonance and eddy current loss in the microwave region. If the magnetic loss is mainly determined by eddy current loss, the value of $\mu''(\mu')^{-2} f^{-1}$ should be a constant. Based on the above, it

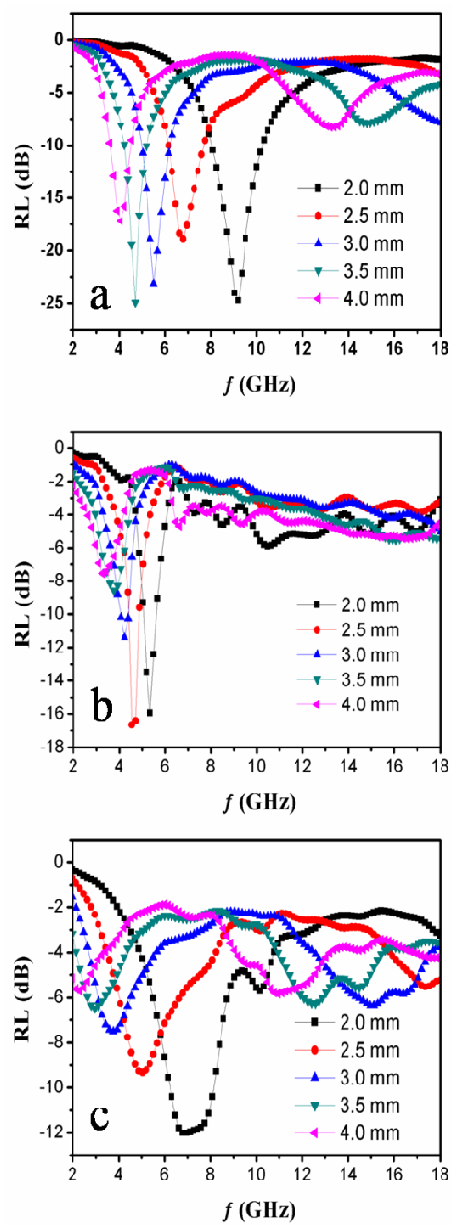

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Fig. 7 Reflection loss curves of composite at different thickness, consisting of mixed paraffin wax with composite for weight fraction of 70%. (a) Fe_3C/GC (b) Fe_2N/GC (c) Fe/GC.

can be concluded that the eddy current loss doesn't play a dominant role in the magnetic loss of the present composites. The low value of $\mu''(\mu')^{-2}f^{-1}$ is attributed to the GC as a separator for suppressing the eddy current loss.[20]

There are two possible contributions for microwave absorption, namely, dielectric loss ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) and magnetic loss ($\tan\delta_\mu = \mu''/\mu'$). The dielectric loss tangent values of the three composites are different as shown in Fig. 6a. The dielectric loss tangent value of Fe_2N/GC composite is decreased in the frequency range of 2–6.5 GHz, and the loss tangent value of Fe_3C/GC composite appears a characteristic peak at 9 GHz. However, the value of Fe/GC composite has no obvious change in the frequency range of 2–18 GHz.

The maximum magnetic loss tangent ($\tan\delta_\mu = \mu''/\mu'$) value of Fe_3C/GC is about 0.03, which is similar to the Fe/GC of 0.05 and Fe_2N/GC of 0.10 (see Fig. 6b). However, all the three composites appear negative values of magnetic loss tangent at 2-18 GHz, which indicates the microwave absorption brings no magnetic loss. The results demonstrate that the dielectric loss plays a dominant role in the three composites. Therefore, the EM attenuation mechanism of the three composites is mainly dependent on the dielectric loss, which is different from the previous reports about the magnetic loss has been regarded as the reason of the main loss."[12-14] The magnetic loss tangent ($\tan\delta_\mu = \mu''/\mu'$) value of Fe_3C/GC is -0.33 at 9.2 GHz, indicating no magnetic loss contribution to the microwave absorption. However, the maximum dielectric loss tangent value of Fe_3C/GC composite is 0.7 at 9.2 GHz, which endows the Fe_3C/GC composite an outstanding microwave absorption property.

Fig. 7 shows the frequency dependence of reflection loss for the sample/paraffin wax composites in the frequency range of 2–18 GHz at different thickness. The three composites have excellent EM wave absorption properties in C-band (4–8 GHz). Especially, Fe_3C/GC composite has the highest EM wave absorption properties. It can be observed that the minimum reflection loss of the Fe_3C/GC composite is –26 dB at 9.2 GHz and the absorption range at −10 dB is from 8–10 GHz with a 2 mm thick layer. The frequency range is quite broader than that of the previously report for a single thickness.[18] Additionally, the minimum reflection loss obviously shifts to the low frequency range with the increase of layer thickness, and the optimum reflection loss of the different thickness layers is concentrated in the low frequency region. The Fe_3C/GC composite exhibits much better microwave absorption properties in C-band than the reported magnetic composites, including Fe/SmO,[12]Fe/Y_2O_3,[13]Fe/CNTs[18] and $CoFe_2O_4$/CNTs.[31]

The magnetic loss tangents of three composites are almost the same, but the corresponding reflection loss values are different, which is may be related to their different dielectric loss tangent caused by different electric resistivity. The Fe_3C/GC composite has the most excellent EM wave absorption properties in C-band (4–8 GHz), indicate that the absorbing performance is determined by the matching degree between dielectric loss ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) tangent and magnetic loss tangent ($\tan\delta_\mu = \mu''/\mu'$). The excellent microwave absorption properties in C-band may be proper combination of the complex permeability and permittivity resulting from the composite of magnetic nanoparticles and GC.

Conclusions

The Fe_3C/GC composite synthesized through a low-cost and scaled-up route exhibited better EM wave absorption properties in C-band (4-8 GHz) than that of the Fe_2N/GC and Fe/GC composites. The minimum reflection loss of Fe_3C/GC composite reaches −26 dB and its absorption range under −10 dB is between 4 to 8 GHz with a thickness layer of 2 mm. The excellent microwave absorption properties of Fe_3C/GC composite could be attributed to the high dielectric loss of light weight graphitic carbon. The composite exhibited well performance of EM wave-absorption in C-band, which may have potential applications in military aircraft, radar and wireless communications.

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