J Low Temp Phys (2013) 170:261–267
DOI 10.1007/s10909-012-0748-7

Low Temperature Solution Synthesis and Microwave Absorption Properties of Multiwalled Carbon Nanotubes/Fe_3O_4 Composites

Q.C. Liu · J.M. Dai · Z.F. Zi · A.B. Pang · Q.Z. Liu · D.J. Wu · Y.P. Sun

Received: 4 June 2012 / Accepted: 13 September 2012 / Published online: 27 September 2012

Abstract Multiwalled carbon nanotubes (MWCNTs)/Fe_3O_4 nanocomposites were synthesized via a simple low temperature solution method. The phase structures and morphologies of the composite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results showed that the Fe_3O_4 spheres of about 150 nm were linked with MWCNTs. The microwave absorption properties of the MWCNTs/Fe_3O_4 nanocomposites were measured by vector network analysis (VNA). A wide region of microwave absorption was achieved due to dual magnetic and dielectric losses. When the matching thickness is 2 mm, the reflection loss (RL) of the sample exceeding −10 dB was obtained at the frequency range of 9.9–12.4 GHz, with an optimal RL of −29.8 dB at 11.04 GHz. A possible mechanism of the improved microwave absorption properties of the composites was discussed.

Keywords Composite materials · Chemical synthesis · Microwave absorption

1 Introduction

In recent years, the microwave absorption materials have attracted much attention because of their potential applications in wireless data communication, local area network, satellite television and self-concealing [1]. Therefore, the demands to develop

---

Q.C. Liu · J.M. Dai (✉) · Z.F. Zi · D.J. Wu · Y.P. Sun
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, P.R. China
e-mail: jmdai@issp.ac.cn

Q.C. Liu · Z.F. Zi · A.B. Pang · Q.Z. Liu
School of Physics and Electronics Information, Huaibei Normal University, Huaibei, Anhui 235000, P.R. China

electromagnetic absorbents with light weight and strong absorption over a broad frequency are ever increasing [2]. Traditional materials, such as carbon black, graphite and ferrite, cannot reach the standards because of their relatively low absorbing abilities [3]. As unilateral dielectric loss or magnetic loss materials are hard to attain impedance match condition, it still remains a great challenge to prepare new types of materials with excellent electromagnetic absorbing properties [4].

Multiwalled carbon nanotubes (MWCNTs) have attracted most interest in the microwave absorption and the applications in the electromagnetic interference shielding owing to their high complex permittivity, low density, and unique electrical transport behaviors [5]. However, the pure MWCNTs contribute to electromagnetic wave energy absorption mostly because of the dielectric loss. The dielectric permittivity and magnetic permeability are out of balance. Therefore, most of the electromagnetic wave radiation incident on MWCNTs is reflected, rather than absorbed. To optimize the performance of MWCNTs as microwave absorbers, it is necessary to modify MWCNTs by decorating with other magnetic nanomaterials, which are expected to exhibit ideal electromagnetic absorption properties. As a high saturation magnetization and low coercivity material, Fe_3O_4 may be a potential candidate for microwave absorption materials at high frequency over the gigahertz range [6]. There are many methods for the preparation of Fe_3O_4/MWCNTs hybrids such as solvo-thermal technique [7], chemical co-precipitation technique [8]. However, there are still some disadvantages in most of these processes such as poor dispersion of Fe_3O_4 and high reaction temperature. In order to solve these problems, low-temperature (120 °C) wet chemical preparation method was employed in this work to prepare MWCNTs/Fe_3O_4 nanocomposites. The dielectric, magnetic loss and microwave absorption properties were investigated by measuring the complex permittivity and permeability of the mixture of paraffin wax and MWCNTs/Fe_3O_4 nanocomposites.

2 Experimental Details

MWCNTs were supplied by Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. The MWCNTs were pretreated with 2 $\mathrm{mol\,L^{-1}}$ nitric acid at 60 °C for 48 h and then washed with distilled water several times until the pH value reached neutral. The resulting MWCNTs are dried in vacuum at 60 °C for further use. All the other reagents used in the experiments were of analytical grade and used without further purification. In a typical synthesis, 0.2 g NaOH was dissolved into 30 mL ethanolamine under stirring. Then the pre-treatment MWCNTs (20–60 mg), 2 mL $Fe(CO)_5$ and 10 mL hydrazine hydrate (85 %) were added and sonicated for 10 min. The as-formed brown solution was transformed to a 50 mL Teflon-lined stainless steel autoclave and kept at 120 °C for 24 h without stirring. The resulted black powder was washed with distilled water and ethanol three times, respectively, and collected with the aid of a magnet. The washed precipitates were dried in a vacuum oven at 60 °C for 8 h. With MWCNTs of different weights (20 mg, 40 mg, 60 mg) adding to the reaction system, the final MWCNTs/Fe_3O_4 inorganic hybrid materials were labeled as S(1), S(2), S(3), respectively.

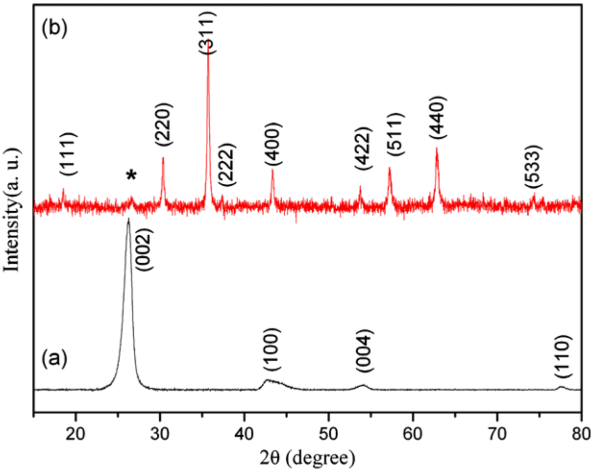


Fig. 1 XRD pattern of MWCNTs (**a**) and MWCNTs/Fe_3O_4 (**b**) (Color figure online)

The phase identification was performed by X-ray diffraction (XRD) on a Bruker Advance D8 X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). The morphologies and chemical composition of the samples were observed by using JEOL-6610LV scanning electron microscopy (SEM), Hitachi H-7650 transmission electron microscopy (TEM) and energy-dispersive X-ray spectrometry (EDS, X-Max, Oxford Instruments). The electromagnetic parameters of the samples were investigated by a vector network analyzer (VNA, AV3629D) by mixing uniformly with 30 wt% molten paraffin wax.

3 Results

Figure 1 shows the XRD patterns of the MWCNTs and MWCNTs/Fe_3O_4 inorganic hybrid materials. In Fig. 1(a), the diffraction peaks at $2\theta = 26.25°$, $42.25°$, $53.97°$, and $77.28°$ are assigned to (002), (100), (004), (110) planes of MWCNTs, respectively. In Fig. 2(b), all the peaks, except for the peak marked by an asterial referring to the typical Bragg peak for pristine MWCNTs, can be indexed as face centered cubic Fe_3O_4 (JCPDS card No. 85-1436). No evidence of impurities such as α-Fe_2O_3 or γ-Fe_2O_3 is found in the XRD pattern. Therefore, a kind of magnetite-MWCNTs heterostructure was formed.

The morphologies and structures of MWCNTs/Fe_3O_4 inorganic hybrid were investigated by SEM and TEM. Figure 2(a) shows a typical SEM image of the MWCNTs /Fe_3O_4 inorganic hybrid. It can be found that the Fe_3O_4 spheres of about 150 nm were linked with MWCNTs. The Fe_3O_4 nanospheres were strongly attached to the surface of MWCNTs. Figure 2(b) is the TEM image of the MWCNTs/Fe_3O_4 inorganic hybrid. We can clearly see that the MWCNTs are wrapped by some Fe_3O_4 nanospheres. The EDS pattern of hybrid is presented in Fig. 2(c). It is quite obvious that the hybrid consist of Fe, O and C elements without any detectable contaminant elements. From the inserted photograph in Fig. 2(c), we can see that as-synthesized MWCNTs/Fe_3O_4 inorganic hybrid can be easily dispersed in ethanol and quickly separated from their dispersion by holding the sample close to a commercial magnet.

Fig. 2 SEM image (**a**), TEM image (**b**) and EDS (**c**) of S(2) (*Insert*: Photograph of CNTs/Fe_3O_4 inorganic hybrid dispersed in ethanol (*left*) and its response to a magnet (*right*)) (Color figure online)

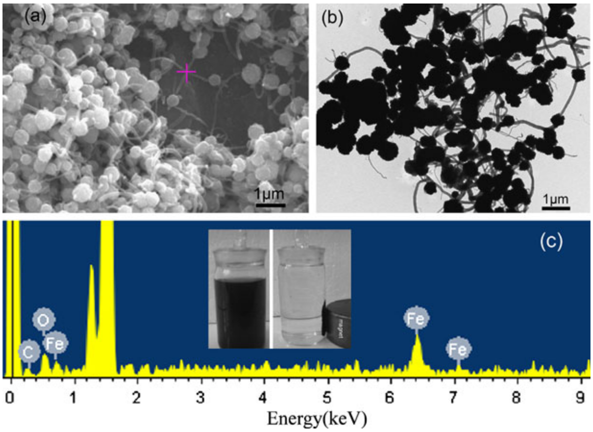
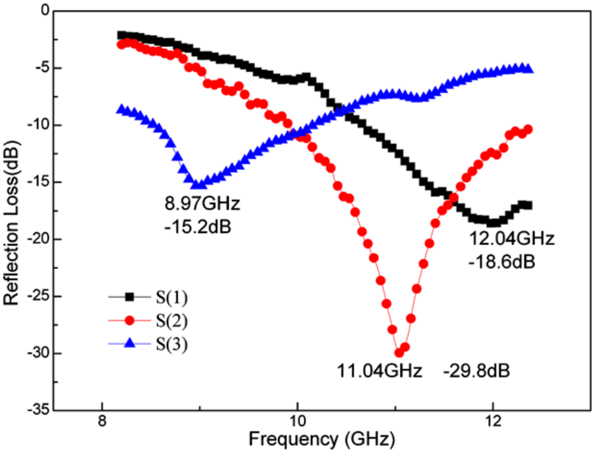


Fig. 3 Reflection losses for MWCNTs/Fe_3O_4 nanocomposites with the same thickness (2.0 mm) (Color figure online)



The reflection loss (RL) abilities of the three samples as a function of frequency are shown in Fig. 3. It can be seen that when the weight of MWCNTs is 20 mg, the maximum RL is −18.6 dB at 12.04 GHz. When the weight of MWCNTs increases to 60 mg, the maximum RL decreases to −15.2 dB at 8.97 GHz. However, an optimal RL of −29.8 dB is reached at 11.04 GHz for the absorber containing 40 mg MWCNTs. Meanwhile, the absorption exceeding −10 dB (more than 90 % of the incident EM-wave is absorbed, which is a typical target from application point of view) is obtained in the 9.92–12.4 GHz range at the thickness of 2.0 mm. The enhanced absorption in this composite is attributed to the existence of a synergistic effect between dielectric loss and magnetic loss at an appropriate mass ratio of the MWCNTs to the Fe_3O_4 nanospheres. It is also clearly found that the maximum RL moves toward low frequency region from 12.04 to 8.97 GHz when the weight of MWCNTs increases from 20 mg to 60 mg.

In order to investigate the intrinsic reasons for microwave absorption, we measured the complex permittivity and permeability of the MWCNTs/Fe_3O_4/paraffin composites by the coaxial line method. Figures 4(a) and 4(b) show the frequency dependence

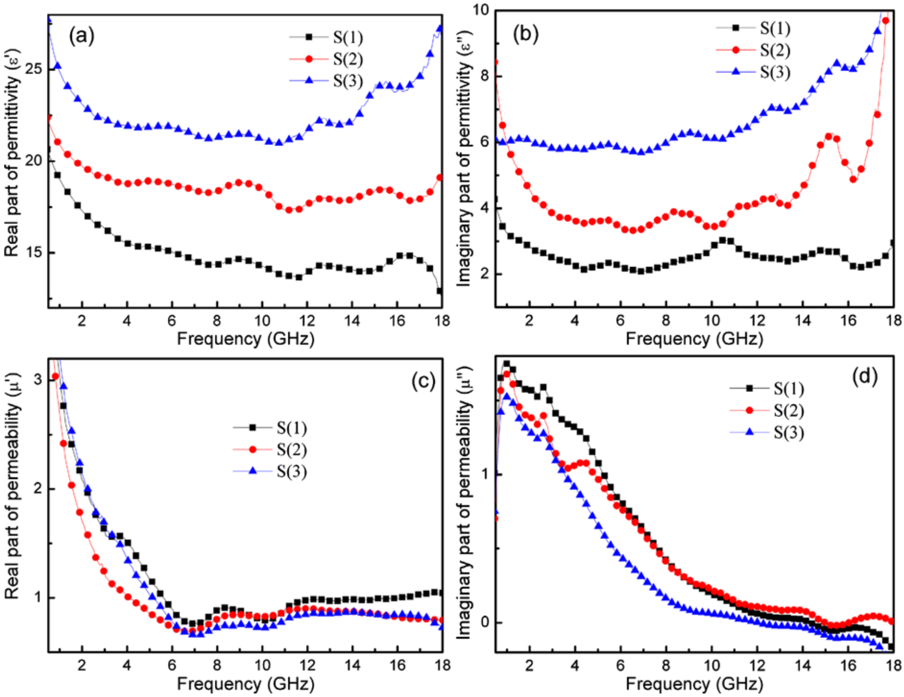


Fig. 4 The frequency dependence real part ε' (**a**), imaginary part ε'' (**b**) of complex permittivity and real part μ' (**c**), imaginary part μ'' (**d**) of complex permeability (Color figure online)

of the real part (ε') and imaginary part (ε'') of the relatively complex permittivity. It can be found that the values of ε' and ε'' are in the range of 12.5–21 and 2.1–4.2, respectively, over the 0.5–18 GHz frequency range when the weight of MWCNTs is 20 mg. Both ε' and ε'' values are relatively higher than those of pure Fe_3O_4 or Fe_3O_4/C [9]. The permittivity spectra of the composites apparently increase as the MWCNTs mass fractions increase. When the weight of MWCNTs increases to 40 mg and 60 mg, the ε' value accordingly increases to 18–22 and 22.5–26, while the ε'' increases to 3.5–9 and 6–10 in the 0.5–18 GHz range. The values of ε' and ε'' represent the energy storage and dissipation capability, respectively. The relatively higher ε'' values of the MWCNTs/Fe_3O_4 hybrid materials indicate a lower electrical resistivity than other microwave-absorption materials such as carbon-coated Ni nanocapsules [10] and carbon-coated Fe nanocapsules [11]. According to the free electron theory [12], $\varepsilon'' = 1/\rho\omega\varepsilon_0$, where ω, ε_0, and ρ are the angular frequency, the dielectric constant of free space, and the resistivity, respectively, it can be speculated that MWCNTs/Fe_3O_4 composites with more MWCNTs components have higher electrical conductivities, i.e., lower electrical resistivities. To our knowledge, MWCNTs can provide conductive bridges between Fe_3O_4 nanospheres based on their special morphology and lead to the increase of the ε'' in composites. Thus, the dielectric loss increases with the increase of MWCNTs mass fraction.

Figures 4(c) and 4(d) show the real part (μ') and imaginary part (μ'') of the relative complex permeability of the MWCNTs/Fe_3O_4 hybrid materials. The values of μ' and

μ'' exhibit the same trend, i.e., the μ' exhibits an abrupt decrease from 3.5 to 0.8 in the 0.5–6.5 GHz and retains an approximate constant over 6.5–18 GHz, while the μ'' presents a normal natural resonance peak at 1.2 GHz and then decreases with frequency. Meanwhile, the values of μ' and μ'' of S(1) are uniformly larger than those of S(2) and S(3) in the range of 0.5–18 GHz.

In general, the excellent microwave absorbing properties are strongly dependent on the efficient complementarities between the relative permittivity and permeability. Only magnetic loss or only dielectric loss leads to weak microwave attenuation. The design of microwave absorbing materials requires two important conditions: impedance matching characteristic and attenuation characteristic. Compared with the permeability, the permittivity of S(3) is so large that it is difficult to attain impedance match, which means most of the incident microwave can not transmit into the absorbing materials. Hence the microwave absorption property of S(3) does not improve correspondingly. For S(1), the real part and imaginary part of permittivity are relatively lower, so the dielectric loss is very small and the microwave absorption property does not improve either. However, the proper complex permittivity and permeability can reach simultaneously in S(2). An optimal RL of −29.8 dB is achieved at 11.04 GHz for the absorber containing 40 mg MWCNTs. This indicates that proper amount of MWCNTs is critical in possessing higher microwave absorption in the X-band.

4 Conclusions

In summary, MWCNTs/Fe_3O_4 nanocomposites have been prepared conveniently by simple chemical solution method at low temperature. The excellent microwave absorption properties in X-band have been obtained due to proper combination of the complex permeability and permittivity resulting from the magnetic Fe_3O_4 nanospheres and lightweight dielectric MWCNTs. For the most excellent microwave absorption properties in X-band, it is found that the RL exceeds −10 dB at the frequency range of 9.9–12.4 GHz for 40 mg MWCNTs. The improvement in absorbing property can be ascribed to the better magnetic loss and matched characteristic impedance. It is believed that MWCNTs/Fe_3O_4 nanocomposites are ideal microwave absorption materials with lighter weight, stronger and wider frequency microwave absorption in X-band.

Acknowledgements This work was financially supported by the National Nature Science Foundation of China (10874051, 51002156, and 11104098).

References

1. A. Katsounaros, K.Z. Rajab, Y. Hao, M. Mann, W.I. Milne, Appl. Phys. Lett. **98**, 203105 (2011)
2. R. Liu, N. Lun, Y.X. Qi, H.L. Zhu, Y.J. Bai, J.Q. Bi, J. Phys. D, Appl. Phys. **44**, 265502 (2011)
3. C. Wang, X. Han, P. Xu, X. Zhang, Y. Du, S. Hu, J. Wang, X. Wang, Appl. Phys. Lett. **98**, 072906 (2011)
4. R.C. Che, L.M. Peng, X.F. Duan, Q. Chen, X.L. Liang, Adv. Mater. **16**, 401 (2004)
5. L. Deng, M. Han, Appl. Phys. Lett. **91**, 023119 (2007)

6. X. Li, B. Zhang, C. Ju, X. Han, Y. Du, P. Xu, J. Phys. Chem. C **115**, 12350 (2011)
7. L.Q. Jiang, L. Gao, Chem. Mater. **15**, 2848 (2003)
8. Y. Zhan, R. Zhao, Y. Lei, F. Meng, J. Zhong, X. Liu, J. Magn. Magn. Mater. **323**, 1006 (2011)
9. Q.C. Liu, Z.F. Zi, D.J. Wu, Y.P. Sun, J.M. Dai, J. Mater. Sci. **47**, 1033 (2012)
10. X.F. Zhang, X.L. Dong, H. Huang, Y.Y. Liu, W.N. Wang, X.G. Zhu, B. Lv, J.P. Lei, C.G. Lee, Appl. Phys. Lett. **89**, 053115 (2006)
11. X.F. Zhang, X.L. Dong, H. Huang, B. Lv, J.P. Lei, C.J. Choi, J. Phys. D, Appl. Phys. **40**, 5383 (2007)
12. S. Ramo, J.R. Whinnery, T.V. Duzer, *Fields and Waves in Communication Electronics* (Wiley, New York, 1984)