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Revealing the interparticle magnetic interactions of iron oxide nanoparticles-carbon nanotubes hybrid materials

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Abstract. Spinel iron oxide nanoparticles capped with organic molecules have been successfully prepared and used to produce iron oxide nanoparticles-single wall carbon nanotubes hybrid materials, which were characterized by a number of experimental techniques. The nanoparticles in both samples have an average particle size of about 10 nm and acquire a chemical composition of the type $Fe_{3-x}O_4$, with $0<x<1/3$. ^{57}Fe Mössbauer spectroscopy and magnetization measurements suggest that the free capped nanoparticles experience stronger superparamagnetic effects with respect to the nanoparticles of the hybrid sample, which show stronger magnetic interparticle interactions. The mutual proximity of the magnetic nanoparticles of the hybrid sample is proposed to be the origin for this behaviour, which is triggered by their denser anchoring to the outer surface of the singe wall carbon nanotubes due to the reduced dimensions of the latter.

1. Introduction

Magnetic nanoparticles (NPs) are important materials with a wide range of technological applications, like media for magnetic data storage [1], drug carriers, identifiers as also contrast and hyperthermia agents in biomedicine [2]. On the other hand carbon nanotubes (CNTs) are novel developed versatile materials with extraordinary structural, mechanical, electronic and magnetic properties and posses a high potential to be used in many aspects of modern technical implementations [3]. The joining of the properties of both categories of materials has given rise to new fields of research and possible future technological applications [3].

Metal alloy (FePt) magnetic nanoparticles-carbon nanotubes (NPs-CNTs) hybrid materials have been prepared recently and their study has revealed very interesting structural, electronic and magnetic properties [4]. In this work we report on the study of the morphological, structural and magnetic properties of iron oxide NPs in NPs-CNTs hybrid materials, using, amongst other experimental techniques, the unique ^{57}Fe Mössbauer spectroscopy, which can give very important atomic-level information on their characteristics.

2. Experimental procedure

Capped iron oxide NPs, and iron oxide NPs-CNTs hybrids where prepared using wet chemical routes described in our previous work [5]. For the preparation of the hybrid samples, single-wall CNTs (Aldrich) were used and the capped iron oxide NPs were attached to the CNTs by means of an interlinker molecule (a carboxylic derivative of Pyrene). The relative mass ratio of capped NPs/single-wall CNTs was 10/1.

The prepared samples were characterized and studied using a number of experimental techniques. X-Ray diffraction (XRD) patterns were collected in a Bruker D8 Advance diffractometer using Cu K_α radiation. Raman and FT-IR spectra were recorded at room temperature (RT) in a RM 1000 Renishaw and a Spectrum GS Perkin-Elmer spectrometer respectively. Transmission Electron Microscopy (TEM) pictures of both samples were captured in a JEOL JEM-2010F microscope. Magnetization and magnetic susceptibility measurements were collected on a LakeShore 7300 Vibrating Sample Magnetometer. ^{57}Fe Mössbauer spectra (MS) were recorded at different sample temperatures using a constant acceleration spectrometer equipped with a ^{57}Co(Rh) source kept at RT and a liquid N_2 bath cryostat (Oxford). The calibration of the spectrometer was done using metallic iron at RT and the isomer shift (IS) values are given relative to this standard.

3. Results and Discussion

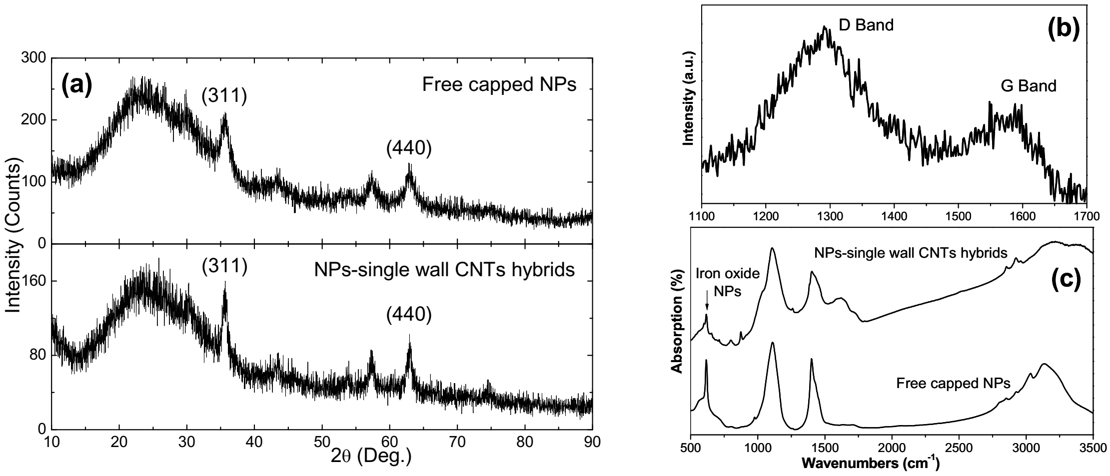

Figure 1. (a) XRD diagrams of the capped iron oxide NPs and the iron oxide NPs-CNTs hybrid samples, (b) Raman spectrum of the NPs-CNTs hybrid sample and (c) FT-IR spectra of the capped NPs and NPs-CNTs hybrid samples.

XRD patterns of both the capped iron oxide NPs and the iron oxide NPs-CNTs hybrids are shown in figure 1(a). The characteristic diffraction peaks of an oxidic spinel phase are shown in both diagrams indicating the presence of either Fe_3O_4 or γ-Fe_2O_3 iron oxide phases. The peaks are broad and determining the exact chemical composition of the iron oxide phase from these diagrams is quite difficult, since the XRD patterns of Fe_3O_4 or γ-Fe_2O_3 show diffraction peaks at almost the same angular positions [6]. The very broad curve between 15 and 40 degrees 2θ is due to the glass sample holder. The absence of a diffraction peak at around 26 degrees 2θ in the diagram of the hybrid sample, which would confirm the existence of the graphitic structure of the CNTs is attributed both to the large contribution of the background of the sample holder and to the reduced dimensions (~ 1-2 nm in diameter) of the single wall nature of the CNTs. Appling the Scherrer formula [7] to the diffraction peaks of the spinel phase we have estimated the average particle size to be about 10 nm for the capped iron oxide NPs and about 11 nm for the NPs of the hybrid sample. The Raman spectrum of the NPs-CNTs hybrid sample is shown in figure 1(b). The spectrum indicates the presence of carbon nanotubes from the two characteristic graphitic signals corresponding to D and G bands with a relative intensity ratio of $I_D/I_G \sim 2.0$. FT-IR spectra appearing in figure 1(c), reveal the presence of the iron oxide magnetic NPs in the final hybrid material which show a characteristic peak at around 610 cm^{-1}.

The TEM image of the capped NPs sample displayed in figure 2(a) shows a quite uniform particle size of about 10 nm. The corresponding image of the hybrid sample shown in figure 2(b), although being not as clear as that of the free NPs sample, shows roughly the same sizes for the iron oxide NPs and some indication of the presence of single wall CNTs could also be found.

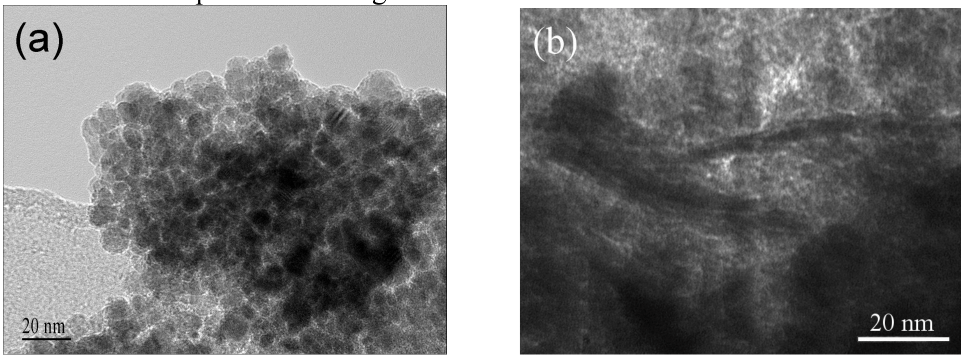

Figure 2. TEM images of the capped NPs (a) and the NPs-CNTs hybrid (b) samples.

^{57}Fe MS of both samples collected at 300 K, 140 K and 77 K appear in figure 3. The main characteristics of the 300 K spectra are the presence of a central paramagnetic doublet accompanied with a set of resolved as well as collapsing magnetically split components. The loss of the doublets' absorption area as the temperature drops reveals their superparamagnetic (SPM) character in both samples. The contribution of the SPM doublet is dominant in the RT spectrum of the capped NPs sample (~50% of the total absorption area (A)), in which also two magnetic components with collapsing hyperfine magnetic fields (B_{hf}) of 29.6(12.0) T and 8.5(4.7) T respectively, appear (the values in parentheses are the -Gaussian type- spreading of B_{hf} allowed for each magnetic component). On the contrary the contribution of the SPM doublet is minor for the RT spectrum of the hybrid sample (~12% of A), where also another 47% of A is occupied by two clearly resolved sextets with B_{hf} of 45.2(2.4) T and 37.2(6.1) T, and the remaining 41% by a collapsing magnetic component with a B_{hf} of 12.4(11.3) T. Here we note that, due to the monodispersed nature of the samples, the different B_{hf} distributed components corresponding to the magnetic part of the spectra, are used to arbitrary parameterize in the fit the intermediate relaxation rate of the NPs. The IS values of all components in both 300 K spectra range between 0.34 mms^{-1} and 0.41 mms^{-1}, suggesting the presence of only Fe^{3+} ions in the iron oxide spinel NPs.

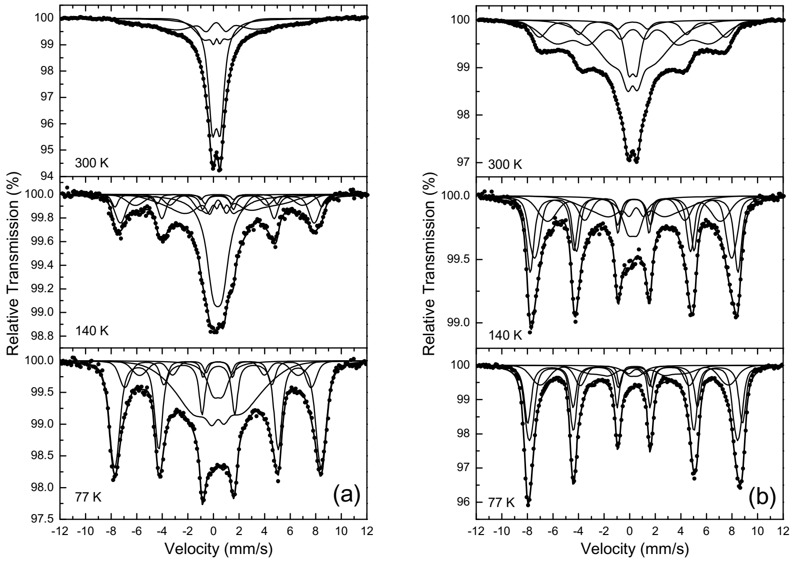

Figure 3. ^{57}Fe MS of capped NPs (a) and NPs-CNTs hybrids (b) samples recorded at different temperatures.

At 140 K the spectrum of the hybrid sample acquires relatively sharper magnetically split absorption lines, while that of the capped NPs sample still posses a large central contribution from collapsing B_{hf} and SPM components. The same characteristics are observed also for the 77 K spectra, where the intense contribution of a major magnetically split component with collapsing B_{hf} is still present for the capped NPs sample. The IS of some of the magnetically split components of the 140 K and 77 K spectra of both samples acquire relatively higher values than those expected from the increase of the corresponding RT values due to the second order Doppler shift effect [8], indicating the possible presence of some $Fe^{2.5+}$ states and suggesting that the iron oxide NPs have an average chemical composition of the type $Fe_{3-x}O_4$, with x between 0 (magnetite) and 1/3 (maghemite).

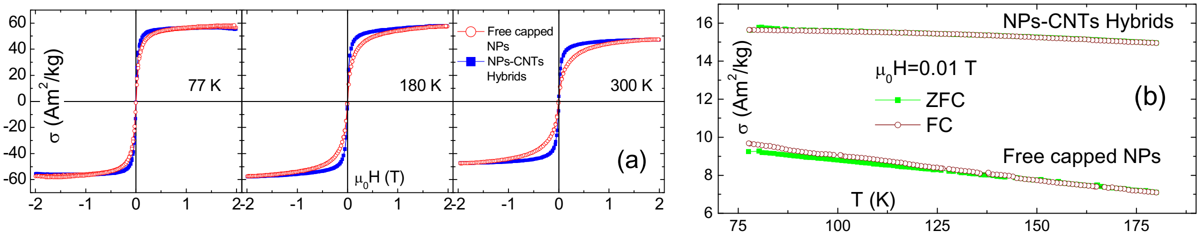

Figure 4. Magnetization measurements of the capped iron oxide NPs and the iron oxide NPs-CNTs hybrid samples as a function of the external magnetic field (a) and temperature (b).

Defining the Blocking temperature (T_B) as that in which the absorption area of the SPM component is half of the total absorption area A, we can estimate the T_B of the capped NPs sample to be around 300 K and that of the hybrid sample to be much higher. This trend comes in agreement with the magnetization measurements shown in figure 4, as the SPM characteristics (relatively low $d\sigma/dH$ slope, lack of saturation at low fields and diversification of zero field cooled and field cooled curves) are more evident in the case of the capped NPs sample.

Given the same average NPs size for both samples as estimated from XRD and TEM, the above results suggest that stronger interparticle interactions are experienced by the NPs of the hybrid sample, relative to those of the capped NPs sample. This is opposite to what we have found for the corresponding capped FePt metal alloy NPs and NPs-CNTs hybrid samples [4], where selective isolation of these FePt NPs on the outer surface of the multi-wall (in that case) CNTs, induced stronger SPM effects for the hybrid sample, relative to the stronger magnetic interparticle interactions observed for the corresponding capped NPs sample. We propose that the stronger magnetic interparticle interactions in our present iron oxide NPs-CNTs hybrid sample are a consequence of the high mutual proximity of these NPs. The reason for such a different behaviour for the NPs of the hybrid sample lies in the use of single- rather than multi-wall CNTs in the present case. The single-wall CNTs of reduced dimensions (1-2 nm) trigger a high local concentration of magnetic NPs, as the NPs anchor around these CNTs with increased density, compared to the case of the multi-wall CNTs.

4. Conclusions

The present work of producing new spinel iron oxide NPs-CNTs hybrids, in which the NPs acquire different magnetic properties when they are attached to the single-wall CNTs in comparison to our previous work on metallic FePt NPs-multi-wall CNTs [4], has shown that it is possible to develop a versatile method for preparation of magnetic NPs-CNTs hybrid materials with tunable magnetic properties, through the control of the NPs and CNTs sizes, as well as their relative mass ratios.

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