Magnetic CoFe$_2$O$_4$/carbon nanotubes composites: fabrication, microstructure and magnetic response

Panfeng Wang, Jingcai Xu, Yanbing Han, Bo Hong, Hongxiao Jin, Dingfeng Jin, Xiaoling Peng, Jing Li, Hongliang Ge* and Xinqing Wang†

College of Materials Science and Engineering, Zhejiang Province Key Laboratory of Magnetism, China Jiliang University, Hangzhou 310018, China

* hongliangge@cjlu.edu.cn
† wxqnano@cjlu.edu.cn

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By combining the unique microstructure of carbon nanotubes (CNTs) with the good magnetism of CoFe$_2$O$_4$ ferrites, CoFe$_2$O$_4$/CNTs nanocomposites were prepared by the solvothermal method for the application of targeting therapy and tumor hyperthermia. X-ray diffraction (XRD), thermal gravity analysis (TGA), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM) were introduced to study the influence of the solvothermal temperature, time and the CNTs content on the microstructure and magnetic properties of CoFe$_2$O$_4$/CNTs nanocomposites. The diameter of CoFe$_2$O$_4$ nanoparticles coating on the surface of CNTs and the saturation magnetization ($M_s$) increased with the solvothermal temperature. CoFe$_2$O$_4$/CNTs nanocomposites prepared at 180°C, 200°C and 220°C exhibited superparamagnetism at room temperature, while the samples prepared at 240°C and 260°C presented ferromagnetism. And the solvothermal time and CNTs content slightly affected the microstructure and magnetic properties, $M_s$ and coercivity ($H_c$) increased slightly with the increasing solvothermal time and the decreasing CNTs content.

Keywords: Carbon nanotubes; CoFe$_2$O$_4$ nanoparticles; magnetic properties.

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1. Introduction

Owing to the unique one-dimensional tubular structure, excellent physical and chemical properties, strong mechanical properties and special electromagnetic properties, carbon nanotubes (CNTs) have presented the huge potential application
in the fields of drug carriers,\textsuperscript{1} hydrogen storage,\textsuperscript{2} nanocomposites and electrical nanodevices.\textsuperscript{3,4} Moreover, due to the large specific surface area and hollow tubular structure, CNTs could act as an excellent template for nanocomposites, and other functional materials could be implanted into the hollow structure or coated on the surface of CNTs to fabricate CNTs nanocomposites. Nowadays, CNTs-based magnetic nanocomposites have been attracting much interest for the potential applications in magnetic data storage, magnetic resonance imaging, electrochemical biosensor, targeting drug carriers and tumor thermotherapy fields.\textsuperscript{5,6}

Owing to the easier preparation and controllable structure, CNTs-coated magnetic nanocomposites have been attracting much more interest compared with CNTs-filled nanocomposites. Combining the magnetic properties of magnetic materials with the excellent chemical and physical performance of CNTs, CNTs-based magnetic nanocomposites exhibited unique mechanical, electrical and magnetic properties. Liu et al.\textsuperscript{7} prepared the \( \text{NiFe}_2\text{O}_4/\text{CNTs} \) magnetic nanocomposites using the Ni(NO\textsubscript{3})\textsubscript{2} and Fe(NO\textsubscript{3})\textsubscript{3} as precursor by the solvothermal method at 110\( ^\circ \text{C} \) for 6 h, and the electrical conductivity of the prepared sample was higher than the pure \( \text{NiFe}_2\text{O}_4 \). Jiang et al.\textsuperscript{8} synthesized CoFe\textsubscript{2}O\textsubscript{4}/CNTs superparamagnetic nanocomposites by the solvothermal method and the saturation magnetization (\( M_s \)) was about 29.6 emu \( \cdot \) g\textsuperscript{−1}. Wang et al.\textsuperscript{9} prepared Fe\textsubscript{3}O\textsubscript{4}/CNTs magnetic nanocomposites using Fe\textsuperscript{2+} and Fe\textsuperscript{3+} salts as the precursors with the co-precipitation method. Li et al.\textsuperscript{10} synthesized the SrFe\textsubscript{12}O\textsubscript{19}/CNTs nanocomposites by the sol–gel method, and the surface of CNTs was coated more completely with SrFe\textsubscript{12}O\textsubscript{19} nanoparticles. Fan et al.\textsuperscript{11} synthesized \( \gamma\)-Fe\textsubscript{3}O\textsubscript{3}/CNTs nanocomposites using Fe(CO)\textsubscript{5} as precursor after aged at 180\( ^\circ \text{C} \) for 1 h under the vacuum condition. Wan et al.\textsuperscript{12} prepared the uniform Fe\textsubscript{3}O\textsubscript{4}/CNTs by refluxing the solution of acetylacetone iron, triethylene glycol and CNTs at 278\( ^\circ \text{C} \) under hydrogen atmosphere. Chen et al.\textsuperscript{13} prepared the Ni–Co alloy coated CNTs by the electroless plating method, which had the potential application in the magnetic recording field.

Combining nanotechnology with modern medicine, magnetic nanoparticles could be applied in the targeting therapy of tumor, and it was helpful to overcome the disadvantage of traditional drug delivery system. As the carrier of targeting therapy, magnetic nanoparticles could realize the exact orientation of targeting therapy and reduce the dosage of the medicine. The magnetic nanocomposites applied in this field should possess a high magnetic response. So far, the following magnetic materials: Fe\textsubscript{3}O\textsubscript{4}, Fe, \( \gamma\)-Fe\textsubscript{2}O\textsubscript{3}, Ni, CoFe\textsubscript{2}O\textsubscript{4} and Co–Fe alloy\textsuperscript{14–17} were used in targeting therapy. The hollow tubes of CNTs-coated magnetic nanocomposites could absorb the drugs and carry the drug to the lesion location and release them. In order to further improve the magnetic response characteristics of targeting drug carrier, CoFe\textsubscript{2}O\textsubscript{4}/CNTs nanocomposites were synthesized by the solvothermal method in this paper. And then the influence of solvothermal temperature, time and CNTs content on the microstructure and magnetic response of CoFe\textsubscript{2}O\textsubscript{4}/CNTs nanocomposites were discussed in detail.
2. Experimental

CNTs used in this study were prepared by CVD method using C$_2$H$_2$ as precursor and Fe/Al$_2$O$_3$ as catalysts. CNTs were dispersed in the mixed solution of the concentrated sulfuric and nitric acids (1:3 by volume), then the mixture were refluxed at 120°C for 5 h, followed by diluting, filtering and washing with the distilled water several times until the pH reached 7. Finally, the purified CNTs could be obtained after drying at 100°C for 10 h. All other chemical reagents were of analytical grade.

Typically, 3 mmol FeCl$_3$·6H$_2$O and 1.5 mmol CoCl$_2$·6H$_2$O were dissolved in 20 ml ethylene diglycol (DEG) at 90°C (marked as A). After stirring for 30 min, 5 ml diethanolamine (DEA) was injected into the A solution, and then 10 ml DEG solution with 12 mmol NaOH was dropped into the A solution. Finally, 10 ml DEG solution with the amount of CNTs (10 mg, 30 mg and 50 mg) was added. After vigorous stirring for 30 min, the mixed liquids were implanted into an autoclave and solvothermal treated at the temperature (180, 200, 220, 240 and 260°C) for a fixed time (6 h, 8 h and 10 h). The products were separated by the magnetic field and washed until the pH reached 7 using the distilled water and alcohol repeatedly.

The phase structure, thermal stability and morphology of CNTs and CoFe$_2$O$_4$/CNTs nanocomposites were characterized by X-ray diffraction (XRD, DX-2700, Cu target, $\lambda = 0.154$ nm, $U = 40$ KV, step was 0.02°), thermal gravity analysis (TGA-DSC, SDT Q600, in air atmosphere, heating rate was 0.5°C·min$^{-1}$) and transmission electron microscope (TEM, JEM-2100). And vibrating sample magnetometer (VSM, LakeShore-7407, up to 2T at room temperature) was used to measure and analyze the magnetic properties of CoFe$_2$O$_4$/CNTs magnetic nanocomposites.

3. Results and Discussion

The influence of the solvothermal temperature on the microstructure and magnetic properties of CoFe$_2$O$_4$/CNTs nanocomposites was discussed. All the samples were solvothermal treated for 10 h with 30 mg CNTs in solution. XRD patterns of the as-prepared CoFe$_2$O$_4$/CNTs nanocomposites and CNTs were presented in Fig. 1. And the intensity of all peaks was normalized according to the maximum peak. As for the pattern of CNTs, there were a sharp peak and a broad peak located at 2θ = 26.4° and 42.6°, respectively, which presented the existence of CNTs. As for the patterns of CoFe$_2$O$_4$/CNTs nanocomposites, the obvious diffraction peaks of CNTs at 180°C and 200°C could be observed. The diffraction peaks of FeCO$_3$ and CoO were detected because of the incomplete reaction at the lower temperature. And the oxide or carbide presented the low valance states for the reducibility of carbon. With the increasing solvothermal temperature, the intensity of diffraction peaks of the FeCO$_3$ and CoO gradually decreased and disappeared completely at 260°C. Moreover, the obvious diffraction peaks of CoFe$_2$O$_4$ spinel phase structure with the space group Fd-3m [227] were detected and marked with “*”.

With the increasing solvothermal temperature, the intensity of diffraction peaks of CoFe$_2$O$_4$ gradually
Fig. 1. XRD patterns of as-prepared CoFe$_2$O$_4$/CNTs at different solvothermal temperatures and purified CNTs.

Fig. 2. TGA curves of CoFe$_2$O$_4$/CNTs and purified CNTs (inset).

increased, indicating that the content and crystallinity of CoFe$_2$O$_4$ particles in the CoFe$_2$O$_4$/CNTs nanocomposites increased (accorded with the results of TEM and TGA). For the samples at higher temperature, the CNTs peaks were normalized according to the CoFe$_2$O$_4$ maximum peak. As the results, the CNTs peaks were pressed to some extent and difficult to distinguish.

TGA curves of CNTs and CoFe$_2$O$_4$/CNTs nanocomposites were shown in Fig. 2. From the weight loss between 450°C and 650°C of CNTs (see the inset of Fig. 2),
Fig. 3. TEM images of CoFe$_2$O$_4$/CNTs at different solvothermal temperatures: (a) 180°C, (b) 220°C, (c) 240°C and (d) 260°C.

it was concluded that the purity of CNTs was about 95%. And TGA curves of CoFe$_2$O$_4$/CNTs nanocomposites showed three-step weight loss. The first gentle slope of the weight loss occurred in the range of 25–240°C should be attributed to the loss of absorbed water. The second steep slope of the weight loss at about 250°C was the decomposition of the impure phase of FeCO$_3$ and the amorphous carbon (oxidized by strong-acid), which disappeared for the sample at 260°C accorded with the analysis of XRD. It could be observed a obvious weight loss ranged from 300°C to 500°C at the third slope, which was the oxidation of CNTs. The final residue of CoFe$_2$O$_4$/CNTs nanocomposites, which consist of CoFe$_2$O$_4$ and impurity, increased from 40 wt.% (180°C) to 95 wt.% (260°C). It could be concluded that the weight ratio of the CoFe$_2$O$_4$ increased with the increasing solvothermal temperature. Moreover, the decomposition temperature (about 350°C) of CoFe$_2$O$_4$/CNTs nanocomposites was lower than the pure CNTs (about 520°C), this should be attributed to the catalysis of Co$_x$Fe$_y$ compounds (deoxidized by amorphous carbon). And the weight increased a little for the Co$_x$Fe$_y$ compounds, which were oxidated to CoFe$_2$O$_4$ when the temperature was higher than 550°C.

TEM was introduced to observe the morphology of CoFe$_2$O$_4$/CNTs nanocomposites, whose corresponding photos were given in Fig. 3. CoFe$_2$O$_4$ nanoparticles coated on CNTs were observed obviously. With the lower solvothermal temperature of 180°C and 220°C, the one-dimensional hollow tube microstructure of CNTs
was detected. But this hollow tube structure became inconspicuous at 240°C and 260°C due to the higher coating efficiency of CoFe$_2$O$_4$ nanoparticles. The diameter of CoFe$_2$O$_4$ nanoparticles was uniform (about 10 nm) at lower temperature (180°C and 200°C) and increased with the solvothermal temperature, which was consistent with XRD results. Moreover, a few dissociative CoFe$_2$O$_4$ nanoparticles were separated from CoFe$_2$O$_4$/CNTs nanocomposites.

The magnetic properties of CoFe$_2$O$_4$/CNTs nanocomposites were discussed by VSM in Fig. 4. The coercivity ($H_c$) of the samples at 180°C, 200°C and 220°C was close to zero and these samples exhibited superparamagnetism. According to the XRD analysis and TEM images, the diameter of CoFe$_2$O$_4$ nanoparticles on CNTs was about 10 nm and smaller than the superparamagnetic critical size of CoFe$_2$O$_4$. With the increasing temperature, the diameter increased up to critical size, and then $H_c$ increased. $H_c$ of CoFe$_2$O$_4$/CNTs nanocomposites at 240°C was 692 Oe and reached 1960 Oe at 260°C. As a result, the magnetic hysteretic loops indicated that CoFe$_2$O$_4$/CNTs exhibited ferromagnetism with the solvothermal temperature of 240°C and 260°C. Based on the results from the XRD, TGA and TEM, the ratio of CoFe$_2$O$_4$ to CNTs increased, and $M_s$ increased from 14 emu/g (180°C) to 76 emu/g (260°C) with the solvothermal temperature accordingly. Furthermore, the as-prepared sample at 260°C was easily separated from the de-ioned water with an outer magnet with the surface field of 1800 Oe in the inset of Fig. 4. Usually, the high $M_s$ could ensure that the samples possess good magnetic response, which was helpful for the application in the field of targeting drug carrier, while the targeting carriers with large $H_c$ would lead to the larger hysteresis losses in the high frequency magnetic field, and which had good potential application in the field of tumor hyperthermia.

In order to further optimize the properties, the influence of the solvothermal time on the morphology and magnetic properties of CoFe$_2$O$_4$/CNTs nanocomposites...
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Fig. 5. Hysteretic loops, XRD and TGA curves of as-prepared CoFe$_2$O$_4$/CNTs for different times.

were also considered, which showed the similar behavior in Fig. 5. All the samples were prepared at 260°C with 30 mg CNTs in solution. It could be concluded that the crystallinity of CoFe$_2$O$_4$ particles slightly increased from XRD patterns and the CoFe$_2$O$_4$ content increased from 88 wt.% to 92 wt.% with the increasing solvothermal time. With the increasing CoFe$_2$O$_4$ content, $M_s$ increased from 67 emu/g to 76 emu/g, $H_c$ increased from 1572 Oe to 1960 Oe, which accorded with the above results from XRD and TGA.

Finally, the influence of the different content of CNTs (10 mg, 30 mg and 50 mg) on the morphology and magnetic properties of CoFe$_2$O$_4$/CNTs nanocomposites (260°C, 8 h) was taken into account and discussed in Fig. 6. With the increasing CNTs content, the smoothness of XRD curves with 50 mg CNTs became relative slightly worse, it could be explained for the decreasing CoFe$_2$O$_4$ content and crystallinity. And the CoFe$_2$O$_4$ content increased from 81 wt.% to 89 wt.% with the decreasing CNTs content. Besides, the residue of the samples with 30 mg and 10 mg CNTs was nearly same. Accordingly, the difference of the XRD and VSM curves between the samples with 10 mg and 30 mg was hardly found, which indicated that the coating density of CoFe$_2$O$_4$ particles reached saturation. TEM images were shown in Fig. 7. The morphology of these samples was similar to those in Fig. 3, and many CoFe$_2$O$_4$ nanoparticles were coated on the surface of CNTs. As for the sample with 10 mg CNTs, the size distribution was not uniform and the maximum size of CoFe$_2$O$_4$/CNTs nanocomposites could reach 40 nm. With the increasing content of CNTs, the possibility of CoFe$_2$O$_4$ coating on CNTs decreased and the diameter of CoFe$_2$O$_4$ nanoparticles decreased to some extent. From the above results, the optimum conditions to synthesize CoFe$_2$O$_4$/CNTs nanocomposites was found to be solvothermal treated at 260°C for 8 h with 30 mg CNTs.
4. Conclusion

CoFe$_2$O$_4$/CNTs nanocomposites were prepared by the solvothermal method, then the influence of the solvothermal temperature, time and the content of CNTs on the morphology and magnetic properties of CoFe$_2$O$_4$/CNTs was discussed in detail. The solvothermal temperature greatly affected the morphology and the magnetic properties, while the solvothermal time and the content of CNTs hardly affected them. And the samples prepared at lower temperature at 180°C, 200°C and 220°C exhibited superparamagnetism and those prepared at 240°C and 260°C showed ferromagnetism. Thus, the CoFe$_2$O$_4$/CNTs nanocomposites with $M_s$ of 75 emu/g and $H_c$ of 1800 Oe were synthesized at 260°C for 8 h with 30 mg CNTs, which had the potential application in tumor hyperthermia.

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Fig. 6. Hysteretic loops, XRD and TGA curves of CoFe$_2$O$_4$/CNTs with different content of CNTs.

Fig. 7. TEM images of the as-prepared CoFe$_2$O$_4$/CNTs (from left to right: 10 mg, 30 mg and 50 mg).
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