Fe₃C/helical carbon nanotube hybrid: Facile synthesis and spin-induced enhancement in microwave-absorbing properties

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ABSTRACT

Exploring effective microwave absorption materials is always a challenge especially in the relatively low frequency range of 2–8 GHz and broad absorption band. Here we developed a Fe₃C/helical carbon nanotube (HCNT) hybrid structures synthesized via catalytic chemical vapor deposition (CCVD) using Fe₃O₄ nanoparticles as catalyst. The microwave-absorbing characteristics of such hybrid nanomaterials were investigated based on the transmission line theory through the evaluation of the experimental data including complex permittivity and permeability. Considering the reaction temperature range of 400–750 °C, the as-prepared hybrid synthesized at 700 °C can be adjusted to have effective performance of RL value less than –10 dB in the relatively lower frequency ranged from 2.9 GHz to 9.9 GHz at the thickness range of 2–5 mm. Furthermore, the hybrid in case of 750 °C bears bandwidths with RL lower than –10 dB from 7.3 GHz to 18 GHz and the minimum RL is about –21 dB. The observed advantageous reflection loss was attributed to the pronounced impedance match owing to the reasonable synergistic effect between magnetic nanoparticles and HCNTs.

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1. Introduction

The pollution of electromagnetic interference (EMI) has raised much more attention with the rapid development of communication devices and extensive use of electronic devices. Exploration and preparation of high-performance microwave absorption materials is an effective approach to resolve the challenge related to EMI pollution. In practical application, excellent the microwave absorbing material usually has the advantages of low density, low

thickness strong absorption at a broad frequency and high thermal stability [1]. At present, microwave absorbing material is one of typical functional materials and has a variety of applications in EMI shielding and countermeasure to radar detection [2,3]. In terms of microwave loss mechanism, the microwave absorbing material can be classified into two categories, namely dielectric and magnetic loss materials. For example, Fe₃O₄, Fe, Ni, Co and their alloy are typical magnetic loss materials. Compared with traditional ferrite materials, CNTs have many advantages in the field of microwave absorption such as the high specific surface area, low density, high values of complex permittivity, etc. [4,5]. Li et al. reported that high specific surface area and a large number of surface suspension parts of CNTs allow for pronounced interfacial polarization and multiple scattering and enhance the absorbing properties of CNTs [6]. In particular, HCNTs are a kind of chiral material which enables the formation of an inductive magnetic field as an electrical current passes through HCNTs [7]. However, most absorbers containing the single component are hard to fulfill requirement of producing high

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dielectric and magnetic loss simultaneously. Recently, hybrid nanotubes [8] and carbon black [9] (the inner cavity of CNTs is filled with foreign atoms [10], molecules [11]), compounds [12] and special structure including hollow [13] and honeycomb structure [14] have drawn much attention since the special structure alleviates the poor dispersion characteristics of bare one-dimensional carbon nanomaterials [15] and improves the impedance match characteristic [16]. Nickel/carbon hybrid nanostructures, multi-walled carbon nanotube (MWCNTs) partially or completely filled by metallic elements were reported with highly enhanced microwave absorption [17–19]. Among metal/CNT hybrid materials, Fe/Fe compounds have attracted increased attention owing to the abundance of Fe in nature and also the observed spin-effect induced enhancement in the microwave absorption properties of magnetic Fe/Fe compounds [20,21]. ENREF_16 Chen et al. reported that in the absorption range from 3.2 to 16.88 GHz, the microwave absorption of $\text{Fe}_3\text{O}_4/\text{SnO}_2$ core/shell nanorods is on the order of -20 dB with a thickness of 2 mm–4 mm [22]. Che et al. prepared carbon nanotube/Fe composites and found the reflection loss reached -25 dB with a thickness of 1.2 mm [23]. Fe/Fe compounds have indeed exhibited promising application potentials in the microwave absorption field despite the complexity of the synthetic routes to these magnetic Fe based hybrid nanomaterials. Therefore, composite technology is an effective method to enhance the performance of functional material [24–28].

In the synthesis of HCNTs, metal catalyst has been frequently employed to realize HCNTs [29]. In addition to the typical catalyst materials such as transition metals Fe, Co and Ni, several novel metal catalysts have also been developed such as Cu, Ag and K [30,31]. However, the catalytic properties of the magnetic metal oxides, a less costly and more accessible catalyst, have not received as much attention and the associated growth mechanism of HCNTs based on such catalysts remains elusive to this date.

In this report, we synthesize a novel Fe_3C –MWCNT hybrid nanotube and HCNTs using Fe_3O_4 nanoparticle catalyst. The introduction of Fe_3C can effectively enhance the magnetic loss of the hybrid materials to improve the microwave absorption performance, and Fe_3C has the advantages of high thermal stability favoring its practical application, which is agreement with the previous reports [32]. The micro-structure of the as-prepared HCNTs and their electromagnetic absorption properties are investigated systematically. The growth mechanism of HCNTs is analyzed and discussed from a kinetics point of view. Our facile synthesis and analysis of such magnetic Fe_3C /HCNT hybrid materials using an advantageous Fe oxide catalyst enhance the application potentials of HCNT-based hybrid nanomaterials in the areas of microwave absorption.

2. Experimental section

2.1. Synthesis of Fe_3O_4 nanoparticles

The hybrid was prepared using 2.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5 g sodium acetate (NaAc) by dissolving in 70 mL and 30 mL of ethylene glycol to form transparent solution, respectively, followed by an ultrasonication for 5 min. Later on, the NaAc solution was dropped into the above suspension slowly with continue magnetic stirring. The mixture was then sealed in a Teflon-lined stainless steel autoclave and aged at 200°C for 24 h. After natural cooled down to room temperature, the as-synthesized products were centrifuged and washed with distilled water and absolute ethanol repeatedly for three times and finally dried in vacuum oven at 60°C for 4 h.

2.2. Preparation of HCNTs

In a typical procedure, Fe_3O_4 particles were dispersed on a ceramic plate, transferred to a horizontal reaction tube located inside a tubular furnace at the room temperature and then heated up to a synthesis temperature (400°C – 750°C) with a heating rate of $5^\circ\text{C}/\text{min}$ with N_2 . After the temperature was stabilized, C_2H_2 and H_2 were introduced for 30 min at a flow rate of 30 mL/min and 15 mL/min, respectively. The samples were cooled to the room temperature in the nitrogen atmosphere furnace.

2.3. Characterizations

The X-ray diffraction (XRD) patterns were obtained with an XRD-7000X. The morphology and size of samples were characterized with Scanning Electron Microscope (SEM) on a JSM-7600F. Transmission electron microscopy (TEM) images were obtained with a JEOL-2010 transmission electron microscope. The complex permittivity and permeability of the products were measured with a coaxial line method at 2 GHz–18 GHz using an AV3618 network analyzer.

3. Results and discussion

3.1. Morphology and structure analysis of the HCNT products

The synthesis of HCNT is achieved typically using two main strategies including the ‘catalyst-component’ adjustment and the ‘growth-condition’ method [33]. To obtain helical nanomaterials and hybrid structures, we choose Fe_3O_4 as catalyst (Fig. S1) and design reasonable growing conditions as shown in Fig. 1. At 400 – 550°C , HCNTs grew upon Fe_3O_4 particles introducing the mixed gas of C_2H_2 and H_2 at flow rates of 30 mL/min and 15 mL/min, respectively. Interestingly, Fe_3C /HCNT hybrid formed at 700°C under the similar gas sources. The Fe-containing particles with catalytic anisotropic properties favor the growth of HCNTs according to the spatial-velocity hodograph theory [34]. In contrast, curved CNTs with hybrid structure formed after relatively faster growth at higher temperature of 700 – 750°C , which is consistent with our previous study [35]. Herein, we demonstrate an effective approach to obtain HCNTs and hybrids CNTs, as shown in Fig. 1.

As shown in Fig. S2, the XRD patterns of the samples synthesized at 450°C confirm that the as-formed Fe compound is Fe_3C . There is a dispersion peak at angles of ~ 26 , which indicates that the

Fig. 1. Schematics of the selective growth for HCNTs and curved Fe_3C /CNTs using Fe_3O_4 as catalyst and C_2H_2 as carbon resource at 550°C and 700°C , respectively.

as-obtained HCNs are quasi-graphene stacks with a relatively low graphitic degree. At 550 °C, the diffraction peaks of the Fe_3C still exist while the dispersion peak shifts to the sharp diffraction peaks of graphite, which indicates that the products have a high graphitic degree. However, in addition to Fe_3C and graphite, the phase of metallic Fe is also detected at a higher reaction temperature of 700 °C, which is attributed to the reduction reaction of Fe_3O_4 by C_2H_2 and H_2 .

Fig. 2 shows the typical morphology of the HCNT products. The reaction temperature has a great influence on the morphology and length of the HCNs. The length of the HCNs evolves with increasing reaction temperature as shown in Figs. S3–S6 and Fig. 2(a, d). In the range of 450 °C–550 °C, the length of these HCNs increased, which was attributed to the enhanced diffusion reaction rates of carbons [36] and the higher catalytic activity of the catalyst nanoparticles at a higher temperature. Further, the morphology of products is also affected by the reaction temperature. HCNs formed at 550 °C were in a helical shape, while product formed at 700 °C exhibited a curved helical morphology [35]. Then it is suggested that the reasonable catalytic anisotropy among catalyst crystal faces is necessary at a proper reaction temperature and favors the helical growth model. HCNs cannot form without catalytic anisotropy between the respective crystal faces [37].

The HRTEM images of the product are shown in Fig. 2. HCNs show a symmetric growth mode at 550 °C, with catalyst particles located in the center of the HCNs (Fig. 2b). This growth pattern is similar to the growth of helical carbon nanofibers [30]. Further, the lattice fringes of catalyst particles can be seen clearly in Fig. 2c, based on the HRTEM images of the catalyst particles; its lattice fringe spacing is determined to be 0.21 nm, corresponding to the (211) diffraction peak of Fe_3C [38]. The outer layer structure has the lattice distance of 0.34 nm, corresponding to the (002) plane of graphite. Interestingly, the HCNs have curved shape at 700 °C as shown in Fig. 2d, e with nanoparticle embedded inside the graphene sheet of HCNs. Fig. 2f shows its HRTEM images along with fast Fourier transformed (FFT) images corresponding to the selected regions. The FFT in the inset also confirms that the nanoparticle is Fe_3C , and the FFT pattern from the HCNs reveals the diffraction rings of the (0 0 2), (1 0 0) and (1 0 1) spots.

Based on the above experimental results and analysis, we then look into the growth mechanism of the helical growth. At a relatively low temperature of 450 °C and 550 °C, the catalytic activity of the particle is relatively low, resulting in a small longitudinal growth velocity V_1 , also named the speed of extrusion. At 700 °C, the catalytic activity of the particles improves and leads to a larger extrusion rate, as demonstrated through the SEM observation that verifies that the HCNT evolves more efficiently at a high temperature.

3.2. Microwave-absorbing performance

In the field of microwave absorption materials, composite and hybrid structure are ideal to get high performance, which usually comes from efficient complementarities between complex permittivity and permeability. To explore the microwave absorption property of the hybrid products synthesized at different temperatures, their real and imaginary part of permittivity and permeability are shown in Fig. 3. As can be seen in Fig. 3a and b, real and imaginary part of permittivity of the 650 and 700 °C samples remain relatively higher level than 400, 500 and 750 °C samples. Besides, the reaction temperature has great effect on the dielectric loss of products shown in Fig. 3c. The dielectric loss value of the products synthesized at a relatively low temperature (400 °C and 500 °C) exhibit similar fluctuation with the slight values of dielectric loss in the range of 2 GHz–12 GHz and relatively stronger dielectric loss in 12 GHz–18 GHz. In case of 650 and 700 °C samples, their corresponding dielectric loss also keeps in the high level especially in the low frequency range of 2–14 GHz. Moreover, the fluctuation of dielectric loss appears with three peaks at 8 GHz, 13 GHz and 15.8 GHz as the reaction temperature increasing to 750 °C. From the dielectric curves, it can be seen that the products synthesized at 650–750 °C exhibit stronger dielectric loss among all the samples, which is due to the increase of CNTs in the as-prepared samples with good conductivity and therefore larger interface between Fe_3C and CNTs resulting in stronger interfacial polarization. In contrast, from the curves of permeability and magnetic loss, we find that the 400, 500 and 750 °C samples performed better compared with 650 and 700 °C samples as shown in

Fig. 2. SEM and HRTEM images of the HCNs synthesized at 550 °C (a–c) and Fe_3C /HCNT hybrid structures formed at 700 °C (d–f). The Inset in (f) shows the corresponding FFT patterns.

Fig. 3. Measured relative (a, b) complex permittivity, (d, e) complex permeability and (c) dielectric and (f) magnetic loss values of HCNs synthesized at 400 °C, 500 °C, 650 °C, 700 °C and 750 °C.

Fig. 3d–f. The enhancement of magnetic property in case of 400, 500 and 750 °C is resulted from the magnetic materials including leftover Fe_3C at 400, 500 °C with larger proportion and more Fe product at higher temperature of 750 °C. In addition, it can be seen that intensive peaks appear and shift to a lower frequency band with the reaction temperature increasing up to 750 °C, indicating that resonance peak can be adjusted by selecting an appropriate reaction temperature.

Based on the free electron theory and Debye theory, three major factors are proposed to account for the enhanced dielectric loss. Firstly, according to the free electron theory $\epsilon'' \approx 1/2\pi\epsilon_0\rho f$, where ρ is the electrical resistivity. The graphene layer of CNTs greatly increased the conductivity of the hybrids especially in range of 600–750 °C, which further increased dielectric loss of the obtained products. Secondly, large amount of interfaces in the hybrids between Fe_3C and CNTs give rise to interfacial polarization and the Maxwell–Wagner effect [39]. Thirdly, the defects in graphene layer with helical structure benefit CNTs being a kind of dipole material; therefore, it can also cause electronic dipole polarization in the hybrid. To further confirm the permittivity dispersion mechanism, some plots of ϵ'' versus ϵ' for Fe_3O_4 and as-synthesized products are given in Fig. 4. Based on Debye dipolar relaxation, the complex permittivity can be expressed in the following equation [40]:

$$\epsilon_r = \epsilon' + i\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau} \quad (1)$$

where τ , ϵ_s , and ϵ_∞ are the relaxation time, the static dielectric constant, and the dielectric constant at infinite frequency. From Eq. (3), it can be deduced that

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (2)$$

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \omega\tau \quad (3)$$

Moreover, it can be further deduced that

$$\left(\epsilon' - \frac{\epsilon_s + \epsilon_\infty}{2}\right)^2 + (\epsilon'')^2 = \left(\frac{\epsilon_s - \epsilon_\infty}{2}\right)^2 \quad (4)$$

Thus, the plot of ϵ'' versus ϵ' should be a single semicircle,

usually denoted as the Cole–Cole semicircle and each semicircle corresponds to a Debye dipolar relaxation. For Fe_3O_4 nanoparticles, a relatively large smooth semicircle is found in Fig. 4a. This large semicircle becomes irregular in case of 400 °C reaction temperature and a few vague semicircles appear for the products synthesized at 500 °C, as shown in Fig. 4b and c, respectively. However, for the products synthesized at 650 °C and 700 °C, some clear small semicircles can be found in Fig. 4d and e. Interestingly, with the reaction temperature increasing to 750 °C, several small semicircles and a whole circle consisting of one large semicircle are found, as presented in Fig. 4f, indicating the existence of several dielectric relaxation processes. The mechanisms of the permittivity dispersion can be interpreted in following description. For pure Fe_3O_4 , there is only a single Debye relaxation process. While $\text{Fe}_3\text{C}/\text{CNTs}$ hybrid in range of 700–750 °C have several continuous Debye relaxation processes. In addition, it is obvious that for as-synthesized hybrids, their Cole–Cole semicircle is distorted, indicating the existence of other loss mechanism, like conductance loss, interfacial polarization and electronic dipole polarization, consisted with the previous analysis. The as-prepared helical CNTs contain both left and right helix at the same ratio of about 50%. In fact, it remains a challenge to prepare helical CNTs with single chirality, which is significant to discuss the effect from the chirality at the nanoscale level of CNTs.

Generally, the magnetic loss is related to the eddy current effect and the anisotropy energy of the hybrids. The values of $\mu''(\mu')^{-2}(f)^{-1}$ should be constant if eddy current loss is a dominate magnetic loss mechanism [19]. In present case, for the products synthesized at 650 °C and 700 °C, the value of $\mu''(\mu')^{-2}(f)^{-1}$ is almost constant in observing frequency ranges. However, for the products synthesized at other temperatures of 400, 500 and 750 °C, the value is not constant, suggesting natural resonance is another important magnetic loss mechanism, described as follow [41]:

$$2\pi f_r = rH_a \quad (5)$$

$$H_a = 4|K_1|/3H\mu_0M_s \quad (6)$$

H_a is the anisotropic energy, r is the gyromagnetic ratio, $|K_1|$ is the anisotropic coefficient and M_s is saturation magnetization. As can be seen in Fig. 5, for the products synthesized at 400 °C and

Fig. 4. Cole–Cole semicircles (ϵ'' versus ϵ') for (a) Fe_3O_4 , and the products synthesized at (b) 400 °C, (c) 500 °C, (d) 650 °C, (e) 700 °C and (f) 750 °C in the frequency range of 2–18 GHz.

500 °C, the value of $\mu''(\mu')^{-2}f^{-1}$ drops at the range of 2–10 GHz, due to the existence of natural resonance attributing to the interactions between the CNTs and Fe_3C particles [42]. However, in cases of 650 °C and 700 °C, their $\mu''(\mu')^{-2}f^{-1}$ values keep constant in observing frequency ranges, suggesting that magnetic loss mainly originating from the eddy current loss. Interestingly, when the reaction temperature increased to 750 °C, the value varied with frequency. Thus, it can be speculated that not only the dielectric property, the magnetic property is also influenced by the reaction

temperature.

On the basis of measured data of complex permittivity and permeability, the values of reflection loss (RL) [43], were calculated according to the transmission line theory, as expressed in Eqs. (7) and (8),

$$Z_{in} = \sqrt{\mu_r/\epsilon_r} \tanh \left[j \left(\frac{2\pi f d}{c} \right) \sqrt{\mu_r \epsilon_r} \right] \quad (7)$$

$$RL(\text{dB}) = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (8)$$

where f is the microwave frequency, d is the thickness of the absorber, c is the velocity of light and Z_{in} is the input impedance of the absorber.

Fig. 6 shows the reflection loss of pure Fe_3O_4 and the hybrids synthesized at different temperatures. For Fe_3O_4 nanoparticles (Fig. 6a), the minimum RL is about −13 dB at 14.5 GHz with a thickness of 3.5 mm and the absorption bandwidths with RL lower than −10 dB is from 13.6 GHz to 15 GHz. Obviously, compared with original Fe_3O_4 nanoparticles, both effective bandwidths and minimum RL value of the hybrids have improved a lot as shown in Fig. 6b–f, indicating that this special $\text{Fe}_3\text{C}/\text{CNTs}$ hybrid is an effective structure to enhance microwave absorption property. Particularly, the hybrid obtained at 700 °C performs well in the relatively lower frequency ranged from 2.9 GHz to 9.9 GHz, and RL value less than −10 dB can be addressed at the thickness range of 2–5 mm.

Fig. 5. Plots of $\mu''(\mu')^{-2}f^{-1}$ vs. frequency for the products synthesized at 400 °C, 500 °C, 650 °C, 700 °C and 750 °C.

Fig. 6. Simulated curves of electromagnetic wave loss of Fe_3O_4 (a) and the $\text{Fe}_3\text{C}/\text{CNTs}$ hybrid prepared at (b) 400 °C, (c) 500 °C, (d) 650 °C, (e) 700 °C and (f) 750 °C.

Besides, for the products synthesized at 750 °C, bandwidths with RL lower than -10 dB is from 7.3 to 11.4 GHz to 16.4–18.0 GHz and the minimum RL is about -22 dB. Compared with other recently reported microwave absorbing materials [44–46], the $\text{Fe}_3\text{C}/\text{CNTs}$ hybrid synthesized at 750 °C have a wider effective absorbing band and a relative larger minimum RL, as shown in Table 1. It is known that the microwave absorption property is determined two factors, impedance matching characteristic and attenuation characteristic of the hybrids. Thus, it can be speculated that reasons for the enhanced microwave absorption property of hybrids are as follows: Firstly, improved level of impedance matching. The loss mechanism of Fe_3O_4 depends mainly on magnetic loss, while the loss mechanism of hybrids consisted of both dielectric (HCNTs) and magnetic loss (Fe_3C), resulting in an improved level of impedance matching. Secondly, the existence of interfacial polarization, electronic dipole polarization, natural resonance and its associated relaxation also greatly improved the microwave absorption property of the hybrids. Thirdly, helical CNTs have special morphology with larger

specific surface area and well dispersion of Fe_3C . Meanwhile, some defects such as vacancies, pentagons and heptagons exist in helical CNTs [47] with the features of short-range order and long-range disorder. Then the electronic spin attributed to these defects and polarized center have the profound effect on the response of helical CNTs [23]. These special features favor higher performance of electromagnetic wave absorbing properties.

4. Conclusion

HCNTs were obtained using Fe_3O_4 nanoparticles as catalyst during the CCVD process. The temperature plays an important role in the growth and micro-structure of the HCNTs. Relatively lower reaction temperature of less than 550 °C favors the formation of HCNTs with a symmetric growth mode, and higher temperature of 700–750 °C benefits $\text{Fe}_3\text{C}/\text{HCNTs}$ hybrids growth. The as-prepared Fe_3O_4 , HCNTs and their hybrids perform different microwave absorbing behaviors. The RL of pure Fe_3O_4 is mainly due to

Table 1
EM absorption properties of some recently reported absorbing materials.

EM absorbing materials	RL _{min} (dB)	Frequency (GHz) (with RL below -10 dB)	Ref.
NiZn	-14.1	8.1–12.5	[44]
$\text{Fe}_3\text{O}_4/\text{ZnO}$	-22.6	10–15.9	[45]
$\text{Fe}_3\text{O}_4/\text{Cu Silicate}$	-23.5	3.5–13.9	[46]
$\text{Fe}_3\text{O}_4/\text{graphene}$	-11.7	15.4–16.5	[48]
FeNi/CNT	-15.4	9–10.5 and 15.7–18.0	[49]
$\text{Fe}_3\text{C}/\text{HCNTs}$	-21.5	7.3–11.4 and 16.4–18.0	This work at 750 °C

magnetic loss while the RL of the samples obtained at 450–600 °C is mainly owing to dielectric loss. The HCNT/Fe₃C hybrids obtained at 700–750 °C perform an improved microwave absorbing behavior especially in the low frequency range, which owing to the novel structure allowing for efficient match between the dielectric loss and the magnetic loss.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval on the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.compositesb.2016.09.003>.

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