CARBON NANOTUBES *VIA* CATALYTIC CHEMICAL VAPOR DEPOSITION METHOD USING INDUCTION HEATING – AN ADVANTAGEOUS ROUTE

Ştefania ŞIMON,[a*] Alexandru R. BIRIŞ,[a] Dan M. LUPU,[a] Ioan MIŞAN,[a] Alexandru S. BIRIŞ,[b] Simona CLICHICI[c] and Cornel IANCU[d]

[a] National Institute for Research and Development of Isotopic and Molecular Technologies, 71-103 Donath Street, P.O. Box 700, Cluj-Napoca, RO-400293, Roumania
[b] UARL Nanotechnologi Center, University of Arkansas at Little Rock, 2801 S University Ave, Little Rock, AR 72204, USA
[c] Department of Physiology, Faculty of Medicine,"Iuliu Hatieganu" University of Medicine and Pharmacy, 8 Victor Babeş Street, Cluj-Napoca, RO-400012 Roumania
[d] Department of Surgical Disciplines, Faculty of Medicine, "Iuliu Hatieganu" University of Medicine and Pharmacy, 3rd Surgery Clinic, 19-21 Croitorilor Street, Cluj-Napoca, RO- 400162 Roumania

The paper presents a comparative study between multiwall carbon nanotubes (MWCNT) grown by the two different versions of catalytic chemical vapor deposition (CCVD) method, namely: the classic method when the heating is performed by an external electrical furnace (EF-CCVD) and an original version of CCVD method based on induction heating and radio frequency (RF-CCVD) excitation of the catalyst system. Distinctive differences were observed in the MWCNTs grown by these two methods. RF-CCVD was also led to high quality single wall carbon nanotubes (SWCNT). Thermogravimetric analyses (TGA) and Raman spectra performed presented the differences among these methods.

INTRODUCTION

Catalytic chemical vapor deposition (CCVD), out of all known synthesis methods, is probably the most promising method for growing carbon nanotubes (CNTs). The difference between the classic CCVD method, when the heating is performed by an external electrical furnace (EF) and the original version of CCVD method based on the induction heating and radio frequency (RF) excitation of the catalyst system, consists in the heat transmission mode. In case of EF-CCVD method the energy is generated by an external furnace that heats the catalyst from the exterior of the quart tube. By RF-CCVD method the catalyst is heated rapidly and equally by the boat at a constant temperature. The CNTs type and diameter are strongly dependent on the size and type of the metal particles in the catalyst. At high temperatures the metal particle in the catalyst can migrate on the supporting matrix, disadvantage that can be avoided by using the RF-CCVD method.

The catalyst systems usually used for CNTs production are composed of transition metal nanoparticles like Fe, Co, and/or Ni embedded within a supporting matrix as: MgO, Al_2O_3, SiO_2, or zeolites.[1,2] The carbon source can include a variety of gaseous or volatilized hydrocarbon compounds like: acetylene, methane, ethanol, hexane, diluted in carrier gas, usually N_2, Ar, H_2, in precise ratios are swept into the reaction chamber at controlled flow rates and temperatures.[3,4] The CCVD method presumes the irreversible deposition of a solid phase from a gaseous phase or a gas mixture, through a heterogeneous chemical reaction.

This present paper presents a comparative study between multiwall carbon nanotubes (MWCNT)

* Corresponding author: stefania.simon@itim-cj.ro

grown by the two different versions of CCVD methods, namely: (a) the classic method EF-CCVD and (b) an the original version RF-CCVD (see Fig. 1). Distinctive differences were observed in the MWCNTs grown by these two methods.
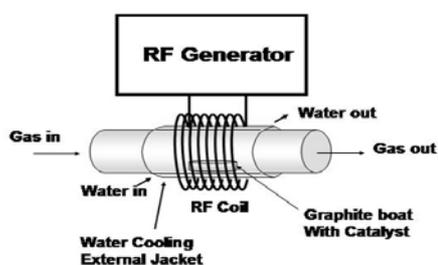

Fig. 1 – Schematic representation of RF-CCVD.

RF-CCVD was performed also to obtain high quality single wall carbon nanotubes (SWCNT).

RESULTS AND DISCUSSION

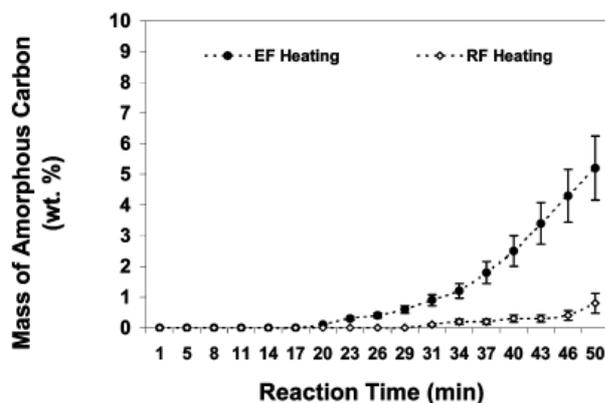The TGA analyses were performed to determine the purity and the burning temperature of the sample that depends on: the crystallinity degree, the possible defects in CNT walls, the impurities and the carbon type.[5] Fig. 2 summarizes the results of the TGA analysis for MWCNTs showing the amounts of amorphous carbon generated as a function of reaction time for the two synthesis methods. It can be seen that after 20 min reaction time the EF process produced significantly greater amounts of amorphous carbon than the RF process.

For SWCNTs, from the analysis of the two curves in the TGA (Fig. 3), it can be seen a single profile for the weight loss, that proves the existence of a single carbonic product in the sample.[6] Also, no variation is detected in the thermogravimetrical curve in the temperature range of 300-400 °C that would correspond to the amorphous carbon decomposition.[6,7] This certifies that the quantity of amorphous carbon obtained as a byproduct during the synthesis reaction is very low, thereby pinpointing one of the most important propriety of RF-CCVD synthesis method.
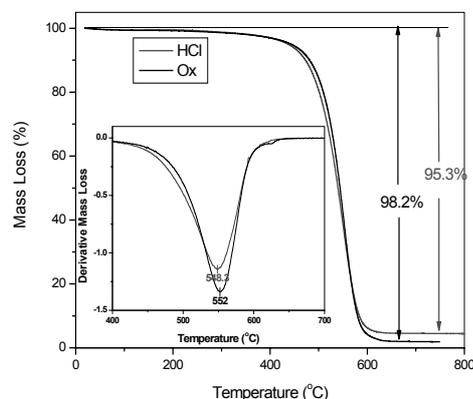

Fig. 2 – Amount of amorphous carbon generated as a function of reaction time for two different heating methods.

Fig. 3 – The TGA and the DTA analysis of purified SWNTs (red-after the first step-HCl) (black-after de second step-ox).

The SWCNT purity after the first step of purification is 95.3% and after the second step of purification is 98.2%.

Raman Spectroscopy is essential for carbon nanotubes characterization.

The Raman spectra for MWCNT (Fig. 4) show all the characteristic bands corresponding to CNT with several numbers of walls, for bought synthesis methods: the D band (1350-1330 cm^{-1}) associated with defects, vacancies, and carbonic impurities (amorphous carbon, glassy carbon); the G band (1500-1600 cm^{-1}) arises from sp2 C crystalline structures and 2D band (2450-2650 cm^{-1}) is associated with the degree of crystallinity of the graphitic layers.

From the ratio of the intensities of the G to D bands it can be observed the increased crystallinity of the MWCNTs grown by RF (I_G/I_D=1.21) relative to those grown by EF(I_G/I_D=0.98).
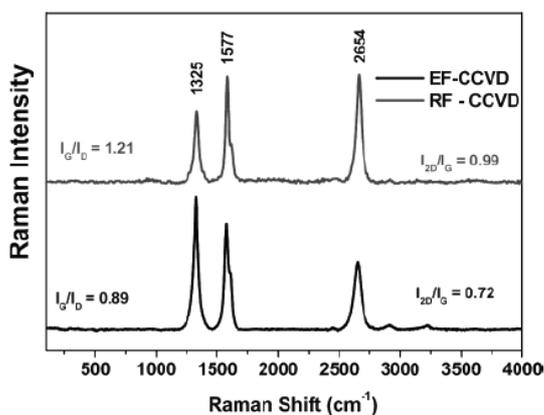
Fig. 4 – Raman spectra at 633 nm for MWCNTs produced by RF-CCVD and EF-CCVD.

Fig. 5 – Raman spectra at 633 nm magnified RBM band for SWCNTs.

The Raman spectra for SWCNT (Fig. 5) together with D, G and 2D band, reveals another band called the "radial breading mode" (RBM). The RBM is the real signature of the presence of SWCNT in a sample and strongly depends on the diameter and chirality of the nanotubes. The RBM frequency (ω) is inversely proportional to the CNT diameter that can be calculated with equation (1):[8]

$$\omega(cm^{-1}) = \frac{223.5}{d(nm)} + 12.5 \qquad (1)$$

Spectral position and corresponding diameter values for our SWNTs are represented in Table 1.

Table 1
Spectral Position and Corresponding Diameter Values from RBM band at λexc= 633 nm

ω_{RBM} (cm^{-1})	d (nm)
192.4	1.24
216.6	1.09
250.7	0.94
281.9	0.83

The intensity of D band for SWCNT is low meaning that our SWCNT contain almost no defects and no carbonic impurities[9] and from the ratio I_G/I_D=9.57 results that SWCNT have a very high crystallinity.

EXPERIMENTAL

1. Catalyst preparation

1.1. The catalyst used for MWCNT synthesis is Fe-Co/CaCO$_3$. This catalyst was prepared by impregnation method.[10] Briefly, Fe(NO$_3$)$_3$·9H$_2$O and Co(CH$_3$-COO)$_2$·4H$_2$O salts were dissolved in distilled water and mixed with CaCO$_3$ to a final ratio of Fe:Co:CaCO$_3$ = 2.5:2.5:95 wt%. The water was removed by vacuum, followed by oven drying at 130 °C overnight.
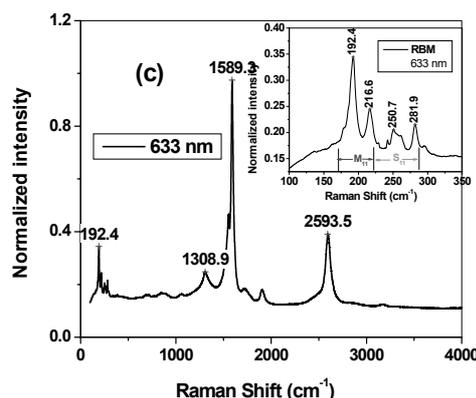
1.2. The catalyst used for SWCNT synthesis is Fe-Mo/MgO. In this case the catalyst was prepared by co-precipitation method. Bough, Fe(NO$_3$)$_3$·9H$_2$O and Mg(NO$_3$)$_2$·6H$_2$O salts were dissolve in ethanol. The (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O was dissolved in NH$_4$OH (25%) and added to the previously mixture in droplets under constant stirring. The catalyst obtained was left to "age" and was filtered after 24h, followed by oven drying at 150 °C and finally annealed in air at 500 °C for 1h. The catalyst final ratio is Fe:Mo:MgO = 1.5:0.15:98.35 wt%.

2. CNT synthesis

2.1. For bought MWCNT synthesis methods, 100 mg of catalyst was spread in a thin layer onto a graphite boat which was subsequently placed inside of a quartz reaction tube and then the reaction tube was positioned inside either a tube furnace or a water cooled induction coil connected to an RF generator, so that the boat was approximately centered in the furnace or coil. The reaction tube was then purged with nitrogen flowing through at 200 mL/min for 10 min to remove the ambient air, and then heated at 720 °C. For RF the temperature fluctuations over the catalyst bed were found to be significantly smaller as compared with the EF heating process, RF induces the heat directly into the graphite boat, which supports the catalyst, allowing a more uniform (and faster if required) heating of the catalyst bed. For both RF and EF, once a stable reaction temperature was reached, acetylene was introduced at a rate of 3 mL/min while maintaining the flow of nitrogen at 200 mL/min.

2.2. For SWCNT synthesis, 50 mg of catalyst was equally spread in the graphitic boat, and then the boat was positioned inside the water cooled induction coil connected to the RF generator. The reaction tube was then purged with argon flowing through at 120 mL/min in order to remove the ambient air, and then heated at 500°C for 10 min. After that the temperature was increase at 850 °C and when the temperature was reached the acetylene gas with a flow rate of 3 mL/min was released into the reaction tube. After 3 minutes the synthesis of SWCNT is done.

3. SWCNT purification

The SWCNT were purified in two steps. In the first step, right after the synthesis, the SWCNT are mix with HCl and sonicated for 15 minutes in a bath type sonicator. The

carbonaceous products obtained were purified in a Soxhlet apparatus with HCl (1:1) for 24 h, washed with distilled water, and dried overnight at 150 ˚C.

In the second step of purification the SWCNT are oxidized in air at 450 ˚C, for 20 minutes to uncover the metallic particles hidden in the nanotubes walls by burning the surrounding carbon and to burn the amorphous carbon. The purification continues with sonication in HCl for 15 minutes, for dissolution of the metal particles uncovered in the oxidation process, followed by filtration, washing with a large quantity of water and drying at 120 ˚C.

4. Thermogravimetrical Analysis

Thermogravimetrical analyses (TGA) were performed on SDT Q600 form TA Instruments. For MWCNT the samples were heated from 25 ˚C to 850 ˚C with a heating rate of 5˚C/min, in air with a flow rate of 150 mL/min.

TGA for SWCNT was performed on purified SWCNT in the temperature range of 25-750 ˚C, with a heating rate of 5˚C/min, in air with a flow rate of 100mL/min.

5. Raman Spectra

The morphology of purified SWCNTs and MWCNTs prepared in bought ways was investigated by Raman spectroscopy, which was performed at room temperature using the Jasco NRS-3300 Raman Spectrometer with a 633 nm laser.

CONCLUSIONS

The RF process is responsible for faster growth rates of CNTs because the catalyst stays active for much longer period of time. The CNTs synthesized by RF have better crystallinities, exhibit significantly smaller amounts of amorphous carbon. By using the RF method the energy consumption is lowered 2-3 times.

REFRENCES

1. Y. Soneda, L. Duclaux and F. Béguin, *Carbon*, **2002, *40*,** 965-969.
2. L. Piao, Y. Li, J. Chen, L. Chang and J. Y. S. Lin, *Catal. Today*, **2002**, *74,* 145-155.
3. D. Lupu, A. R. Biris, I. Misan, N. Lupsa, A. S. Biris, D. A. Buzatu and M. Kleeve, *Particul. Sci. Technol.,* **2002**, *20*, 225-234.
4. D. Lupu, A. R. Biris, A. Jianu, C. Bunescu, E. Burkel, E. Indrea, G. Mihailescu, S. Pruneanu, L. Olenic and I. Misan, *Carbon,* **2004**, *42*, 503-508.
5. S. Srepalli, P. Nicolaev, O. Gorelik, V. G. Hadjiev, W. Holmes, B. Files and L. Yowell, *Carbon*, **2004**, *42*, 1783-1791.
6. S. B. Gregg and S. Vecchio, *J. Phys. Chem. B,* **2006,** *110*, 1179-1186.
7. P. Ramesh, T. Okasaki, T. Sugai, J. Kimura, N. Kishi, K. Sato, Y. Pzeki and H. Shinohara, *Chem. Phys. Lett*., **2006,** *418,* 408-412.
8. S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley and R. B. Weisman, *Science,* **2002**, *298,* 2361-2366.
9. S. Jeong, K. K. Kim, S. J. Jeong, K. H. An, S. H. Lee and Y. H. Lee, *Synthetic Metals,* **2007**, *157,* 570-575.
10. E. Couteau, K. Hernadi, J. W. Seo, L. Thien-Nga, Cs. Miko, R. Gaal and L. Forro, *Chem. Phys. Lett*., **2003,** *378*, 9-17.