

## Synthesis of Multi Wall Carbon Nanotube (WCNT) over thin films of SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> deposited by Combustion Chemical Vapor Deposition

M. D. Lima\*, S. S. Stein, R. Bonadiman, M. J. de Andrade, C. P. Bergmann  
Av. Osvaldo Aranha, 99, sala 705-c, CEP 90035-190, Porto Alegre, Rio Grande do Sul,  
Brasil.

e-mail: [m.dlima@brturbo.com](mailto:m.dlima@brturbo.com)

Laboratory of Ceramic Materials, LACER, Materials Department, Federal University of  
Rio Grande do Sul.

*Carbon nanotubes (CNT) constitute a new class of materials discovered in 1991 by Sumio Iijima that present unusual mechanical, electrical and thermal properties. CNT synthesis directly over metallic or ceramic substrates is of great interest in the electronic industry for the development of circuits or displays. Many ceramic catalysts have been reported for CNT growth, and a great part of them is based on the formation of a solid solution between transition metallic oxides (Fe, Ni, Co) and ceramic oxides. In this report homogeneous mixtures of Fe<sub>2</sub>O<sub>3</sub> and amorphous SiO<sub>2</sub> were prepared through their co-deposition by Combustion Chemical Vapour Deposition (CCVD). This technique allows the deposition of thin films using low cost equipment and precursors. After that, they were kept in an atmosphere of H<sub>2</sub>/CH<sub>4</sub> to promote the CNT growth. The temperatures of synthesis were varied from 950 to 1100 °C. The efficiency of the synthesis process was evaluated according to its thermal analysis, mass variation during the synthesis, purification, scanning and transmission electron micrographies. Multiwall Carbon Nanotubes were obtained with diameters of less than 15 nm.*

Key words: carbon nanotubes; CVD; silica.

### INTRODUCTION

The Combustion Chemical Vapor Deposition (CCVD) technique has been recently developed [5], and it has advantages when compared to the conventional systems, mainly because of the low cost of the employed precursors and equipment. The energy needed to the dissociation of the precursors and to the activation of nucleation and diffusion processes during film formation is provided by the combustion of gases,

such as H<sub>2</sub>, acetylene, methane or any other non-contaminating combustible. The deposition process is carried-out at room pressure and usually at open air. Precursors are dissolved in a combustible solvent that is atomized and burned, and the flame produced by the combustion of the solvent can be used as the main heat source of the process, while a second flame acts as a pilot-flame.

The deposition of amorphous silica coatings by CCVD technique has already been reported by Hampikian and Carter [4]. In their work, they used Ni-20Cr as the substrate, and the precursor was tetraethyl orthosilicate (TEOS) diluted in ethylic alcohol (0.0025M). Several different oxides, both amorphous and crystalline, have been deposited by this technique [4].

Carbon nanotubes (CNT) are a new class of materials discovered in 1991 by Iijima [6], and they have remarkable mechanical, electrical and thermal properties. They have the highest known ultimate tensile stress, of about 200 GPa, 100 times greater than the most strength steel, with only 1/6 of its density. Several processes regarding carbon nanotubes synthesis are being developed, among them electrical discharge between graphite electrodes and Catalytic Chemical Vapor Deposition (Catalytic CVD), the last having the greatest potential for mass production of nanotubes. The catalysts used are transition metals such as Fe, Ni and Co, or their oxides. These catalysts, used in the form of nanoparticles with diameters smaller than 20nm, are submitted to a carbon-rich environment at a temperature between 600 and 1200°C, and become supersaturated with carbon. Hence, the carbon precipitation occurs, in the shape of a curved graphite plan, forming a tube. The hybridization type of these tubes is sp<sup>2</sup>, and they can have one plane (single-wall carbon nanotubes, CNTPS), or several planes, forming multi-walled carbon nanotubes (CNTPM). The catalysts or their precursors can be dispersed over a plane substrate, such as a silicon wafer, or over some inert material with a large surface area. Several ceramic catalysts have already been developed to promote the growth of CNT. Most of them are based on the formation of a solid solution between transition metals oxides (Fe, Ni, Co) and thermal stable ceramic oxides. This way, the metallic catalyst is homogeneously dispersed and “diluted” within the ceramic matrix. The atmospheres used in the synthesis of nanotubes by the Catalytic CVD technique cause the reduction of the oxides. The formation of metallic nanoparticles of different diameters depends on factors such as surface tension between the metal and the ceramic matrix and the metal surface concentration. Proper conditions to the formation of carbon nanotubes are achieved when the diameter of such particles is smaller than 15-20 nm.

The growth of carbon nanotubes over both ceramic and metallic substrates has a great potential for technological applications, mainly because of their electronic properties. Surfaces coated with CNT could be used as electrodes with high surface area or as electron emission field guns, which could be used in high efficiency and high luminosity displays. In this work, amorphous silica films deposited by Combustion CVD were used as a matrix to the solution and dispersion of iron oxide. There are papers [1, 2, 3] regarding the deposition of Fe-SiO<sub>2</sub> over Si-substrates by sol-gel/impregnation techniques; however, no references concerning the use of Combustion CVD technique to the synthesis of carbon nanotubes were found in the literature.

## **EXPERIMENTAL PROCEDURE**

**Fe-SiO<sub>2</sub> films deposition.** The Fe-SiO<sub>2</sub> films were deposited over stainless steel AISI 316L substrates, with 19.05mm diameter and 2mm thick. One side of the substrates was ground to 400 grit sand paper and then polished with 1.5μm alumina. On the opposite side, a hole with 2mm diameter and 1.5mm deep was made on the center of the sample, so a type-K thermocouple could be fixed on it. The equipment utilized for the CCVD depositions is schematically shown in figure 1. A Bunsen burner was used as pilot flame, and propane was employed as combustible. The atomization system is constituted by 2 needles arranged perpendicularly. The precursors solution is injected on the thinner needle (0.6mm diameter), while the atomizer gas is injected on the thicker one (1.5mm diameter). The deposition parameters are listed in Table 1. The liquid precursor is pumped by a peristaltic pump, and the thermocouple under the substrate is connected to a data acquisition system. The used precursor was TEOS (MERCK) diluted in absolute ethylic alcohol at a fixed concentration of 0.043M, and iron was added as Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (VETEC). Iron nitride was added in several different proportions, as stated in Table 2.

**Nanotubes synthesis.** The nanotubes synthesis was carried-out in a tubular mullite furnace, with 50mm internal diameter and 500mm length, as seen in figure 2. The furnace is externally heated by electrical resistances. Several atmospheres with different compositions, as shown in Table 2, were tested. The employed carbon source was natural gas (Table 3), and the nanotubes synthesis was done at room pressure. The

catalysts were put in a small alumina container, which was located right below the internal thermocouple, as shown in figure 2. Starting from room temperature, the synthesis temperature - 1000°C – was reached after 30 minutes, and after that the natural gas was purged during 10 minutes. After that, the flux of natural gas was stopped, and the carrying gas flux was increased to 400l/h during two minutes, in order to quickly remove all the natural gas from the furnace interior. The flux of carrying gas was kept during furnace cooling down. After the synthesis, some sample were submitted to a treatment with 36% HCl, in order to remove the metallic catalyst particles.

The coatings characterization was firstly made by X Ray diffractometry (Philips X'Pert MDP diffractometer) equipped with a graphite monochromator and using a copper anode operating at 40kV and 40mA. Electron microscopy – both scanning and transmission – were also done, using a JEOL JSM 5800 and a JEOL JEM2010 (operated at 200kV and 0.25 point resolution), respectively.

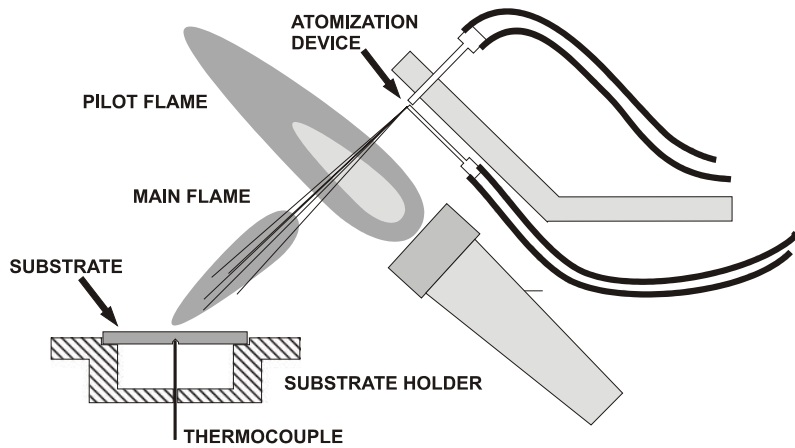


Figure 1. Deposition system – schematic.

Table 1. Deposition parameters.

Air flux	16l/min
Precursor flux	2.5 ml/min
Substrate temperature	700 ±50°C
Susbtrate to atomizer distance	90 mm
Substrate/atomizer angle	55°

Table 2. Employed formulations. Fixed concentration of Teos: 0.043M.

Formulation	Teos g/l	Fe(NO <sub>3</sub> ).9H <sub>2</sub> O g/L	Fe concentration in the precursor solution (M)	Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> wt%	Fe/SiO <sub>2</sub> wt%
0	9.35	0.00	0.0000	0.00	0.00
1	9.35	8.40	0.0208	1.27	44.28
2	9.35	4.20	0.0104	0.63	22.14
3	9.35	2.10	0.0052	0.32	11.07
4	9.35	1.05	0.0026	0.16	5.53
5	9.35	0.53	0.0013	0.08	2.77

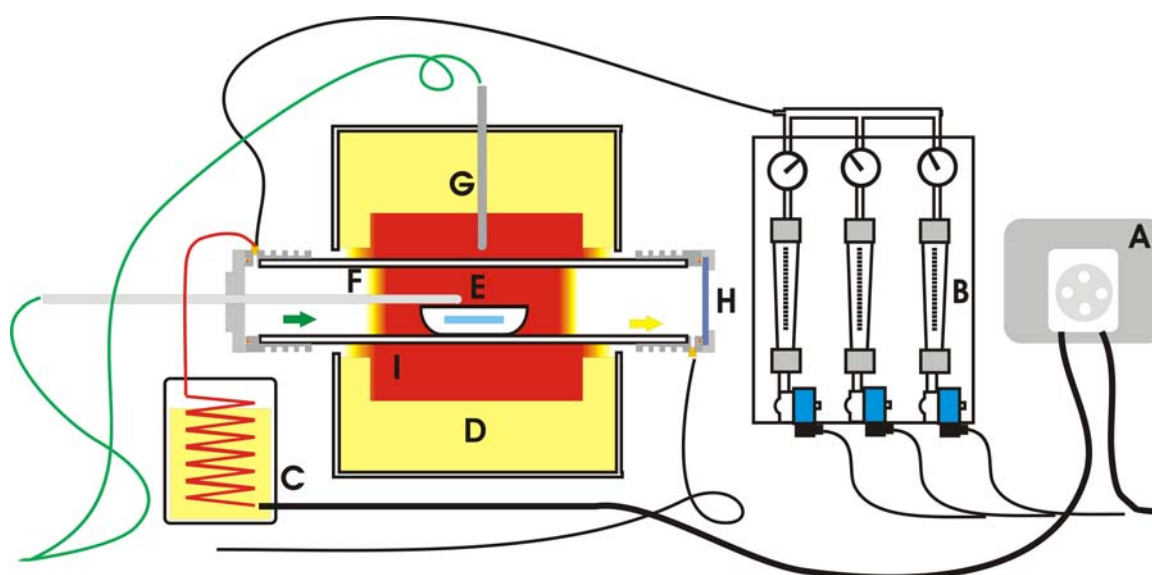


Figure 3. Equipment used for the synthesis of CNT: a) peristaltic pump used for liquid precursors injection; b) flux meters; c) liquid precursors evaporators; d) electric furnace; e) nanotubes growth substrate; f) thermocouple; g) mullite tube; h) boron silicate viewing window.

Table 3. Composition of the employed natural gas (NG) – volume %

Methane	CH <sub>4</sub>	91.800
Ethane	C <sub>2</sub> H <sub>6</sub>	5.580
Propane	C <sub>3</sub> H <sub>8</sub>	0.970
Iso-Butane	C <sub>4</sub> H <sub>10</sub>	0.030

N-Butane	$C_4H_{10}$	0.020
Pentane	$C_5H_{12}$	0.100
Carbon Dioxide	Q	0.800
Nitrogen	$N_2$	1.420

## RESULTS AND DISCUSSION

The X Ray diffraction analyses of the coated substrates (Figure 2) revealed that the coatings were almost completely amorphous, containing traces of tridimite. This indicates that there was no iron segregation in the form of crystalline phases in the deposited coating, and that iron was homogeneously dispersed within the film.

Films submitted to NG/H<sub>2</sub> atmosphere had different performances regarding carbon nanotubes synthesis (Figure 4). Formulations 1 and 2 led to the formation of films that produced a little amount of thin CNT, while formulations 4 and 5 led to the formation of thin CNT, thick fibres and embedded iron particles in carbon, as shown in Figure 4.5). A good production of random oriented CNT in the film surface was obtained with formulation 3.

Films produced with formulation 3 had approximately 10% wt% of metallic iron after the reduction of Fe<sub>2</sub>O<sub>3</sub>, assuming that it was completely reduced during the heating stage and that both Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> had the same deposition synthesis. Such iron concentration was found to be the most suitable for the synthesis process. For the films containing higher iron concentrations, which were produced using formulations 1 and 2, it is probable that coarse iron particles or even metallic iron films were formed after the hydrogen reduction, leading only to the deposition of amorphous carbon. Films with lower iron concentration produced dispersed catalyst particles, resulting in low density of carbon nanotubes.

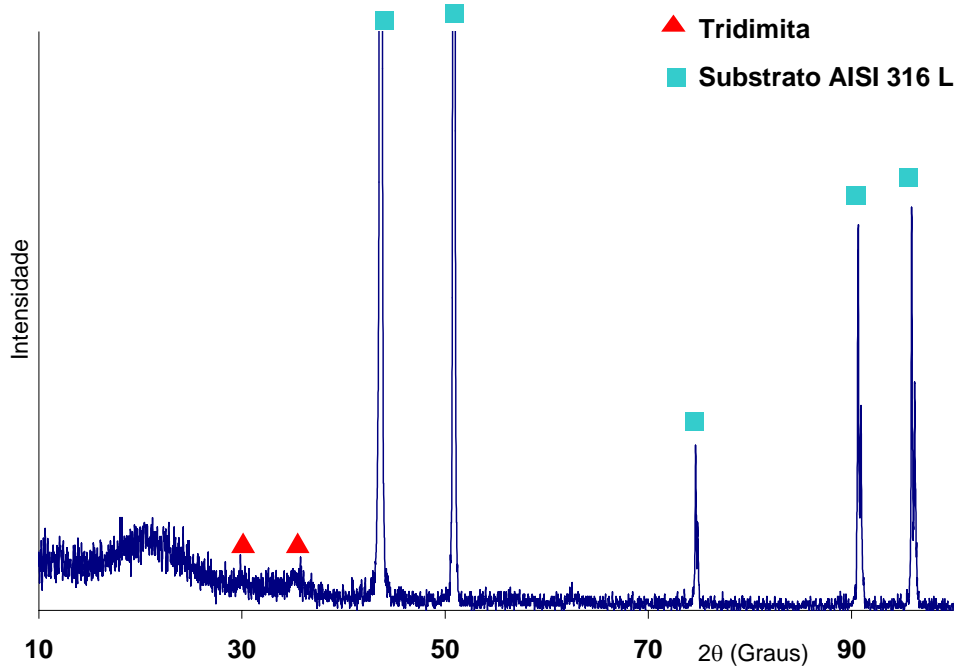


Figure 3. X Ray diffraction of the coated AISI 316L steel substrate. Coating prepared according to formulation 3.

Films prepared from formulation 3, which produced the highest amount of CNT seen by SEM, were also characterized by TEM. After the carbon nanotubes synthesis, the film was stripped and their fragments were immersed in concentrated HCl and ultrasound cleaned during 30 minutes, in order to remove particles of metallic iron and iron carbides. The acid dispersion containing the film and the CNT was neutralized in a  $\text{Na}_2\text{CO}_3$  solution, and the solid particles were separated by filtration and rinsed several times in deionised water to remove salts from neutralizing process.

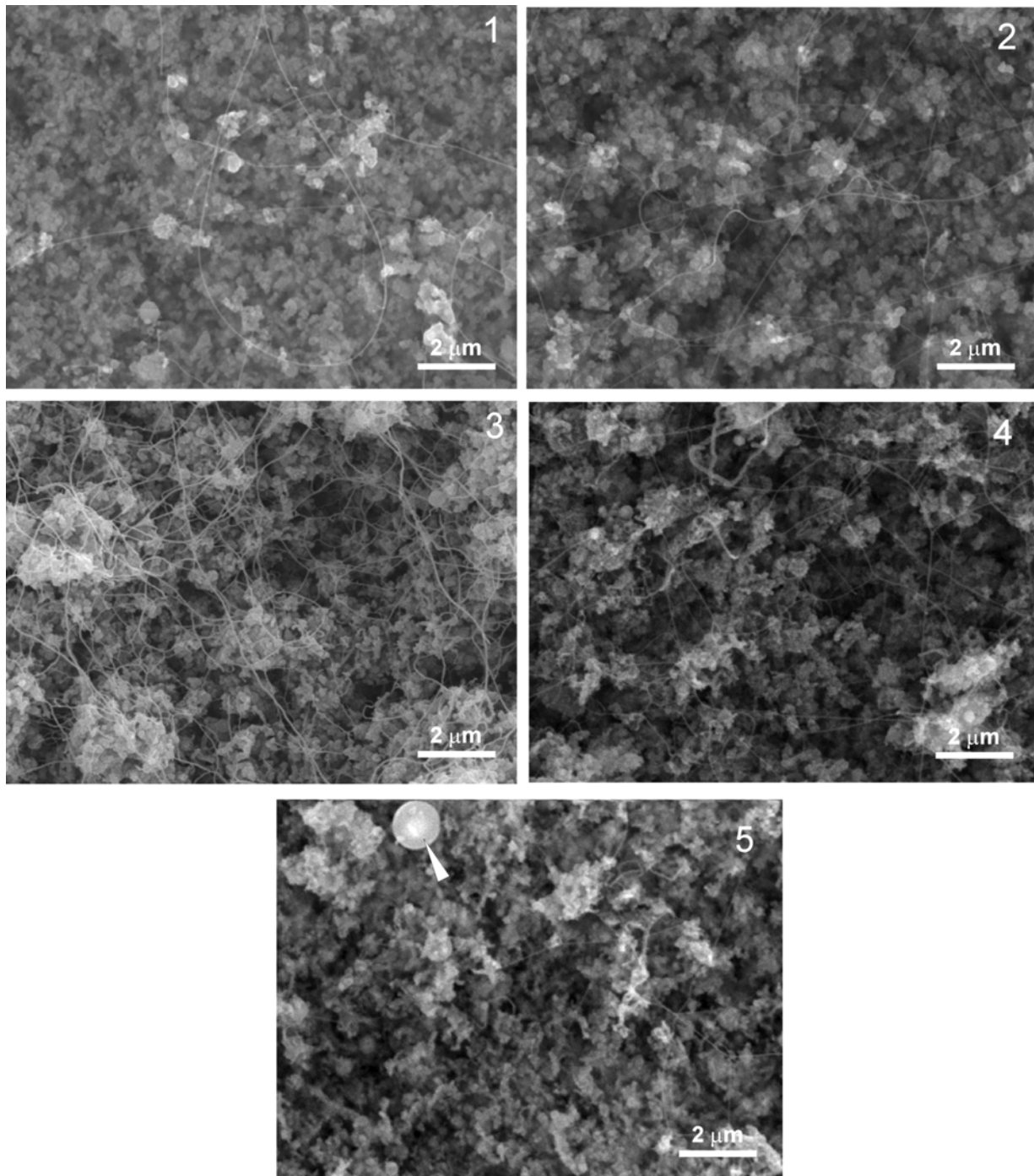


Figure 4. SEM micrographs of the coatings after the CNT synthesis in H<sub>2</sub>/N<sub>2</sub> atmosphere. Number at the upper-right corner indicates the formulation used.



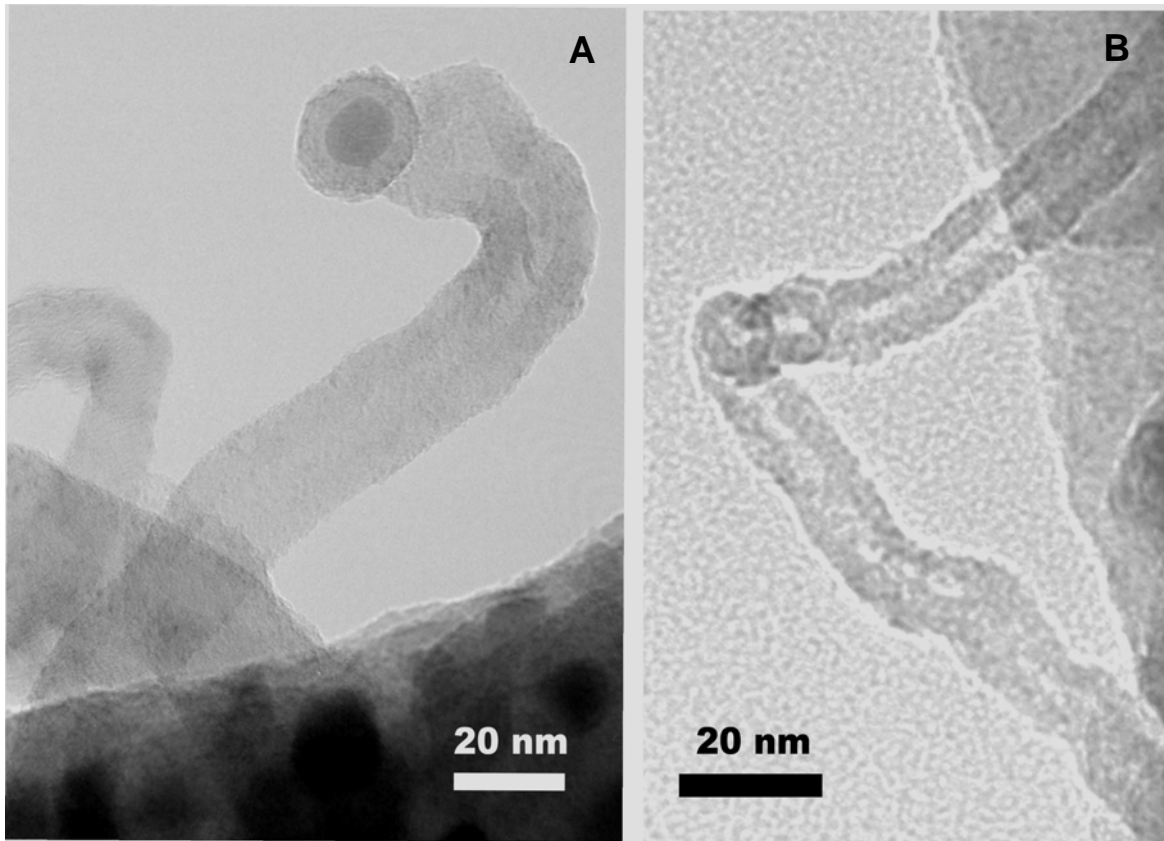


Figure 5. TEM micrograph of the Fe-SiO<sub>2</sub> film prepared according to formulation 3.

Figure 5 shows that the CNT produced using formulation 3 are multi-walled, with diameters ranging from 10 to 20nm. Despite the HCl treatment, nanometric iron particles remained embedded at the nanotubes endings (Figure 5.A) or in concentric layers of carbon (buckonions).

## CONCLUSIONS

It was possible to produce CNT over Fe-SiO<sub>2</sub> films deposited by the Combustion CVD technique. The obtained films were almost totally amorphous, indicating that iron was well dispersed within the silica matrix. Those films, when exposed to a H<sub>2</sub>/GN atmosphere, led to the production of CNT in different amounts, depending mainly on the iron concentration in the film. Higher amounts of carbon nanotubes were achieved

with films made from precursor solutions containing 0.0052M Fe and 0.043M SiO<sub>2</sub>. Nanotubes produced with this formulation were multi-walled and had diameters between 10 and 20 nm.

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## **REFERENCES**

1. Murakami Y., Yamakita S., Okubo T, Maruyama S., , Chemical Physics Letters 375 , p. 393–398, 2003.
2. Huang L., Wind S. J., O'Brien S. P., , NANO LETTERS vol. 3, No. 3, p. 299-303, 2003.
3. Zheng F, Liang L, Gao Y, Sukanto J. H., Aardahl C.L., , NANO LETTERS, Vol. 2, No. 7, p. 729-732, 2002.
4. Hampikian , J.M. ; Carter, W.B. ;, Materials Science and Engineering A267 (1999) 7–18.
5. Hunt, A.T.; Carter, W.B.; Cochran, J.K. , Jr., Appl. Phys. Letts. 63 (2) (1993) 266.
6. Iijima S. , *Nature* 354, p. 56 – 58, 1991.