Materials Letters 62 (2008) 4059–4061

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Decorating carbon nanotubes with Cobalt nanoparticles

Zhengping Dong, Kun Ma, Jianguo He, Juanjuan Wang, Rong Li *, Jiantai Ma *

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, PR China

ARTICLE INFO

Article history:
Received 28 February 2008
Accepted 5 June 2008
Available online 10 June 2008

Keywords:
Multiwalls carbon nanotubes
Cobalt nanoparticles
Magnetic property

ABSTRACT

A magnetic composite of multiwalls carbon nanotubes (MWNTs) decorated with Cobalt nanoparticles was synthesized successfully by a simple chemical precipitation and deoxidization method. The composite was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The pattern of XRD indicated that MWNTs and Cobalt nanoparticles coexisted in the composite. The TEM images revealed that the Cobalt nanoparticles were distributed on the surface of the MWNTs, with the size ranging from 5 to 15 nm. The hysteresis loops of the decorated MWNTs were measured by a vibrating sample magnetometer (VSM), the ferromagnetic signature emerged with the saturated magnetization of 5.8 emu/g, and the coercive of 310 Oe.

1. Introduction

Since the discovery by Iijima [1], carbon nanotubes (CNTs) have received considerable attention over the past decade from scientific studies and industrial applications [2]. Decorating the surface of CNTs can improve dispersity of CNTs in solvents [3] or impart new optical, electric, magnetic properties [4–7]. Magnetic nanocomposites have potential applications in various areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging. Therefore, studies on magnetic nanocomposites, especially on magnetic carbon nanotubes (CNTs), are rapidly expanding. Recently, Gao et al. and co-workers successfully synthesized novel "tadpole" like Fe_3O_4/MWNTs by position-selectively attaching Fe_3O_4 balls on tips of MWNTs through a straightforward and effective polyol-medium solvothermal method [8]. Sun et al. fabricated magnetic carbon nanotube composites by the decomposition of ferrocene on MWNTs at different temperatures [9]. Ma et al. proposed a new method to produce magnetic tubes by filling MWNTs with Fe nanoparticles [10]. Various magnetic materials including iron [10–11], iron oxide [12–14], nickel [15–16] decorated on CNTs have been prepared. Magnetic materials of cobalt decorated MWNTs have also been prepared. Radinka Kozhuharova prepared well-aligned Co-filled multi-walled carbon nanotubes [17]. Xicheng Ma and co-workers produced Co-filled CNTs by decomposition of benzene over Co/silica-gel catalysts [18]. Nevertheless, there is no study concerning the magnetic properties of the Cobalt nanoparticles attaching on the outside surface of MWNTs. In this work, we synthesized the composite of MWNTs decorated with Cobalt nanoparticles by a simple chemical precipitation and deoxidization method. In particular, the nanocomposite exhibits excellent magnetic property and the reaction is time saving.

2. Experimental

MWNTs (diameters: 20–40 nm, purity: 95–98%) prepared by the catalytic decomposition of CH_4 and were provided by Shengzhen Nanotech Port Ltd. Co (China). The typical procedure is as follows: The raw MWNTs with closed ends were re-fluxed in 6 M nitric acid (37 wt.%) at 383 K for 5 h. This milder treatment removed amorphous carbon and catalyst while keeping the caps intact. The pure MWNTs were dispersed in a solution of Cobalt nitrate with the help of an ultrasonic bath. The ammonia solution (2.5 wt.%) was slowly added into the solution with vigorous stirring till the pH value reached 9.5. Then the solution was filtered with 0.65 mm filter membrane and washed with distilled water repeatedly. Later the product was dried overnight at 373 K in an oven. After that the sample was annealed at 573 K for 2 h in a steam of nitrogen. We got the materials of CoO decorated MWNTs. The resulting materials were reduced using H_2 at 623 K for 2 h successively.

The final products were characterized by an X-ray powder diffractometer (XRD, D/max 2400 V, Rigaku, Japan) with Cu Kα radiation (λ=0.15406 nm). The morphologies of the samples were observed through transmission electron microscopy (TEM, Hitachi-600, Japan) with an accelerating voltage of 100 kV. Qualitative analysis of particle composition was carried out using energy dispersive X-ray analysis (EDX) equipped with TEM. Magnetic properties of the samples were measured by a vibrating sample magnetometers (TOEI, VSM-5S-15) with a maximal applied field of 16 kOe. The samples were measured under a magnetic field of 10 kOe at room

* Corresponding authors. Tel./fax: +86 931 8912311.
E-mail addresses: majiantai@lzu.edu.cn (J. Ma), liyirong@lzu.edu.cn (R. Li).

0167-577X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2008.06.017

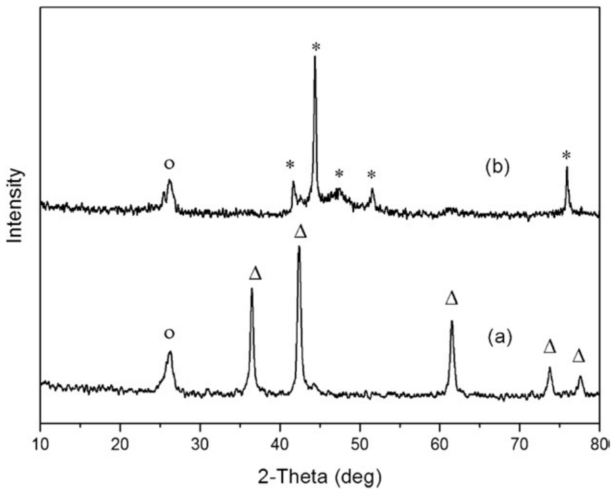

Fig. 1. XRD patterns of: (a) CoO-MWNTs and (b) Co-MWNTs. (○) MWNTs, (△) CoO and (*) Co.

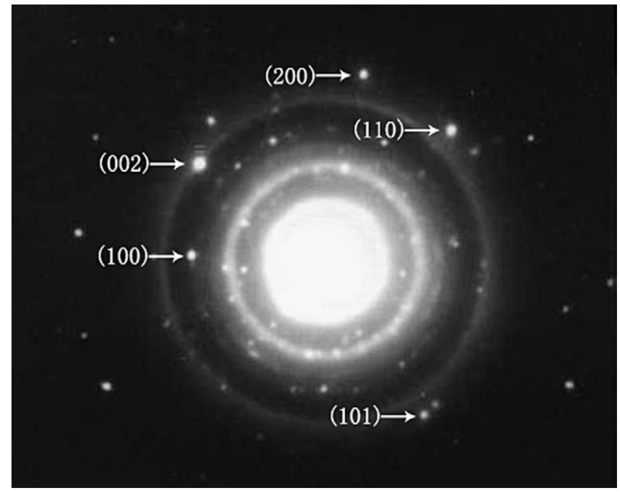

Fig. 3. SAED pattern of the Cobalt nanoparticles decorated MWNTs.

temperature, and the amount of the sample for the measurement was 0.237 g.

3. Results and discussion

The magnetic composite of Co decorated MWNTs was prepared in four steps — (i) when the MWNTs were re-fluxed in 6 M nitric acid, –OH or –COOH could be generated on the surface, (ii) titrating the well-dispersed MWNTs and Cobalt nitrate solution with ammonia solution, when the pH value reached 9.5, most of the precipitate (Cobalt hydroxide) was coated on the surface of the MWNTs, maybe the –OH or –COOH was the center of the precipitate, (iii) annealing the sample at 573 K in inert atmosphere, the Cobalt hydroxide nanoparticles were converted to CoO nanoparticles and (iv) when reduced using H_2 the desired product was obtained.

Fig. 1a shows the XRD pattern of the CoO decorated MWNTs. The diffraction peak at 2θ=26.24° is assigned to (002) plane of MWNTs. The position of other characteristic peaks in Fig. 1a shows good agreement with PDF (74-2392) data of the cobalt oxide. The diffraction angles at 2θ=36.53°, 42.41°, 61.60°, 73.74°, 77.50° can be assigned to scattering from the (111), (200), (220), (311) and (222) planes of the CoO crystal lattices, respectively. Fig. 1b is the XRD pattern of the Cobalt nanoparticles decorated MWNTs. The characteristic peak of MWNTs still exists. It should be noted that the peak intensity of MWNTs decreases after the reduced procedure. According to the PDF cards No. 05-0727 for the magnitite (Co) ,diffraction peaks at 2θ=41.64°, 44.36°, 47.10°, 75.90° can be assigned to (100), (002), (101), (110) crystal planes of Co nanoparticles, respectively. And the peak at 2θ=51.52° is the fcc-Co (200) crystal plane agreement with PDF (15-0806).

Typical TEM images of the Cobalt nanoparticles decorated MWNTs are shown in Fig. 2. It can be seen from Fig. 2a that MWNTs after modification shows rough surfaces, indicating the intense deposition of nanoparticles. Fig. 2b reveals that the highly dispersed Cobalt nanoparticles are mainly deposited on the outer walls of MWNTs, and the size of most of the particles is 5 nm to 15 nm, which is in consistent with predictions of Scherrer equation.

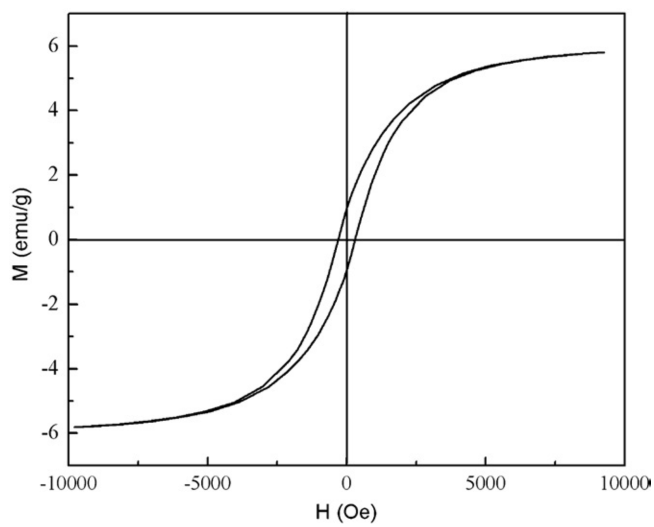

Fig. 4. Magnetization curves of the Cobalt nanoparticles decorated MWNTs.

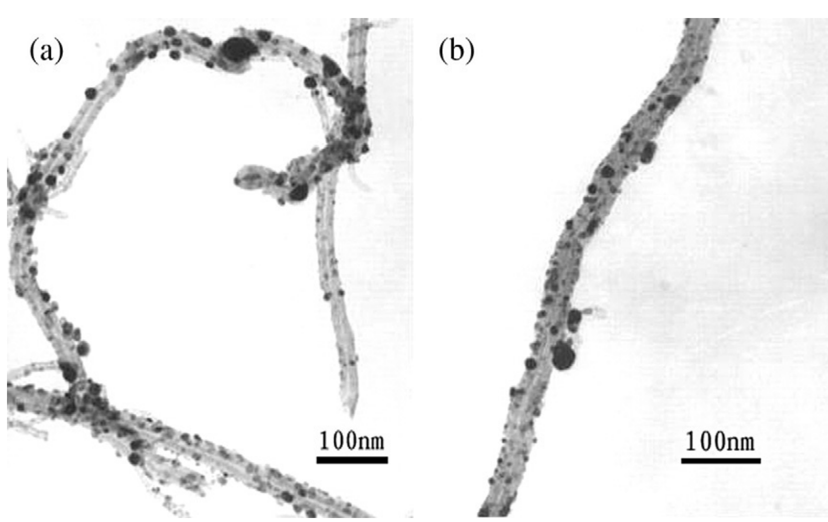

Fig. 2. TEM images of Cobalt nanoparticles decorated MWNTs.

The SAED pattern of the Cobalt nanoparticles decorated MWNTs is shown in Fig. 3. The pattern presents a pair of arcs from carbon nanotube. In addition to the reflection from the carbon nanotube, we observed some spots and rings, which were identified as the diffraction from Cobalt nanoparticles. The appearance of the diffraction rings and spots indicates the polycrystalline property of the nanoparticles loaded.

The magnetic properties of the decorated MWNTs were measured in fields between ±10 kOe at room temperature. The magnetization curve is presented in Fig. 4. It demonstrates the composite's ferromagnetic properties with saturated magnetization (Ms) and coercivity (Hc) values of 5.8 emu/g and 310 Oe, respectively.

4. Conclusion

In summary, we presented a simple and effective chemical method for the modification of MWNTs by magnetic composites of Cobalt nanoparticles. The sample exhibits excellent magnetic properties, which provides an opportunity for the applications in the fields of electronic–magnetic nanodevices, absorbing materials and data storage systems. We also supply a method of preparing one-dimensional magnetic nanomaterials.

References

[1] Iijima S. Nature 1991;354:56.
[2] Jang BJ, Yoon H. Adv Mater 2003;15:2088.
[3] Oh-Kil K, Jongtae J, Jeffrey WB, Steven K, Pehr PE, Leonard JB. J Am Chem Soc 2003;125:4426.
[4] Chin KC, Gohel A, IElim H, Ji W, Chong GL, Lim KY, et al. Chem Phys Lett 2004;383:72.
[5] Oymak H, Erkoc S. Chem Phys 2004;300:277.
[6] Watts PCP, Hsu WK, Randall DP, Kotzeva V, Chen GZ. Chem Mater 2002;14:4505.
[7] Wu YH, Qiao PW, Qiu JJ, Chong TC, Low TS. Nano Lett 2002;2:161.
[8] B. Jia, L. Gao. J Phys Chem B 2007;111:5337.
[9] Sun ZY, Liu ZM, Wang Y, Han BX, Du JM, Zhang JL. J Mater Chem 2005;15:4497.
[10] Jin J, Li R, Wang H, Chen H, Liang K, Ma J. Chem Commun 2007:386–8.
[11] Jang Jae-Won, Lee Kyu Won, Oh IH, Lee EM, Kim IM, Lee Cheol Eui, et al. Solid State Commun 2008;145:561.
[12] Pradhan BK, Toba T, Kyotani T, Tomita A. Chem Mater 1998;10:2510.
[13] Cao H, Zhu M, Li Y. J Magn Magn Mater 2006;305:321.
[14] Cao H, Zhu M, Li Y. J Solid State Chem 2006;179:1208.
[15] Elias AL, Rodriguez-Manzo JA, McCartney MR, Golberg D, Zamudio A, Baltazar SE, et al. Nano Lett 2005;5:467.
[16] Bittencourt C, Felten A, Ghijsen J, Pireaux JJ, Drube W, Erni R, et al. Chem Phys Lett 2007;436:368.
[17] Kozhuharova R, Ritschel M, Elefant D, Graff A, Leonhardt A, Groudeva-Zotov S, et al. Appl Surf Sci 2004;238:355.
[18] Ma X, Cai Y, Lun N, Ao Q, Li S, Li F, et al. Mater Lett 2003;57:2879.