

# FILLING OF CARBON NANOTUBES WITH SELENIUM

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## Introduction

Carbon nanotubes are unique nanostructures with remarkable electronic, mechanical, chemical,... properties, which make them attractive candidates for a variety of applications ranging from composite materials to molecular electronics [1,2].

Some of the interesting applications of these nanometer size tubes is linked to their tubular structure, indeed carbon nanotubes could be used as nanoscale molds. Therefore their filling raises the possibility of novel nanomaterials synthesis with technologically interesting properties on a nanometric scale, and offers the possibility to enhance the physical properties of both the encapsulated and encapsulating materials [3,4]. Filled nanotubes can be synthesized by capillary action [5] or by using composite anodes in arc discharge [6], resulting in formation of encapsulated compounds or elongated nanostructures of different materials (carbides, oxides, or even pure metals). In the present study, multiwall nanotubes, synthesized by catalytic and thermal decomposition of hydrocarbons, and single wall nanotubes (from Rice University) were filled with Se. The control of Se partial pressure in our reactor allows to control the nanotube filling rate, which also depends on the nanotube inner diameter. Such 1D nanowires are ideal systems allowing to investigate the influence of confinement on Se structure and nanocomposite properties.

## Experimental

For this study, carbon nanotubes (NTs) having different inner diameters were selected. Multiwall carbon nanotubes (MWNTs) are synthesized in our laboratory by two different ways. The larger inner diameter nanotubes used are produced by a template method [7] using commercially porous alumina membranes with a pore diameter of 200 nm. MWNTs are obtained after thermal decomposition of propylene at 800 °C during 3 hours. MWNTs with a small inner diameter (3-5 nm) are synthesized via catalytic decomposition of acetylene ( $C_2H_2$ ) on a  $Co_xMg_{(1-x)}O$  solid solution at 600 °C for 1 hour [8]. As for SWNTs, they are provided by Rice University (Houston US), their inner diameter is about 1.2 nm. Before filling, catalytic MWNTs need to be opened, it is done with concentrated nitric acid at 120°C, then  $CO_2$  treatment at 525°C.

For filling carbon nanotubes, a vapor phase method was carried out, because Se is easy to vaporize due to its low melting (221°C) and boiling (685°C) points and low surface tension (97 mN/m). Experiments were performed in a sealed glass reactor, where the control of Se partial pressure allows to control the nanotube filling rate, which

will depend also on the nanotube diameter. Knowing the initial mass of nanotubes, we plot the nanotube mass up-take as a function of selenium pressure for different filling temperatures (400, 500 or 600°C). After filling samples were characterised by HRTEM and EDX analysis (Phillips CM 20) and X ray diffraction.

## Results and Discussion

To better understand the nanotube filling mechanism, we reported the nanotube mass uptake as a function of selenium pressure for the three different kind of nanotubes, i.e. the different nanotube inner diameters (Figure 1).

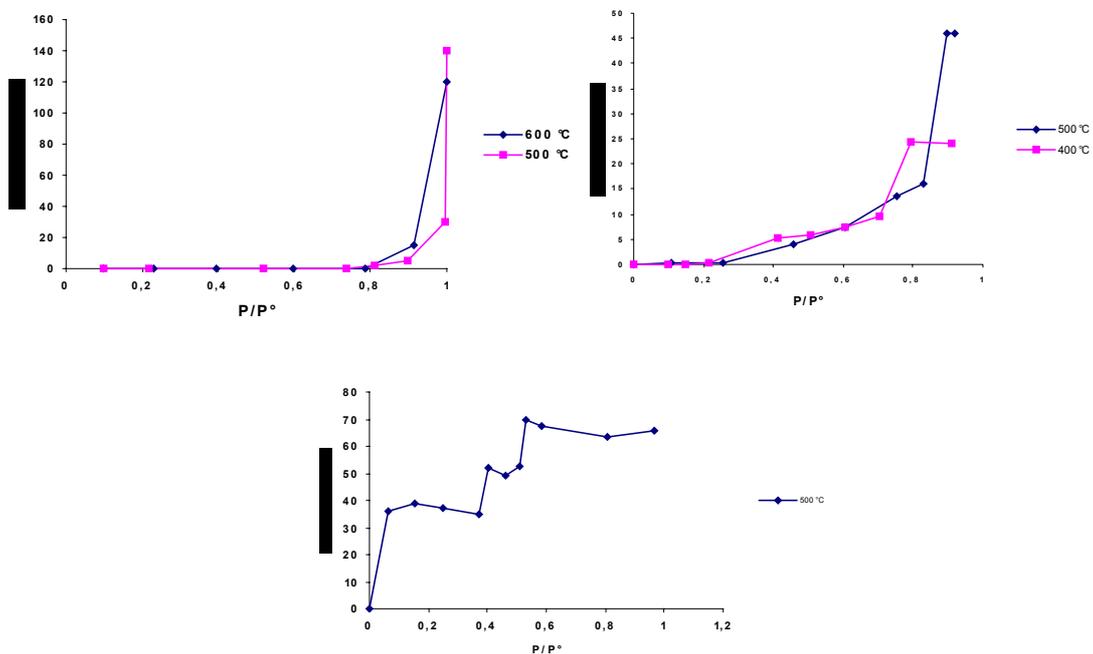


Figure 1. Nanotubes mass uptake as a function of selenium partial pressure, for the “template” MWNTs (top left), the catalytic MWNTs (top right) and the SWNTs (bottom)

What is important to notice is, on one hand, filling takes place in one or several steps, depending on the nanotube type, and on the other hand, an efficient filling is only possible if a control of the selenium partial pressure in the reactor is achieved.

Concerning the filling steps, their numbers and positions are directly connected to the nanotubes diameter. As the nanotubes diameter decreases, filling occurs at lower Se pressure.

In the case of “template” MWNTs (inner diameter of about 200 nm), filling occurs at high pressure: over 0.8 at 600°C, over 0.9 at 500°C and condensation transition is close to  $P/P^\circ = 1$ . When samples are characterized by HRTEM, MWNTs filling rate up to 90% is observed [9].

For catalytic MWNTs (inner diameter ranging from 3 to 5 nm), filling occurs at lower  $P/P_0$ , i.e. close to 0.2, whatever the filling temperature. Transition is observed at  $P/P_0 = 0.79$  at 400°C,  $P/P_0 = 0.84$  at 500°C and  $P/P_0 = 0.88$  at 600°C. In HRTEM, only partial MWNTs filling is observed before transition (Figure 2 left), whereas all opened MWNTs are Se-filled after transition (Figure 2 right). It is also important to notice that no selenium particles are observed on MWNTs external surface, meaning our vapor-phase filling method is very efficient and selective. Filling modifies Se structure, indeed X-ray diffractograms show a slight decrease of the  $a$  lattice parameter due to Se confinement inside MWNTs inner channel.

As the nanotubes diameter decreases, i.e in the case of SWNTs filling, Se adsorption is more complex. Three steps are observed, at  $P/P_0 = 0.03$ , at  $P/P_0 = 0.38$ , at  $P/P_0 = 0.53$ , probably due to different Se adsorption sites.

The influence of such confinement on Se structure is at present studied by EXAFS.

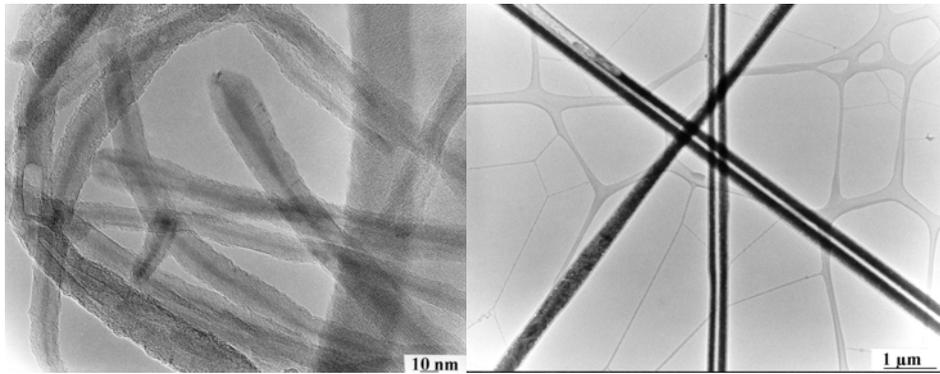


Figure 2. HRTEM micrographs showing partially filled catalytic MWNTs (left) and filling of all the opened MWNTs after transition (right).

Se is an interesting guest for nanotubes filling due to its low melting (221°C) and boiling (685°C) points, its low surface tension (97 mN/m) and good wettability on carbon surface. Se filling occurs by steps. In catalytic MWNTs (inner diameter: 3 to 5 nm), it starts in the smaller diameter MWNTs, then all the opened ones are filled. That means filling is governed by capillary condensation phenomenon. In SWNTs, the three steps observed probably correspond to different Se adsorption sites, computation is in progress to take into account adsorption possibilities according to geometry of pores and SWNTs structural organization.

## Conclusions

We developed a vapor-phase method allowing to efficiently fill MWNTs and SWNTs with selenium. The control of Se partial pressure and temperature in our sealed reactor

allows to control the nanotube filling rate, therefore filling rates up to 90% can be achieved. We observed a nanotube size-dependence filling. As nanotube inner diameter decreases, filling occurs at lower Se partial pressure. In our case the filling mechanism results of capillary condensation, so steps observed depend on the size of adsorption sites available. The influence of confinement on Se structure and electronic properties is in progress, followed by Raman spectroscopy and EXAFS.

## References

- [1] S. Iijima, *Nature* 354, 56 (1991)
- [2] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* 15, 5, 353-389 (2003)
- [3] J. Sloan and M.L.H. Green, *Handbook of nanostructured materials and nanotechnology*, ed. H.S. Nalwa, vol.5, Academic Press (2000)
- [4] M.S. Dresselhaus, Y.M. Lin, O. Rabin, A. Jorio, A.G. Souza Filho, M.A. Pimenta, R. Saito, Ge.G. Samsonidze, G. Dresselhaus, *Mat. Sci.and Eng. C233*, 129-140 (2003)
- [5] M. R. Pederson and J. Q. Broughton, *Phys. Rev. Lett.* 69, 2689 (1992); P. M. Ajayan and S. Iijima, *Nature (London)* 361, 333 (1993); E. Dujardin, T. W. Ebbesen, H.Hiura and K. Tanigaki, *Science* 265, 1850 (1994)
- [6] R. S. Ruoff, D. C. Lorents, B. Chan, R. Malhorta and S. Subramoney, *Science* 259, 346 (1993)
- [7] T. Kyotani, L. Tsai et A. Tomita, *Chem. Mater.*, 8, 2109 (1996)
- [8] Y. Soneda, K. Szostak, S. Delpeux, S. Bonnamy and F. Béguin, in *Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth, *AIP Conference Proceedings* 591, 2001, pp 199-203
- [9] J. Chancolon, F. Archaimbault, S. Delpeux, A. Pineau, M.L. Saboungi and S. Bonnamy, in *Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth, *AIP Conference Proceedings* (2002).