Observation of a superparamagnetic breakdown in gadolinium chloride filled double-walled carbon nanotubes

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ABSTRACT

In this article, the magnetic properties of gadolinium chloride-filled double-walled carbon nanotubes ($GdCl_3$@DWNTs) in the temperature range 2-300 K are explored. The temperature-dependent phonon frequencies of the G-band were studied from 80-300 K to investigate the effect of temperature on the magnetic ordering. Temperature-dependent susceptibility measurements show that the $GdCl_3$@DWNTs sample has a pronounced superparamagnetic phase from 83 K. The temperature dependence of the G-band frequency for filled tubes exhibited a distinct difference compared to pristine nanotubes, where a sharp phonon hardening at low temperatures was observed. A correlation between the onset temperature of superparamagnetism and the abrupt G-band phonon hardening in the filled tubes was verified. $GdCl_3$@DWNTs were characterized by a finite remnant magnetization at 300 K which decreased as the temperature was lowered because of the presence of the discontinuous magnetic nanoparticles, providing a superparamagnetic contribution characterized by an S-shaped non-saturating hysteresis loop at 2 K. Remarkably, the onset of superparamagnetism, marked by the bifurcation point, occurred at roughly the same temperature where the G-band phonon frequency showed a pronounced hardening at approximately 80 K, indicating a close correlation between phonon modes and spin clusters.

I. INTRODUCTION

Nanoscale magnetic ordering in exotic and artificial materials and devices has attracted attention due to the wide applicability of nanomagnets for technological advancements[1–3] forming a new branch in condensed matter physics. Superparamagnetism, first described by Louis Néel, is a property arising out of single-domain behaviour when a bulk ferromagnet (FM) or an antiferromagnet (AFM) is reduced to a size below about 50 nm.[4,5] Magnetic phase transitions as a function of temperature and crystallite size have been extensively studied in the past[6–8] for biomedical applications and ferrofluids.[9,10] Double-walled carbon nanotubes (DWNT) are of interest because of their coaxial nature which makes them better candidates for nanoscale engineering in the biomedical field.[9] Further, by introducing nanomagnets into the interior of DWNT the expectation is that magnetic and electronic properties significantly will vary significatly.[11,12] The Gd^{3+} ion is known as a key component for the design of paramagnetic complexes as it has the largest number of unpaired electrons within the rare earth elements.[13] Its presence in the carbon nanotube (CNT) is expected to have a direct effect on the interwall interaction because of the proximity of the inner and outer wall.[14] The structural and complementary magnetic properties presented here, are novel as the phonon dependent magnetic properties of DWNTs modified with gadolinium has not been reported before, as most studies have focused on either single-walled (SWNTs) or multiwalled carbon nanotubes (MWNTs).[15,16]

This work reports how the encapsulation of Gd^{3+} ions into the inner core of a CNT changes the magnetic ordering of the CNT-lanthanide composite at low temperatures. The temperature-dependent magnetization and Raman phonon frequency shift are investigated to explore the superparamagnetic relaxation which is assumed to happen by coherent rotation of the spins.

II. EXPERIMENTAL METHODS

DWNTs and $GdCl_3$ filled DWNTs were prepared using a method described previously[17] and characterized through high-resolution transmission microscopy (HRTEM) and inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Field dependent magnetization, $M(H)$, at different constant temperatures were measured using a Cryogenic high field measurement system with a vibrating sample magnetometer (VSM). Susceptibility as a function of temperature, $\chi(T)$ was also measured using the VSM in the field cooled (FC) and zero field cooled (ZFC) modes from 300-2 K in an applied magnetic field of 0.01 T. Raman spectroscopy measurements were done from 80-300 K using a Bruker laser Raman spectrometer.

III. RESULTS AND DISCUSSION

Fig. 1 presents an HRTEM image of the $GdCl_3$@DWNTs clearly showing the successful filling of the nanotubes where the $GdCl_3$ nanocrystals could be identified as discontinuous rod-like structures with varying lengths of 5 to 30 nm within the core of the innermost tube. The technique for filling DWNTs was reported before,[17,18] and HRTEM studies confirmed the filled material as $GdCl_3$ through investigations of the crystal lattice structure.[18] The $GdCl_3$ was randomly distributed within the DWNTs and the effect of the filling is correlated to the magnetic properties. Through ICP-OES it was established that the $GdCl_3$@DWNTs had an elemental composition of Co: 1.21%, Mo: 0.48%, Gd: 6.90% weight percentage.

Fig. 2 depicts the magnetic and Raman data for $GdCl_3$@DWNTs. Fig. 2(a) shows the $\chi(T)$ measured in the FC and ZFC modes. A clear downturn at 16±5 K was observed, indicative of a superparamagnetic transition.[19] Fig. 2(b) shows typical $M(H)$ loop as a function of the applied magnetic field measured at different temperatures (2 and 300 K). In Fig 2(c) the temperature dependant Raman G-band is shown. The clear peak shift observed at wavelength 1588 cm^{-1} to 1591 cm^{-1} respectively, is associated with the G-band confirming phonon hardening.[20] The phonon hardening coincides with the onset of superparamagnetism depicted in Fig. 2(a).

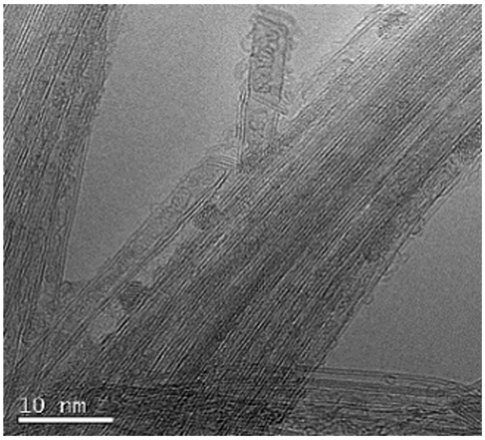

FIG. 1. HRTEM images of $GdCl_3$-filled double-walled carbon nanotubes (DWNTs) showing different filling morphologies in the inner core of the DWNTs.

It is known that CNTs modified with Gd undergo superparamagnetic transitions at low temperatures.[21,22] The hallmark of this effect is the bifurcation observed between FC and ZFC susceptibility, $\chi(T)$, as shown in Fig. 2(a), indicating how the non-interaction of ferromagnetic centers leads to superparamagnetism.[5] The bifurcation starts at 83±7 K and upon decreasing the temperature the gap between the FC and ZFC broadens. At 16±5 K, there is a sudden downward turn observed in the ZFC data associated with the blocking temperature, (T_B), defined as the maximum temperature in the ZFC curve. The maximum observed at T_B results when the thermal fluctuations within the nanoparticles are comparable to or greater than the energy barrier for moment reversal, allowing rapid random flipping of the nanoparticles' magnetic moments.[19]

Two significant temperatures have thus been identified, the higher one being the bifurcation temperature which signifies the onset of the superparamagnetic phase, and the second lower temperature is the blocking temperature which indicates the dominance of the superparamagnetic phase.[5,19] The broad bifurcation transition is a consequence of the inhomogeneity in the magnetic particles' sizes, seen in the HRTEM image (Fig. 1), resulting in a range of blocking temperatures corresponding to the different sized particles.[5]

The inverse of the ZFC susceptibility ($1/\chi$) was plotted as a function of temperature (Fig. 2(a) Inset) to determine the coupling mechanism. For the $GdCl_3$@DWNTs the $1/\chi$ versus T curve was linear in the temperature range from 300 K down to approximately 83 K, which is close to the determined bifurcation temperature in the $\chi(T)$, followed by a steeper decrease. This is an indication of a magnetic phase transition.[5] Using the Curie-Weiss law, a negative Weiss constant of -155 K was obtained, indicating antiferromagnetic (AFM) exchange interaction. AFM exchange requires the existence of an interaction between two spin sublattices of different spin orientation.[19] In the $GdCl_3$ filled DWNT studied here, the AFM features are most likely due to the exchange coupling between neighbouring clusters of $GdCl_3$ inter particle interactions dominating over intra-particle interactions. The delocalized electrons of the nanotubes are candidates for mediating the AFM through the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction.[1] The exchange coupling provides an additional magnetic anisotropy to help align the ferromagnetic spins in a certain direction[19] and it diminishes above a critical temperature called the blocking temperature.

The $M(H)$ curves, Fig. 2(b), show that the $GdCl_3$@DWNTs is weakly ferromagnetic (FM) at room temperature, characterized by a weak coercive field of 0.030 ± 0.005 T and remanence of 0.2 ± 0.02 emu. g^{-1}. This is characteristic of FM Gd ions with a Curie temperature, T_C, of 292 K.[23] The pristine DWNTs are paramagnetic.[24] Thus, the observed magnetization in $GdCl_3$@DWNTs is considered to be because of the presence of Gd^{3+} ions. As the temperature is lowered below the T_B, the $M(H)$ loop shows a transition

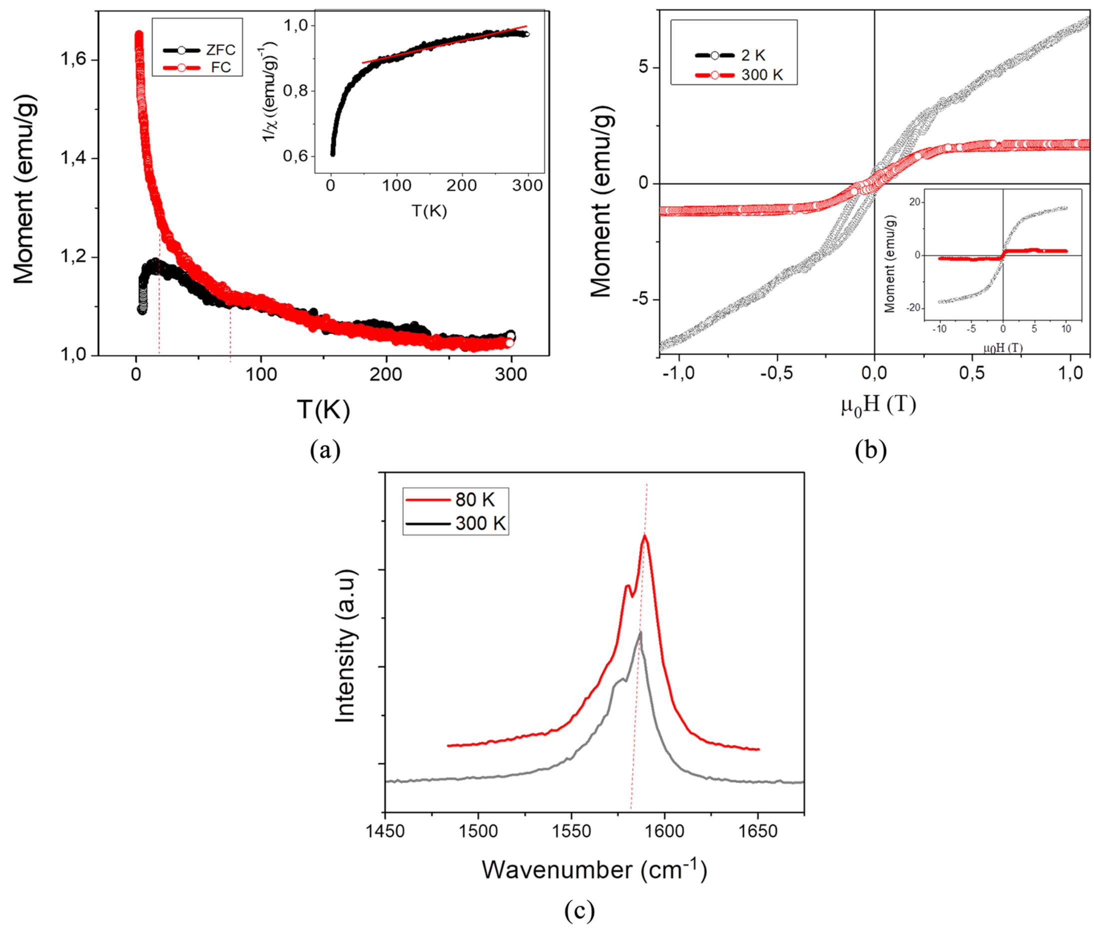

FIG. 2. Magnetic and Raman data for $GdCl_3$@DWNTs (a) $\chi(T)$ measured in the FC and ZFC showing a downturn at 16±5 K indicative of a superparamagnetic transition, inset shows the inverse FC susceptibility, $1/\chi(T)$ (b) Typical magnetization loops as a function of the applied magnetic field measured at different temperatures (2 and 300 K). The Inset shows the full-scale magnetization as function of field measurements (c) Temperature dependant Raman G-band showing a shift to higher wavenumbers at low temperatures.

from weakly ferromagnetic to superparamagnetic behaviour as shown in the inset of Fig. 2(b). This is characterized by a non-saturating hysteresis and a distinct change in the shape of the hysteresis at 2 K which coincides with the superparamagnetic region in the $\chi(T)$. Hence, the magnetization of the noninteracting Gd^{3+} ions randomly flips direction under the influence of temperature.[21] As the temperature is lowered below the T_B, the $M(H)$ loop is characterized by a nonzero coercivity, due to surface defects in nanocomposites that create high exchange energy increasing the coercivity of a system that has an antiferromagnetic exchange interaction.[25] This phenomenon is generally termed as superferromagnetism, often observed when the nanoparticles are brought very close to each other[26] and arises due to the $GdCl_3$ dipolar interaction at low temperatures in this system.

Fig. 2(c) shows the polarized Raman spectra highlighting the change in the position of the G-band phonon frequency with temperature. The G-band, which is normally found at 1580 cm^{-1}, is shifted from 1588 cm^{-1} to 1594 cm^{-1} in $GdCl_3$ filled DWNTs as the temperature is lowered. This is known as phonon hardening which arises from spin-phonon coupling.[20,27] A significant change of the phonon frequency with temperature is a manifestation of the anharmonic terms in the lattice potential energy, which is determined by the anharmonic potential constant described by the Balkanski model.[28] This model describes how the Raman frequency shift linked to the temperature variation is affected by a change of lattice parameter resulting from cubic anharmonic interactions between nearest-neighbour atoms.[28,29] Hence the observed phonon hardening in $GdCl_3$ filled DWNTs can be correlated to spin reorientation and the influence of the single-domain behaviour arising from the superparamagnetic phase transition that onsets at the bifurcation temperature.

IV. DISCUSSION AND CONCLUSION

It has been shown that DWNTs filled with $GdCl_3$ undergo a superparamagnetic transition that can be correlated to phonon hardening at low temperatures. As seen in the susceptibility data, superparamagnetism is verified in the filled DWNTs through the bifurcation observed in ZFC and FC measurements, which onsets at 83±7 K. The blocking temperature for the superparamagnetic phase was determined to be 16±5 K. This is particularly interesting when considering the spin relaxation mechanisms known for the superparamagnetic breakdown.[30,31] The superparamagnetic breakdown becomes apparent as a result of the induced limit attributed to the particle size of the Gd ions. At this point, the formation of several domains becomes energetically unfavourable and the particle becomes a magnetic single domain. At low temperatures, the superparamagnetic relaxation of the magnetization of small non-interacting particles under the influence of an external magnetic field can be described by a phonon-mediated spin relaxation in which the total spin of the monodomain particle interacts with strain fields. This work furthers the understanding of the spin-phonon interactions in low dimensional systems and can contribute to the design of superparamagnetic complexes for biomedical applications.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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