Structural and mechanical properties of double wall carbon nanotubes

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ABSTRACT

Narrow diameter double wall carbon nanotubes can be grown with high yield by catalytic chemical vapor deposition. Double walled carbon nanotubes are the molecular analogs of coaxial cables. The external tube protects the internal tube from its environment and isolates the electric conductor of sub-nanometer dimension over micrometer long distances. While it is still particularly difficult to grow tubes of controlled helicity, inelastic light scattering is a powerful tool to find the helicity of narrow diameter internal tubes and explore their mechanical properties. We have examined the inelastic light scattering spectrum of narrow double walled carbon nanotubes to specify their helicity and to study their mechanical stability under hydrostatic pressure.

Keywords: nanotubes, carbon, microscopy, light scattering, phonons

1 INTRODUCTION

Carbon nanotubes (CNTs) are model systems in nanoscience. They combine molecular extension in two dimensions and macroscopic extension in one dimension. The electronic properties of carbon nanotubes depend on the orientation of the two dimensional honey-comb lattice of graphite with respect to the tube axis. This is described by two indices (m,n) which define the circumference in the honey comb lattice and determine the helicity. For each helicity there are two chiralities (left and right). Depending on the helicity the boundary condition of the electronic wave functions is different and accordingly the electronic properties depend on helicity. The combination of a metallic internal tube with an insulating external tube forms an interesting example of a nanowire in its most simple form. In the case of two metallic tubes, they represent the molecular analog to a coaxial cable. Deviations from sp^2 hybridized carbon are larger for narrow diameter CNTs due to their larger curvature. The weak interaction between the walls makes it possible to slide the two tubes with respect to each other. The double wall CNT's (DWCNTs) we report here have external diameters comparable to single wall CNTs (SWCNTs). We find that DWCNTs have a higher mechanical stability towards deformations than SWCNTs. The internal tube is furthermore well protected from its environment.

Double walled carbon nanotubes were first observed by Dai et al (1) who reported the presence of a small amount of DWCNTs along with SWCNTs during the disproportionation of CO on alumina supported Mo particles at 1200°C. The presence or absence of double walled tubes was related to the nature of the catalyst by Hafner et al (2). Double walled tubes were also observed by Laurent et al (3) during the decomposition of methane on iron catalysts generated *insitu* during the reduction of a solid solution of iron and aluminum oxides. In this process, a mixture of single and double walled tubes was obtained. Similar results were obtained for Co catalyst. A high proportion of double walled tubes could be obtained also by the selective removal of single walled tubes from a mixture of the two. The interesting feature in the last two results is that the diameter of the internal tube is often smaller than that of the smallest observed diameter for single walled tubes in the sample. Double walled tubes have also be obtained by filling C_{60} molecules in single shell carbon nanotubes followed by annealing (4) or by changing the catalyst in the sublimation of graphite in an electric arc (5).

Inelastic light scattering provides information about the dynamics of the atomic lattice and mechanical properties and can also provide information on low energy electronic excitations. The technique is extremely sensitive to small structural changes of the atomic lattice. The inelastic light spectrum depends on the energy, momentum and polarization of the incident photon. At low Raman shifts (50-450cm^{-1}) a radial symmetric breathing mode is observed for nanotubes whose energy is inversely proportional to the diameter ($\propto 1/d$) (6). This means that the sensitivity of this mode to the diameter increases with smaller tube diameter. The calibration factor depends, however, on the environment of the tube and ranges from *224-248cm^{-1}/nm* (6). Some authors have reported that the interaction with the support surface shifts the mode energy by 10-20cm^{-1} (7). The fact that helicity and diameter are related to each other and the number of helicities for a given energy range of the breathing mode decreases with smaller diameter gives the possibility to attempt to assign the helicity of the internal tubes (8). We report here the assignment of the radial breathing mode of DWCNT's an the corresponding optical phonon bands, we show the influence of tube-tube interaction using spectroscopic imaging and we investigate the mechanical properties under hydrostatic pressure to learn about the pressure gradient in DWCNTs.

2 EXPERIMENTAL RESULTS

We use a micro Raman setup (Dior XY, Renishaw) with an argon or a krypton ion laser.

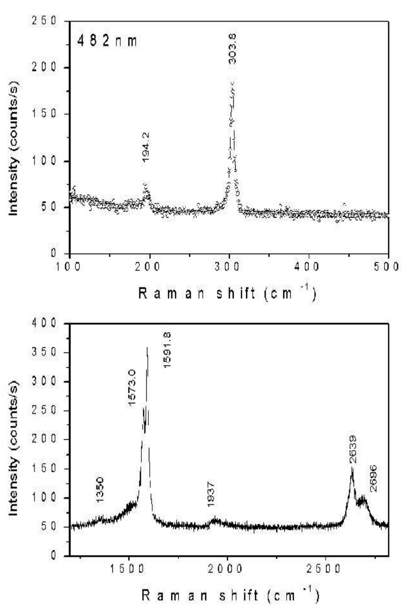

Figure 1

Inelastic light scattering spectrum of a double wall carbon nanotube in the low (top) and high (down) energy range.

Figure 1 shows an inelastic light spectrum of double wall carbon nanotubes with the incident beam set at 482nm. The tubes have been diluted in ethanol and sonicated. A droplet of the nanotube solution has been dried on glass slide before the spectroscopic inspection. Figure 1 shows a spectrum of a highly diluted region were we believe that we detect the signal of only a few DWCNTs. The top figure shows the low energy part with the radial breathing modes and at the bottom we show the corresponding high energy part of the spectrum. We can deduce the diameter of (0.75nm/ 0.83nm, error 0.01nm) from the two peaks at 294.2cm^{-1} and 303.8cm^{-1}. The uncertainty in the calibration factor translates into a uncertainty in the assignment of the helicity which ranges (m,n) for the peak at 194.2cm^{-1} between (9,3) and (10,0) and for the peak at 303.8cm^{-1} between (6,6) and (9,1). When we compare the so determined tube diameters and observed energy of the radial breathing modes with the calculated values for DWCNTs using the valence force model (9) we find that the peak at 303.8 agrees well with determined diameter using a calibration factor of 223.75cm^{-1}. The peak at 194.2cm^{-1} falls between the values calculated for internal and external tubes. Using the same calibration factor, the calculated values are in agreement with the observed spectra for a external tube if we assume that the interaction with the substrate shifts the radial mode by 20cm^{-1}. The two corresponding diameters are too close to come from the same DWCNT. The fact that we do not see corresponding radial mode of the internal or external tube indicates that the observed intensity is strongly diameter dependent. The one dimensional tubes give rise to particularly strong singularities in the electronic density of states which has the effect that the observed scattering intensity is expected to depend on tube diameter.

At high energy we observe a narrow doublet (1572cm^{-1}/1592cm^{-1}, G-band) of the tangential optical modes, a shoulder at 1500cm^{-1} attributed to the optical modes of metallic tubes and a small band at 1350cm^{-1} (D-Band) attributed to disorder induced double resonant scattering (10). Second order spectral bands are observed at higher energy shifts (G' band at 2600cm^{-1}). The doublet at 1580cm^{-1} falls in the same energy range of the optical phonon bands found for SWCNTs but differs by the fact that the lower energy peak is more intense.

Figure 2 shows a collection of spectra recorded in the energy range of the radial breathing mode along a single tube bundle in steps of 0.2μm. Each line corresponds to a radial breathing mode of a single tube. They are well defined and change significantly within a distance of 0.2μm, the step size. For tubes with a diameter below 1 nanometer the low energy breathing modes are very sensitive to the diameter and the peak positions are for neighbouring helicities are displaced by more than the spectral width (2-5cm^{-1}) of the peak. The number of spectroscopic lines or radial breathing modes corresponding to a particular tube changes along the tube bundle (vertical axis in figure 2). One of the most intense peaks at 255cm^{-1} can be traced along the entire image. The number of peaks changes in particular between 1-2 µm in figure 2 which we attribute to a tube intersection. The phonon peak at 255cm^{-1} in this same region (1-2µm, figure 2) shifts slightly and shows that the intersection with the tubes influences the local strain in the CNTs.

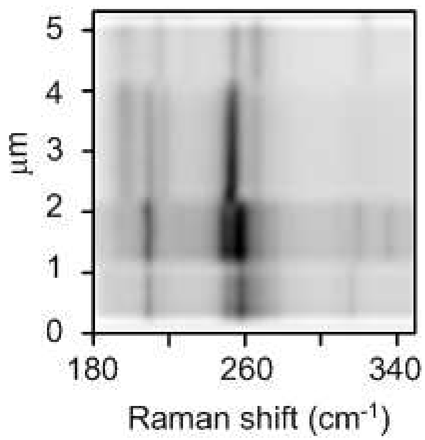

Figure 2

Raman image of a double wall carbon nanotube along a single tube bundle in steps of 0.2µm.

The mechanical properties of DWCNT's can be examined by applying a hydrostatic pressure to a liquid pressure medium where the tubes are suspended, and observe the changes of the phonon bands as a function of the applied pressure. For DWCNT we expect that the external tube protects the internal tube and the pressure is reduced for the internal tube. Fig. 3 shows the spectra at low and high pressure. With increasing applied pressure we observe that the optical phonon band splits into two bands. For SWCNTs and graphite only one band is observed which shifts linearly with applied pressure. The two bands observed for DWCNT's can be associated to the optical phonon band of the internal and external tube. The linear pressure coefficient for the two bands is 3.11 cm^{-1}/GPa for the internal tube and 5.59 cm^{-1}/GPa for the external tube. The pressure coefficient for the internal tube is the lowest observed for three folded carbon and directly indicates that the pressure reduction due to the external tube. It is interesting to note that the boundary conditions for the internal and external tubes are different. While the external tube experiences a radial stress from the pressure medium from outside and the internal tube from within, the internal tube experiences only a radial stress from the external tube. While the radial stress is continuous, the weak inter-tube interaction leads to a discontinuous tangential stress component. This explains why the optical phonon band, sensitive to the tangential strain, splits into two bands for DWCNT's corresponding to the optical phonon band of the internal and external tubes. If we can apply the elastic continuous shell model with a continuous radial and discontinuous tangential stress component and we find perfect agreement with our experimental observation (11).

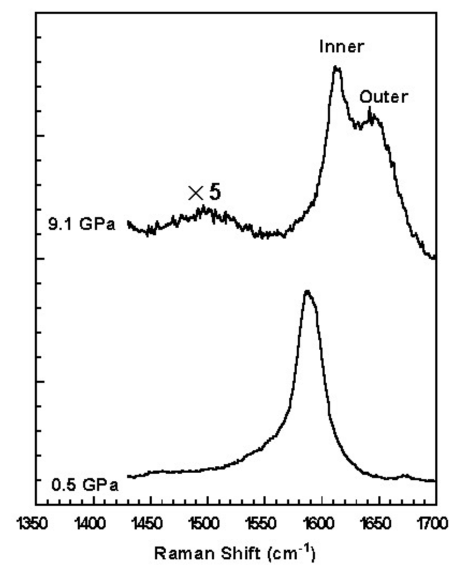

Figure 3

Inelastic light scattering spectra (633nm) of double wall carbon nanotubes under hydrostatic pressure.

In figure 3 we also see that the band due to the external tube which shifts more strongly has a large line width while the band from the internal tube has a constant width. We find that due to the different boundary conditions that the pressure coefficient for the external tube depends on the diameter while for the internal tubes the pressure coefficient is constant. The external tube is stabilised by the internal tube. Our sample contains a distribution of DWCNTs, centred at 1.1 nm and ranging from 0.6 to 2.4nm. The diameter distribution has therefore the effect to broaden the optical phonon line of the external tubes. Each external diameter will shift differently with applied hydrostatic pressure. But for the internal tubes of different diameter, all the internal tubes will shift the same amount with applied hydrostatic pressure.

3 Conclusion

We have assigned the helicity of radial breathing modes of internal and external tubes of DWCNT's and compared the experimental results to valence force calculations. This comparison shows that the smaller value of the calibration factor for the radial breathing mode is in better agreement and this indicates that the interaction with the substrate shifts the energy of the external tube by 10-20cm^{-1} as has been suggested by earlier model calculations (7). Systematic spectroscopic inspection along a line shows that the radial breathing mode is influenced by the presence of intersecting tubes. When applying a hydrostatic pressure on DWCNTs we observe a discontinuity of the tangential stress. The optical phonon due to the in-plane mode is very sensitive to tangential stress and splits with applied pressure. This observation can be explained by the elastic continuum shell model. The same model can also explain the different line broadening observed for internal and external tubes. The tangential stress depends for external tubes on the diameter whereas it stays constant for the internal tubes. The different mechanical behaviour of DWCNTs are expected to find interesting applications in sensors and activators in the near future [12].

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