Caracterisation of double wall carbon nanotubes by Transmission Electron Microscopy and optical absorption

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Single wall carbon nanotubes (SWNTs) have shown outstanding capabilities in realising new functional devices such as ultrasensitive gas sensors, electronics on a molecular scale and quantum devices. However, due to their one-dimensional structure, the SWNTs are extremely sensitive to any slight changes in their environment, which change their properties like electrical conduction. A strategy to overcome this difficulty is to use double wall carbon nanotubes (DWNTs), consisting of two concentric tubes. The outer tube is used as a sacrificial layer, in order to preserve the electronic structure of the inner wall. However, little is known about the properties of such tubes and especially the interaction between the two layers and the impact of these interactions on their physical and chemical properties.

My thesis is in the context of a partnership ANR (The wall project) which was formed to study and exploit the potential of double-walled tubes for the development of transducers. The aim of my thesis is to study the interaction between the two walls and to establish correlations between the structure of DWNTs and their electronic and optical properties. These properties are very sensitive to the structure of the tubes. Thus, according to the winding angle of the carbon network (called helicity) and its diameter, a SWNT may be metallic or semi-conductor, with a variable gap according to the diameter. The optical transitions are also directly dependent on diameter and helicity, so the optical spectroscopy is a fine probe of the electronic properties. The general experimental approach is to combine structural analysis of electronic transmission microscopy (TEM) and optical absorption and luminescence measurements, through cooperation between the LEM and LPQM (ENS Cachan), which co-frame the thesis. Electron microscopy allows to determine the atomic structure of tubes either from atomic resolution images either from their diffraction. Both methods are implemented on the TEM Zeiss in the LEM and TEM Jeol ARM in the MPQ laboratory (University Paris 7) to which the LEM has access. Optical measurements will be carried out in the LPQM. The tubes will be studied from the CIRIMAT (Toulouse) who has developed a method for specific synthesis of this kind of tubes and with which the LEM has developed cooperation. The produced tubes as a mixture of different structural configurations in terms of diameter and helicity, must be sorted to have batches of pure samples. For this, we take advantage of a effective sorting density technique (Density Gradient Ultracentrifugation or DGU), developed by LEM-LPQM consortium , which can distinguish several populations of nanotubes selected by their diameter or their electronic character [1]. The aim is to apply this technique to DWNTs and study on nanotube diameter and chirality given and known, the nature of the transfer, which may occur between the two layers when the tube is optically excited.

The first stage of the first year of the thesis was to inventory the population of tubes in unsorted samples provided by the CIRIMAT through statistical analysis by TEM. A typical view is given in Figure 1. We have determined that the original sample contained about 66% of DWNTs and 20% of SWNTs. The outer diameter of DWNT ranges between about 1.2 and 4 nm. From images of very high resolution (HRTEM) performed on the ARM that allows access to a spatial resolution of 50pm for an accelerating voltage of 80kV (Figure 1), we could determine the helicity of the two layers and corresponding Hamada indices (n,m). From the study of thirty tubes, we have thus established that if the helicity of the outer tube seems almost random, it is not the same for the inner tube. The tubes are rotated relative to the each other so as to avoid certain values. If the origin of these values is still poorly understood, this result shows a first correlation between the structure of the tubes.

The second stage was to perform an initial sort by DGU of unsorted tubes to separate SWNTs and DWNTs and separate tubes according to their diameter. We initially used the sorting conditions to separate SWNTs by diameter [2]. Fifteen fractions resulted from ultracentrifugation, which were then analyzed by TEM and optical absorption. According to the TEM observations, the upper fractions, with lower densities, contain only SWNTs with diameters increasing as the number of the fraction. DWNTs appear only from the fraction 4, while SWNTs disappear from the fraction 9. We tested the reliability of our double methods of analysis on fractions containing SWNT (Figure 2) to identify if the populations of sorted SWNT, which have been observed in TEM, are consistent with energy bands measured on absorption spectra. For this, we used semi- empirical relationships, which are used to calculate the optical transition energies as a function of diameter of metal tubes (transitions M11 , M22) and semiconductors (transitions S11, S22, S33 , etc ...) [3]. The example of the layer 3, analyzed in Figure 2, shows the consistency of the two types of analysis. A thinner test will be soon realized directly from the TEM identification of sorted tubes indices (n,m).

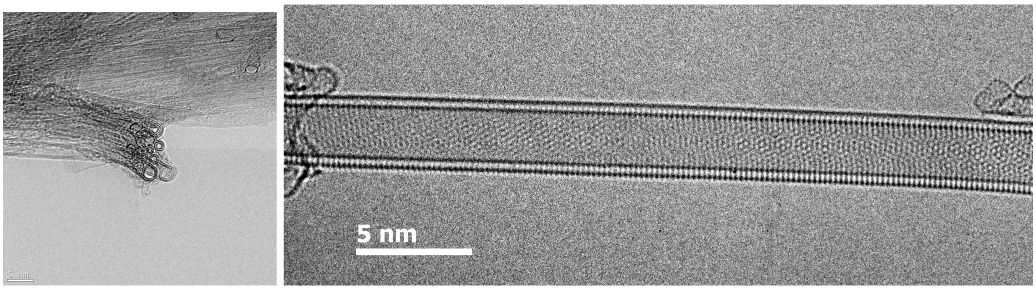

Fig. 1 – (left) Image TEM of carbon nanotubes in bundle in the unsorted sample. (right) Image of DWNT by HRTEM.

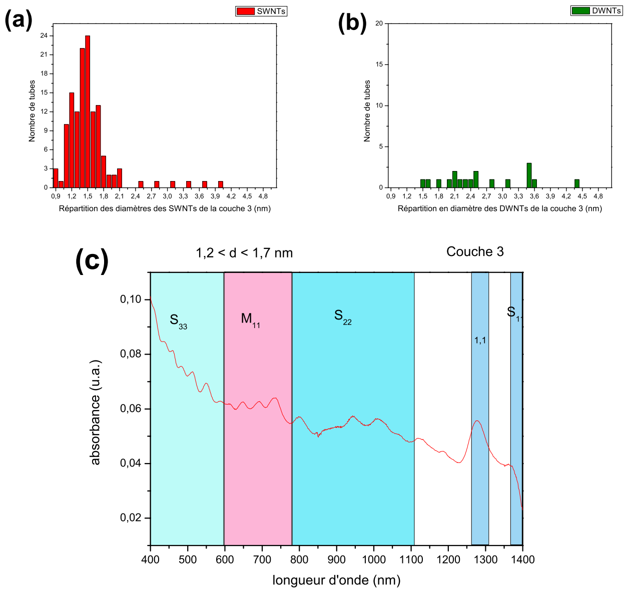

Fig. 2 – Statistics in diameter of (a) SWNTs and (b) DWNTs. (c) We draw energy transition bands on the absorption spectrum of the layer 3, thanks to statistics made by TEM and equations relating diameter and transition energy.

Références

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