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Influence of treatment conditions and nanotube type on the decoration of multiwalled carbon nanotubes with magnetic particles

E.G. Uc-Cayetano[a], R. Schönfelder[b], F. Avilés[a], J.V. Cauich-Rodríguez[a], A. Bachmatiuk[b], M.H. Rümmeli[b], F. Rubio[c], M.P. Gutiérrez-Amador[d] and G.J. Cruz[e].

[a] Centro de Investigación Científica de Yucatán, A.C., Unidad de Materiales, Calle 43 # 103, Col. Chuburná de Hidalgo, 97200 Mérida, Yucatán, México. Email: eguc_2909@hotmail.com
[b] Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden). Helmholtzstrasse 20 D-01069 Dresden, Germany.
[c] Instituto de Cerámica y Vidrio Campus de Cantoblanco. C/ Kelsen, 5 28049 Madrid España.
[d] Escuela Superior de Apan, UAEH. Chimalpa Tlalayote, Municipio de Apan, Hidalgo, México.
[e] Instituto Nacional de Investigaciones Nucleares, Departamento de Física. Carretera México-Toluca s/n, La Marquesa Ocoyoacac, Edo. Mex. C.P. 52750, México.

Abstract

Multiwalled carbon nanotubes (MWCNTs) are attractive materials which are generally used to render multifunctionality to polymeric matrices; such multifunctionality can be enhanced when the MWCNTs are decorated with suitable particles. In this work, oxidized MWCNTs were decorated with iron oxide nanoparticles obtained by hydrolization at high temperature in the presence of triethylene glycol and Iron (III) chloride as metal precursor. The influence of the concentration of iron precursor and reflux time in the hydrolysis, as well as the structural ordering and diameter of the MWCNT on the decoration was investigated. EDS, HRTEM, Raman spectroscopy, XRD, TGA, XPS and vibrating sample magnetometry were used to characterize the decorated MWCNTs. The results indicate that a more homogeneous decoration and higher saturation magnetization is achieved for MWCNTs with smaller diameter and greater density of defective/reactive sites at a concentration of 1:2 (MWCNTs: $FeCl_3*6H_2O$) with 30 minutes of reflux time.

1. Introduction

Decoration of MWCNTs consists of depositing nanoparticles on the MWCNTs walls or ends, bonded by physical interactions. In recent years, MWCNT decoration has received increased attention because of their promising applications in fields such as catalysis, biosensors, biomedical, magnetic data storage, and electronic devices, and many of them include incorporation into polymer matrices [1, 2]. There are several methods to achieve this goal, such as precipitation, hydrolysis at high temperature or chemical decomposition of a metal precursor. A critical aspect in this type of procedures is the homogeneity of the deposit of nanoparticles on the surface of the MWCNTs. The type of metallic nanoparticle used in the decoration can be very diverse; depending on the application in mind this can range from transition metals such as Co particles, Ni, Ru, to noble metals such as Ag, Au or Pt, but the most commonly used are maybe iron oxide nanoparticles [1-3]. Many studies on MWCNT decoration emphasize the need of surface modification through an oxidative treatment in the success of decoration [3-5]. In these studies, the MWCNT morphology and the methodology used for decoration varies, but the influence of the MWCNT morphology, structural ordering and concentration of precursors on the final outcome of the MWCNTs decoration is still unclear.

We report here the use an iron precursor to obtain a material with magnetic properties for prospective applications in electrochemical biosensing. The influence of the concentration of iron precursor and treatment time on the homogeneity of the decoration of MWCNTs with magnetic

particles for two types of MWCNTs with different morphology and structural ordering is investigated.

2. Experimental

Commercial 95 wt% pure MWCNTs, Baytubes C150P (outer diameter = 13-16 nm, inner diameter = 2-6 nm, length 1 μm) provided by Bayer MaterialScience (labeled as "A"), and MWCNTs acquired from Cheap Tubes Inc (outer diameter = 50-80 nm, inner diameter = 5-10 nm, length = 10-20 μm, labeled as "B"), were used for this research.

The functionalization of MWCNTs used a method based on a mixture of HNO_3 and H_2SO_4 as oxidizing agents because it has shown its efficiency in the generation of OH, CO and COOH functional groups on the surface of MWCNTs with minimum structural damage [6].

The methodology used for the decoration of MWCNTs with nanoparticles of iron oxide (Fe_3O_4, γ-Fe_2O_3) consisted on dispersing 100 mg of oxidized MWCNTs in 50 ml of triethylene glycol for 1 h in an ultrasonic bath. After the dispersion, 400 mg of $FeCl_3*6H_2O$ (200 and 100 mg of $FeCl_3*6H_2O$ for the other weight ratios) and 3.6 g of anhydrous sodium acetate were added to the solution. The resulting mixture was brought to reflux at 200 °C for 120 and 30 min. The MWCNTs obtained were centrifuged with acetone, subsequently washing and filtering was performed with distilled water to remove the remaining particles and finally dried at 100 °C for 12 h.

Decorated MWCNTs were characterized by TEM, Raman Spectroscopy, EDX, XRD, TGA, XPS and their magnetic response was determined by vibrating magnetometry.

Both types of MWCNTs (A and B) were used for decoration at different weight concentration ratios of MWCNTs: $FeCl_3*6H_2O$ and variations in the reflux time, as shown in Table 1.

Table 1. Decorating treatments performed at oxidized Bayer MaterialScience (A) and Cheap Tubes Inc (B) MWCNTs.

MWCNT type	**Bayer MaterialScience (A)**					**Cheap Tubes Inc. (B)**	
Identification	**1:4-120**	**1:4-30**	**1:2-120**	**1:2-30**	**1:1-30**	**1:2-30**	**1:1-30**
Ratio of MWCNTs: $FeCl_3*6H_2O$	1:4	1 :4	1:2	1:2	1:1	1:2	1:1
Reflux time (min)	120	30	120	30	30	30	30

3. Results and discussion

3.1 Transmission electron microscopy

TEM micrographs of decorated MWCNTs with the iron nanoparticles attached to the MWCNTs outer walls are seen in Figure 1 for two types of decoration treatment. Treatments 1:4-120(A) and 1:4-30(A) yielded inhomogeneous decoration with large clusters of iron oxide particles and undecorated regions of MWCNTs (not shown), as seen in the first row of Figure 1, where 1:4-30(A) is shown as example. Similar results were observed for treatment 1:2-120(A). For both nanotubes, treatments 1:1-30 and 1:2-30 resulted in a good density, distribution and

homogeneity of the iron nanoparticles. For 1:2-30 the decorating particle size ranges from 5-20 nm in diameter. Both treatments 1:1-30 the resulted in decreased particle diameter and density, maintaining a good dispersion and homogeneity. Treatments using MWCNTs of type A showed a slightly more homogeneous decoration and with more density of particles on the MWCNTs surface than those for nanotube type B, maybe because of the more density of defective/reactive sites for MWCNTs of the A-type.

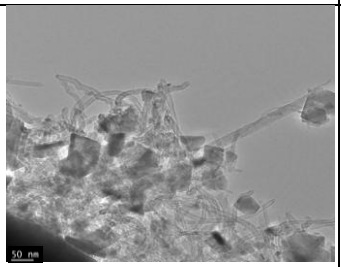
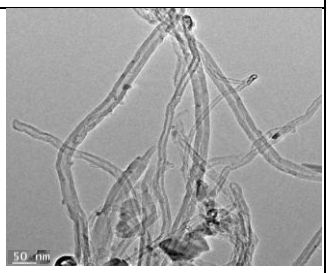
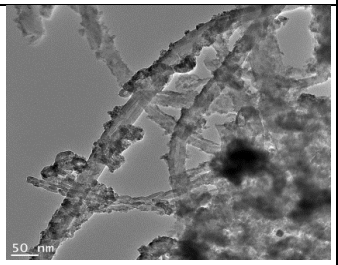
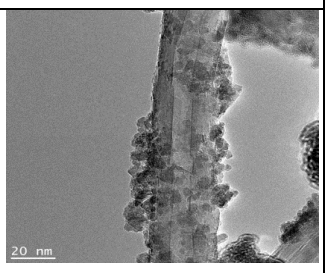
MWCNT type	Treatment ID label (description)	Low magnification	High magnification
A	**1:4-30(A)** (1:4 weight ratio at 30 min of reflux time)		
B	**1:2-30(B)** (1:2 weight ratio at 30 min of reflux time)		

Fig. 1. Selected TEM micrographs obtained from MWCNTs decorated following treatment 1:4-30(A) and 1:2-30(B).

3.2 Elemental analysis

Elemental analysis of decorated MWCNTs was obtained by EDS. The major elements present in our samples are carbon, oxygen and iron. Treatment 1:4-120(A) had the highest content of carbon and the smallest percentage of iron (79.3 wt% and 6.2 wt%, respectively), indicating that the density of the iron oxide particles generated is low. Treatment 1:4-30(A) showed a significantly larger amount of Fe (~28 wt%) but not homogeneously dispersed in the sample (as seen from TEM micrographs). Treatments 1:2-120(A), 1:2-30(A) and 1:2-30(B) showed similar amounts of carbon (~60-63 wt%), oxygen (~18 wt%) and iron (~18-21 wt%), but there was a reduction in the amount of Fe (~12 wt%) when the concentration is reduced to 1:1. The increase in oxygen content (~10 wt%) with respect to the samples that were not decorated suggests that the samples containing iron may be forming iron oxides.

3.3 Raman spectroscopy

A marked difference in the Raman I_G/I_D intensity ratios was found for both MWCNTs previous to decoration. For MWCNTs of type A, $I_G/I_D = 0.47 \pm 0.02$, while for MWCNTs of type

B, I_G/I_D = 0.83±0.03, which denotes larger density of defective/reactive sites for MWCNTs of type A. No further important differences in the Raman spectra were observed upon decoration.

3.4 X-ray powder diffraction spectrometry

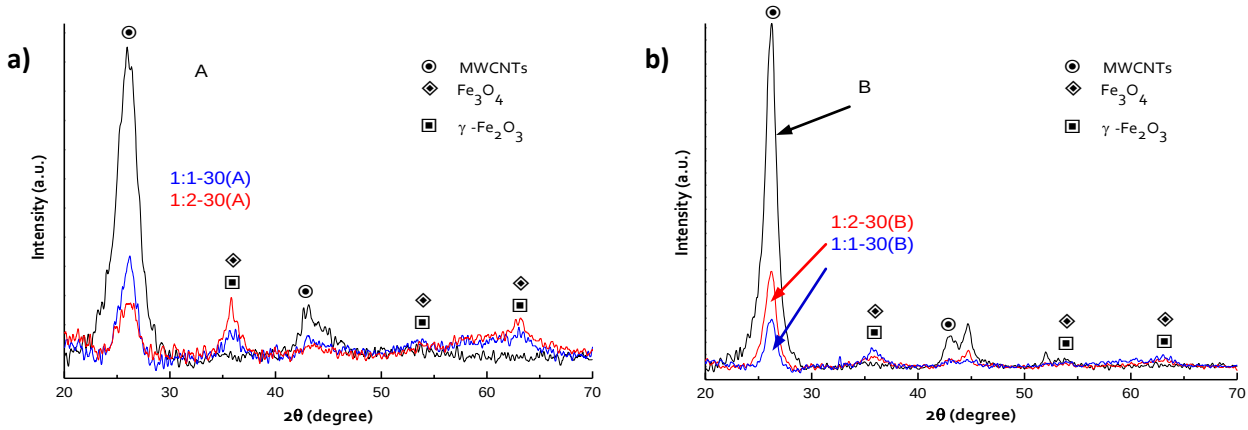


Fig. 2. XRD patterns of oxidized and decorated MWCNTs with different weight concentrations. a) MWCNT type A, b) MWCNT type B.

Both types of oxidized MWCNTs had diffraction peaks at 2θ = 26.6° and 43.5° which are attributed to the (002) and (100) planes of the MWCNTs (see Fig. 2). These peaks are still present in the decorated MWCNTs but new peaks confirm the presence of iron oxide particles. Decorated MWCNTs of type A exhibited new diffraction peaks at 2θ = 35.5°, 54.0°, 57.0° and 63.0° which correspond to the planes (311), (422), (511) and (400) of magnetite (Fe_3O_4) but also overlape with some of maghemite (γ-Fe_2O_3). The XRD pattern of magnetite is very similar to that of maghemite, and the results seem to indicate that both phases coexist in the decorated samples. The XRD pattern of decorated MWCNTs of type B exhibited only less intense peaks at 2θ = 35.5°, 54.0°, 57.0° and 63.0° that confirming the coexistence of Fe_3O_4 and γ-Fe_2O_3.

3.5 Thermogravimetric analysis

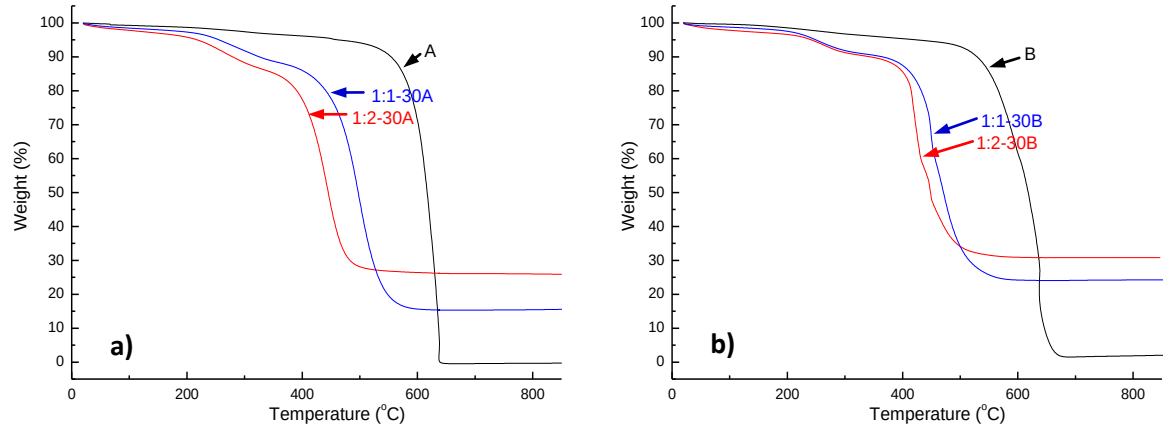


Fig. 3. TGA thermograms of oxidized and decorated MWCNTs with different weight concentrations. a) MWCNT type A, b) MWCNT type B.

TGA analysis in synthetic air (Fig. 3) shows the weight loss ratio (decomposition) of MWCNTs as a function of temperature and provides valuable information about the amount of iron oxide particles in the samples. While both MWCNTs loss all their mass at ~640 °C, decorated MWCNTs retain 20-30 wt% after all the MWCNT material is burned off, suggesting that this percentage corresponds to the weight of Fe_3O_4/γ-Fe_2O_3 and some metallic impurities already present (<5 wt%) in the undecorated MWCNTs. The weight percentage remaining after elimination of the MWCNTs is consistent with the percentage of Fe present in the sample quantified by EDS.

3.6 X-ray photoelectron spectroscopy

The XPS spectrum (Fig. 4) of decorated MWCNTs showed bands at ~285, 532, and 711 eV which are attributed to the energetic distribution of C 1s, O 1s and Fe 2p orbitals, respectively. Fe 2p 1/2 and Fe 2P 3/2 peaks located at 711 and 724.9 eV can be related to Fe chemical states in Fe_3O_4 [7], but the shoulder between Fe 2p 1/2 and Fe 2p 3/2 suggests that additional Fe states could be found in Fe_2O_3 form [8]. There is also a shifting (from 532 to 530 eV) and widening of the O 1s band for the decorated samples, which further indicates formation of iron oxides. This confirms that magnetite is the dominant phase present in the nanoparticles, which may coexist with another iron phases such as maghemite.

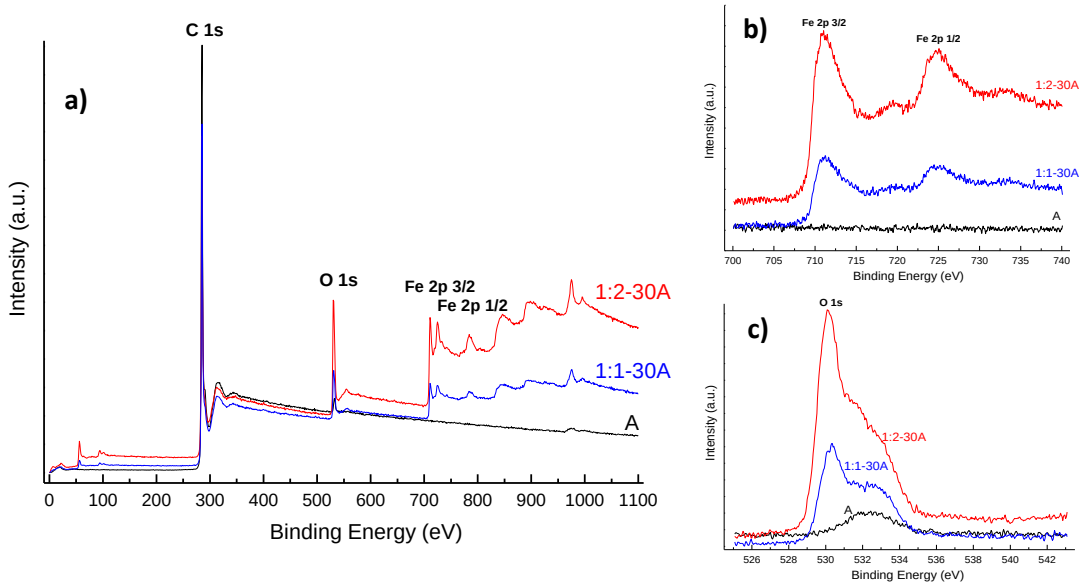


Fig. 4. XPS spectrum of decorated MWCNTs (A) with different weight concentrations. a) Survey, b) Fe 2p orbitals, c) O 1s orbitals.

3.7 Vibrating Sample Magnetometer

The magnetic hysteresis loops of the decorated MWCNTs (Fig. 5) were obtained in a vibrating sample magnetometer and exhibit a ferrimagnetic behavior (coercitive fields or the order of ~90 Oe). The saturation magnetizations ranges from ~2 to 6 emu/g with the maximum magnetization value observed for sample A decorated by treatment 1:2-30. The differences in

saturation magnetizations values in our samples may be attributed to the differences in the Fe_3O_4/Fe_2O_3 degree of coverage on the MWCNTs, dispersion and particle size.

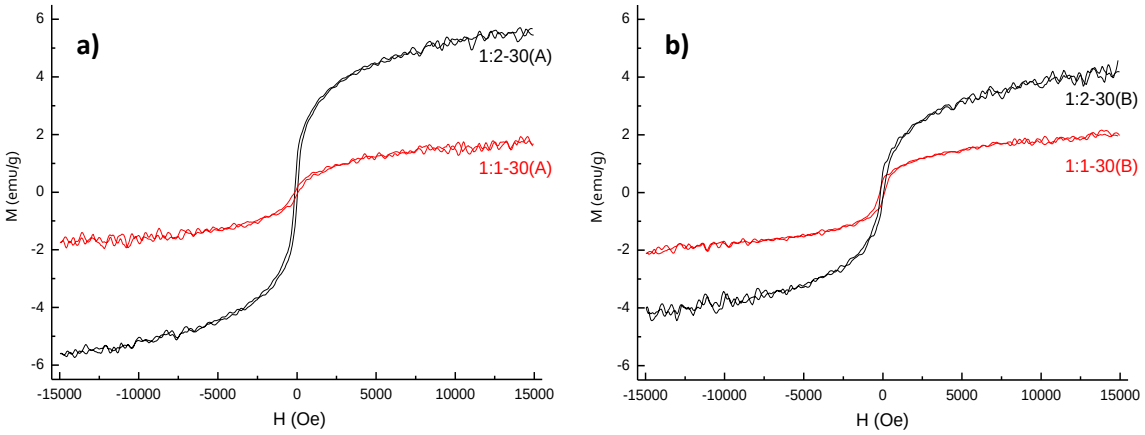


Fig. 5. Magnetization curves of decorated MWCNTs with different weight concentrations. a) MWCNT type A, b) MWCNT type B.

5. Conclusions

MWCNTs were decorated with magnetic nanoparticles with diameters ranging between 5-20 nm. EDS and TGA indicate that the weight content of the nanoparticles present in MWCNTs is around 20-25 %. XRD and XPS showed the presence of magnetite and maghemite (Fe_3O_4, γ-Fe_2O_3) in cubic arrangements coexisting in the samples of decorated MWCNTs. Magnetic hysteresis loops of the samples of decorated MWCNTs showed a low hysteretic ferrimagnetic behavior of the decorated MWCNTs. Treating the MWCNTs with a 1:2 weight concentration of MWCNT: $FeCl_3*6H_2O$ using a reflux time of 30 min produced the most homogeneous decoration. By comparing the two types of MWCNTs a more homogeneous decoration with more intense peaks of diffraction corresponding to Fe_3O_4 and higher value of magnetization saturation was found for MWCNTs of type A with respect to type B, probably due to their higher density of defective/reactive sites (I_G/I_D ratio in Raman) and its smaller diameter.

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