Raman investigation of the defect modes of metallic and semiconducting enriched single walled carbon nanotubes

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Motivation:

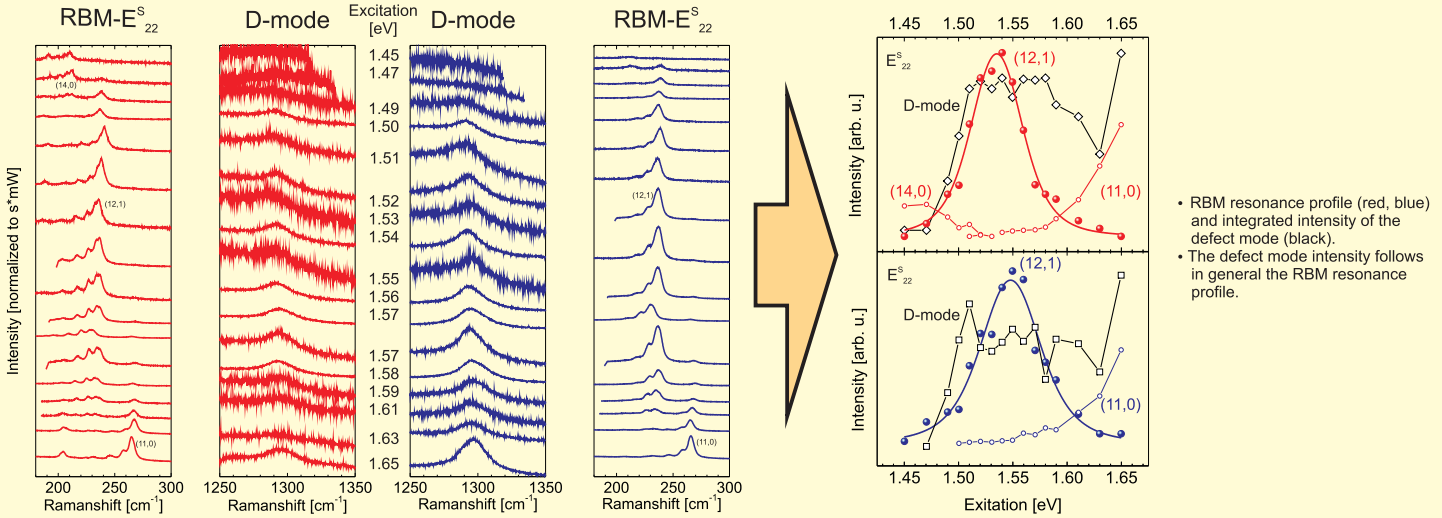
Functionalization of single-walled carbon nanotubes (SWCNTs) typically leads to an increase in intensity of the defect induced Raman bands. A large intensity of the defect modes is therefore often used as an evidence for successful functionalization [1,2]. However, there is no hint if a selective functionalization of metallic or semiconducting SWCNTs can be confirmed with the help of the intensity or position of the defect mode. A necessary condition for that would be that the resonance profiles of the defect modes are known in comparison to the profiles of the well-known radial-breathing modes [3]. Here we analyze the Raman defect modes of metallic and semiconducting enriched HiPCO SWCNT samples. By resonance Raman spectroscopy we study the evolution of the lineshape of the defect mode of SWCNTs for excitation energies in the range of 1.45 to 1.65 eV and 1.96 to 2.34 eV. Furthermore, we discuss differences of the defect modes between the semiconducting and metallic enriched samples.

Sample:

HiPCo single-walled carbon nanotubes. Enriched by density-gradient ultracentrifugation and solved in SDS [4].

Resonance profiles of the defect mode of semiconducting SWCNTs in comparison to the profiles of the RBMs:

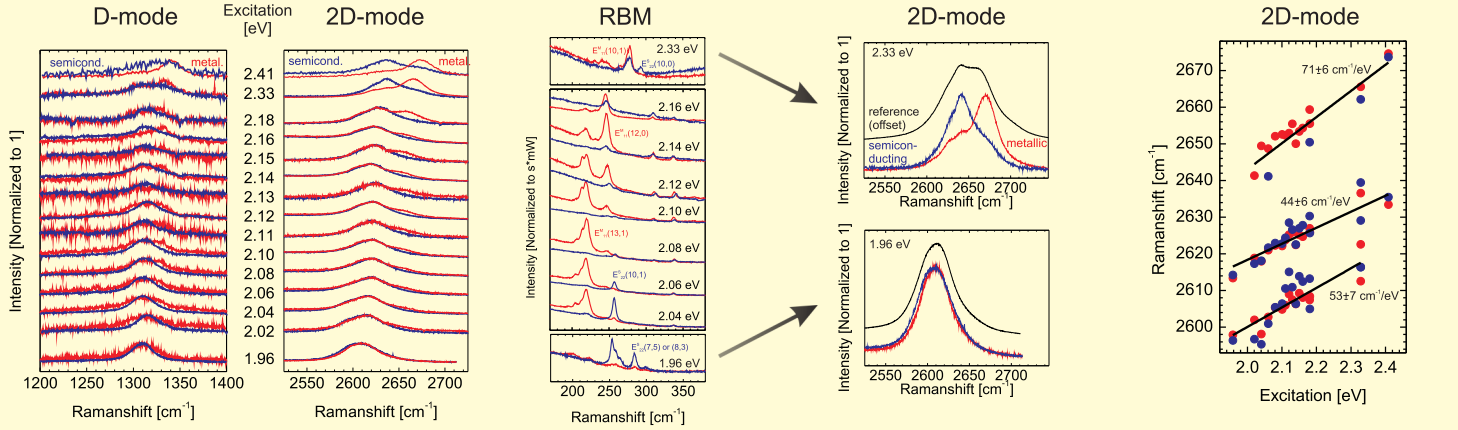
metallic enriched (~80%) semiconducting enriched (~95%)



- Raman measurements of enriched samples with only semiconducting branches in resonance.
- D-mode intensity shows similar variations like the RBM.
- In the metallic enriched sample semiconducting tubes are still present.

- RBM resonance profile (red, blue) and integrated intensity of the defect mode (black).
- The defect mode intensity follows in general the RBM resonance profile.

Differences of the defect-modes position between the semiconducting and metallic enriched samples:



- Line shape of metallic (red) and semiconducting (blue) enriched samples.
- The D- and 2D-mode positions differ for differently enriched samples.
- The D- and 2D-mode of the metallic enriched sample consist of several peaks. These peaks seem to appear and disappear successively.

- RBMs from metallic (red) and semiconducting (blue) enriched samples with metallic and semiconducting tubes in resonance.

- 2D mode at 2.33 eV and 1.96 eV laser energy (normalized to 1). Black line shows a scaled spectrum of a reference (not enriched) sample.
- The difference in 2D-mode position between the two laser energies seems larger for the metallic enriched tubes than for the semiconducting ones, due to the larger dispersion of the high-frequency peak.

- The intense high-frequency component of the D- and 2D mode in metallic enriched sample is more dispersive than the other components.

Conclusion:

- The defect mode seems to have a similar resonance behavior as the RBM. The resonance window of the D-mode is larger due to larger phonon frequency, double-resonant scattering and contributions of different nanotube branches.
- Measurements of enriched samples show that different components of the defect modes might belong to different branches that are in resonance for distinct laser energies.
- In addition, the diameter dependence of the double-resonance might play a role [5,6].
- These findings can help in future to confirm a selective functionalization of SWCNT by the intensity and position of the defect mode for distinct laser energies.
- Further investigation on assemble VS individual tube effects are needed.

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