Electron Microscopy as a means to validate Raman spectroscopy for qualifying single-walled carbon nanotubes

Jiang, H.[1], Tian, Y.[1] and Kauppinen, E.[1]

[1] Aalto University School of Science, Finland

Recently there is a growing trend of using resonance Raman technique to quantify the population of a specific type of conductivity in a bulk material. In this work, we use electron microscope/electron diffraction as a means to evaluate its validity. Three SWNTs samples with different diameter distributions, including a ferrocene decomposition floating catalyst chemical vapor deposition (ferrocene-FC-CVD)[1] SWNT sample and a spark-based FC-CVD (spark-FC-CVD)[2] sample, in addition to a NIST SWNT reference sample (RM8281), have been investigated. Raman spectroscopy study with three excitation wavelengths of 514, 633, and 785nm was performed to quantify the metallic SWNT concentrations (M%) in the samples. To evaluate the Raman results, electron diffraction (ED) technique was used to directly map the chirality distribution. In the ferrocene-FC-CVD sample, M% was estimated over 90% from Raman analysis at 633nm, but 0% at 514nm, while ED analysis gave about 24%. For the spark-FC-CVD sample, the 633nm Raman analysis led to about 55% metallic tubes, but the 514 laser resulted in less than 2% though ED analysis turned out to be 33%. In particular, the Raman assessment of the well-known (6,5)-dominated NIST reference sample at all three wavelengths of 633nm, 514nm and 785nm, however, showed a small minority of (6,5) tubes, due to the weak resonance of the (6,5) tube with any of those lasers.

To conclude, our results prove that the Raman RBM intensities depend largely on the resonant conditions at certain wavelengths, rather than simply on concentrations. Up to the resonance conditions, some majority nanotube species revealed by electron diffraction measurements induce relatively weak, or even missing RBMs, and vice versa. This certainly leads to an uncertainty over Raman spectroscopy for quantitative assessment of metallic tube concentrations calculating from the relative peak intensities[3].

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