Temperature effects in the Raman spectra of bundled single-walled carbon nanotubes

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Raman spectra of bundled single-walled carbon nanotubes (SWCNTs) were measured at various temperatures up to 400°C. The SWCNTs were synthesized by the arc discharge method in helium atmosphere at a pressure of 0.86 bar, using a metallic Ni/Y catalyst. The multistep oxidation in air, followed by reflux in HCl, resulted in a ~90 wt.% pure SWCNT (no surfactants were applied). The average diameter of the tubules was 1.5 nm (ranging from 1.4 to 1.6 nm) as anticipated for the preparation method applied, as well as by TEM and Raman characterization. The final product was annealed in vacuum at 600°C for 5 hours. The main impurities were graphite particles, while the content of metal impurities was ~1.3%.

Raman spectra were recorded *in-situ* by means of a triple monochromator DILOR XY system equipped with a nitrogen cooled CCD detector system, and a high temperature cell for temperature up to 400°C with an accuracy of ±2°C. The 514.5 nm Ar^+ laser line was focused on the sample by means of a 20× objective in a spot of ~3 μm diameter, while the beam intensity on the sample was ~1 mW.

Raman spectra were measured during two successive temperature runs. The first one from 25°C up to 250°C and then down to 25°C, indicated by open and solid circles in Fig.1, respectively. The second run from 250°C up to 370°C and then down to 25°C is indicated by open and solid squares, respectively. The reversible shift for the G-band peaks is characterized by a temperature coefficient of 0.024 cm^{-1}/K, while for the RBM bands a partially irreversible shift is observed. Upon heating, the temperature coefficient of the frequency is 0.014 and 0.027 cm^{-1}/K, for smaller and larger tube diameters, respectively. The residual temperature shift of the RBM modes increases for increasing tube diameter. The irreversible temperature behavior of the RBM modes may be related with randomly created C-C inter-tube bonds in the bundle, which break at high temperature, resulting in irreversible increase of the inter-tube distances.

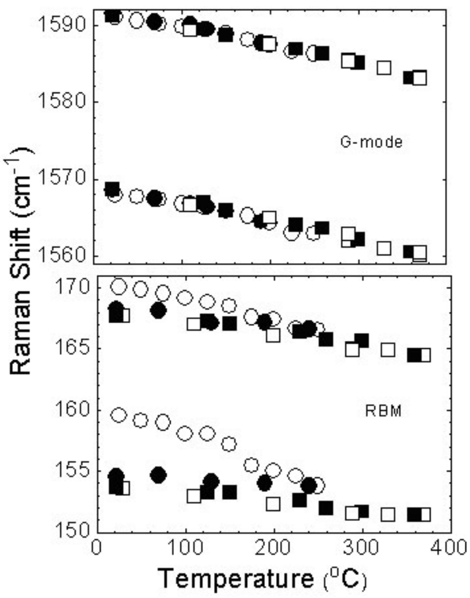

Fig.1. Temperature dependence of the RBM and the G-band Raman peak frequencies of the SWCNT material.

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