The growth of nanophases in the clean room inside single-wall carbon nanotubes[☆]

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Abstract

The interior of single-wall carbon nanotubes is studied by filling fullerenes into the one-dimensional nanospace inside the tubes using different filling methods. Filling from solution is demonstrated as efficient as filling from the vapor phase. Evidence for successful filling comes from a transformation of the encapsulated carbon atoms to a secondary tube centered inside the primary tube. Isotope-labeled fullerenes are used to disentangle the Raman response from the two shells in double-wall carbon nanotubes.
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1. Introduction

The hollow inside of single-wall carbon nanotubes (SWC-NTs) is an attractive space to grow materials with nano-scaling dimension in radial direction and quasi-infinite extension in axial direction. From experiments reported previously from our group and from work done by other research groups, a material science for the inside of the tubes has already been established [1–3].

In this contribution, we compile previous results and present new results on the filling of the tubes with fullerenes from the gas phase and from solution. Transformation to double-wall carbon nanotubes (DWCNTs) is used as a proof for the efficiency of the filling processes. In addition, isotope labeled carbon source material is used to grow inner shell tubes in the primary SWC-NTs. By this technique, Raman lines from the inner shell tubes and from the outer shell tubes can be disentangled even if their frequency depends only weakly on the diameter.

1.1. Filling the tubes

The insertion of material into the tubes can be performed in several ways, depending essentially on the type of material to be enclosed. For fullerenes the classical method is the fill-ing from the gas phase at elevated temperatures of the order of 870 K, where the filler is sealed into a quartz tube together with SWCNT in the form of bucky paper. Alternatively, filling is also possible for tubes deposited on a substrate. If the substrate is stable versus reaction with carbon at high temperatures transformation to DWCNTs is possible. In this way DWCNTs thin films on PT were successfully prepared [4]. C_{60} fullerenes, C_{70} fullerenes and metallo-fullerenes or other endohedral fullerenes were inserted. Recently, cold filling from solution was demonstrated and applied to filling the tubes with temperature sensitive material such as $N@C_{60}$ [5]. Smart filling processes were developed which allow to learn about properties and dynamics of the tubes by the filling and subsequent transformation process in the case of carbonaceous fillers [6].

Reactions of the inserted material are another interesting subject. Reactions of fullerenes inside the tubes to a second inner tube is one example which leads to DWCNTs with extremely narrow radial breathing mode (RBM) Raman lines [7]. The other reaction which was demonstrated so far was a transformation to a polymeric phase of charged C_{60} inside the tubes [8], most likely with single bonded cages in a linear arrangement. Most recently, reaction of PbO inside the tube with the tube walls was observed [9].

Table 1 provides an overview of the preparative processes needed for the filling and of results obtained so far or demonstrated in this paper. This table shows that a material science of inner tubes has already been developed.

Table 1
Filling of single-wall carbon nanotubes with inorganic and organic material as reported here or in some recent papers

Operation	Details of the technique	Resulting structures
1. Opening the tubes	Etching with HNO_3 or O_2 at elevated temperatures	Tubes with holes
2. Filling the tubes	From the gas phase: by heating to 720–890 °C together with fullerenes	Peapods
	From the melt: PbO, by heating to 1161 K	Tubes filled with PbO
	From solution: fullerenes, $N@C_{60}$	Peapods, molecules in the tubes
	Smart filling and isotope engineering: filling with isotope labeled fullerenes or combination of labeled and non labeled fillers	Diameter-selective filling, isotope labeled peapods, carbon source analysis
3. Reactions inside the tubes	Reduction of the fullerenes inside the tubes Polymerization to a linear chain	Charged C_{60}, $C_{60}{}^{6-}$-polymer
	Fusion or evaporation and re-condensation of the fullerenes at very high (1620 K) temperatures	Beanpods, DWCNTs, ^{13}C labeled inner tubes
	Covalent bonding reaction of carbons in smart filled tubes	Diameterselective DWCNTs
	Oxidation of the tubes from the inside	PbO nanowires
4. Molecular kinetic reactions on the tubes	Partial recovery of tube openings by heat treatment	Constraints in the filling process, diameter selective DWCNTs

2. Experimental

Raman spectra reported in this paper were recorded with a Dilor xy spectrometer at temperatures between 20 and 300 K.

Normal resolution (1.4 cm^{-1} for red lasers) as well as high resolution (0.4 cm^{-1} for red lasers) configuration were used. Excitation of the spectra was performed with a large number of laser lines between deep red and blue. The spectra were recorded with a back-thinned, blue enhanced CCD detector.

3. Results

3.1. Peapods and double-wall carbon nanotubes

Filling of SWCNTs and a subsequent heating to form DWC-NTs can be traced quantitatively by Raman spectroscopy. Fig. 1 gives an example. The spectrum at the bottom was recorded for pristine SWCNTs and exhibits the well known lines around 175 cm^{-1} from the radial breathing mode (RBM), around
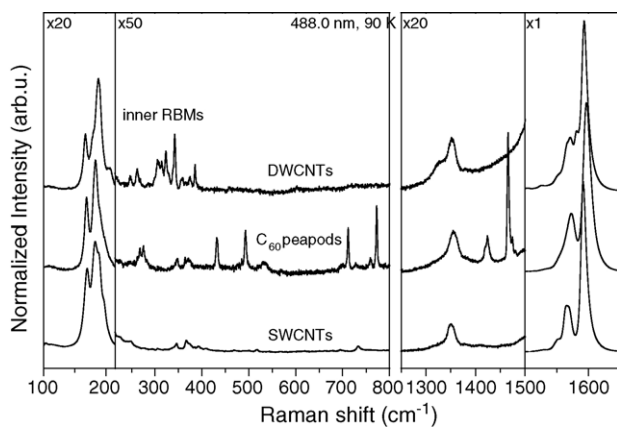

Fig. 1. Raman spectra of carbon nanophases as excited with a 488 nm laser. Pristine SWCNTs (bottom), peapods (center), DWCNTs (top). A scale magnification is indicated.

1350 cm^{-1} from the defect induced mode (D-line), and around 1580 cm^{-1} from the graphitic line (G-line). The small feature at 350 cm^{-1} is an overtone of the RBM mode. After filling the tubes with C_{60} (spectrum in the center of Fig. 1) additional peaks appear which originate from the encapsulated fullerenes. The most prominent line originates from the pentagonal pinch mode Ag(2) of C_{60} and is located at 1464 cm^{-1}. Thus, it is down-shifted from the free molecule by about 4 cm^{-1}. For narrow tubes and green laser excitation this line is split into two components peaking at 1464 and 1474 cm^{-1}, respectively. This splitting is unusual since a total symmetry mode cannot split on symmetry reduction. In a recent analysis this splitting was assigned to dynamical behavior of the peas in the tubes [10]. The relative intensity between the response from the pentagonal pinch mode and the G-line can be used as a check on the filling concentration. For a 60% filling (60% of the possible fullerene sites inside the tubes are occupied) the integrated intensity ratio $I_{Ag(2)}/I_{G\text{-line}}$ is 0.003 [11]. After heating the peapod system for several hours to 1620 K the fullerenes transform to an inner shell tube and thus establish the DWCNT system. The Raman response of the DWCNTs is depicted as the top spectrum in Fig. 1. It is characterized by the very narrow lines of the RBM from the inner tubes, clustered around 300 cm^{-1}. Lines as narrow as 0.4 cm^{-1} were observed which is ten times more narrow than RBM lines recorded so far [7].

3.2. Low temperature filling and smart filling

One of the difficult problems with the filling experiments is a reliable proof that filling has taken place. For carbon rich fillers we have developed an alternative technique to check the filling. After the filling the sample is heated to 1620 K to transform the carbons into an inner shell tube. If there was sufficient carbon available a RBM response from these tubes is observed. The latter exhibits very strong Raman lines which means very accurate detection is possible. In addition, intensities can be related to the response from the outer tube RBM which is another advantage
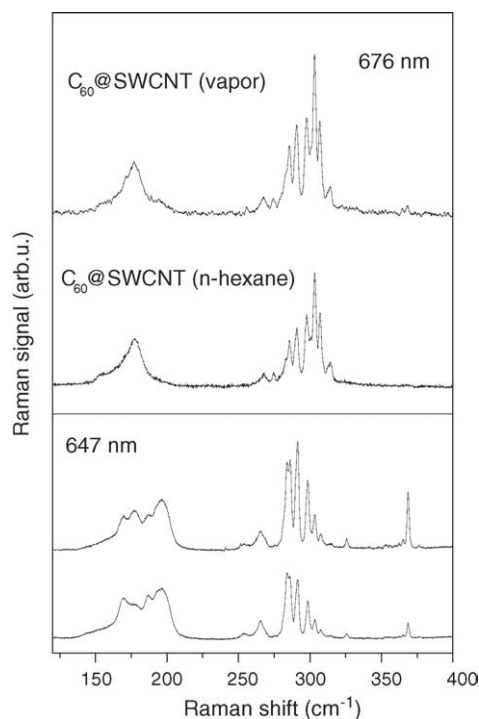
Fig. 2. Raman response of the RBM from DWCNTs after filling by various methods: 676 nm excitation—filling with C_{60} from the gas phase (top), with C_{60} in *n*-hexane solution (second from top); 647 nm excitation—reference (second from bottom), filling after annealing the opened tubes (bottom).

of this technique. It can be used to compare high temperature filling and low temperature filling (filling from solution) for C_{60}. Examples are depicted in Fig. 2.

The sharp lines from the inner tubes are clear evidence that the corresponding carbon material has entered the tubes and acted as a carbon source for the inner tubes. The identical line pattern as seen in the figure proves that the growth process of the inner tubes is independent from the filling method. For the spectrum at the bottom of Fig. 2 the tubes were annealed at 800 K before filling. Small diameter tubes were closed during this treatment. Thus, high frequency RBMs are missing or at least reduced in intensity.

In another process of smart filling we used ^{13}C isotope labeled carbon as source material. C_{60} or C_{70} made of ^{13}C is appropriate. In the resulting DWCNT structures the inner tubes consist only of ^{13}C whereas the outer tubes and any carbon contamination consist of ^{12}C. This helps to separate the Raman response from inner tubes and outer tubes for vibrations where the frequency is only weakly dependent on the tube diameter. Examples are the response form the G-line or from the D-line. Fig. 3 depicts the influence of the substitution on the latter and on the RBM. DWCNTs were grown from 29% enriched and from almost 90% ^{13}C enriched C_{70} fullerenes. Whereas in the case of the RBM (Fig. 3 (left)) the response from the outer tubes remains constant the response from the inner tubes exhibits the expected downshift of $9\,cm^{-1}$ according to the higher mass of the carbon atoms. In the case of the D-lines the response of the two tubes overlap strongly and since the D-line even from SWCNTs can have a fine structure [11] it is not straight forward to disentangle the contributions from the two tubes. In contrast, after isotope substitution, the $42\,cm^{-1}$ downshift clearly separates the contributions as demonstrated in Fig. 3 (right).

4. Discussion

The use of relative Raman intensities for the determination of SWCNT filling is for the moment restricted to C_{60} fullerenes, since this is the only material where calibration curves exist. The ratio between the response from the inner tubes to the outer tube intensity is a direct measure for the carbon atoms inside the tubes. The experiments where the opened tubes were annealed prior to transformation (Fig. 2, bottom) provides a way to control the filling. Annealing at 900 K closes the holes in the tubes with a tube diameter selective behavior.
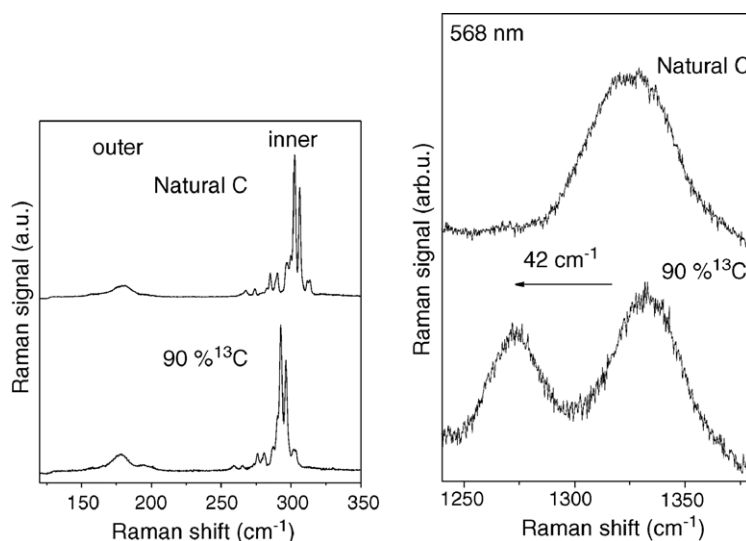

Fig. 3. Raman response of ^{13}C labeled DWCNTs. RBM for material grown from only ^{12}C and for material where the inner shell tubes are grown from 90% ^{13}C, downshift $9\,cm^{-1}$ (left). Similar results for the D-line, downshift $42\,cm^{-1}$ (right).
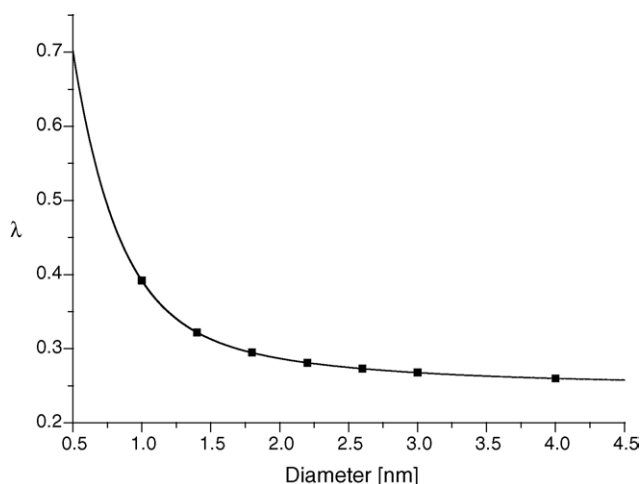
Fig. 4. Electron–phonon coupling in SWCNTs vs. tube diameter, extrapolated from calculations in Ref. [13].

Isotope substitution can be expected to turn into a valuable analytical tool for nanotube research. In the present case the existence of a D-line from the inner-shell tubes was demonstrated. This is not trivial, since the inner-shell tubes are expected to be highly defect-free which would strongly suppress the Raman response form the D-line. On the other hand, the electron–phonon coupling is known to increase with increasing curvature of carbon cages. This was demonstrated in early theoretical work on fullerenes [12] but more recently also confirmed for nanotubes [13,14]. A result from such calculations as extrapolated to diameters characteristic for the inner-shell tubes is depicted in Fig. 4. Even though the calculation was for the SWCNT conduction band the trend can be expected to be the same for the higher excitations. Since the electron phonon coupling enters as a square into the Raman intensity enhancement of a factor five can be expected, for equal defect concentration. In addition the high quality of the inner-shell tubes may increase the lifetime of the excited electronic states and thus further enhance the Raman cross section. The role of the tube ends as a source of phonon scattering with high wave number must still be explored.

5. Summary

A new method is demonstrated to control the filling of SWCNTs with molecules containing a large amount of carbon. After the filling process the carbons inside the tubes are transformed to a new inner-shell tubes which can easily be detected. The method is applied to filling fullerenes from solution, and to study ^{13}C labeled fullerenes and carbon nanotubes.

Acknowledgements

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