Synthesis of a hierarchical carbon fiber@cobalt ferrite@manganese dioxide composite and its application as a microwave absorber

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In this study, a novel hierarchical carbon fiber@cobalt ferrite@manganese dioxide (CF@CoFe2O4@MnO2) composite was facilely prepared via a sol–gel method and hydrothermal reaction. The morphology, structure, chemical and element composition, crystal form, elemental binding energy, magnetic behavior and microwave absorbing performance of the composite were carefully investigated. According to its hysteresis loops, the composite exhibits a typical soft magnetic behavior, with a $M_s$ value of 30.2 emu g$^{-1}$. Besides, the as-synthesized CF@CoFe2O4@MnO2 composite exhibits superior microwave absorption performance mainly due to reasonable electromagnetic matching, and its minimum reflection loss value can reach $-34$ dB with a sample thickness of just 1.5 mm. The composite can be regarded as an ideal microwave absorber.

1. Introduction

In recent years, the universal applications of computer technology, electromagnetic medicine, broadcasting, and communication have made microwaves part of human beings’ daily lives. Thus, the harm caused by microwaves to humans and their interference with related equipment is receiving increasing attention from all over the world. Simultaneously, in order to achieve microwave protection, research on microwave absorbing materials has also been rapidly growing. According to the dielectric loss and magnetic loss mechanisms of the microwave, an ideal microwave absorber ought to possess both selective dielectric properties and magnetic properties. Therefore, the combination of dielectric materials (such as carbon-based materials, conductive polymers, and transition metal oxides) and magnetic materials (metal iron, cobalt, nickel and their compounds) by chemical reactions has been a classic research method for obtaining superior microwave absorbing composites.

As a typical soft magnetic material, cobalt ferrite has been widely applied in the preparation of efficient microwave absorption composites. Lv et al. developed a novel coin-like core/shell $\alpha$-Fe$_2$O$_3$/CoFe$_2$O$_4$ composite, which showed excellent EM wave absorbing performance, with a minimum reflection loss value of $-41$ dB. Besides, RGO/CoFe$_2$O$_4$, CNT/CoFe$_2$O$_4$ (ref. 20) and PANI/CoFe$_2$O$_4$ (ref. 21) also exhibit superior microwave absorption performance due to the fair electromagnetic matching.

In view of its strong dielectric properties, manganese dioxide has become an interesting research material when regarded as a microwave absorber. Among others, MnO$_2$ possesses many advantages such as strong designability, simple synthesis method, good stability, and low price. Recently, an ideal microwave absorber comprising a hierarchical Fe$_2$O$_3$@carbon@MnO$_2$ hybrid has been reported by Chen et al. The hybrid showed an excellent microwave absorption capacity based on the improvement of dielectric properties by MnO$_2$ with a minimum reflection loss value of $-35$ dB when the sample thickness is 2.7 mm. Besides, numerous other superior microwave absorbers related to MnO$_2$ such as PANI/MnO$_2$/CF, NiFe$_2$O$_4$/MnO$_2$, carbonyl iron/MnO$_2$ (ref. 25) were also reported. Thus, it is significant to develop a microwave absorber by using MnO$_2$.

In this study, a novel CF@CoFe$_2$O$_4$@MnO$_2$ composite was facilely prepared. First, a typical sol–gel reaction was adopted to prepare the CF@CoFe$_2$O$_4$ composite. Then, the as-synthesized CF@CoFe$_2$O$_4$ composite was further coated with MnO$_2$ via a hydrothermal reaction to obtain the CF@CoFe$_2$O$_4$@MnO$_2$ composite. The morphology, structure, chemical and element composition, crystal form, elemental binding energy, magnetic behavior, and microwave absorbing performances of the composite were carefully investigated. According to its hysteresis loops, the composite exhibited a typical soft magnetic behavior, with a $M_s$ value of 30.2 emu g$^{-1}$. Besides, the as-synthesized CF@CoFe$_2$O$_4$@MnO$_2$ composite possesses a superior microwave absorption performance mainly due to reasonable electromagnetic matching, and its minimum reflection
loss value can reach −34 dB with a sample thickness of just 1.5 mm. The composite can be regarded as an ideal microwave absorber.

2. Experimental

2.1 Sol–gel method for the synthesis of CF@CoFe2O4 composite

The CF@CoFe2O4 composite was facilely prepared by a sol–gel method. 2.7 g of FeCl3·6H2O, 1.2 g of CoCl2·6H2O and 0.5 g of CF were uniformly mixed with a moderate amount of C6H8O7. After grinding the material into powder, the mixture was transferred into a flask maintained at 90 °C in a water bath and then 0.5 g ethylene was slowly added to the flask. Then, the pH of the solution was adjusted to 8 using ammonia, after agitating for more than 180 min, the mixture became uniform and the gel was formed. Finally, the gel was calcined at 750 °C for 360 min under an N2 atmosphere to obtain the CF@CoFe2O4 composite.29–31

2.2 Preparation of the CF@CoFe2O4@MnO2 composite

The CF@CoFe2O4@MnO2 composite was facilely prepared via a hydrothermal reaction. 200 mg of the as-synthesized CF@CoFe2O4@MnO2 composite was homogeneously distributed in 75 mL deionized water by high speed agitation for 1 h. Then, 1.5 mL hydrochloric acid and 1.0 g potassium permanganate were added successively. After another 10 min of high-speed agitation, the liquid mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and reacted at 150 °C for 120 min. After naturally cooling it to room temperature, the as-prepared CF@CoFe2O4@MnO2 composite was separated via centrifugation at 10 000 rpm, successively washed with absolute ethanol for about 7–8 times, and put into a 100 °C blast drying oven for 12 h.32–35

2.3 Characterization

The specimen morphology, structure, chemical and element compositions were determined via a scanning electron microscope (FESEM, Quanta600FEG) equipped with an energy dispersive X-ray (EDX) spectrometer. Besides, X-ray diffraction (XRD, ESCALAB 250) in the 2 theta range of 10° < 2θ < 80° was adopted to measure the crystal structures of CF, CF@CoFe2O4 and CF@CoFe2O4@MnO2 composites. The bonding energy of the CF@CoFe2O4@MnO2 composite was examined via X-ray photoelectron spectroscopy (XPS, Thermal Scientific Kz). The hysteresis loops of CoFe2O4, CF@CoFe2O4 and CF@CoFe2O4@MnO2 composites were characterized using a vibrating sample magnetometer (VSM, Lake Shore7307). For the microwave absorbing performance measurement, the complex permittivity (εr) and permeability (μr) of CF, CF@CoFe2O4 and CF@CoFe2O4@MnO2 composites were investigated using an Agilent HP8720ES vector network analyzer in the frequency range of 2.0–18.0 GHz based on a coaxial method. First, the samples were uniformly distributed in a paraffin phase with the weight ratio of 30%, and then pressed into a cylindrical mold (φin = 3.04 mm, φout = 7.00 mm). Based on the obtained parameters of the samples, the corresponding reflection loss curves were further calculated and their microwave absorption performances could be identified.

3. Results and discussions

The preparation process of the CF@CoFe2O4@MnO2 composite is briefly illustrated in Fig. 1. First, a typical sol–gel reaction was adopted to synthesize CF@CoFe2O4. Then, in order to make the MnO2 nanocrystals in situ grow along the surface of the CF@CoFe2O4 composite, another hydrothermal reaction was carried out to complete the redox reaction of potassium permanganate and carbon, and the CF@CoFe2O4 composite was further coated with MnO2 to obtain the CF@CoFe2O4@MnO2 composite. The reactions occurring during the synthesis process are shown as eqn (1) and (2).36–39

\[
\text{Co}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Co(OH)}_2 + 2\text{Fe(OH)}_3
\]

\[
\rightarrow \text{CoFe}_2\text{O}_4 + 4\text{H}_2\text{O} \quad (1)
\]

\[
4\text{KMnO}_4 + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{K}_2\text{CO}_3 + 2\text{KHC}O_3 \quad (2)
\]

Fig. 2 exhibits the SEM images of CF (a), CF@CoFe2O4 (b), CF@CoFe2O4@MnO2 composites (c) and the EDS spectra of CF@CoFe2O4@MnO2 composite (d). It can be observed from
the images that the pre-reaction carbon fiber possesses a smooth surface, and its diameter is about 6–7 μm. After the sol–gel reaction, the surface CF was homogeneously cladded by CoFe₂O₄ nanoparticles (Fig. 2b), and the thickness of overburden was about 600 nm. Fig. 2c reveals the morphology of the CF@CoFe₂O₄@MnO₂ composite, the CF@CoFe₂O₄ was uniformly coated with MnO₂ after the hydrothermal reaction, and the diameter further increased to around 8.2 nm. The total thickness of the coating layer could be calculated from the size difference (about 750 nm). The CF@CoFe₂O₄@MnO₂ composite’s EDX patterns illustrate that the composite was composed of the elements of C, O, Mn, Fe and Co, the composition ratio (wt%) of these elements were 26.13%, 28.06%, 19.17%, 18.82% and 7.82%, respectively. The C element is mainly from the carbon fiber, while the O element can be attributed to the components of CoFe₂O₄ and MnO₂. The above results confirm the successful synthesis of the CF@CoFe₂O₄@MnO₂ composite. Meanwhile, the composite’s EDX elemental mapping images (Fig. 3a–f) further identifies the components in the as-synthesized product.⁴⁰–⁴³

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**Fig. 2** SEM images of CF (a), CF@CoFe₂O₄ (b), CF@CoFe₂O₄@MnO₂ composites (c) and the EDS spectra of CF@CoFe₂O₄@MnO₂ composite (d).

**Fig. 3** EDX elemental mapping images (a–f) of CF@CoFe₂O₄@MnO₂ composite.
Fig. 4 displays the XRD patterns of CF, CF@CoFe₂O₄ and CF@CoFe₂O₄@MnO₂ composites, which can be used to investigate the samples’ crystal structures. From this figure, the broad peak between 2θ = 20°–40° represents the crystal plane diffraction peak of CF. After the sol–gel reaction, there are seven diffraction peaks located at 2θ = 18.51°, 30.41°, 35.71°, 43.5°, 53.9°, 57.5° and 63° signifying the (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes, respectively, of CoFe₂O₄ (JCPDS card no. 22-1086), in the XRD pattern of CF@CoFe₂O₄. Compared with the CF@CoFe₂O₄ sample, the additional two peaks of CF@CoFe₂O₄@MnO₂ composite located at 36.1° and 74.2° belong to MnO₂ crystal’s (2 1 1) and (3 1 2) plane diffraction peaks, respectively, which can further confirm the successful synthesis of CF@CoFe₂O₄@MnO₂ composite.

Fig. 5 exhibits the XPS spectra of CF@CoFe₂O₄@MnO₂ composite. Fig. 5a is the survey scan spectra, from which the C 1s, Fe 2p, O 1s, Mn 2p, Co 2p binding energy can be observed. In Fig. 5b, the two peaks located at 283.5 eV and 284.6 eV are corresponding to the C–C/C≡C and C–O binding energy of C element, respectively. The two peaks located at 711.5 eV and 726.4 eV represent Fe 2p₃/₂ and Fe 2p₁/₂ binding energies (Fig. 5c). From Fig. 5c, the 2p₁/₂ and 2p₃/₂ belonging to Mn element can obviously be observed. And the Co 2p₁/₂ and Co 2p₃/₂ binding energies of Fig. 5d and 5f are located at 780.5 eV and 796.2 eV, respectively.
$2p_{1/2}$ binding energy peaks are located at 782.8 eV and 798.2 eV, respectively, which can be observed in Fig. 5f. The above results jointly verified the elemental composition of the as-synthesized CF@CoFe$_2$O$_4$@MnO$_2$ composite.

In view of the magnetic loss mechanism of electromagnetic waves, the magnetic behaviors of microwave absorbers have a great effect on their microwave absorbing performance, thus the magnetic hysteresis loops of CoFe$_2$O$_4$, CF@CoFe$_2$O$_4$ and CF@CoFe$_2$O$_4$@MnO$_2$ composites were measured by utilizing VSM and the results are exhibited in Fig. 6. The CoFe$_2$O$_4$, CF@CoFe$_2$O$_4$ and CF@CoFe$_2$O$_4$@MnO$_2$ composites all displayed a typical soft magnetic behavior, which is very beneficial for the absorption of microwaves. The magnetic saturation values of CoFe$_2$O$_4$, CF@CoFe$_2$O$_4$ and CF@CoFe$_2$O$_4$@MnO$_2$ composites were 65.5 emu g$^{-1}$, 54.8 emu g$^{-1}$ and 30.2 emu g$^{-1}$, respectively. The reduction in their magnetic saturation can mainly be attributed to the decrease of the mass ratio of the unique magnetic material CoFe$_2$O$_4$ among these samples.

Normally, when the microwave is incident upon the surface of the sample, it would be reflected or transmitted, meanwhile, the contained microwave energy would be absorbed by magnetic loss and dielectric loss or transformed into heat energy and scattered in the air. In view of the loss mechanism of the microwave, the absorption mode of the microwave can mainly be divided into magnetic loss and dielectric loss, which can be calculated by utilizing its permeability $\mu'$, $\mu''$ and permittivity $\varepsilon'$, $\varepsilon''$, respectively. The parameter's real part $\mu'$ and $\varepsilon'$ represent the storage capability of a material, while the imaginary part $\mu''$ and $\varepsilon''$ on behalf of the dissipation capability of magnetic energy and electric energy, respectively. Based on $\mu'$, $\mu''$, $\varepsilon'$ and $\varepsilon''$, the corresponding reflection loss patterns of the measured samples can be calculated by using eqn (3)–(6).

$$\Gamma = \frac{Z_{in} - Z_0}{Z_{in} + Z_0}$$  \hspace{1cm} (3)$$

$$Z_0 = (\mu_0/\varepsilon_0)^{1/2}$$  \hspace{1cm} (4)$$

$$Z_{in} = Z_0 \left( \sqrt{\frac{\mu_0}{\varepsilon_0}} \tanh \left[ j \frac{2\pi df}{c} \left( \sqrt{\frac{\mu_0}{\varepsilon_0}} \right) \right] \right)$$  \hspace{1cm} (5)$$

$$R_L = 20 \log \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right)$$  \hspace{1cm} (6)$$

In these formulas, $Z_{in}$ represents normalized input impedance of the absorbing material, $Z_0$ on behalf of the impedance of free space, parameter $d$ stands for the thickness of absorber, parameter $c$ means the light velocity in the vacuum and another parameter $f$ signifies the frequency of the input microwave. Thus, the measured sample’s thickness possesses a great effect on its microwave absorption performance. In addition, the absorbers’ microwave absorption performances were mainly codetermined by their magnetic property and dielectric property. The
electromagnetic parameters of CF, CF@CoFe₂O₄ and CF@CoFe₂O₄@MnO₂ composites are exhibited in Fig. 7, and the corresponding dielectric loss (\(\tan \delta_e = \varepsilon''/\varepsilon'\)) and magnetic loss (\(\tan \delta_m = \mu''/\mu'\)) were also calculated and shown in Fig. 8. By comparing the three samples’ electromagnetic parameters, as a conductive material, the CF sample possesses high dielectric parameter value (real part \(\varepsilon'\) and imaginary part \(\varepsilon''\)). However, as a nonmagnetic material, the magnetic parameter values of CF are the lowest among these samples (real part \(\mu'\) and imaginary part \(\mu''\)), which is unfavorable to the magnetic loss for electromagnetic waves. After the sol–gel reaction, the dielectric parameter values and \(\tan \delta_e\) of CF@CoFe₂O₄ decreased while its magnetic parameters (real part, imaginary part and magnetic loss) were all increased, which can mainly be attributed to the introduction of magnetic material CoFe₂O₄. Compared with CF@CoFe₂O₄, the CF@CoFe₂O₄@MnO₂ composite’s magnetic loss was reduced, while the dielectric loss was improved (real part ~ 10.8 and imaginary part ~ 3.2), which can result in a more reasonable electromagnetic matching, further enhancing the sample’s microwave absorbing performance. Besides, the CF@CoFe₂O₄ sample the CF@CoFe₂O₄@MnO₂ composite sample exhibited resonance phenomenon, which is considered to be associated with local confinement, natural resonance and exchange resonance loss.58–62

![Reflection loss curves of CF (a), CF@CoFe₂O₄ (b) and CF@CoFe₂O₄@MnO₂ composites (c) at a different thickness, the effective absorption band width of CF@CoFe₂O₄@MnO₂ composite (d).](image)

Fig. 9 Reflection loss curves of CF (a), CF@CoFe₂O₄ (b) and CF@CoFe₂O₄@MnO₂ composites (c) at a different thickness, the effective absorption band width of CF@CoFe₂O₄@MnO₂ composite (d).

According to the measured \(\varepsilon', \varepsilon'', \mu', \mu''\), the reflection loss patterns at different thicknesses ranging from 2–18 GHz of CF (a), CF@CoFe₂O₄ (b) and CF@CoFe₂O₄@MnO₂ composite (c) samples were calculated and the results are exhibited in Fig. 8. As shown in Fig. 8a, as a nonmagnetic material, the EM wave absorbing capacity of a pure carbon fiber is poor and its minimum reflection loss (\(R_L\) min) value is −15 dB with a specimen thickness of 1.6 mm. However, when combined with magnetic material CoFe₂O₄ via the sol–gel method, the CF@CoFe₂O₄, its microwave absorbing performance was enhanced, and the minimum reflection loss value is less −20 dB. Fig. 10

![Mechanism illustration of microwave absorption for the CF@CoFe₂O₄@MnO₂ composite.](image)

Fig. 10 Mechanism illustration of microwave absorption for the CF@CoFe₂O₄@MnO₂ composite.
The above results illustrate that the as-synthesized CF@CoFe$_2$O$_4$@MnO$_2$ composite exhibits superior microwave absorption performance both in absorbing efficiency and EAB width with a low thickness. The mechanism sketch illustration of microwave absorption for the CF@CoFe$_2$O$_4$@MnO$_2$ composite is shown in Fig. 10. First, the dielectric material CF, MnO$_2$ and magnetic material CoFe$_2$O$_4$ can achieve fair electromagnetic matching. Second, the multiple interfaces that emerged from its layer-by-layer cladding structure can increase absorption times of EM wave. Third, the interfacial polarizations and interface relaxation between MnO$_2$ and NiFe$_2$O$_4$ can further enhance its microwave capacity. These factors code-termined the excellent microwave absorbing properties of the CF@CoFe$_2$O$_4$@MnO$_2$ composite.66–71 When compared with other reported homologous microwave absorber including Fe$_3$O$_4$@Co@MnO$_2$,52 CNT/CoFe$_2$O$_4$,64 PANI/MnO$_2$/CF,61 NiFe$_2$O$_4$@MnO$_2$,63 carbonyl iron/MnO$_2$,68 PANI@Ni@CF,69 and z-Fe$_2$O$_3$/CoFe$_2$O$_4$ (ref. 59) (Table 1), the as-synthesized CF@CoFe$_2$O$_4$@MnO$_2$ composite showed excellent EM wave absorption performance.

4. Conclusion

In summary, a uniform CF@CoFe$_2$O$_4$@MnO$_2$ composite was facilely fabricated via a two-step method, a sol–gel method and a hydrothermal reaction. The morphology, structure, chemical and element composition, crystal form, elemental binding energy, magnetic behavior, and microwave absorbing performances of the composite were carefully investigated. According to its hysteresis loops, the composite exhibited a typical soft magnetic behavior, with an $M_r$ value of 30.2 emu g$^{-1}$. Besides, the as-synthesized CF@CoFe$_2$O$_4$@MnO$_2$ composite possesses superior microwave absorption performance mainly due to a reasonable electromagnetic matching, and its minimum reflection loss value can reach $-34$ dB with a sample thickness of just 1.5 mm. The composite can be regarded as an ideal microwave absorber.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was financially supported by the Natural Science Foundation of Shandong Province (ZR2019YQ24), the Qingchuan Talents Induction Program of Shandong Higher Education Institution (Research and Innovation Team of Structural-Functional Polymer Composites), National Natural Science Foundation of China (51407134, 51801001), China Postdoctoral Science Foundation (2016M590619, 2016M601878), Qingdao Postdoctoral Application Research Project, Key Laboratory of Engineering Dielectrics and Its Application (Harbin University of Science and Technology), Ministry of Education (KFZ1803), Provincial Key Research and Development Program of Shaanxi (2019GZ-197), Key Project of Baoji University of Arts and Sciences (ZK2018051), Baoji Science and Technology Project (16RKKX-1-29) and Baoji Engineering Technology Research Center for Ultrafast Optics and New Materials (2015XNL-1-3). Feng AL is supported by The Thousand Talents Plan for Young Professionals of Shaanxi Province.

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