ELSEVIER Journal of Magnetism and Magnetic Materials 231 (2001) L9–L12

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Letter to the Editor

Magnetic properties of Fe nanoparticles trapped at the tips of the aligned carbon nanotubes

X.X. Zhang[a,*], G.H Wen[a], Shaoming Huang[b], Liming Dai[b], Ruiping Gao[c], Zhong L. Wang[c]

[a] Department of Physics, Univeristy of Science and Technology Hong Kong, Clear Water Bay, Kawloon, Hong Kong, China
[b] CSIRO Molecular Science, Bag 10, Clayton South, Victoria 3169, Australia
[c] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta GA 30332-0245, USA

Received 23 November 2000

Abstract

The magnetic properties of iron nanoparticles partially encapsulated at the tips of aligned carbon nanotubes have been studied. The carbon nanotube wall not only protects the metallic particles from oxidization, but also reduces the inter-particle dipolar interaction by non-magnetic separation. Magnetic characterizations performed in the temperature range of 5–350 K with magnetic field up to 3 T show that these carbon-nanotube-supported iron particles are good candidates for high-density magnetic recording media. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 36.40.Cg; 61.48.+C; 75.50.Tt; 61.46.+W

Keywords: Fe nanoparticles; Aligned carbon nanotube; Recording media

Magnetic nanoparticles have been fabricated using a variety of techniques [1–3], and many interesting phenomena have been observed [1,3–5]. Their novel properties are the focus of many fundamental research and practical applications [1,2,4–7]. Most of the current studies are on oxide nanoparticles, because it is difficult to prevent metallic magnetic (Fe, Co, Ni) nanoparticles from oxidization at conventional experimental conditions. Several techniques, such as carbon encapsulation [8–11], reagent stabilizing [12], and passivation of nanoparticles [13], have been developed to protect the metallic particles. Magnetic properties of the carbon-encapsulated nanoparticles and nanowires have been investigated recently [14,15]. The metallic particles in the carbon cages and films are believed to be a potential candidate for the high-density magnetic recording media [8,9].

It is well known that transition metals, such as Fe and Co, are mandatory for the nucleation and growth of carbon nanotubes by pyrolysis [16]. In preparation of aligned carbon nanotubes by pyrolyzing iron (II) phthalocyanine, FePc, it has been demonstrated that the nanotube growth involves two iron nanoparticles [17]. A small particle serves as the nuclei of the nanotube and a large particle locates at the growth front to be responsible for the growth of the nanotubes [17].

*Corresponding author. Fax: +852-2358-1652.
E-mail address: phxxz@ust.hk (X.X. Zhang).

0304-8853/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0304-8853(01)00134-2

Magnetic nanoparticles are useful for magnetic data storage. In this paper, the magnetic properties of the large iron particles encapsulated at the tips of the aligned carbon nanotubes are characterized and the potential applications of the magnetic particles for data storage are discussed.

The aligned carbon nanotubes on quartz glass plates were prepared by pyrolysis of FePc under Ar/H_2 in a dual furnace fitted with independent temperature controllers according to published procedures [17,18]. Briefly, a predetermined amount of FePc and a quartz glass plate pretreated with or without alkanethiols were placed over the first and second furnaces, respectively. We then proceeded the pyrolysis process by first heating the second furnace up to 900°C and the first furnace at 650–750°C for ca. 10 min, followed by keeping both furnaces at 900°C for ca. 10 min. As previously demonstrated, the aligned nanotubes produced at 900°C showed cork-like Fe rods aligned along the longitudinal axis [17] as seen in the SEM image shown in Fig. 1. In order to demonstrate the possibility of transferring the aligned nanotubes with full integrity and to facilitate the magnetic measurements, we have developed a dry lefting-up technique apart from the contact transfer method involving an aqueous hydrofluoric acid solution as reported earlier [18]. In the case of dry transferring, we simply peeled off the aligned nanotube film from the quartz substrate through a Scotch tape, which was prepressed on the nanotube layer [19].

Microstructure of the carbon nanotubes was studied using transmission electron microscopy (TEM) at 400 kV using an JEOL 4000EX and at 100 kV using an JEOL 100C. The as-prepared carbon nanotubes are well aligned in a direction normal to the substrate surface. A bunch of the aligned carbon nanotubes observed in TEM is shown in Fig. 2a. The large iron particles at the growth front are clearly seen (Fig. 2b). The carbon nanotube has a bamboo-like structure. The inner tube is almost empty but subdivided by single or double graphitic layers. The wall thickness is $\sim$9 nm. The average particle size is $\sim$70 nm. The body of the iron particles is capsulated by graphitic layers, while growth front at the tip is only covered by a few atomic layers of carbon.

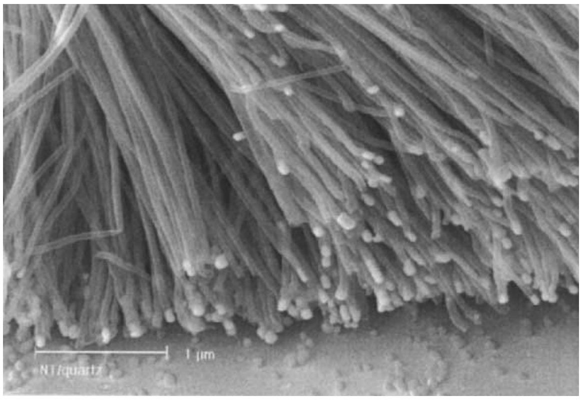

Fig. 1. SEM image of the iron particles within tips of the aligned nano tubes.

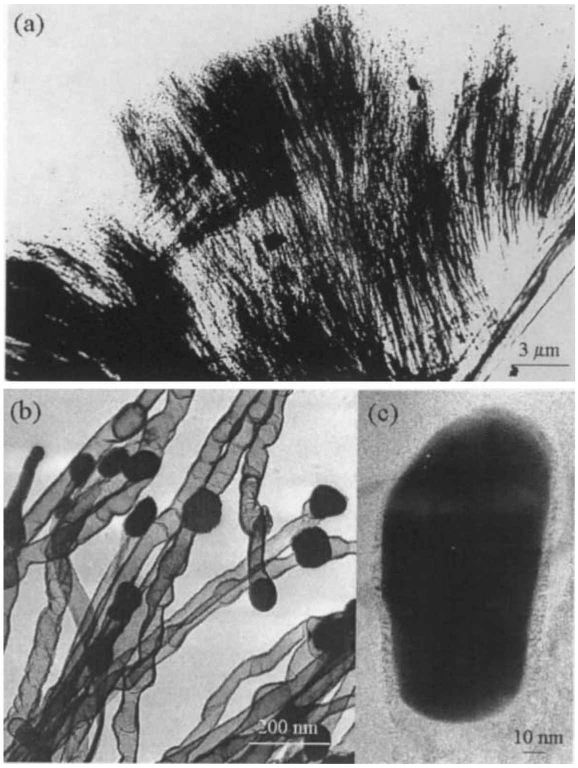

Fig. 2. TEM image of the particles and the nanotubes. (a) A bunch of the aligned carbon nanotubes; (b) top view of the aligned nanotubes, showing the large iron particles; (c) HR-TEM image of the nanotube tips.

This structure is clearly shown by the image given in Fig. 2c, where the graphitic shells from the carbon nanotube are clearly observed. This structure is unique for data storage because it is not necessary to deposit an amorphous carbon as a lubricant which may enhance the sensitivity for data reading and writing.

Magnetic properties of the particles have been characterized using quantum design SQUID magnetometer equipped with 5 T magnet in the temperature range 5–360 K. Since the cork-like Fe particles are at the tips of the aligned nanotubes (Figs. 1 and 2), it is natural to expect that the sample (film) should show the perpendicular anisotropy, i.e. the magnetization prefers to be perpendicular to the film plane. In order to characterize the macroscopic anisotropy of the sample which is an average anisotropy of the individual particles, the magnetic field, H, has been applied along the tube direction (i.e. H perpendicular to the film plane) and perpendicular to the tubes (H parallel to the film plane). Fig. 3 shows the temperature-dependent magnetization as a function of temperature with H parallel to the tubes in a field of 5 kOe. It is evident that the particles behave ferromagnetically with Curie temperature much higher than 350 K. The inset shows the magnetization as a function of temperature obtained at the zero-field-cooled (ZFC) and field cooled (FC) processes with a small applied magnetic field of 0.1 kOe. The procedure for the ZFC-FC magnetization measurements has been described previously [3,4]. The ZFC-FC magnetization curves clearly indicate that the particles are quite thermally stable without blocking (or superparamagnetic behavior). For BCC α-Fe, the critical size for single domain particles is about 20 nm [20], above which there will be domain walls in the particles. The particles in this study have an average size of ~70 nm, thus they should be considered as non-single-domain particles. Even for the single domain particles with size of 20 nm, the blocking temperature T_B should be much higher than 350 K (The blocking temperature T_B can be estimated by $25k_BT_B = KV$ [3,4], where k_B is Boltzmann constant, V is the particles volume and $K = 4 \times 10^4$ J/m^3 is an anisotropy constant of iron). Since our particle size is about 70 nm, the proportional dependence of the magnetization on temperature seen in the ZFC curve can be ascribed mainly to the domain wall depinning processes

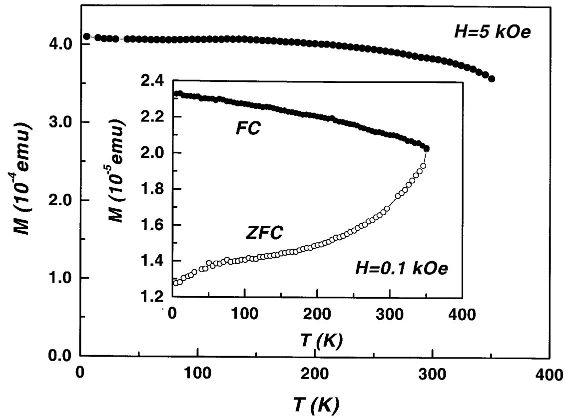

Fig. 3. Temperature dependence of magnetization in the field of 5 kOe. The inset is the magnetization as a function of temperature obtained in the zero-field cooled and field cooled process with filed of 0.1 kOe.

[21]. The magnetization curve in Fig. 3 obtained with applied magnetic field of 5 kOe is actually the temperature-dependent saturation magnetization. The ZFC-FC magnetization measured with H perpendicular to the tubes are very similar to that shown in Fig. 3.

The magnetic hysteresis loops have been measured at different temperatures from 5 to 320 K with the applied magnetic field perpendicular and parallel to the carbon nanotubes. No significant difference has been observed in the two directions. The coercive field was found to be the same for the two directions within the experimental resolution. The hystereses obtained at 5 and 320 K are given in Fig. 4a, which shows the ferromagnetic behavior. Shown in Fig. 4b is the temperature dependence of the ratio of M_r/M_s and coercive field, H_C, extracted from the hysteresis loops, where M_r, and M_s are the remanent and saturation magnetization, respectively. It is evident that both the M_r/M_s ratio and coercive field H_C decreases monotonically with increasing temperature, as expected for small particle systems [4]. Although that both M_r/M_s and H_C decrease with temperature, they are still larger than that for Co–C nanocrystalline films [9]. For single-domain particles with a uniaxial anisotropy and randomly distributed easy axes, the ratio of M_r/M_s is know to be ~0.5 at a temperatures well below the blocking temperature. Therefore, the decrease in both M_r/M_s and H_C

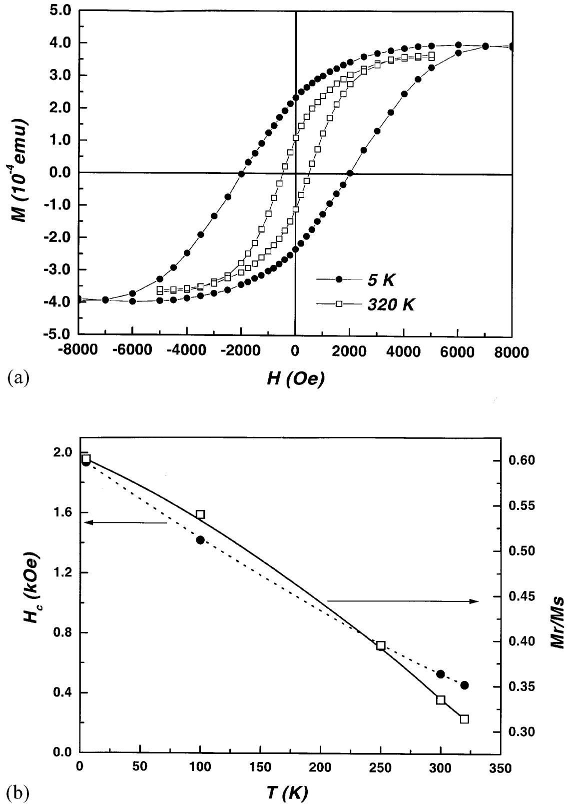

Fig. 4. (a) Hysteresis loops obtained at 5 and 320 K with magnetic field parallel to the tubes; (b) the temperature dependence of the ratio M_r/M_s and coercive field H_C.

with increasing temperature can be attributed to the depinning of domain walls in the particles.

The similar magnetization curves observed for the applied magnetic field in both parallel and perpendicular directions can be explained by taking account of the random distribution of the easy axes (the longitudinal of particles) and the shape of the particles, as shown in the TEM and SEM images. If the Fe particles used as the seeds for the nucleation of the nanotube are small enough, say, less than 20 nm, the particles will be single domain and will exhibit very high uniaxial anisotropy due to the stress of the nanotube and the shape [1]. Consequently, the coercive field will be greatly enhanced, which may satisfy the requirement of $H_C \sim 2.5$ kOe for the next generation high-density recording media [22]. Another advantage of the particles in the tips of the nanotubes, is that the walls of the nanotubes act as a non-magnetic separation, which is essential for the high magnetic recording media to eliminate the dipolar interaction between the neighboring particles [23]. Furthermore, the exceptional electronic properties and the hollow structure characteristic of carbon nanotubes could have important implications for the use of the magnetic nanotubes in many other potential applications ranging from electromagnetic devices to magnetically guided drug delivery systems.

XXZ and GHW are supported by HKUST6111/98P and ISF (AF/155/99). RPG and ZLW thank the support of NSF grants DMR-9733160 and DMR-9971412.

References

[1] D.L. Leslie-Pelecky, R.D. Rieke, Chem. Mater. 8 (1996) 1770, and references therein.
[2] R.F. Ziolo et al., Science 257 (1992) 219.
[3] J.S. Yin, Z.L. Wang, Phys. Rev. Lett. 79 (1997) 2570.
[4] X.X. Zhang, J.M. Hernandez, J. Tejada, R.F. Ziolo, Phys. Rev. B 54 (1996) 4101.
[5] J. Tejada, X.X. Zhang, E. del Braco, J.M. Hernandez, E.M. Chudnovsky, Phys. Rev. Lett. 79 (1997) 1754.
[6] R.D. Shull, IEEE Trans. Magn. 29 (1992) 2614.
[7] L. Gunther, Phys. World 2 (1990) 28.
[8] J. Hery, J. Scott, S. Majetich, Phys. Rev. B 52 (1995) 12564.
[9] T. Hayashi et al., Nature 381 (1996) 772.
[10] V.P. Dravid et al., Nature (London) 374 (1995) 602.
[11] S. Subramoney, Adv. Mater. 10 (1998) 1157.
[12] S.H. Sun, C.B. Murray, J. Appl. Phys. 85 (1999) 4325.
[13] K.K. Fung, B.X. Qin, X.X. Zhang, Mater. Sci. Eng. A 286 (2000) 135.
[14] J.J. Host et al., J. Appl. Phys. 83 (1998) 793.
[15] N. Grobert et al., Appl. Phys. Lett. 75 (1999) 3363.
[16] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[17] De-Chang Li, Liming Dai, Shaoming Huang, Albert W.H. Mau, Zhong L. Wang, Chem. Phys. Lett. 316 (2000) 349.
[18] Shaoming Huang, Liming Dai, Albert W.H. Mau, J. Phys. Chem. B 103 (1999) 4223.
[19] Y. Yang, S. Huang, H. He, A.W.H. Mau, L. Dai, J. Am. Chem. Soc. 121 (1999) 10832.
[20] A.H. Morrish, The Physical Principal of Magnetism, Robert E. Krieger Publishing Company, Malabar, FL, p. 1983.
[21] X.X. Zhang et al., Phys. Rev. B 53 (1996) 3336.
[22] E.S. Murdock et al., IEEE Trans. Magn. 28 (1992) 3078.
[23] T. Yogi, T.A. Nguyen, IEEE Trans. Magn. 29 (1993) 307.