Preparation of multi-walled carbon nanotube–Fe composites and their application as light weight and broadband electromagnetic wave absorbers

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Multi-walled carbon nanotube (MWCNT)–Fe composites were prepared via the metal organic chemical vapor deposition by depositing iron pentacarbonyl on the surface of MWCNTs. The structural and morphological analyses demonstrated that Fe nanoparticles were deposited on the surface of the MWCNTs. The electromagnetic properties of the MWCNTs were significantly changed, and the absorbing capacity evidently improved after the Fe deposition on the MWCNT surface. A minimum reflection loss of −29.4 dB was observed at 8.39 GHz, and the less than −10 dB bandwidth was about 10.6 GHz, which covered the whole X band (8.2–12.4 GHz) and the whole Ku band (12.4–18 GHz), indicating that the MWCNT–Fe composites could be used as an effective microwave absorption material.

Keywords: multi-walled carbon nanotube, nano composites, electrical properties, microwave absorber

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1. Introduction

Numerous studies have been conducted on high-performance and multi-functional microwave absorption materials for dealing with the electromagnetic (EM) pollution problem and the development of stealth technology for military platforms.[1–5] The traditional microwave absorbers face particular common problems, such as large specific gravity, narrow absorption bandwidth, and large match thickness.[6] Therefore, microwave absorption materials that exhibit wide wave band, strong absorption, light weight, and thin thickness have become the core of most research.

As a lightweight microwave absorber, multi-walled carbon nanotubes (MWCNTs) have been considerably researched because of their good compatibility and small density.[7,8] However, MWCNTs are resistive loss materials with no magnetic property and poor absorption property when used alone. Thus, MWCNTs are always used with magnetic loss materials to attain the desired electrical properties.[9–11] Carbonyl iron (CI) powders have a wide range of applications as absorbing materials with high saturation magnetization and relative permeability at microwave frequencies.[12,13] According to the related studies, the CI powders can effectively improve the high-frequency dielectric properties by coating iron on the samples.[14] However, the applications of CI are limited because of its narrow absorption bandwidth and heavy weight. Therefore, the deposition of iron pentacarbonyl [$Fe(CO)_5$] on the MWCNT surface is expected to produce a composite that possesses the above mentioned advantages, and is able to obtain remarkable absorption in the 2–18 GHz frequency range.

In this study, a process is developed to design an MWCNT–Fe composite via the metal organic chemical vapor deposition method, which has the following significant features: low deposition temperature, fast deposition, and flexible deposition rate.[15,16] The crystal structure, morphology, complex permittivity, complex permeability, and microwave absorption properties of the sample are also investigated.

2. Experiment

2.1. Sample preparation

Exactly 1 g of MWCNT powder (purity: > 90%, diameter: 10–30 nm, from Nanchang SUNNANO Co., Ltd.) and 15 mL of $Fe(CO)_5$ (99.9%, from Shaanxi XingHua Chemical Co., Ltd., carbonyl iron power plant) were placed in an airproof reactor and an evaporator, respectively. N_2 was passed through the system to ensure that the air in the tube was blown out. The MWCNT powder was heated and maintained at 200 °C, and $Fe(CO)_5$ was evaporated at 80 °C. The $Fe(CO)_5$ vapor was blown into the reactor by N_2 at a rate of 30 mL/min for 20 min. The N_2 flow was controlled by using a gas flow meter. An HH-SA digital thermostat oil bath pot was used to heat $Fe(CO)_5$. The pipings were coated with a layer of insulation sleeve to prevent $Fe(CO)_5$ gas condensation at low temperatures before it entered the reactor. To obtain a uniform coating, the reactor was vigorously and continuously stirred mechanically. MWCNT–Fe composites were obtained after slow cooling to room temperature, and the whole experiment was protected by N_2.

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2.2. Measurement of properties

The resulting crystalline phases were characterized using X-ray diffraction (XRD; D/max-IIB, Japan). The data were recorded using Cu $K\alpha$ radiation of 40.0 kV and 100.0 mA in the 2θ region, from 20° to 70°, with a scanning speed of 15°/min. The FEI Quatan250FEG field emission scanning electron microscopy (FESEM) and JEOL JEM-2100 transmission electron microscope (TEM) were employed for morphological analyses. The EM parameters (complex permeability and permittivity) were measured using a vector network analyzer (HP-8720ES) in the frequency range of 2–18 GHz. The samples used for the EM parameter measurements were prepared by dispersing the powders into paraffin wax at a mass fraction of 10% and then pressing the mixtures into a compact toroidal shape with outer and inner diameters of 7.0 mm and 3.0 mm, respectively.[4]

3. Results and discussion

3.1. Crystalline structure and morphology analysis

Figure 1(a) shows the XRD patterns of MWCNTs and MWCNT–Fe composites. The peaks of the samples at $2\theta = 26.6°$ are the characteristic XRD peaks of carbon (002). The figure shows that the MWCNT–Fe composites have a diffraction peak at $2\theta = 26.6°$, similar to that of the MWCNTs, whereas the intensity of the peak decreases. In addition, a (110) peak around $2\theta = 44.6°$ is observed in the XRD pattern of the MWCNT–Fe composites, which indicates that the shell layer is composed of iron. The FESEM images of MWCNTs and MWCNT–Fe composites are shown in Figs. 1(b) and 1(c), respectively. Figure 1(b) shows that the MWCNTs are wrapped together with high purity, and no granular amorphous carbon is observed on the surface. From Fig. 1(c), it is found that the surfaces of the MWCNTs are coated with nano-iron powder, and a small amount of iron in the form of large spherical particles gather around the MWCNTs. As shown in the TEM image of MWCNT–Fe (Fig. 1(d)), most of the MWCNT surface is coated with a layer of iron. Iron particles (deep color spherical particles) with an average diameter of approximate 20 nm are presented on the MWCNT surface. The EDS analysis shows that the major component of pure MWCNTs is carbon (97.87 wt.%), and the minimal iron (2.13 wt.%) is the activator of the MWCNT production. After Fe coating on the MWCNT surface, the content of Fe obviously increases to 25.13 wt.%, as shown in Fig. 1(e).

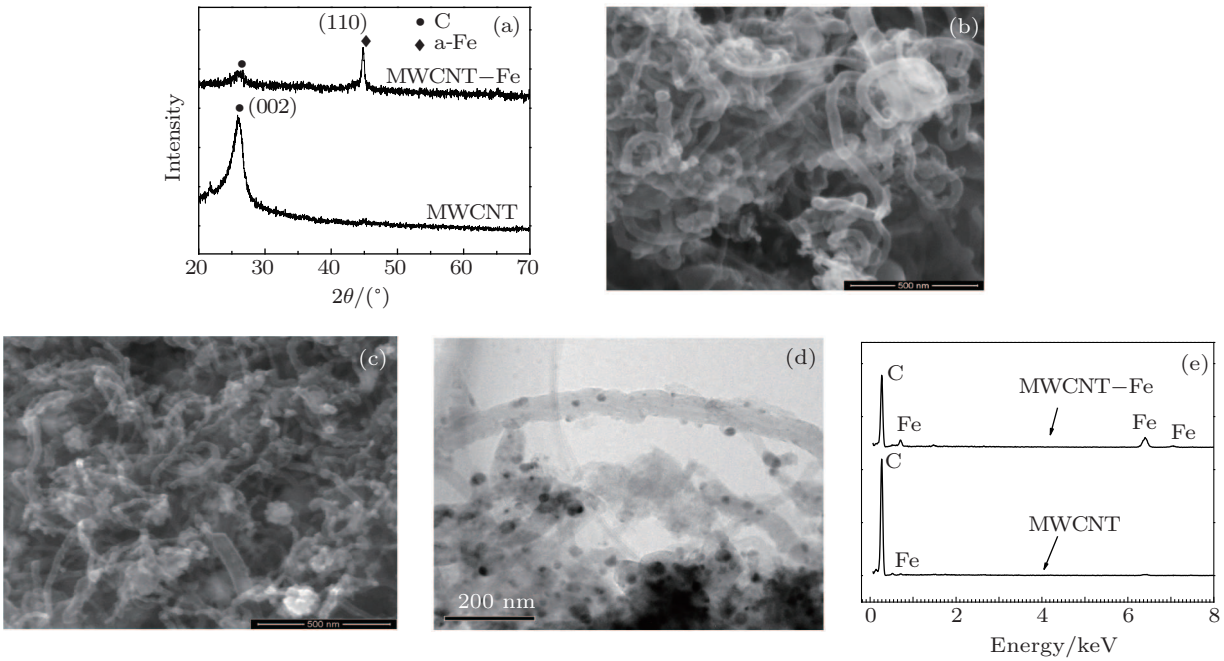


Fig. 1. (a) XRD patterns and (b), (c) FESEM images of MWCNTs and MWCNT–Fe composites. (d) TEM image of MWCNT–Fe composites. (e) EDS patterns of MWCNTs and MWCNT–Fe composites.

3.2. Complex permittivity and permeability

In Fig. 2(a), the real ε' and the imaginary ε'' parts of the complex permittivities of MWCNTs and MWCNT–Fe composites both exhibit significant variations with the frequency, and the ε'' values of the MWCNT–Fe composites are obviously higher than those of the MWCNTs at the 2–18 GHz range. The resistivity of the MWCNT–Fe composites is higher than that of the MWCNTs, which shows that the Fe shell can increase the conductivity of the sample.[17] This high resistivity is ascribed to the effective dispersion and the im-

provement of the microwave absorption. Multiple dielectric resonant behaviors exist in the complex permittivity of the MWCNT–Fe composites. The resonance behavior typically comes from space charge, dipole, ionic, and electronic polarizations.[18] The dipole polarization has a dominant function in the metal matrix composite and operates at high frequencies compared with the space charge polarization. The ionic and the electronic polarizations generally operate at THz and PHz, respectively.[18] Thus, the multiple dielectric resonant behavior of the complex permittivity should be derived from the dipole polarization in the MWCNT–Fe composites.

Figure 2(b) shows the real μ' and the imaginary μ'' parts of the complex permeability of the MWCNT–Fe composites as a function of frequency at the 2–18 GHz range. The μ' and μ'' values of the MWCNT–Fe composites gradually change with increasing frequency, which are in the ranges of 1.22–1.48 and 0.15–0.69, respectively. The data for the MWCNTs are not shown in Fig. 2(b) because their μ' and μ'' are almost 1 and 0, respectively. The general losses of microwave magnetic materials mainly come from eddy current losses, magnetization vector rotation, natural resonance, and magnetic domain wall resonance.[19] The magnetization vector rotation occurs only in a strong magnetic field, and the magnetic domain wall resonance at the microwave frequency is very small and can be neglected.[20] Therefore, the electromagnetic wave (EMW) loss in the MWCNT–Fe composites is primarily caused by eddy currents or natural resonances. If the MWCNT–Fe magnetic loss only is the eddy current loss, then $f^{-1}(\mu')^{-2}\mu''$ should be a constant.[21] Figure 2(c) shows $f^{-1}(\mu')^{-2}\mu''$ versus the frequency for the MWCNT–Fe composites. A downward trend is found as the frequency increases. Hence, the eddy current loss could be ruled out, and the MWCNT–Fe magnetic loss is dominated by the natural resonance.

Figure 2(d) shows the dielectric $(\tan\delta_\varepsilon = \varepsilon''/\varepsilon')$ and the magnetic $(\tan\delta_\mu = \mu''/\mu')$ losses that contribute to the microwave absorption. The dielectric and the magnetic losses increase after Fe coating on the MWCNT surface. The higher magnetic loss of the MWCNT–Fe composites compared with that of the pure MWCNTs is mainly due to the contribution of the two-dimension complex microstructures. Furthermore, a proper dielectric loss can also be obtained by coating a suitable Fe content on the MWCNT surface. The material is able to consume incoming EMW with a large attenuation constant α to achieve a low reflection.[22] The attenuation constants α of the MWCNTs and the MWCNT–Fe particles are shown in Fig. 2(e). After the Fe growth on the MWCNT surface, the attenuation constant increases significantly. This result means that the absorbing performance of the MWCNT–Fe composites is better than that of the pure MWCNTs.

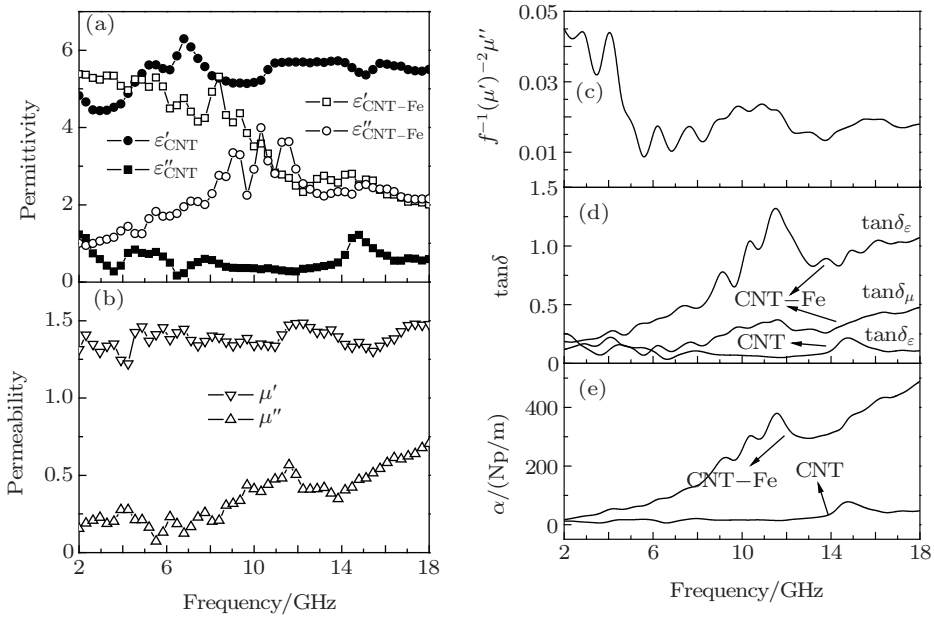


Fig. 2. (a) Complex permittivity, (b) complex permeability, (c) $f^{-1}(\mu')^{-2}\mu''$, (d) dielectric and magnetic loss factors, and (e) attenuation constant of the samples versus frequency.

3.3. Microwave absorption properties

Based on transmission line theory,[23,24] the reflection losses (RL) of MWCNTs and MWCNT–Fe composites with varying thicknesses are obtained and shown in Figs. 3(a) and 3(b), respectively. The figures indicate that the Fe coating on the MWCNT surface can effectively improve the absorbing properties of the MWCNTs. After the surface modification of the MWCNTs, an RL exceeding −10 dB is obtained at the

7.4–18.0 GHz frequency range. A minimum RL of −29.4 dB is found at 8.39 GHz, which corresponds to a matching thickness of 3.4 mm (Fig. 3(c)).

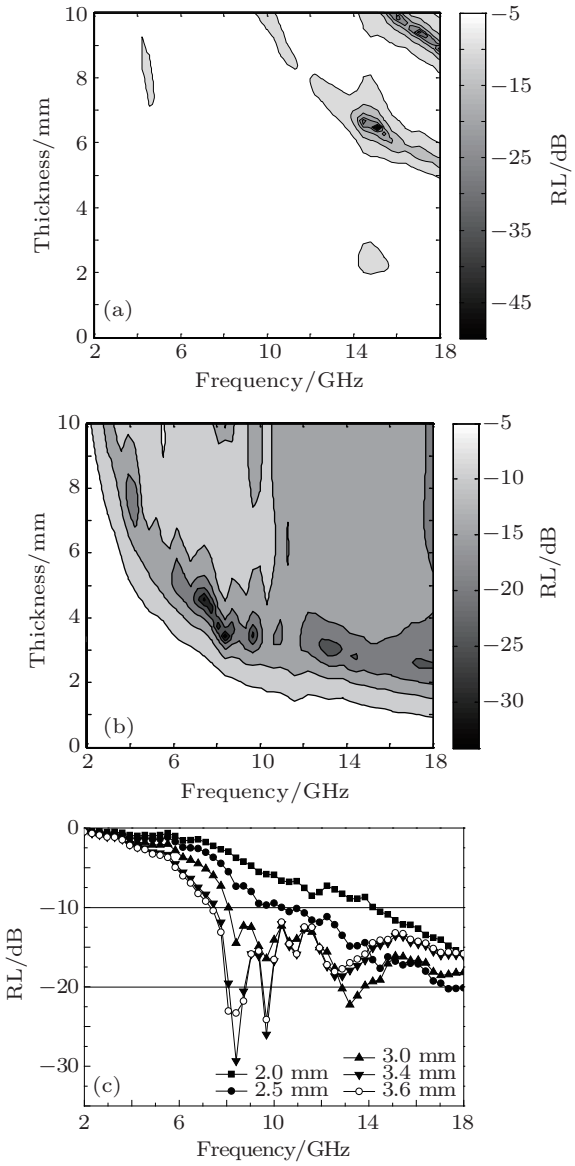


Fig. 3. Reflection losses of (a) MWCNTs and (b), (c) MWCNT–Fe composites with varying thicknesses.

4. Conclusion

The deposition of $Fe(CO)_5$ on the MWCNT surface successfully produced MWCNT–Fe composites, and the EMW absorbing properties of the MWCNTs were effectively improved. An RL exceeding −10 dB was obtained at the 7.4–18.0 GHz frequency range, with a minimum RL of −29.4 dB at 8.39 GHz, which corresponds to a matching thickness of 3.4 mm. This study developed a unique method for obtaining MWCNT–Fe composites with good absorption properties, simple process, and low cost, which can be potentially applied in engineering.

References

[1] Wang W J, Zang C G and Jiao Q J 2013 *Chin. Phys. B* **22** 128101
[2] Liu Y, Liu X X, Wand X J and Wen W 2014 *Chin. Phys. Lett.* **31** 047702
[3] Wei C Y, Shen X Q and Song F Z 2012 *Chin. Phys. B.* **21** 028101
[4] Liu Y, Liu X X and Wang X J 2014 *J. Alloy. Compd.* **584** 249
[5] Liu Y, Liu X X and Wang X J 2014 *Adv. Appl. Ceram.*
[6] Zhang T, Huang D Q, Yang Y, Kang F Y and Gu J L 2013 *Mat. Sci. Eng. B* **178** 1
[7] Rajesh K S, Narayanan T N, Reena Mary A P, Anantharaman M R, Anchal S, Robert V and Pulickel M A 2011 *Appl. Phys. Lett.* **99** 113116
[8] Wen F S, Zhang F and Liu Z Y 2011 *J. Phys. Chem. C* **115** 14025
[9] Lee D H, Seo S D, Lee G H, Hong H S and Kim D W 2014 *J. Alloy. Compd.* **606** 204
[10] Tong G X, Liu F T, Wu W H, Du F F and Guan J G 2014 *J. Mater. Chem. A* **2** 7373
[11] Yu L M, Li B, Sheng L M, An K and Zhao X L 2013 *J. Alloy. Compd.* **575** 123
[12] Min S K, Ying D L, Bong J P, Chun-Yeol Y and Hyoung J C 2012 *J. Ind. Eng. Chem.* **18** 664
[13] Ni X M, Zheng Z, Xiao K, Huang L and He L 2010 *Mater. Chem. Phys.* **120** 206
[14] Cheng Y L, Dai J M, Wu D J and Sun Y P 2010 *J. Magn. Magn. Mater.* **322** 97
[15] Manasevit H M 1968 *Appl. Phys. Lett.* **12** 156
[16] Li Z M, Li J P, Jiang H Y, Han Y B, Yin J Q, Xia Y J, Chang Y M, Zhang J C and Hao Y. 2013 *J. Cryst. Growth.* **368** 29
[17] Lacrevaz T, Flechet B, Farcy A, Torres J, Gros-Jean M, Bermond C, Vo T T, Cueto O, Blampey B, Angenieux G, Piquet J and Decrecyc F 2006 *Microelectron. Eng.* **83** 2184
[18] Dong X L, Zhang X F, Huang H and Zuo F 2008 *Appl. Phys. Lett.* **92** 013127
[19] Zhang S Y and Cao Q X 2012 *Mat. Sci. Eng. B* **177** 678
[20] Zhang X F, Dong X L, Huang H, Liu Y Y, Wang W N, Zhu X G, Lv B, Lei J P and Lee C G 2006 *Appl. Phys. Lett.* **89** 053115.
[21] Yang Y, Xu C L, Xia Y X, Wang T and Li F S 2010 *J. Alloy. Compd.* **493** 549
[22] Lu B, Huang H, Dong X L, Zhang X F, Lei J P, Sun J P and Dong C 2008 *J. Appl. Phys.* **104** 114313
[23] Naito Y and Suetake K 1971 *IEEE Trans. Microw. Theory Techn.* **19** 65
[24] Meshram M R, Agrawal N K, Sinha B and Misra P S 2004 *J. Magn. Magn. Mater.* **271** 207