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Synthesis of superparamagnetic iron(III) oxide nanowires in double-walled carbon nanotubes†

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The synthesis and characterization of superparamagnetic iron(III) oxide nanowires confined within double-walled carbon nanotubes by capillary filling with a melted precursor (iron iodide) followed by thermal treatment is reported for the first time.

Carbon nanotubes (CNT) are undoubtedly one of the most striking discoveries in recent years, as these structures possess unique properties, including the ability to encapsulate foreign materials inside their cylindrical cavity, for applications in different fields.^{1,2} One simple approach to fill nanotubes is to use capillary forces, which induce the filling with either a solution^{3,4} or a melted material.^{5,6} The latter was proved to lead to a better filling rate in comparison with the wet chemistry route. In the present study we have explored the filling of double-walled CNT (DWNT) with melted iron diiodide (FeI₂), as precursor for CNT-encapsulated magnetic iron nanowires, which are planned to be used for biomedical applications, such as hyperthermia.⁷

DWNT with a selectivity of *ca.* 80% were synthesized by catalytic chemical vapour deposition (CCVD) as described in earlier work.⁸ The resulting DWNT-containing composite powder was then soaked in an aqueous HCl solution, in order to separate the CNT, by dissolving all the remaining oxide material, as well as unprotected metal (Co, Mo) particles. Unlike nitric acid or other oxidizing acids, HCl does not damage the DWNT (no opening of the DWNT, no oxidation of the tips and defects which may be present in the outer sidewall⁹). The acidic suspension was filtered on 0.45 µm pore size cellulose nitrate membrane (Whatman) and washed with deionized water until neutrality. The resulting DWNT, denoted extracted DWNT (pristine), were then dried overnight in an oven at 80 °C.¹⁰ DWNT (*ca.* 15 mg) with median inner diameter of 1.35 nm and median outer diameter of 2.05 nm,⁸ were intimately mixed in glove-box conditions with anhydrous

iron(II) iodide (*ca.* 500 mg), with a purity of 99.99+ % (Aldrich), in an approximate molar ratio of 1 : 1.3 (volumic excess = 36). The violet–black mixture-powder was then transferred into a quartz ampoule and sealed under vacuum. It was then placed in a tubular furnace and heated at 5 °C min⁻¹ to 690 °C (*ca.* 100 °C above the melting point of FeI₂, 587 °C). The sample was kept for 300 min at this temperature and melted FeI₂ entered within the DWNT, due to capillary forces. It was then slowly cooled in two steps, at 0.1 °C min⁻¹ to a temperature of 567 °C (20 °C below the melting point of FeI₂) and then at 1 °C min⁻¹ to room temperature. A black aggregate with metallic reflects was obtained, which was again ground in a mortar, until a powder was obtained. In order to eliminate the iron(II) iodide which was obviously in excess at the surface of the tubes, the resulting powder was then transferred in a small quantity of deionized water, sonicated for *ca.* 1 min in a sonication bath, filtered and then washed with deionized water, until the yellow colour of the filtrate could no longer be observed. The FeI₂@DWNT powder was dried overnight at 80 °C and then reduced in hydrogen at 250 °C for 5 h. The sample was then stored (in air) before observation by high-resolution transmission electron microscopy (HRTEM) and characterization by ⁵⁷Fe Mössbauer spectroscopy as well as magnetic measurements.

The filled DWNT were first imaged by HRTEM with a JEOL-JEM-2100 (operated at 200 kV), before and after the treatment in hydrogen.

Fig. 1(a) and (b) show two typical HRTEM images of FeI₂@DWNT observed before the reduction in hydrogen. Most of the DWNT were found to be clean of deposits on the outer wall, and were filled with crystallized material. Either in the case of bundles (Fig. 1(a)) or for separated tubes (Fig. 1(b)), strong contrasts arranged in a regular fashion could be clearly detected inside the DWNT and on almost all their observable length. This regular alignment of dark spots indicates a very nice crystallization of FeI₂ (structure model of bulk FeI₂ represented in Fig. 1(f)). Based on the visual inspection of all HRTEM images, the filling yield was estimated to be higher than *ca.* 60%. In a previous study,⁴ similar DWNT were filled with a much lower yield starting from a precursor in solution (FeCl₃). The presence of some FeI₂ nanocrystals located outside the DWNT was observed to a very limited extent, suggesting that the washing conditions with deionized water are efficient, but could still be optimized (longer time). EDX analysis† confirmed the concomitant presence of both iron and iodine in the sample. Besides,

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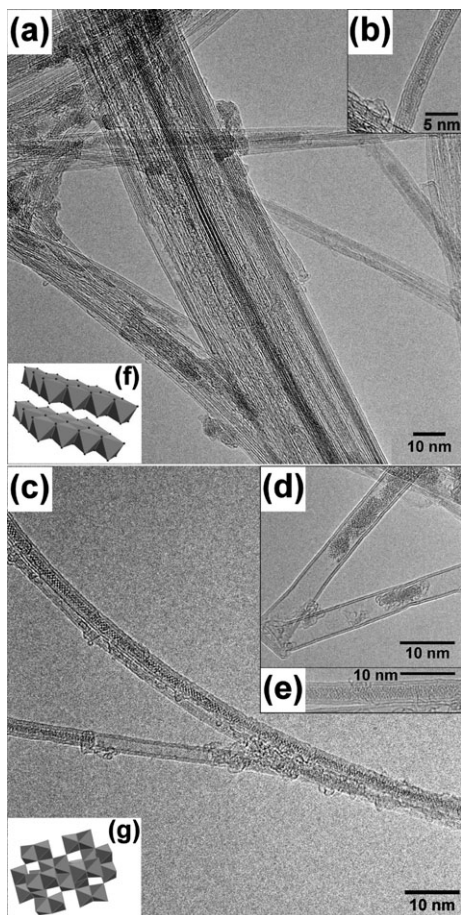


Fig. 1 HRTEM images of Fe_2O_3 filling within (a) a DWNT bundle; (b) a single DWNT; (c) DWNT filled with superparamagnetic iron(III) oxide nanowires; (d) DWNT with large diameter, filled with iron(III) oxide nanoparticles; (e) smaller diameter DWNT filled with iron(III) oxide nanowire; (f) structure model of bulk Fe_2O_3 ; (g) structure model of bulk iron(III) oxide.

elemental analysis indicated 12.3 wt% of iron in the sample, which is a quantitative confirmation of the good filling rate evidenced by the HRTEM images.

Fig. 1(c)–(e) present HRTEM images of filled DWNT after the treatment in hydrogen. In Fig. 1(d), a discontinuous filling with apparently poorly organized material is shown, while in Fig. 1(c) and (e) the filling was achieved on all the observable length of the tubes. Although the filling yield was still estimated to be over 60%, the crystallized filling material was found

more discontinuous than before the reduction treatment, with the frequent observation of crystals only a few tens of nanometres in length (Fig. 1(c)), suggesting that some chemical modification occurred. This was confirmed by EDX analysis which indicated the absence of iodine (oxygen was also detected but could not be related to the presence of an iron oxide because the starting DWNT already contained traces of oxygen¹¹). The XRD pattern shows the presence of low-intensity broad peaks at the angles corresponding to $\gamma\text{-Fe}_2\text{O}_3$, although the small quantity and small size do not allow a full analysis of the data (size of crystallites). It is however clear that no peak of bcc-Fe was present, unlike in our previous work.⁴

The observation of crystalline material inside the DWNT is not an evidence that the final compound obtained after reduction in hydrogen is actually iron metal. After treatment in hydrogen, the sample was analyzed by ^{57}Fe Mössbauer spectroscopy at three different temperatures (RT, 77 K and 45 K) and the results (Fig. 2) indicated that the iron within the tubes was in the form of superparamagnetic (SPM) iron(III) oxide nanoparticles, both at RT and liquid nitrogen temperature.

At 45 K, a magnetic contribution (39% area, present as a large hyperfine magnetic field distribution, with two relative maxima at 160 kG and 460 kG) was superimposed with the SPM quadrupolar doublet. The fact that at 45 K the magnetic contribution was 39% of the total area indicates that the Mössbauer blocking temperature T_{BM} has not been reached (this temperature is determined when the respective areas of the SPM and magnetic contributions are equal).¹²

In order to confirm the superparamagnetism of the iron(III) oxide nanowires, magnetic measurements were also performed, with a Quantum Design MPMS SQUID, from 2 to 300 K. Usual zero-field-cooled (ZFC) and FC measurements were performed to observe magnetic irreversibility.

For the hysteresis loop $M(H)$ measurements were obtained between + 10 KOe and – 10 KOe.

Fig. 3(a) shows the FC and ZFC curves for the iron oxide nanowires inside the DWNT from 2 to 300 K at different constant magnetic fields ($20 \leq H \leq 1000$ Oe). On the one hand, the ZFC susceptibility curves exhibit a broad peak indicating the blocking temperature $T_{\text{B}\chi}$, as found in superparamagnetic compounds ($T_{\text{B}\chi} = 32$ K for $H = 20$ Oe), related to the mean particle size. The $T_{\text{B}\chi}$ decreased monotonically with increasing the magnetic field. Such a peak in the ZFC curve generally implies a distribution in particle size and anisotropy.¹³ On the other hand, the FC branch

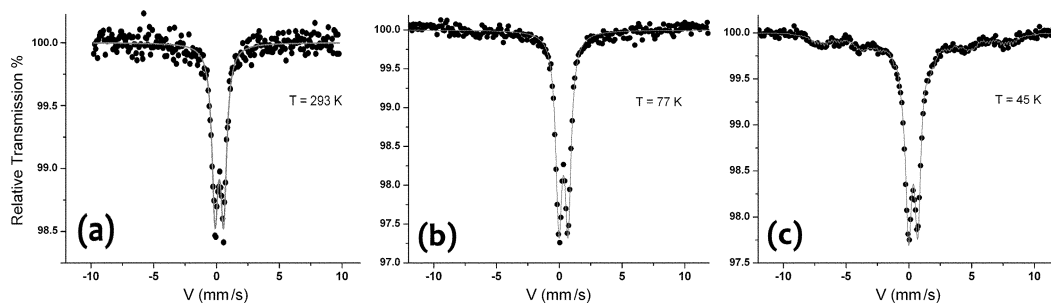


Fig. 2 Mössbauer spectra of the reduced samples at RT, 77 K and 45 K. The experimental result (black dots) and the theoretical fit (continuous line) are shown.

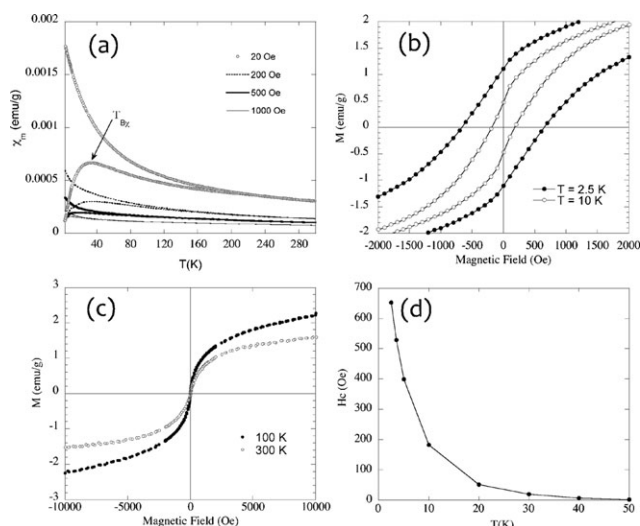


Fig. 3 Magnetization as a function of temperature at different magnetic fields. (a) The ZFC curve shows the blocking temperature T_{BL} of superparamagnetic behaviour. (b) Magnetization vs. H showing the symmetric hysteresis at two temperatures below T_{BL} . (c) In the superparamagnetic region the magnetization curves exhibits no hysteresis. As an example we show the magnetization at 100 and 300 K. (d) Temperature dependence of the coercivity (zero above T_{BL}).

displays a continuous increase when decreasing T , without tendency to magnetization saturation below T_{BL} , showing a $M_{FC}(T_{BL}) \approx 0.61M_{FC}(10\text{ K})$ and an irreversibility of $M_{ZFC}(T_{BL}) \approx 0.63M_{FC}(T_{BL})$. Above T_{BL} , the ZFC and FC data show a perfectly reversible behaviour at all fields. The lack of FC saturation points out to the existence of a (quasi) independent relaxation and then a magnetically ideal SPM behaviour. In a similar system comprising Co nanoparticles in mesoporous (SiO_2) media,¹⁴ the increasing magnetic inter-particle (dipolar) interactions by increasing Co concentration were deduced from the FC curves. This resulted in a saturation ($M_{FC}(T_{BL}) \approx M_{FC}(10\text{ K})$ and $M_{ZFC}(T_{BL}) \approx M_{FC}(T_{BL})$) of that FC branch, visible at 14% Co in pores. Indeed, this FC feature is here providing some useful information on the arrangement of the wires in the tubes; namely, the Fe-oxide nanowires encapsulated with a high filling ratio should be then separated in discrete long portions in a chain-like arrangement, which is supported by TEM observations (Fig. 3(c) and (d)). The distance between chain wires should be some tenths of nanometers to result in a very weak dipolar interaction ($\propto 1/r^3$) to allow the observed ideal SPM behavior displayed in Fig. 3(a). Furthermore, to display such a behaviour, we suggest that the randomly arranged wires (possibly $\gamma\text{-Fe}_2\text{O}_3$) present a feeble inter-wire magnetic coupling through the carbon wall, due to the average distance around 1 nm. Indeed, nanometric sols of $\gamma\text{-Fe}_2\text{O}_3$ in PVA in various arrangements and interparticle distances have been the subject of extensive research, from independent to highly-coupled nanoparticles and chains.^{13–15} In the case of particles of 8 nm size, separated by an average distance of ca. 64 nm, a blocking temperature very similar to the present results was observed in the ZFC/FC curves,¹⁵ with a ZFC peak $\approx 40\text{ K}$, and a FC continuous increase with $M_{FC}(T_{BL}) \approx 0.79M_{FC}(10\text{ K})$ and $M_{ZFC}(T_{BL}) \approx 0.85M_{FC}(T_{BL})$. The ideal superparamagnetism

of the iron oxides is also obvious in the $M(H)$ hysteresis data. Between 2.2 and 40 K, a symmetrical hysteresis loop was observed, indicating the ferromagnetic nature of the iron nanosystem (either nanowires or particles) in this range of temperatures which is below the blocking temperature ($T_{BL} = 32\text{ K}$).

As an example Fig. 3(b) shows the hysteresis loops at 2.5 and 10 K. In the superparamagnetic region ($T_{BL} > 32\text{ K}$) the magnetization curves exhibit no hysteresis and both remanence and coercivity are equal to zero. Fig. 3(c) shows the magnetization curves at 100 and 300 K with no hysteresis loop. From the hysteresis curves at different temperatures (Fig. 3(d)) we can obtain the values of the coercivity. As predicted by the theory of superparamagnetism¹³ the coercivity is equal to zero (no hysteresis) for temperatures above T_{BL} .

In agreement with ⁵⁷Fe Mössbauer spectroscopy and magnetic measurements data, the reduction of FeI_2 in hydrogen was probably directly followed by oxidation, leading to superparamagnetic iron(III) oxide crystallized nanowires (supported by HRTEM observations) forming chain-like structures inside DWNT (the exact nature of those structures, wires or particles, is under investigation).

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