Comparing TEM and resonant Raman spectroscopy for diameter distribution assessment of single wall carbon nanotubes

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Characterization of single wall carbon nanotube (SWCNT) population plays a key role to study the influence of growth parameters during their formation. Despite this crucial step, statistical data extracted from more than one characterization technique are rarely compared in publications claiming for SWCNT growth selectivity. Transmission Electron Microscopy and Raman spectroscopy are widely used to obtain an accurate measurement of the SWCNT diameters [1]. We used both techniques and observed a systematic shift between the diameter distributions assessed by Raman spectroscopy and TEM imaging in our typical SWCNT samples, CVD grown on SiO_2/Si wafers (Figure 1)[2]. TEM image analyses were performed on samples transferred on TEM grids using the methodology we proposed in [3] whereas Raman spectra are recorded on the as grown samples and tube diameters were deduced from their radial breathing mode by following a procedure widely used in the literature [4]. Observed shift can be as high as 0.4 nm, which represents 20 to 30 % of the diameter values while measurement accuracy is estimated to be equal to 0.05 nm for both techniques. Furthermore, small tube diameters below 1.2 nm seem to be under-detected by TEM with respect to Raman whereas the opposite trend is observed for tube diameters larger than 1.5 nm. In this work, we explore the comparison between TEM imaging and Raman spectroscopy capabilities for determining the diameter distribution of a CVD grown sample, in an effort to validate, or invalidate, currently used methodologies.

First, comparisons between TEM- and Raman-extracted diameter distributions on our CVD grown samples will be shown. Then, a study on diameter-sorted SWCNTs will be presented, in an attempt to understand the differences observed between TEM- and Raman-extracted diameters below 1.2 nm. To explain the observed shift, we have put forward a few hypotheses linked to potential intrinsic biases of both TEM and Raman spectroscopy as characterization techniques, or to potential deficiencies in our methodology. In order to scrutinize the relevance of these hypotheses and gain more insight into the differences between TEM and Raman spectroscopy for diameter distribution assessment, especially in the Raman dominant diameter range, we have conducted a study on diameter-sorted SWCNTs by a gradient density ultra-centrifugation technique as described in [3, 5], with a distribution centered around 1.0 - 1.2 nm (Figure 2).

This study has enabled us to show that TEM is a technique that is perfectly adapted to the characterization of small-diameter SWCNTs, and that the transfer process from SiO_2/Si wafers used for SWCNT growth is not responsible for the difference in abundance of SWCNTs within the diameter range of 0.5 - 1.3 nm between our growth results as measured by TEM and Raman spectroscopy. The relative accordance on the diameter range between TEM and Raman spectroscopy for the diameter distribution assessment of the diameter-sorted SWCNT sample, and the large discrepancy observed in the case of our wide diameter distribution growth samples, show the importance of a cross characterization methodology. In this respect, our study highlights the biases, introduced by the resonance conditions mandatory for detecting SWNTs by Raman spectroscopy, which can severely distort SWNT population identification and artificially lead to conclude on an apparent tube selectivity. Complete identification of the atomic tube structure using aberration corrected HRTEM [6] will be discussed as a tool for gaining quantification on the detection conditions using Raman spectroscopy.

[1] for a review see *Understanding carbon nanotubes : from basics to applications ,*

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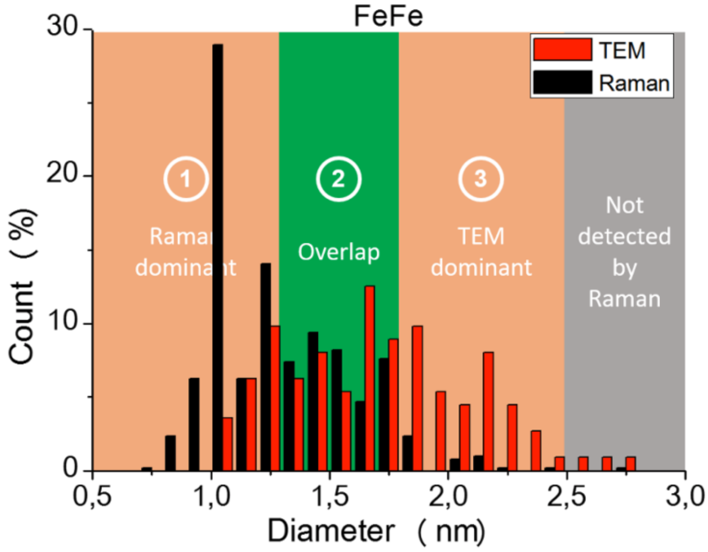

Figure 1 : Superimposed diameter distribution histograms as determined by Raman and TEM, for a sample of SWCNTs grown at 800 °C from Fe nanoparticles as catalysts [2]. Four diameter ranges are distinguished. Domain 1: Ø < 1:3 nm, Raman dominates; domain 2: 1.3 < Ø < 1.7 nm, Raman and TEM seem to be in certain agreement; domain 3: 1.7 < Ø < 2.5 nm, TEM dominates; finally for the highest diameters a range where only TEM allows to detect the SWCNTs.

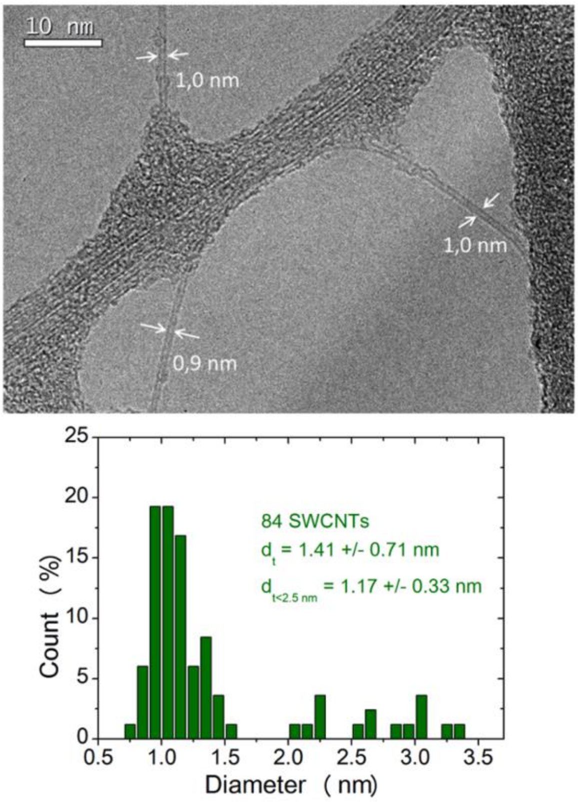

Figure 2: typical TEM image of the transferred diameter-sorted SWCNTs, with the measured diameters instructed in white; diameter distribution histogram extracted from the measurement of the diameters of 84 SWCNTs on random locations on the grid.