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Decoration of carbon nanotubes with iron oxide

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Abstract

A magnetic composite of multiwalls carbon nanotubes (MWNTs) decorated with iron oxide nanoparticles was synthesized successfully by a simple and effective chemistry precipitation method. The composite was characterized by X-ray diffraction analysis (XRD), Mössbauer spectrum (MS), transmission electron microscopy (TEM), and Fourier transform spectroscopy (FTIR) techniques. The patterns of XRD and MS indicated that MWNTs, γ-Fe_2O_3, and Fe_3O_4 coexisted in the composite. The TEM observation indicated that the nanoparticles of iron oxide were attached on the surface of the MWNTs, and the sizes of the particles ranged from 25 to 80 nm. FTIR spectra showed that SO_4^- functional groups existed on the surface of MWNTs after modification by sodium dodecylbenzene sulfonic acid (SDBS), which could immobilize Fe^{3+} ions onto the MWNTs. The hysteresis loops of the MWNTs and decorated MWNTs were measured by vibrating sample magnetometer (VSM), and the results showed that the composite was ferromagnetism with the saturated magnetization of 20.07 emu/g, and the coercive of 163.44 Oe.

Keywords: Multiwalls carbon nanotubes; Composite; Decorating; Magnetic properties; Iron oxide

1. Introduction

Carbon nanotubes (CNTs) have received a considerable amount of attention over the past decade from the view point of scientific studies and industrial applications [1]. Decoration of the surface of CNTs can improve dispersity of CNTs in solvents [2] or impart new optical, electric, magnetic properties of CNTs [3–6]. Many efforts have been devoted to decorate CNTs with diverse organic compound by the covalent attachment, polymer wrapping and surfactant treatment by non-covalent attachment [7]. Various CNT-based composites have been derived from decorating CNTs with metals, metal oxides, and semiconducting nanoparticles [8–11]. The resultant CNTs derivations show promising features for nanoelectric and other applications.

Recently, more and more researches have been conducted towards decorating CNTs with iron oxide and preparing magnetic carbon nanomaterials due to their potential applications in electric device, magnetic data storage and heterogeneous catalysis. The studies are focused on the process of impregnating CNTs with iron oxide [1,12], the electric and magnetic properties of the composite [13,14], catalysis using of magnetic carbon nanomaterials [15,16], and so on. For CNTs impregnated with iron oxide, Jang et al. [12] reported a process to fabricate γ-Fe_2O_3-impregrated magnetic CNTs using polymer nanotubes as the carbon precursor. For the electric and magnetic properties of the composite, Jiang et al. [13] prepared MWNTs-magnetite nanocomposites by in situ solvothermal method and discussed the electric properties of them; Correa-Duarte et al. [14] achieved the magnetic functionalization of CNTs by coating with iron oxide nanoparticles through the polymer wrapping and layer-by-layer assembly techniques, and aligned magnetic CNTs under low magnetic fields. For the catalysis using of magnetic carbon nanomaterials, Tsang et al. [15] reported the synthesis of magnetically separable catalyst carriers, consisting of carbon-encapsulatated nanomagnets by a

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nanochemistry approach that involves sequential spraying, chemical precipitation, and controlled pyrolysis, which could be used for preparing carbon supported nanocatalyst for the manufacture of fine chemicals; Lu et al. [16] synthesized ordered mesoporous carbon with surface-grafted magnetic particles by using a sequence of well designed manipulation steps, and demonstrated the applications of the synthesized composite as magnetically separable adsorbent and catalyst. However, in general, most of the processes of preparing CNTs-iron oxide composite are time-consuming and expensive. In this paper, we describe a simple and effective chemistry precipitation method to synthesize a magnetic composite of multiwalls carbon nanotubes (MWNTs) decorated with iron oxide nanoparticles. The reaction time is much less than that of in the literature [12–14,16]. In particular, the magnetic properties as well as the microstructures of the nanocomposites have been systematically investigated.

2. Experimental

The MWNTs (diameters: 20–40 nm, purity: 95–98%) prepared by the catalytic decomposition of CH_4 were provided by Shengzhen Nanotech Port Ltd. Co (China). The typical procedure was described as follows: the commercial MWNTs were treated in a hydrofluoric acid and concentrated nitric acid, respectively, and then separated by filtering with a 0.65 μm filter membrane and washed repeatedly with distilled water for removing the catalyst and impurity. To modify the surface of MWNTs, the purified MWNTs was homogeneously dispersed in a 1 wt% sodium dodecylbenzene sulfonic acid (SDBS) aqueous solution for 4 h. After further rinsing and drying, 1 g SDBS-absorbed MWNTs was dispersed into 50 ml 0.1 M $Fe(NO_3)_3$ solution by ultrasonic treatment. Then the ammonia solution with a concentration of 2.5 wt% was added dropwise into the suspension with vigorously agitation until the pH value reached 9.5. After 30 min reaction, the insoluble black product was filtered with 0.65 μm filter membrane, washed with distilled water and then the final product was dried at 100 °C for 5 h in an oven. The sample was heated in a steam of nitrogen from room temperature to 250 °C at the rate of 5 °C min^{-1}, kept for 1 h and ramped to 700 °C at the rate of 10 °C min^{-1}, and then it was annealed at 700 °C for 2 h.

The synthesized samples were characterized by an X-ray powder diffactometer (XRD, D/max 2550 V, Rigaku, Japan) with Cu$K\alpha$ radiation ($\lambda = 0.15418$ nm). Mössbauer spectroscopic studies (MS, Wissel, Germany) for the obtained composites were performed using a source of ^{57}Co in a Pd matrix at room temperature. The velocity transducer was operated in the constant-acceleration mode. Hyperline interaction parameters were derived from the MS using a least-squares method. The morphologies of the samples were observed through transmission electron microscopy (TEM, JEM 2010, JEOL, Japan) with an accelerating voltage of 200 kV. High-resolution electron microscopy (HRTEM) image was taken on JEM2010 to. The FTIR spectra were obtained by using a Fourier transform infrared spectrometer (FTIR, NEXUS-5670, Nicole, America). Magnetic properties of samples were measured by a vibrating sample magnetometer (VSM, LH-3, China) under a magnetism field of ±4 kOe at room temperature.

3. Results and discussion

Fig. 1a shows the XRD pattern of the MWNTs. It can be seen that the diffraction peaks at $2\theta = 26.24°$, 42.58° are assigned to (002), (110) planes of MWNTs. Fig. 1b is the XRD pattern of the decorated MWNTs. The characteristic

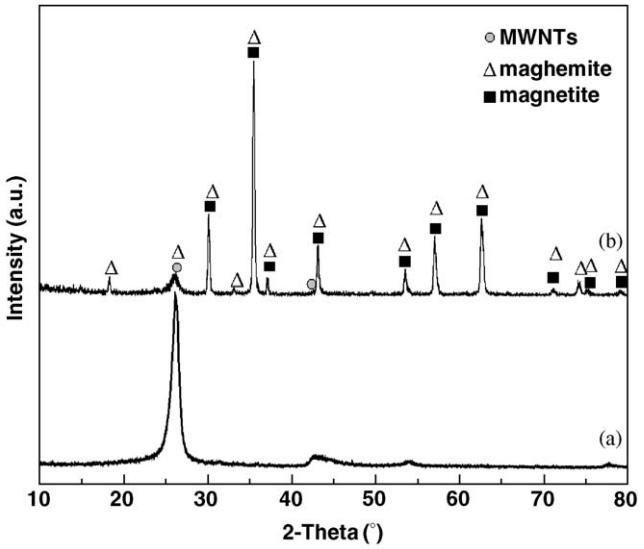

Fig. 1. XRD patterns of (a) MWNTs and (b) decorated MWNTs.

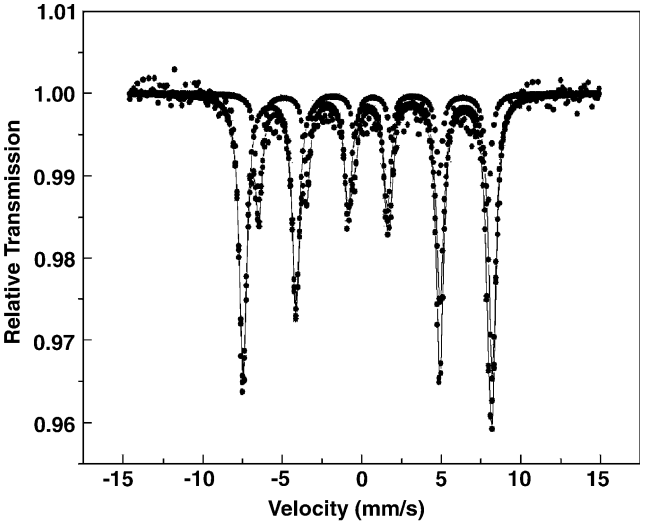

Fig. 2. Mössbauer spectrum of decorated MWNTs measured at room temperarue.

peaks of MWNTs still exist, which indicates that the structure of MWNTs is not destroyed during the decorating process. It should be noted that the peak intensities of MWNTs decrease after decorating. According to the JCPDS cards No. 19-629 for the magnitite (Fe_3O_4) and No. 39-1346 for the maghemite (γ-Fe_2O_3), diffraction peaks at $2\theta = 35.48^\circ$, 30.12°, 62.64°, etc. can be assigned to iron oxides. The mean particle size of iron oxide nanoparticles calculated by Scherrer equation is about 45 nm. However, the XRD pattern of magnetite is very similar to that of maghemite, it is difficult to ascertain the accurate phase of iron oxides.

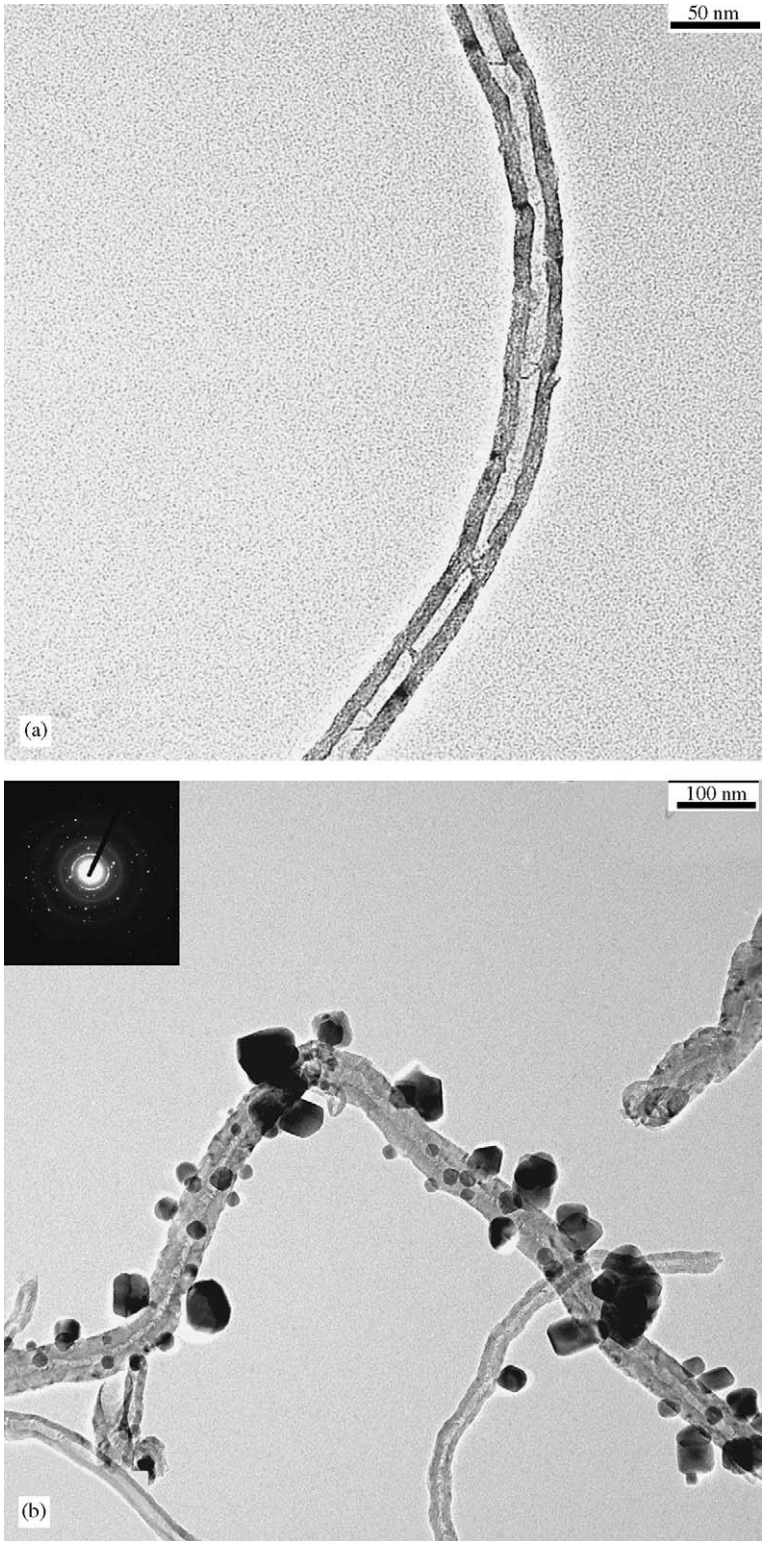

Fig. 3. TEM images of the samples (a) MWNTs, and (b) decorated MWNTs.

Since the MS of magnetite, which is two sextet peaks, obviously differs from that of maghemite, which is a sextet peak. The MS was measured to further ascertain the phases of the obtained sample. Fig. 2 shows the experimented and calculated MS of the composite. The interpretation of the spectrum is consistent with the well-established site assignment of magnetite. In this structure the Fe^{2+} ions reside in site B, whereas Fe^{3+} ions are distributed over sites A and B of the magnetite crystal structure. This spectrum is fitted by two sextets; for the sextet attributed to site A (Fe^{3+}) we obtain the hyperfine parameters $H_{eff} = 486\,kOe$, IS = $0.37\,mm\,s^{-1}$ and the ratio of the peak area is 0.76. Corresponding to site B (Fe^{3+} and Fe^{2+}) the magnetic hyperfine field is $H_{eff} = 447\,kOe$, IS = $0.72\,mm\,s^{-1}$ and the ratio of the peak area is 0.24. The data of H_{eff} and IS obtained are in accordance with the well-known hyperfine parameters for magnetite, which provides evidence for the existence of magnetite in the composite. The ratio of the area of absorption of A (Fe^{3+}) and B (Fe^{3+} and Fe^{2+}) is about 1/2 in well-established spectrum of magnetite. However, the area of absorption of A (Fe^{3+}) is 76% of the total absorption for the decorated MWNTs, indicating that more Fe^{3+} ions exists in the magnetite phase. XRD pattern of the sample also shows maghemite peaks together with peaks corresponding to magnetite. From the results of XRD and MS, it can be concluded that magnetite and maghemite coexist in the as-synthesized composite, which is consistent with the result reported in the literature [14].

Under the TEM observation of MWNT (Fig. 3a), the MWNT shows well-graphitized walls without any remarkable coverage of other materials, the diameter of the nanotubes is about 30 nm. Fig. 3b shows a TEM micrograph of typical decorated MWNTs. It is found that iron oxide nanoparticles are covered on the surface of the MWNTs. The sizes of the nanoparticles ranges from 25 to 80 nm, which is consistent with the result calculated using the Scherrer equation. The select area electron diffraction (SAED) pattern of the decorated MWNTs (inset of Fig. 3b) shows diffraction rings very clearly, which indicates that the iron oxide are polycrystal. The HRTEM micrograph of the composite (Fig. 4) also confirmed that the composite is consisted of the graphitized walls and iron oxide nanoparticles. The fringe spacing between two carbon layers of MWNTs is about 0.34 nm and the (311) lattice spacing of iron oxide is around 0.25 nm.

Fig. 5 shows the FTIR spectra of the SDBS, SDBS-absorbed MWNTs and decorated MWNTs. The peaks near $3452\,cm^{-1}$ in curve (a) and (b) correspond to the bending vibrating of adsorbed water or hydroxyl group in samples. The curve (c) also appears a very weak peak near $3452\,cm^{-1}$ due to a small amount of absorbed water. The main characteristic bands of SDBS are assigned as follows: the asymmetrical and symmetrical stretching of $-CH_2$ are represented at 2926 and $2855\,cm^{-1}$. The peak at $2958\,cm^{-1}$ is assigned to asymmetrical stretching vibration of $-CH_3$, and those at 1378 and $1466\,cm^{-1}$ are assigned to

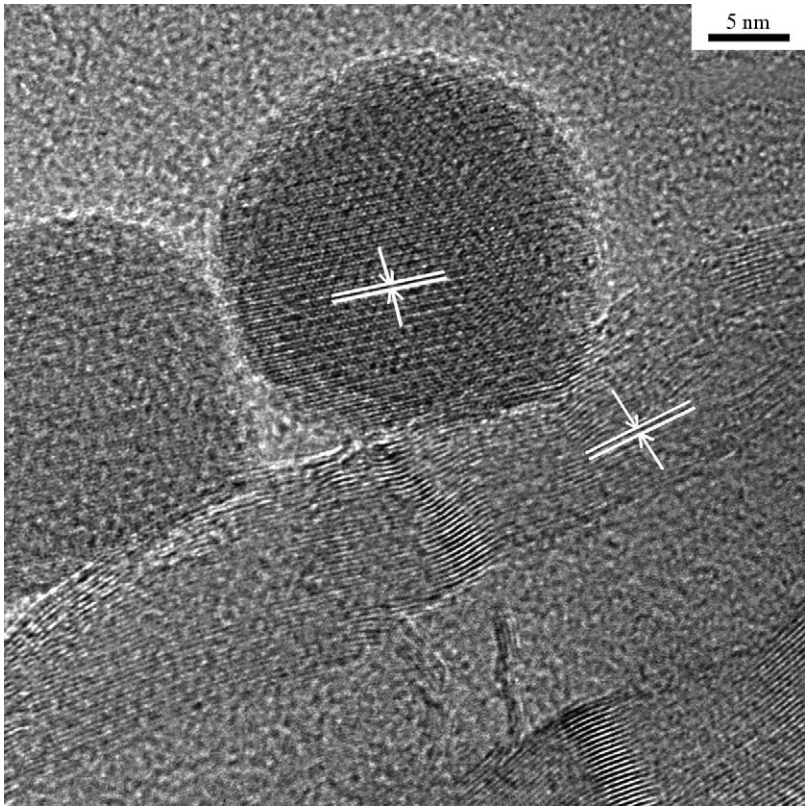

Fig. 4. HRTEM image of decorated MWNTs.

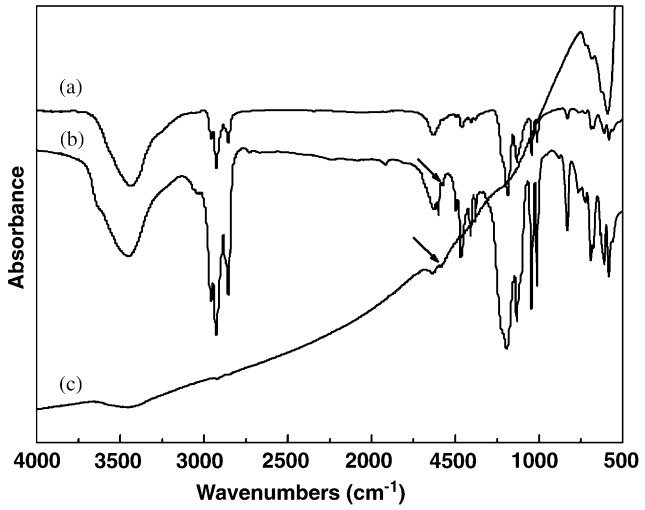

Fig. 5. FTIR spectra of (a) SDBS, (b) SDBS absorbed MWNTs, and (c) decorated MWNTs.

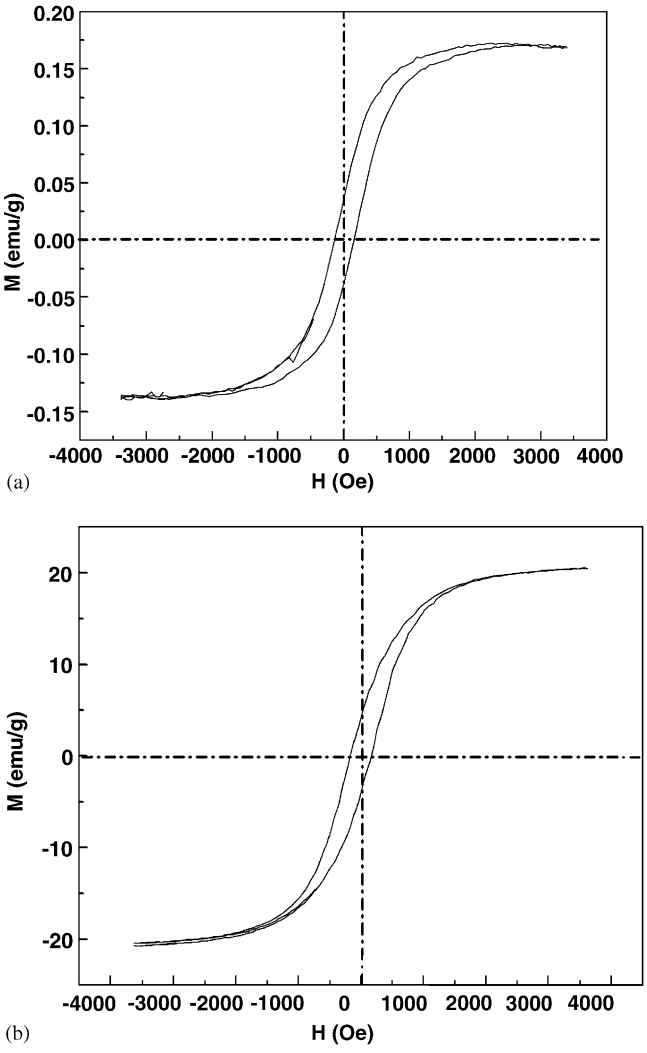

Fig. 6. Magnetization curves of (a) MWNTs and (b) decorated MWNTs.

Table 1
The magnetic properties of the samples

Samples	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
MWNTs	0.17	0.038	145.30
Decorated MWNTs	20.07	4.10	163.44

symmetrical and asymmetrical deform vibrations of $-CH_3$. Peaks at 1602 and 1497 cm^{-1} are attributed to the c=c stretching vibration for benzenoid ring, and the characteristic peak of SO_4^{2-} is at 1220 cm^{-1}. Except that, a characteristic peak of MWNTs at 1835 cm^{-1} (arrowed in curve (b)) appears, indicating that the SDBS modified MWNTs contained the SDBS and MWNTs. The existence of SO_4^{2-} in the SDBS modified MWNTs is benefit to immobilize the Fe^{3+} onto the MWNTs by the electrostatic attraction. In curve (c), the peak near 1585 cm^{-1} is associated with the vibration of carbon skeleton of the MWNTs, the peak at 591 cm^{-1} is attributed to the Fe–O bond absorbing and all the characteristic peaks of SDBS disappear. These results indicate that the SDBS decomposes completely after the decorated MWNTs are annealed at 700 °C.

The magnetic properties of the MWNTs and decorated MWNTs were measured in fields between ±4kOe at room temperature. The hysteresis loops of the MWNTs and decorated MWNTs are presented in Fig. 6(a) and (b), respectively. Their magnetic parameters are summarized in Table 1. The hystertsis loops of the MWNTs and the decorated MWNTs are of similar shapes. The MWNTs possess weak magnetic properties, attributed to a small amount of residual catalyst in the product and/or the nanotube itself [17]. The hysteresis loops of the decorated MWNTs exhibits typical ferromagnetic behavior. The saturation magnetizations is found to be 20.07 emu/g from the hysteresis loop, which is smaller than that of bulk magnetite (84 emu/g) and maghematite (34 emu/g) for the non-magnetic (weak magnetic) substance of CNT existes in the composite. The coercivity ($Hc \approx 163$ Oe) of the decorated MWNTs is between the values of bulk magnetite ($Hc = 305-335$ Oe) and bulk maghematite (75–150 Oe), which is dependent on the particle sizes and different degrees of vacancy ordering of the particles related to the preparation methods.

4. Conclusion

A simple and effective chemical method to decorate the MWNTs with iron oxide nanoparticles has been developed in this research. Through SDBS modification, SO_4^{2-} groups are introduced on the surface of the MWNTs, which facilitates the dispersion of the MWNTs and the attachment of the metal ions on their surface. Moreover, the use of ammonia solution can avoid the positive ion impurities entering the system. The polycrystal iron oxide nanoparticles are attached on the surface of the MWNTs, and the

sizes of the particles range from 25 to 80 nm. It should be further noted that the MWNTs decorated with iron oxide nanoparticles exhibits typical ferromagnetic behavior at room temperature, which provides an opportunity for the application in the fields of electronic-magnetic nanodevices, absorbing materials and data storage systems.

Acknowledgments

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References

[1] B.J. Jang, H. Yoon, Adv. Mater. 15 (2003) 2088.
[2] K. Oh-Kil, J. Jongtae, W.B. Jeffrey, K. Steven, P.E. Pehr, J.B. Leonard, J. Am. Chem. Soc. 125 (2003) 4426.
[3] K.C. Chin, A. Gohel, H. IElim, W. Ji, G.L. Chong, K.Y. Lim, C.H. Sow, A.T.S. Wee, Chem. Phys. Lett. 383 (2004) 72.
[4] H. Oymak, S. Erkoc, Chem. Phys. 300 (2004) 277.
[5] P.C.P. Watts, W.K. Hsu, D.P. Randall, V. Kotzeva, G.Z. Chen, Chem. Mater. 14 (2002) 4505.
[6] Y.H. Wu, P.W. Qiao, J.J. Qiu, T.C. Chong, T.S. Low, Nano Lett. 2 (2002) 161.
[7] B.J. He, W.L. Sun, M. Wang, Z.Q. Shen, Mater. Chem. Phys. 95 (2005) 202.
[8] G. Vasilios, T. Vasilios, G. Dimitrios, P. Dimitrios, Chem. Mater. 17 (2005) 1613.
[9] C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, Nature 372 (1994) 159.
[10] B.K. Pradhan, T. Toba, T. Kyotani, A. Tomita, Chem. Mater. 10 (1998) 2510.
[11] M. Monthioux, Carbon 40 (2002) 1809.
[12] J. Jang, K.J. Lee, Y. Kim, Chem. Commun. (2005) 3847.
[13] L.Q. Jiang, L. Gao, Chem. Mater. 15 (2003) 2848.
[14] M.A. Correa-Duarte, M. Grzelczak, V. Salgueiriño-Maceira, M. Giersig, L.M. Liz-Marzán, M. Farle, K. Sierazdki, R. Diaz, J. Phys. Chem. B 109 (2005) 19060.
[15] S.C. Tsang, V. Caps, I. Paraskevas, D. Chadwick, D. Thompsett, Angew. Chem. Int. Ed. 43 (2004) 5645.
[16] A.H. Lu, W. Schmidt, N. Matoussevitch, H. Bönnemann, B. Spliethoff, B. Tesche, E. Bill, W. Kiefer, F. Schüth, Angew. Chem. Int. Ed. 43 (2004) 4303.
[17] J.H. Wu, L.B. Kong, Appl. Phys. Lett. 84 (2004) 4956.