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Controlling the magnetic response of carbon nanotubes filled with iron-containing material

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ABSTRACT

Magnetic nanoparticles and/or nanowires are being encapsulated in carbon nanotubes (CNTs) as an alternative to introduce a magnetic response to CNTs. This work proposes a novel route to control the magnetic response of CNTs filled with iron-containing nanomaterial through the synthesis process and heat treatment. CNTs were synthesized through chemical vapor deposition from ferrocene at 750 °C. They were characterized by Raman spectroscopy and microscopy. In addition, the CNTs were heat treated after the synthesis; CNTs were heated at 1000 °C for 10 min in an inert atmosphere. The magnetic properties of CNTs as grown and after heat treatment were evaluated using the hysteresis loop and Mössbauer spectroscopy. Results show that there is a correlation between the manufacturing process – considering synthesis parameters and heat treatment – and the composition of iron-containing phases in the CNTs. By varying the temperature and dwell time of synthesis, the composition of the phases encapsulated by CNTs will be different. Heat treatment performed on the CNTs after the synthesis, also resulted in significant modification of the final phases trapped by the nanotubes. These methods enabled the control of which phases remained encapsulated by the nanotubes. This study shows it is possible to control the final magnetic properties, e.g. coercivity, of CNTs filled with magnetic material so as to synthesize the most appropriate magnetic nanomaterial for a specific application.

1. Introduction

Magnetic nanomaterials have been the focus of research of numerous scientists due to their large range of possible applications [1], e.g. the use of magnetic nanoparticles to produce nanocomposites and ferrofluids [2]; and the use of these nanoparticles to control magnetic hyperthermia [3]. Studies in the field of magnetic nanomaterials are mainly focused on the use of iron nanoparticles, which have the disadvantage of easy oxidation. Recently, researchers have proposed the use of magnetic nanoparticles and/or nanowires encapsulated in carbon nanotubes (CNT) as an alternative to solve this issue [4,5]. Depending on the synthesis method and precursor materials, CNTs can be filled with different nanoparticles [6,7]. The chemical vapor deposition (CVD) method is the most successful method to encapsulate these materials. A feasible route to grow CNTs that does not require high temperatures and expensive precursors relies on the use of ferrocene ($Fe(C_5H_5)_2$) as both precursor and catalyst of the synthesis [8–11]. Iron-containing phases filling CNTs are known [12–14] to be inherent to the production process when ferrocene is used as the precursor. Researchers have acquired CNTs filled with α-iron, γ-iron and iron carbides [12,15,16]. These phases provide a magnetic response to the nanotubes, which is seen to have potential applications in magnetic devices.

The following work correlates the composition of the phases encapsulated in the CNTs with the synthesis method and heat treatment to which these nanotubes are submitted. This work shows that there is a correlation between the manufacturing process – considering synthesis parameters and heat treatment – and the composition of iron-containing phases in the CNTs. By varying the synthesis temperature and dwell time used for the CNT production, the authors could control which phases remained encapsulated by the nanotubes. Heat treatment after the synthesis can also modify the final phases inside the nanotubes. The results presented in this work prove that it is possible to control the final magnetic properties, e.g. coercivity, of CNTs filled with magnetic material so as to synthesize the most appropriate magnetic nanomaterial for a specific application.

2. Materials and methods

The CNTs were synthesized in a CVD apparatus, composed basically of a 30 mm inner diameter quartz glass tube placed into a

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cylindrical furnace that can slide along the tube. Highly pure Helium gas was pumped into the tube reactor at 300 sccm (5×10^{-6} m^3/s). High surface area silica nanopowder was used as substrate for the nucleation and growth of CNTs. The silica nanopowder was supplied by Evonik Industries (Aerosil 200). Ferrocene, which was used as iron and carbon precursor, was purchased from Sigma Aldrich. The synthesis temperature was 750 °C with a ramp up ratio of 30 °C/min. The employed dwell time was 2 min.

Before the synthesis, the ferrocene was placed into the quartz tube next to the heat zone of the reactor and the silica substrate was placed in the heat zone. The temperature was ramped up to 750 °C and once this temperature was reached, the ferrocene was subjected to the heat to undergo pyrolysis, with CNT nucleation and growth occurring, therefore, in a few seconds. When the synthesis was done, a black powder containing CNTs was obtained over the silica nanopowder and nearly no remaining material was observed on the tube walls. Further details of the synthesis can be read in previous work [17]. The employed synthesis method was optimized from ferrocene routes that were previously proposed [8–10]; in the current synthesis method, the usage of a high surface area powder as substrate guarantees high efficiency at relatively low synthesis times and temperatures.

After the synthesis, the CNTs were exposed to heat treatment, with the temperature being increased to 1000 °C and maintained at this level for 10 min. This process was performed under highly pure Helium gas, to assure an inert atmosphere. Inert atmosphere prevents the CNTs structure to be destroyed; in fact several researchers use synthesis temperature up to 1300 °C to guarantee the synthesis of CNTs with less defects on their structure [18–20]. Moreover, high temperature heat treatment under inert atmosphere has already been used to eliminate amorphous carbon and defects of the structure of CNTs without damaging their structure [21].

The product of the synthesis was evaluated regarding its structure with a Raman Spectroscope, model Renishaw in Via Spectrometer System. The experiments were performed at room temperature, at a range of 0–3100 cm^{-1} using a laser of 514 nm. A transmission electron microscope (TEM) was also used to evaluate the CNTs' morphology. The equipment used was a TEM Jeol JEM 1200ExII. In addition, tests of the chemical composition and magnetic properties of the contents before and after the heat treatment were carried out on the synthesized material in order to evaluate the magnetic response of the final product.

The phase composition and magnetic properties of the nanoparticles and nanowires trapped in the CNTs were evaluated by X-ray diffractometry (XRD), Mössbauer spectroscopy and the magnetization curve. The equipment used for XRD was a Philips Diffractometer, model X'Pert MPD, with a graphite monochromator and fixed anode operated at 40 kV and 40 mA using the Cu-Kα radiation. Three syntheses using the same process and parameters were performed and analyzed by XRD in order to assure the reliability of the results.

The Mössbauer spectra were obtained at room temperature, using a constant acceleration electromechanical drive system with a multichannel analyzer for collecting and storing the data. The hyperfine parameters, independent for each phase, were obtained by least-squares fitting assuming Lorentzian line shapes. ^{57}Co in rhodium was used as source, with nominal activity of 50 mCi. A high-purity Fe metal foil was used for calibration of the velocity scale. The samples prepared for the Mössbauer spectroscopy consisted of four syntheses performed under the same conditions and mixed together. As in XRD, a larger sampling assures more reliable results.

Magnetic characterization was also performed at room temperature, using an alternating gradient-field magnetometer (AGFM) with the magnetic field, H, of ±6000 Oe.

3. Results and discussion

3.1. Evaluation of the morphology of CNTs before and after heat treatment

According to the obtained results, CNTs nucleate and grow on the surface of the substrate as entangled bundles of nanotubes (not shown). Raman spectroscopy and TEM images obtained for the CNT bundles on the silica nanopowder before heat treatment show that the synthesis of CNTs produces multi-wall CNTs, although the presence of single-wall CNTs cannot be discarded. In addition, the presence of nanoparticles and nanowires can be observed inside the nanotubes (indicated with arrows in Fig. 1b).

According to literature [18,19], CNTs growth using the ferrocene synthesis route tend to exhibit a mixture of single and multi-wall CNTs as well as a large variety in lengths. Evaluating the TEM image (Fig. 1c), one can notice the presence of a single-wall CNT on the bottom right side of the figure. Nevertheless, the length of the CNTs produced in the current work cannot be estimated due to the bundle-like nature in which these nanotubes tend to grow as a result of the nanopowder substrates.

This bundle-like nature of CNTs here synthesized guarantee that iron-based nanoparticles formed during this synthesis route are encountered inside the tubes. Previous work performed showed that when high surface area nanopowder is used as substrate for the growth of CNTs, these nanotubes tend to nucleate on the nanoparticles and they are not easily released from it during the synthesis, maintaining the extremity of the tubes blocked. Hence, the authors assume that iron-containing phases remain inside the nanotubes after the synthesis because there is no way out. However, syntheses performed without the nanopowder presented iron-based particles attached to the external walls of the tubes.

Fig. 2 shows the Raman spectra obtained for the synthesized CNTs before and after the heat treatment. The TEM images and Raman spectra obtained demonstrate the presence of CNTs in all the performed syntheses.

In the high-frequency region of the spectrum, the two bands characteristics of carbon nanotubes are observed; these bands indicate the graphite peak (G-band) at about 1600 cm^{-1}, and the disorder and defects of the structure, named D-band, at about 1380 cm^{-1}. A G′-band related to the graphitic structure is also observed at higher frequencies. In the low-frequency part of the spectrum, there is a second region characteristic of CNTs, this region is named Radial Breathing Mode (RBM). This region at 100–300 cm^{-1} is very visible for CNTs that present diameter sizes lower than 2 nm [22,23]. Bands on the RBM region may not exist in cases where the diameter size of the nanotube is higher than 2 nm.

Raman spectroscopy also indicates the degree of graphitization based on the ratio of the intensities of the D and G bands. The ratio between the D and G bands (known as $I_{D/G}$) is related to the presence of structural defects and disorder in the nanotubes [22]. When the $I_{D/G}$ values of as grown and heat treated CNTs are compared, one can observe that the ratio value decreases after the heat treatment (Fig. 2). This can be attributed to a highly organized material obtained after the heat treatment because of the extra energy and time to which this material is submitted during the heat treatment.

TEM images obtained after the heat treatment indicate the presence of CNTs filled with nanowires. These nanowires are indicated by black arrows in Fig. 3b. These results demonstrate that the structure and morphology of CNTs exposed to heat treatment are not damaged by this process. Moreover, one can observe that the $I_{D/G}$ ratio obtained for samples before and after the heat treatment decreases considerably after the heat treatment, suggesting a lower amount of defects in the walls of the nanotubes.