Magnetic characterization of Fe-nanoparticles encapsulated single-walled carbonnanotubes†

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Magnetic Fe nanoparticles less than 1 nm have been successfully filled in single-walled carbon nanotubes (SWNTs), and their magnetic properties are characterized by means of SQUID measurements in the temperature range of 5–300 K.

Single-walled carbon nanotubes (SWNTs) represent a fascinating candidate for the construction of nanoscale electronic devices owing to their special properties and intriguing applications in many fields. Theoretical and experimental work have indicated that the introduction of foreign materials into their hollow cavities will have interesting effects both on the properties of filling materials and the filled SWNTs.[1–3] In particular, it is very attractive that SWNTs can be filled with ferromagnetic metals such as Fe, Co or Ni into their cavities. In these hybrid systems, the SWNTs not only effectively prevent these magnetic metals from oxidation, but also exhibit both novel ferromagnetism and electronic properties. For example, it may allow us to use both charge and spin of electrons for transport in SWNTs-based spintronic devices by introducing magnetic elements.

However, early studies of filling have mainly been focused on multi-walled carbon nanotubes (MWNTs)[4–6] although many related theoretical studies have predicated that SWNTs filled with Fe atoms will exhibit more interesting electronic and magnetic properties.[7,8] In contrast to MWNTs, SWNTs with diameter of 1–2 nm and high aspect ratio represent a genuine one-dimensional nano-system. Magnetic properties of ferromagnetic metals (such as Fe) filled SWNTs are certainly of great interest in nanophysics. Nevertheless, to the best of our knowledge, experimental studies on the synthesis of Fe-filled SWNTs remain a challenging issue due to the experimental limitations. Therefore, the encapsulation of magnetic metals in SWNTs is becoming a promising and challenging research area.

In this communication, the synthesis of Fe-encapsulated SWNTs is explored for the first time using ferrocene as a starting material. Firstly, ferrocene molecules are filled in SWNTs by a vapour diffusion method. Secondly, ferrocene-filled SWNTs are further annealed in vacuum to release Fe atoms inside SWNTs. Magnetic properties of Fe-filled SWNTs are examined, and our results have revealed that most of encapsulated nanoparticles are pure iron.

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Pristine SWNTs used here are made by an arc discharge using Fe/Ni as catalyst. The raw SWNTs are purified by filtration and acid treatment.[9] After purification, air oxidation process for SWNTs is carried out in static air at 450 °C for 30 min in order to create SWNTs with open ends. The purified SWNTs mixed with excess ferrocene powder (about 1 : 20 by weight) are placed in a glass ampoule. The ampoule is then evacuated to 2×10^{-5} Torr and sealed. The vacuum glass ampoule is heat-treated in a electric furnace at 180 °C for 48 h. As a result, ferrocene-filled SWNTs are obtained from the above filling process. A purification process is performed to remove the ferrocene attached on the outer side of the SWNTs, then the purified ferrocene-filled SWNTs are heated by a flash annealing process in vacuum (10^{-6} Torr) during which ferrocene is decomposed and transformed into Fe atoms inside SWNTs. The detailed synthesis process for Fe-filled SWNTs has been described in our previous work.[10] Samples of both ferrocene-filled SWNTs and Fe-filled SWNTs are characterized in detail by a Hitachi HF-2000 transmission electron microscope (TEM) operated at 200 kV, equipped with an energy dispersive X-ray spectrometer (EDX, Noran Instruments). The amount of Fe nanoparticles in SWNTs are analyzed by X-ray fluorescence spectroscopy (XRF, RIX2100). Magnetic properties of samples are characterized using a Quantum Design MPMS-5 superconducting quantum interference devices (SQUID) magnetometer with applied magnetic field $-5.5\ \mathrm{T} \leqslant H \leqslant 5.5\ \mathrm{T}$ in the temperature range of 5–300 K. During the measurements, samples of SWNTs (1 mg) are uniformly deposited on a quartz substrate ($7 \times 7\ \mathrm{mm}^2$). In order to subtract the diamagnetic contributions, blank samples of quartz are measured independently and subtracted from the Fe-filled SWNTs flake-quartz contributions.

Fig. 1(a) shows a typical TEM image of an individual single-walled carbon nanotube (SWNT) filled with clusters of ferrocene molecules. The diameter of the SWNT is about 1.4 nm, and the length of the filling part in this nanotube is over 5 nm, as marked by a rectangle. The contrast between the SWNT and clusters of ferrocene is noticeable, which evidently confirms that ferrocene molecules have been incorporated in SWNTs. In comparison with Fig. 1(a), Fe nanoparticles in SWNTs exhibit a different morphology during TEM observations, as shown in Fig. 1(b) where several dark spots (indicated by arrows) can clearly be identified, which reveals that these Fe particles are encapsulated. It is seen that these dark spots have an average diameter of about 0.5–0.7 nm, suggesting each of them contains only several iron atoms. In addition, EDX spectroscopy has been further performed to confirm the existence of Fe in SWNTs (see ESI†). For the sake of comparison, Fig. 1(c) shows a TEM image for a carbon-coated catalyst particle over 30 nm which exists as an impurity in pristine

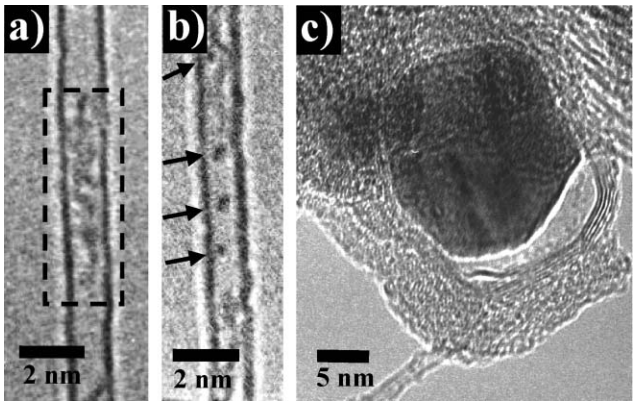

Fig. 1 TEM images of ferrocene-filled SWNT (a), Fe-filled SWNT (b) and a carbon-coated Fe catalyst particle (c).

SWNTs. By comparison, TEM observations indicate that Fe nanoparticles less than 1 nm have successfully been incorporated in SWNTs.

Fig. 2 presents magnetization *vs.* applied magnetic field for pristine SWNTs and Fe-filled SWNTs measured at 5 K (a) and 300 K (b), respectively. Fig. 2(a) shows that both samples exhibit ferromagnetic behavior with a hysteresis loop at low temperature. The measurements indicate clearly that the magnetization of Fe-filled SWNTs is much larger than that of pristine SWNTs. This result provides an indirect evidence for the encapsulation of Fe nanoparticles in SWNTs since they are easily oxidized and lose their magnetization without the protection of SWNTs. In addition,

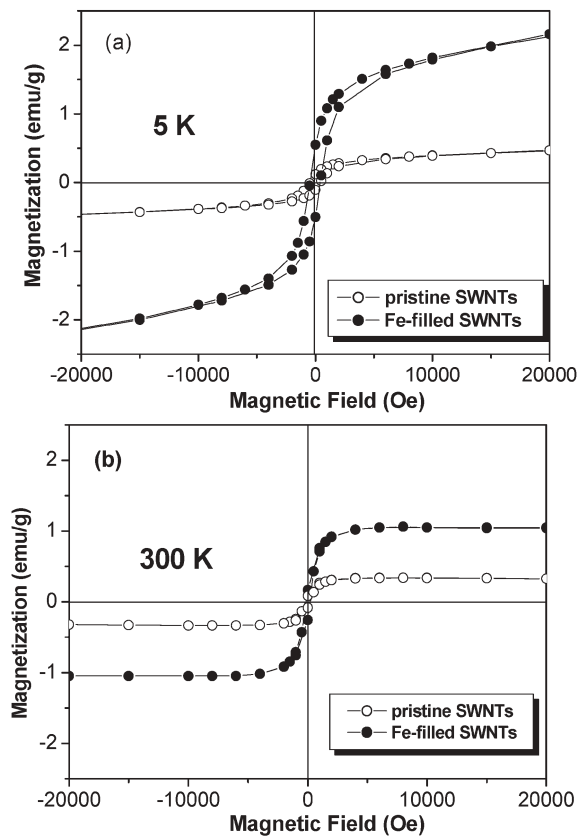

Fig. 2 Magnetization curves of pristine SWNTs and Fe-filled SWNTs at 5 K (a) and 300 K (b).

the Fe-encapsulated nanotube samples show saturation of magnetization much more slowly compared to the pristine nanotube samples, suggesting some Fe particles are in a super-paramagnetic state. In our case, the magnetization of pristine SWNTs results from the magnetic impurities, since it is very difficult to remove all of the magnetic catalysts coated by carbon layers in pristine SWNTs, as shown in Fig. 1(c), even though they have been purified by acid treatment. In other words, the pristine SWNTs are a mixture of magnetic catalyst particles and pure carbon nanotubes. The pure carbon nanotubes are well known to exhibit diamagnetic behavior.[4] Thus, the magnetization of pristine SWNTs is directly related to the existence of a small amount of magnetic particles with diameter over 30 nm. For the Fe-filled SWNTs, the magnetization is therefore attributed to the presence of both catalysts and Fe nanoparticles encapsulated inside SWNTs. In addition, we have investigated the magnetic properties of ferrocene-filled SWNTs, and the magnetization data reveals that their magnetic properties appear similar to the magnetic properties of pristine SWNTs due to the diamagnetic properties of ferrocene molecules. Fig. 2(b) shows the room-temperature hysteresis loops for pristine and Fe-filled SWNTs. By comparison, the magnetization loops indicate that temperature exerts a significant effect on the sample of Fe-filled SWNTs in contrast with that of pristine SWNTs. It is obvious that small iron particles are very sensitive to the measurements, suggesting clear size dependent behavior. The saturation magnetization (M_s), coercivity (H_c), and remanent magnetization (M_r) for both samples are summarized in Table 1.

The saturation magnetization (M_s) values for both the samples show a decrease with increasing the temperature. For Fe-filled SWNTs, the value is observed to decrease from 2.6 to 1.1 emu g^{-1} when the temperature is increased from 5 to 300 K. In contrast, for pristine SWNTs, only a small decrease is observed. In relation to the iron element content in both the samples, they are measured to be about 1.9 and 0.6% for Fe-filled and pristine SWNTs, respectively, by XRF analysis. It is of note that the amount of iron content in pristine SWNTs is almost the same for each different measurement by XRF. Therefore the content of encapsulated Fe nanoparticles in SWNTs is determined to be about 1.3% by subtracting the magnetic contribution of pristine SWNTs, and their magnetization can be roughly estimated to be 171 emu g^{-1}, indicating that most encapsulated Fe nanoparticles are in the metallic phase. On the other hand, this value is less than 220 emu g^{-1} for bulk pure iron,[11] therefore, the presence of iron carbide such as Fe_3C cannot be ruled out since nanosized iron particles are very active towards carbon.[12] Consequently, the magnetization of Fe-filled SWNTs may result from both pure iron and iron carbide. In addition, the coercivity (H_c) for Fe-filled SWNTs is found to show little change compared with that for pristine SWNTs, and both the samples exhibit a similar change with variation in temperature. The observed results may be due to

Table 1 M_s, H_c and M_r for pristine and Fe-filled SWNTs at 5 and 300 K

T/K	Sample	M_s/emu g^{-1}	H_c/Oe	M_r/emu g^{-1}
5	Pristine	0.38	418	0.12
	Fe-filled	2.6	423	0.55
300	Pristine	0.32	196	0.084
	Fe-filled	1.1	200	0.17

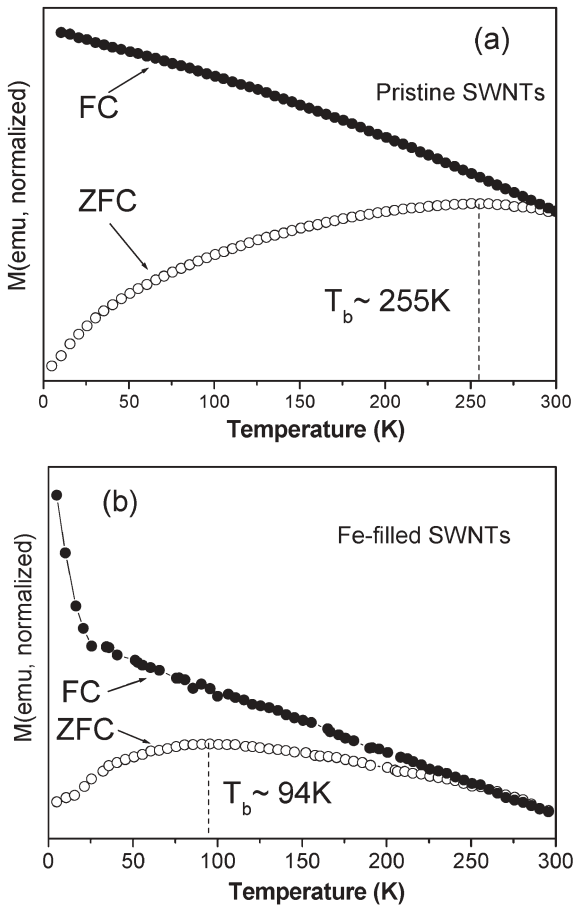

Fig. 3 Temperature dependence of ZFC and FC measurements recorded at a magnetic field of 100 Oe for pristine SWNTs (a) and Fe-filled SWNTs (b).

the reason that the coercivity depends mainly on magnetocrystalline anisotropy of magnetic catalysts particles.[11] In our case, it is difficult to form Fe crystals in SWNTs because each encapsulated Fe particle contains only several Fe atoms. Moreover, Table 1 shows that a relatively large change is observed for the remanent magnetization at 5 and 300 K for Fe-filled SWNTs compared with that for pristine SWNTs.

To gain a better understanding of the magnetic behavior of Fe-filled SWNTs, we have performed zero-field-cooled (ZFC) and field cooled (FC) magnetization measurements. For the ZFC measurements, the sample is first cooled from 300 to 5 K in zero magnetic field. After applying a 100 Oe magnetic field, the magnetization is measured in a warming cycle. For the FC measurements, the SWNTs sample is cooled in the magnetic field (100 Oe) from room temperature to 5 K, and then the magnetization is measured in the warming cycle keeping the field on. Fig. 3 shows the temperature dependence of ZFC and FC measurements under the applied magnetic field of 100 Oe for pristine SWNTs (a) and Fe-filled SWNTs (b).

The trace in FC and ZFC curves represents the characteristic feature for the different samples. For both the samples, as the temperature increases, the magnetization for FC measurements shows a decrease, which is attributed to the thermal activation effect since the magnetic moment is frozen along the direction of the applied magnetic field at low temperatures. Meanwhile, for the sample of Fe-filled SWNTs, it is noticed that a striking sharp decrease can clearly be observed in the FC curve at about 25 K, corresponding to the existence of small magnetic particles in the superparamagnetic state. For ZFC curves, as the temperature increases, the magnetization shows an increase because the magnetic moment is thermally activated along the magnetic field direction. For Fe-filled SWNTs, a blocking temperature (T_b, transition temperature from ferromagnetic to superparamagnetic state) peak can be observed in the ZFC curve at about 94 K. By contrast, the T_b peak can be identified at near room temperature of 255 K for pristine SWNTs, which is similar to the magnetic behaviour of iron-filled MWNTs,[11,13] suggesting the presence of large magnetic particles in the case of our SWNTs. Undoubtedly, the above results reveal an obvious difference between pristine and Fe-filled SWNTs, and superparamagnetic properties of Fe-filled SWNTs can be observed due to the small size distribution of Fe nanoparticles inside the SWNTs. However, owing to the unexpected effect of magnetic catalysts in Fe-filled SWNTs, we are not able to detect the blocking temperature in the range of low temperatures.

In conclusion, we have demonstrated the possibility of filling magnetic Fe nanoparticles in SWNTs using ferrocene as a starting material. TEM observations confirm that dot-like Fe particles with diameter less than 1 nm have successfully been filled inside SWNTs. Magnetic measurements taken from 5 to 300 K have confirmed that most of the encapsulated Fe nanoparticles are in the metallic phase, and superparamagnetic behavior is observed due to their small size, which shows a great difference compared with this feature observed for pristine SWNTs in which only large catalyst particles exist.

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