Asian Journal of Chemistry; Vol. 24, No. 10 (2012), 4281-4284

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis and Characterization of Cobalt-Doped Carbon Nanotubes

A. KAZEMZADEH[1,*] and B. MEHDIZADEH NARAGHI[2]

[1]Material and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran
[2]International University of Imam Khomeini, Qazvin, Iran

*Corresponding author: Fax: +98 261 6201888; Tel: +98 261 6204131; E-mail: asg642001@yahoo.com

(*Received*: 16 June 2011; *Accepted*: 30 April 2012) AJC-11372

Carbon nanotubes have been synthesized using chemical vapour deposition method in a catalytic bed. Catalyst was prepared by a sol-gel method and then methane was introduced to decompose by the catalyst. After purification of the obtained carbon nanotubes, cobalt was introduced to the carbon nanotube bundles. In order to prevent the cobalt oxidation, the experiment was done under 2×10^{-5} torr vacuum. $CoCl_2$ was used as cobalt source and the furnace temperature increased up to 790 ºC. In this temperature, $CoCl_2$ decomposed and cobalt added to the carbon nanotubes as an additive. SEM images show no difference between carbon nanotube structures before and after annealing. XRD and Raman spectroscopy were used to analyze the samples.

Key Words: Carbon nanotube, Cobalt, Doping, Raman spectroscopy.

INTRODUCTION

Elemental carbon in sp^2 hybridization can form a variety of amazing structures, such as graphite (3D), graphene (2D), carbon nanotubes (CNTs, 1D) and fullerene (0D). Carbon nanotubes defined by Ijima in 1991[1] have a unique tubular structure with nanometer scale diameters and large length/diameter ratios. Owing to the covalent sp^2 bonds formed between individual carbon atoms, carbon nanotubes are stiffer and stronger potentially than any other known material[2]. Since their discovery, carbon nanotubes have been extensively studied because of their unique structure and remarkable mechanical, electronic, magnetic, photonic and transport properties[3]. In the mass production of carbon nanotubes, it was found that nanotubes form nanotube bundles (nanorope) with close-packed two-dimensional triangular lattices[4] which might offer a host lattice for intercalation and storage of guest atoms or molecules. All these fascinating characteristics make carbon nanotubes the focus of current nanoscience and nanotechnology with many potential applications, including nanoelectronic devices, field emitters and bio sensors[4].

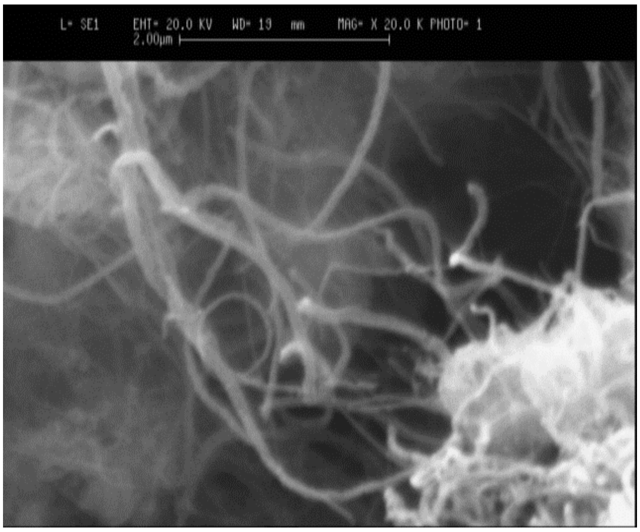
In this report, carbon nanotube was synthesized by chemical vapour deposition and catalyst was prepared by a sol-gel method. After that, cobalt added to the carbon nanotube bundles and the effect of the cobalt concentration on the structure and properties of carbon nanotubes was studied by means of different spectroscopic techniques.

EXPERIMENTAL

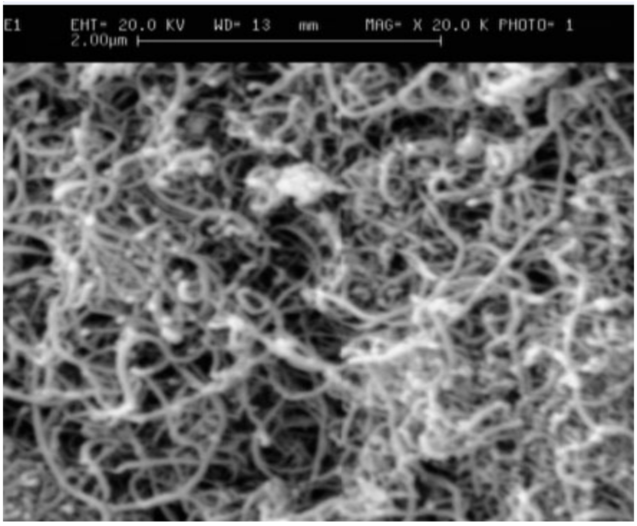
The catalyst was prepared by a sol-gel method. For a typical procedure, 2 g alumina powder, 100 mL ethanol and 4.4 mL TMOS were dissolved in 10 mL distilled water to form a gel by vigorous stirring. The precursor gel was first annealed at 90-100 ºC in the nitrogen to vapourize water and ethanol for 6 h and then reduced in the laboratory environment for 2-3 days to form Al_2O_3-SiO_2 hybrid. In order to make iron-based metal catalyst, 1 g Al_2O_3-SiO_2 was dissolved in 70 mL deionized water. Then 0.167 g $Fe_2(SO_4)_3$ and 0.2 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ added to the suspension by vigorous stirring for 15 min and then was annealed in the nitrogen for 2 h. The obtained powder was milled and raw orange catalyst was gained. Finally the powder was annealed in the O_2 at 500 ºC for 90 min to remove the organic quaternary ammonium salts. For a methane chemical vapour deposition experiment, 0.2 g catalyst was placed in a quartz tube mounted in a tube furnace. An argon flow was passed through the quartz tube as the furnace was heated to reach 900 ºC. From room temperature up to 700 ºC, the furnace temperature increased by a slower rate. When the furnace reached to 900 ºC, the argon flow was replaced by methane (4 L/min, 1/27 atm) for 20 min. After that methane was changed by argon and the system was cooled to room temperature under argon atmosphere. In the next step, cobalt-doped carbon nanotubes were fabricated using a high vacuum process and $CoCl_2$ was used as cobalt source. In order to this, carbon nanotube powder was mixed by different concentrations of $CoCl_2$ homogeneously *i.e.*, four samples (each sample contains 60 mg CNT powder) with 0 % wt (undoped), 0.85 % wt, 1.7 and 2.5 % wt cobalt. The prepared samples were placed in an alumina crucible, coverd by a shield and mounted in a high vacuum furnace. The furnace pressure was 2×10^{-5} torr. Reaching this pressure took 1.5 h long. Because of covering the samples, the furnace temperature increased up to 803 ºC and allowed the sample temperature to increase up to 790 ºC (the $CoCl_2$ melting point is 735 ºC). This process took 2 h long. In order to cobalt substitutions betweeen CNT bundles, the samples remained in this temperature for 2 h as $CoCl_2$ decomposed. Finally, furnace was cooled to room temperature in 2 h. This procedure was done for every three samples. An undoped target was also prepared as a standard for comparison in this systematic study. SEM images show no difference between CNTs before and after doping process. It means that the CNT structure was intact and didnt burn as we expect. XRD and Raman spectroscopy were used to characterize pristine and cobalt-doped carbon nanotubes. Powder X-ray diffraction measurments were carried out with a Cu source (philips PW-3710). Data were collected between 20 and 80º with 1.54 Å wavelength. 40 kV and 30 mA current. Raman scattering studies were carried out using laser excitation wavelength 532.12 nm. The groove density of the grating is 1800 grooves/mm. Nd-YAG (532 nm) was used as excitation source. The excitation beam was brought to a strip or spot focus on to the samples at a power level of 4 mw. All data are the average of the two sets and were collected from samples maintained at room temperature under ambient conditions. The illumination time was 1 min.

RESULTS AND DISCUSSION

Fig. 1a,b showes the SEM images (Auto Probe, Stereo Scan S360, Cambridge) of carbon nanotubes before and after annealing, respectively. It can be seen from these images that CNTs remained intact during doping process because of using a high vacuum condition, that is the expectant result and shows that CNTs didnt burn.



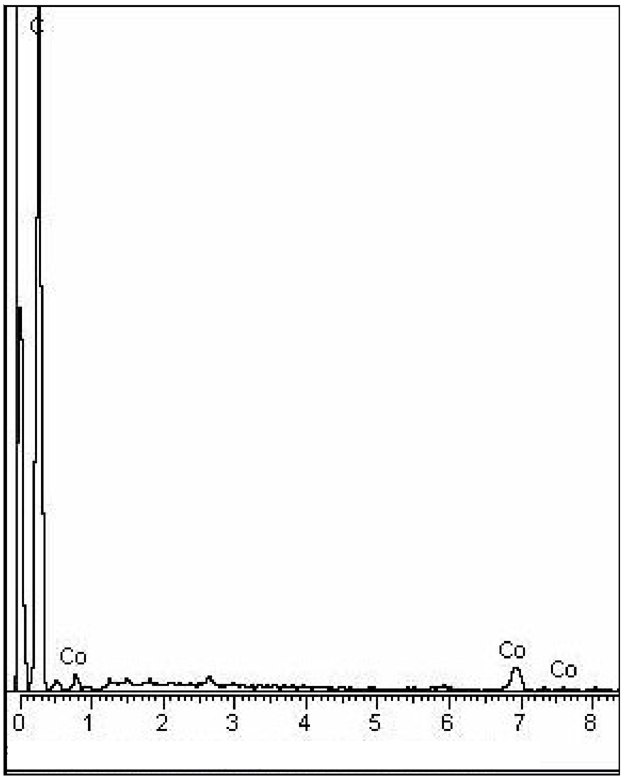
(a)



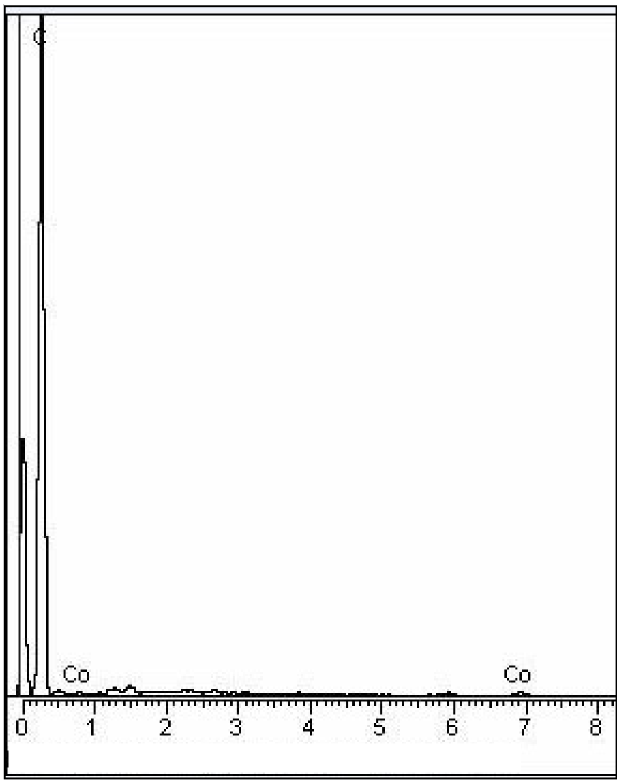
(b)

Fig. 1. SEM image of carbon nanotubes (a) before and (b) after annealing

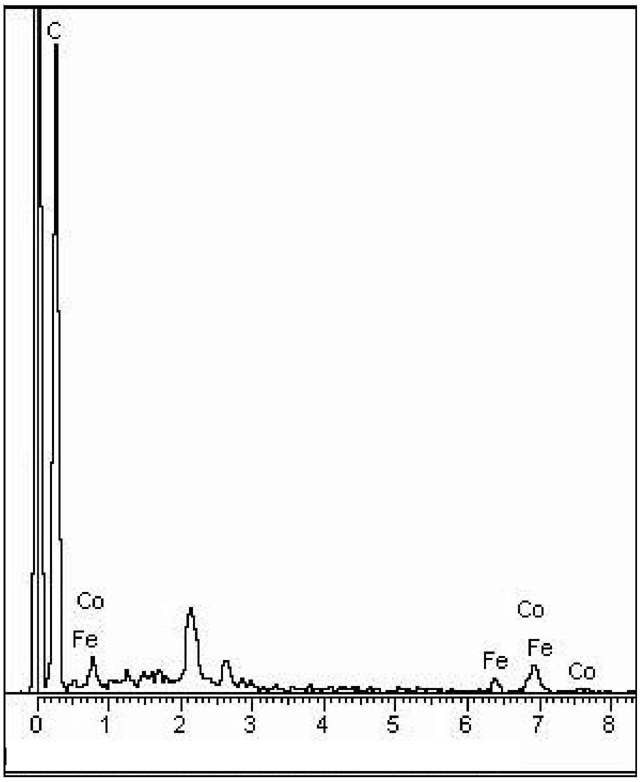
Fig. 2 shows the EDS spectra of doped samples that obviously confirm the presence of cobalt in CNT bundles. Fe peak is related to the Fe-contained catalyst that used as substrate to synthesize carbon nanotubes. The XRD patterns of the carbon nanotubes doped with cobalt are shown in Fig. 3. Due to the low cobalt doping, there is no obvious difference between XRD patterns. The (002) reflection observed at about diffraction angle 2θ = 26º corresponds to interlayer spacing d = 3.4 Å, 2.2 % higher than that in pyrolitic graphite (3.35 Å). The broad asymmetric (100) band around 42.3Å corresponds to the carbon layers in a turbostatic arrangement. Obtained XRD patterns correspond to the XRD patterns of multiwalled carbon nanotubes in references.



(a)



(b)



(c)

Fig. 2. EDS spectra of doped samples (a) 0.85 %, (b) 1.7 %, (c) 2.5 %

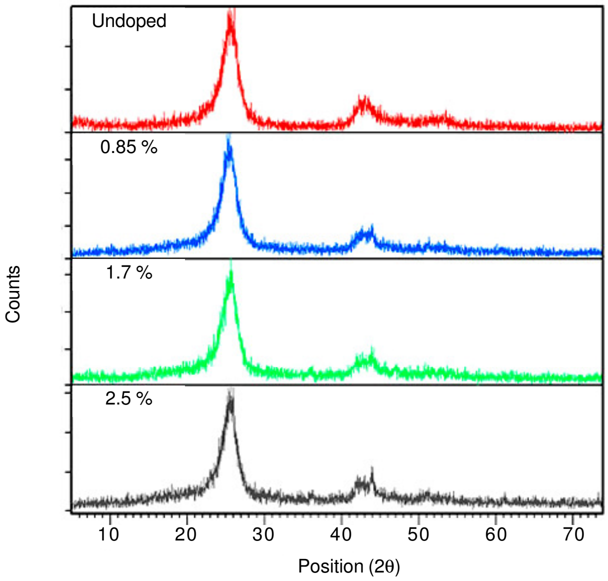


Fig. 3. XRD pattern of pristine and doped samples (the cobalt concentration increased from up to down)

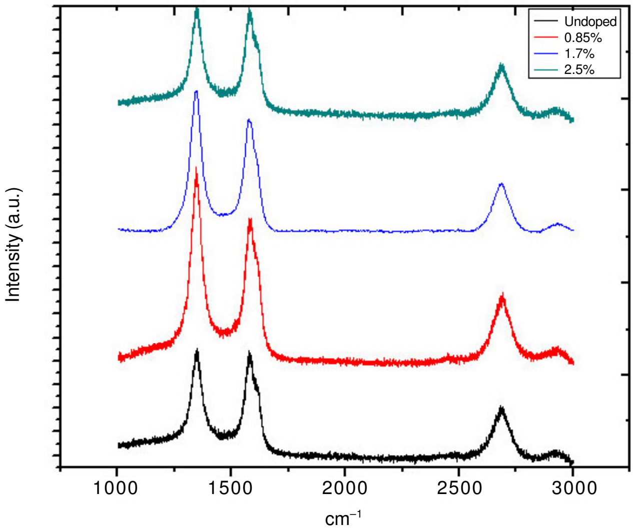


Fig. 4. Raman spectra of the samples

Fig. 4 shows the Raman spectra of the four samples. Table-1 depicts the important features of the Raman spectra. It can be seen that by increasing the cobalt concentration, the tangential mode (G-band) at *ca.* 1590 cm^{-1} and the disorder induce D-band at *ca.* 1340 cm^{-1} does show a general increase in intensity which suggest that the increasing presence of cobalt in the target is in fact, bringing about a noticeable change in the degreee of ordering in the hexagonal lattice[5]. This increase in the D-band intensity is attributed to the activation of off-zone-center phonons due to relaxation of the strict selection rules for Raman scattering due to a double resonance process[6]. Based on a lorenzian line fit to the data, the G'-band intensity increased by increasing the cobalt doping. The G' intensity is comprabable to the G intansity[7].

According to the Table-1, the linewidth of the D-band shows a detectable increase that indicates a simultanous formation of graphitic by-products such as carbon nano-capsules[8], with an increase of defects on surfaces[9]. Also, there are no detectable shift in the k_D, k_G and $k_{G'}$ that can be attribted to the low cobalt doping.

Conclusion

According to the obtained results, the XRD sensitivity to cobalt doping is not obvious enough, but Raman spectrum

TABLE-1
IMPORTANT FEATURES OF RAMAN SPECTRA

Sample	I_D	I_G	I_D/I_G	$FWHM_D$	$FWHM_G$	$I_{G'}$	K_D	K_G	$K_{G'}$
Undoped	1100	880	1.3	60 cm^{-1}	80 cm^{-1}	480	1346.1	1587.2	2685.4
0.85 %	1850	1500	1.2	60	70	900	1341.7	1586.6	2684.9
1.7 %	1180	900	1.3	70	60	400	1343.5	1581	2683.4
2.5 %	1100	1090	1.0	70	70	600	1349.2	1586.2	2684.4

shows a good sensitivity to even low concentrations of cobalt. The relative increase in the G and D band intensities shows that the increasing presence of cobalt in target is in fact, bringing about a noticeable change in the degree of ordering in the hexagonal latice and also cobalt may be doped into the impurities, respectively. By increasing the cobalt concentration, we can study the other features of Raman spectra and also any shifts in wavenumbers more carefully.

REFERENCES

1. S. Ijima, *Nature*, **354**, 56 (1991).
2. P.-X. Hou, C. Liu and H.-M. Cheng, *Carbon*, **46**, 2003 (2008).
3. J.J. Zhao, X.S. Chen and J.R.H. Xie, *Anal. Chim. Acta*, **568**, 161 (2006).
4. A. ThessA, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tmoanek, J.E. Fischer and R.E. Smalley RE *Science*, **273**, 483 (1996).
5. K. McGuire, N. Gothard, P.L. Gai, M.S. Dresselhaus, G. Sumanasekera and A.M. Rao, *Carbon*, **43**, 219 (2005).
6. D.L. Carroll, P.M. Ajayan and S. Curran, *J. Mater. Res*., **13**, 2389 (1998).
7. A.M. Rao, E. Ritcher, S. Bandow, B. Chove, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, G. Dresselhaus and M. S. Dresselhaus, *Science*, **275**, 187 (1997).
8. H. Hiura, T.W. Ebbsen, K. Tanigaki and H. Takahashi, *Chem. Phys. Lett*., **202**, 509 (1993).
9. K. Kobayashi, R.o Kitaura, Y. Kumai, Y. Goto, S. Imagaki and H. Shinohara, *Carbon*, **47**, 722 (2009).