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Evaluation of iron-containing carbon nanotubes by near edge X-ray absorption technique

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HIGHLIGHTS

- CNTs filled with Fe-based nanoparticles were heat treated in inert atmosphere.
- EXAFS analysis was performed on CNTs, and LCF and FT were obtained.
- *In situ* XANES measurements were performed during the heating of the samples.
- Fe-based particles change from Fe carbide to metallic Fe during the heat treatment.
- The applied synthesis method guarantees that Fe phases are not oxidize.

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ABSTRACT

The synthesis of carbon nanotubes (CNTs) via Chemical Vapor Deposition method with ferrocene results in CNTs filled with Fe-containing nanoparticles. The present work proposes a novel route to characterize the Fe phases in CNTs inherent to the synthesis process. CNTs were synthesized and, afterwards, the CNTs were heat treated at 1000 °C for 20 min in an inert atmosphere during a thermogravimetric experiment. X-Ray Absorption Spectroscopy (XAS) experiments were performed on the CNTs before and after the heat treatment and, also, during the heat treatment, *e.g.*, *in situ* tests were performed while several Near-Edge X-Ray Absorption (XANES) spectra were collected during the heating of the samples. The XAS technique was successfully applied to evaluate the phases encapsulated by CNTs. Phase transformations of the Fe-based nanoparticles were also observed from iron carbide to metallic iron when the *in situ* experiments were performed. Results also indicated that the applied synthesis method guarantees that Fe phases are not oxidize. In addition, the results show that heat treatment under inert atmosphere can control which phase remains encapsulated by the CNTs.

1. Introduction

The most feasible route to grow carbon nanotubes (CNTs) is the Chemical Vapor Deposition (CVD) method, where ferrocene ($Fe(C_5H_5)_2$) is used as precursor and/or catalyst (Bhatia and Prasad, 2010; Osorio and Bergmann, 2012). This synthesis process does not require high temperatures and expensive precursors (Bhatia and Prasad, 2010; Kuwana and Saito, 2005; Hembram and Rao, 2011; Gui et al., 2008). Nonetheless, iron-containing phases filling CNTs are known to be inherent to this production process (Antunes et al., 2011; Dillon et al., 2012; Nagata et al., 2013). Researchers have acquired CNTs filled with α-iron, γ-iron and iron carbides (Antunes et al., 2011; Resende et al., 2009; Longbottom et al., 2007). and the literature indicates that depending on the synthesis method and precursor materials, CNTs can be filled with different nanoparticles (Gao et al., 2004; Liu and Wehmschulte, 2005). For several years these nanoparticles were seen as contaminants of the CNT synthesis process.

Recent papers are revealing that magnetic nanoparticles and/or nanowires could be encapsulated in CNTs as an alternative to provide a magnetic response to the nanotubes (Morelos-Gomez et al., 2010; He et al., 2008; Mero et al., 2014; Castrejón-Parga et al., 2014; Kim et al., 2012). A previous study (Osorio et al., 2013) has therefore suggested that iron-based phases inherent to the synthesis process of CNTs using ferrocene provides a magnetic response to the nanotubes and the synthesis parameters can ensure that the nanoparticles are completely encapsulated by CNTs (Osorio and Bergmann, 2012). Thus, this material may have potential applications in magnetic devices. In order to apply this

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material to commercial application, however, it is necessary to have a better understanding of the phases grown within the nanotubes and to evaluate their behavior.

A previous study (Osorio et al., 2013) has shown that by varying the synthesis temperature and dwell time used for CNT production, one can have different phases trapped in the CNTs, which will result in different magnetic behavior. The following study analyzes for the first time the behavior of these phases trapped in the CNTs using the Near Edge X-Ray Absorption (XANES) technique. XANES is an absorption spectroscopy that can give valuable information regarding the oxidation state of elements. Knowing that the material encapsulated by CNT is iron-based, XANES is introduced as an alternative to study the behavior of these phases during a heat treatment. This innovative approach will enable us to examine the material trapped in the CNTs from a fresh point of view.

2. Experimental

CNTs were synthesized through the CVD process using ferrocene as precursor and catalyst; and SiO_2 as a support for the nucleation and growth of CNTs, according to previously published work (Osorio and Bergmann, 2012). The temperature used for the growth of CNTs was 750 °C. The morphology of the synthesized CNTs was evaluated by Raman Spectroscopy and Transmission Electron Microscopy (TEM). The Raman Spectroscope used was a Renishaw inVia Spectrometer System at a range of 0–3100 cm^{-1}, using a laser of 532 nm. TEM images were obtained in a JEOL microscope, model JEM-1200 ExII.

In order to evaluate the behavior of phases inherent to the performed synthesis process, samples were also evaluated in a Thermogravimetric/Differential Scanning Calorimeter (TG/DSC) and in a X-ray Absorption Near Edge Structure Spectroscope (XANES). The equipment used for TG/DSC analysis was a Netzsch STA 449F3. Samples were heated until 1000 °C, at a heating rate of 10 °C/min and with a dwell time of 20 min, in an inert atmosphere of argon.

X-ray absorption spectra at the Fe K-edge were collected at the bending magnet station D04B of the Brazilian Synchrotron Light Laboratory (LNLS) in Campinas/SP, Brazil. All samples were prepared as powders mixed with boron nitrite and pressed into a disk. XANES spectra were collected in transmission mode. A Fe foil reference absorption spectrum was simultaneously acquired for every sample using the transmitted beam. The energy was calibrated by defining the first derivative peak of the Fe foil spectrum to be 7112.0 eV.

First, X-ray absorption (XAS) spectra were collected for each sample. Then, *in situ* XANES analyses were performed in order to simulate a heat treatment and evaluate the behavior of phases encapsulated by CNTs under different temperatures. Sequential spectra were therefore recorded while the temperature was increased up to 1000 °C and kept at that level for 20 min. For the X-ray absorption spectra the data was acquired as follows: the pre-edge region from 7032 to 7092 was collected with a step size of 2 eV and acquisition time of 1 s; the edge region ranging from 7092 to 7192 with a 0.3 eV step size and 2 s acquisition time; and the region above 7192 with a 0.05 eV step size and 2 s of acquisition time. *In situ* XANES spectra were recorded from 7062 to 7248.8 using a 2 eV step size for the pre-edge region (7062–7092); a 0.35 eV step size for the edge region (7092–7182); and a 0.07 eV for the region above 7182. An acquisition time of 1 s was used for all regions. Table 1 indicates the temperature range of each spectrum acquired during the *in situ* XANES experiments. According to acquisition parameters used, the temperature range was, hence, obtained.

XAS data and linear combination fitting were carried out with the ATHENA software, which is based on the IFEFFIT library of numerical and XAS algorithms. Spectra were compared after subtraction of a constant baseline and normalization.

Table 1
In situ XANES experiment indicating the temperature range of each spectrum measured.

Measurement-code	Average temperature (°C)	Range of temperature (°C)
01	21.0	21
02	33.5	21–88
03	127.5	91–164
04	200.5	165–236
05	271.0	237–307
06	343.0	308–378
07	414.0	379–449
08	485.0	450–520
09	556.5	522–591
10	627.5	593–662
11	698.0	663–733
12	769.5	735–804
13	841.0	806–876
14	911.5	877–946
15	974.5	949–1000
16	1000.0	1000

EXAFS (Extended X-ray Absorption Fine Structure) data was also analyzed with the aid of ATHENA software. Bulk Fe and Fe_2O_3 standard compounds used on the analysis were measured by the authors; Fe_3C standard data was obtained from the online XAFS Database[1]. The steps performed for extraction of the oscillatory part of an X-ray absorption spectrum were: (a) pre-edge background removal; (b) edge position determination; (c) post-edge background removal and normalization; and (d) transformation of the EXAFS spectrum to k-scale. Hence radial distribution function can be obtained by Fourier Transform (FT).

3. Results and discussion

The TEM images and Raman spectrum (Figs. 1 and 2) indicate the growth of CNTs filled with nanoparticles. The black spots seen in Fig. 1 point to the presence of nanoparticles inside the nanotubes synthesized by the CVD technique, using ferrocene as precursor/catalyst and SiO_2 as a support for CNT nucleation. The Raman peaks characteristic of CNTs can be seen in Fig. 2.

Fig. 3 shows the result obtained with the TG/DSC experiment. The TG curve shows that there was no significant mass gain and/or loss during the heating of CNTs in an inert atmosphere. The DSC curve, however, indicates an endothermic reaction occurring between 500 and 700 °C, followed by an exothermic reaction that carries on until the end of the experiment, at 1000 °C.

According to the data previously obtained through the Mössbauer Spectroscopy (Osorio et al., 2013), iron carbide and α-Fe are the major phases found in the CNT samples. This data also revealed that after the CNTs are exposed to high temperatures, the amount of iron carbide decreases considerably, whereas the amount of α-Fe increases. Recent publications have proposed that during CNT synthesis the carbon dissolves in the metal catalyst, followed by the diffusion of the carbon through the metal. Once the catalyst is saturated with carbon, it achieves the proper condition to nucleate and grow CNTs and, hence, carbon is expelled from the metal, forming the tubular structure (Kuwana and Saito, 2005; Leonhardt et al., 2006; Schape et al., 2004; Esconjauregui et al., 2009). In addition, a study conducted by Rodriguez-Manzo

[1] http://millenia.cars.aps.anl.gov/cgi-bin/newville/Model-Search.cgi/ModelData/fe3c_rt01_mar02.xmu