Pressure dependence of Raman modes in double wall carbon nanotubes filled with amorphous selenium

E. Belandria[1], J. M. Broto[2], E. Flahaut[3], F. Rodríguez[4], R. Valiente[5], E. del Corro[6], M. Taravillo[6], V. G. Baonza[6] and **J. Gonzalez**[4,7]

[1]Centro de Estudios Avanzados en Óptica, Universidad de los Andes, 5201 Mérida, Venezuela,[2]Laboratoire National des Champs Magnétiques Intenses (LNCMI) - CNRS UPR 3228,Université de Toulouse, 143 Avenue de Rangueil, 31400 Toulouse, France [3]CIRIMAT, Université de Toulouse, F-31400 Toulouse, France,[4]DCITIMAC-Malta Consolider Team, Universidad de Cantabria, 69005 Santander, Spain,[5] Dto de Fisica Aplicada- Malta Consolider Team, Universidad de Cantabria, 69005 Santander, Spain [6] MALTA-Consolider Team, Departamento de Quimica Fisica I, Facultad de Ciencias, Universidad Complutense de Madrid, Plaza de Ciencias 3, 28040- Madrid, Spain,[7] Centro de Estudios de Semiconductores, Universidad de los Andes, Mérida 5201,Venezuela.

jesusantonio.gonzalez@unican.es

The synthesis of mono-dimensional nanocrystals is complex due to the lack of stability of such structures. One way to stabilize them is to prepare them within a container, such as carbon nanotubes (CNTs). CNTs are good candidates for this application due to their inner diameter in the nanometer range, as well as their good chemical and thermal stability. Selenium, which is a p-type semiconductor, exhibits both photovoltaic and photoconductive properties. It is utilised in many devices ranging from solar cells to rectifiers and xerography [1]. Trigonal selenium (hexagonal) is the most stable allotrope under normal temperature and pressure. Selenium has also monoclinic allotropes although it is generally commercially available in the amorphous state. The confinement of Se inside CNT was only scarcely studied but Chancolon et al. [2] proposed a method for filling CNT in the vapour phase and performed a comprehensive study of the structure of Se within the CNT by X-Ray diffraction and X-ray absorption spectroscopy. They found that the Se present inside the CNT was mainly amorphous in their synthesis conditions. Earlier studies have revealed that the space available within CNT may play an important role on the crystal structure of the confined material, especially in the case of narrow DWCNT where materials are often found in amorphous state even if they crystallise in singlewalled CNT of similar inner diameter [3]. The samples are characterized by high resolution transmission electronic microscopy and Raman spectroscopy.

A systematic analysis of TEM images reveals that samples produced by this method contain approximately 77% of double wall carbon nanotubes (DWCNTs), the high proportion of DWCNTs was also confirmed by electron diffraction with a small admixture of about 18% single-wall CNTs (SWCNTs), and roughly 5% triple-wall CNTs . The inner and outer diameters range from 0.53 to 2.53 nm and from 1.23 to 3.23 nm, respectively. The median inner diameter is 1.2 nm and the median outer diameter is 1.9 nm [4,5,6]. They were filled using a high filling yield capillary wetting technique [6]. Filling yield was roughly estimated to be *ca*. 50%, straight from transmission electronic microscopy (TEM) observation, presented in Figure 1.In order to investigate their structural stability and unravel the differences induced by intershell interactions, unpolarized room temperature Raman spectra of radial and tangential modes of DWCNTs filled with 1D nanocrystalline Se excited with 514 nm were studied at high pressures (figure 2). Up to 12 GPa we found a pressure coefficient of 4.9 $cm^{-1}GPa^{-1}$ for the internal tube and 7.5 $cm^{-1}GPa^{-1}$ for the external one. In addition, the tangential band of the external and internal tubes broadens and decreases in amplitude. Under pressure, we note that the pressure coefficient of the G-bands of the internal and external CNTs filled with amorphous Se are larger than the pressure coefficients of empty CNTs and this has been attributed to the effect of charge transfer from the Selenium nanowires to the CNTs. Finally, we unravel that the outer tubes act as a protection shield for the inner tubes (figure 3).

References

[1] H. Fana, Z. Wanga, X. Liua, W. Zhenga, F,Guoa, Y. Qian,Solid State Communications **135**, (2005).319.

[2] W. C. Cooper, R. A Westbury, *Selenium,* 87-147, (1974).

[3] J. Chancolon, F. Archaimbault, S. Bonnamy, A.Traverse, L. Olivi, G. Vlaic, Journal of Non-Crystalline Solids **352**, (2006) 99.

[4] José Jorge, E. Flahaut, F. González- Jiménez, Gema González, J. González, E. Belandria,J.M.Broto, B. Raquet, Chemical Physics Letters, **457**, (2008) 347.

[5] E. del Corro, J. Gonzalez, M. Taravillo, E. Flahaut and V. G. Baonza, *Nano Lett.*, ***8*** (8), (2008) 2215

[6] E. Belandria, M. Millot, J.M. Broto, E. Flahaut, F. Rodriguez , R. Valiente , J. Gonzalez, Carbon, **48**, (2010) 2566.

Figures

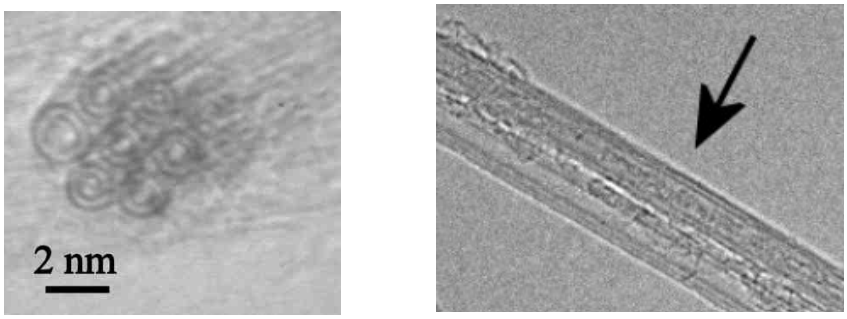

Figure 1: HRTEM images of Se@DWCNT

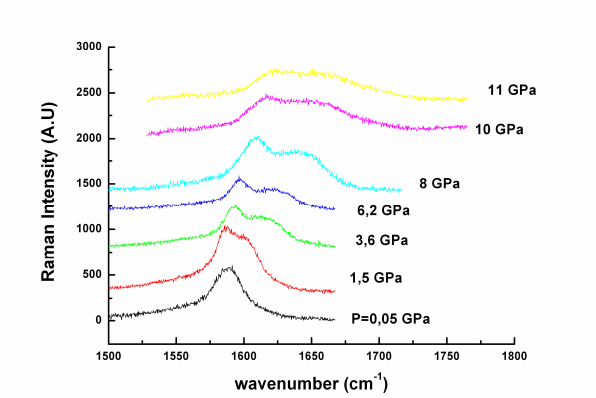

Figure 2: Raman spectra at different pressures in the upstroke of Se@DWCNTs

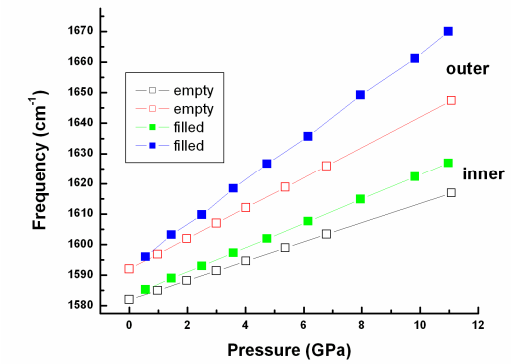

Figure 3: Pressure dependence of tangential modes of DWCNT@Se for the inner and outer tubes.