Highly perfect inner tubes in CVD grown double-wall carbon nanotubes

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Available online 30 August 2005

Abstract

The synthesis of double-wall carbon nanotubes (DWCNTs) with highly unperturbed inner shells is reported using the catalytic vapor deposition method. Temperature dependent and high resolution Raman measurements show an enhanced phonon life-time of the inner tubes with respect to the outer ones and similar diameter SWCNTs. This proves that the inner tubes are unperturbed similar to the inner tubes in peapod-grown DWCNTs. The presence of the outer tube is argued to protect the inner tube from interaction with impurities and also to stabilize the growth of defect free inner tubes. The current material underlines the application potential of DWCNTs.

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1. Introduction

Double-wall carbon nanotubes (DWCNTs) are on the borderline between single-wall (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). As a result, they share common features with both classes of materials. Generally, SWCNTs are considered to be of fundamental interest and MWCNTs are known to be more application-friendly. SWCNTs exhibit a number of compelling physical properties such as superconductivity [1], the Tomonaga-Luttinger liquid state [2,3] and a predicted Peierls state [4,5]. DWCNTs are fundamentally interesting as their physical properties are determined by the well defined inner and outer tube chiralities [6,7] and are candidates for applications such as, e.g., reinforcing composites or scanning microscopy probeheads due to the improved elastic properties as compared to the SWCNTs but still of smaller diameter than MWCNTs. In addition, the small diameter inner tubes enable us to study the behavior of highly curved nanostructures such as curvature induced deviations from the electronic structure of graphite [8,9].

DWCNTs can be grown from fullerenes encapsulated inside SWCNTs, peapods [10] (PEA-DWCNTs) by a high temperature treatment [11,12] without any catalysts. Raman studies on the inner tubes in PEA-DWCNTs indicated at least an order of magnitude longer phonon life-times, i.e., narrower line-widths, as compared to the outer tubes [6]. This was associated with the highly unperturbed nature of the inner tubes that are grown in the nano clean-room interior of SWCNTs. The defect content of the tube shells is crucial for applications such as the possibility of ballistic transport and improved mechanical properties.

An alternative DWCNT synthesis is based on catalytic SWCNT growth methods such as arc-discharge [13] and catalytic chemical vapor deposition (CCVD) methods [14–20]. So far, Raman studies on such samples have given a similar linewidth for the inner and outer tubes indicating comparable number of defects for the two shells [14,17–19,21]. However, no low temperature
and high resolution Raman data have been reported that is needed for the accurate observation of the inner tube line-widths. As a result, inner tubes in PEA-DWCNTs are the only tubes known to be highly defect free among all kinds of CNT materials.

Here, we report that CCVD grown DWCNTs (CVD-DWCNTs) can also have very narrow Raman line-widths indicating their high perfectness as the inner tubes in PEA-DWCNTs. Interestingly, the inner tube diameter distribution in the current CVD-DWCNT is very similar to the PEA-DWCNT samples and it is discussed whether perfectness of small diameter inner tubes is a general phenomenon of small diameter inner tubes.

2. Experimental

2.1. Catalyst preparation

The CVD catalyst was a modified version of the Fe/Mo/MgO system developed by Liu et al. [22] for SWCNT synthesis. (NH₄)Mo₇O₂₄ (Reanal) and Fe(NO₃)₃·9H₂O (Aldrich) were dissolved in distilled water and the solution was added to the aqueous suspension of MgO and sonicated for 30 min at room temperature. The resulting slurry was dried in two steps, under vacuum at 90 °C for 1 h and then at atmospheric pressure at 120 °C overnight. The catalyst possessed a molar Fe:Mo:MgO ratio of 1:0.1:110.

2.2. Nanotube synthesis

Nanotubes were synthesized in a fixed bed horizontal quartz tube reactor with a diameter of 60 mm and a length of 110 cm. 0.30 g catalyst was placed in a quartz boat and shoveled to the middle of the reactor. After purging the system with Ar at room temperature, the gas stream was changed to the C₂H₂:Ar (10 cm³/min:150 cm³/min volume at room temperature, the gas stream was of 110 cm³. 0.30 g catalyst was placed in a quartz boat and quartz tube reactor with a diameter of 60 mm and a length in 2.2. Nanotube synthesis

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2.3. Raman spectroscopy

Multi frequency Raman spectroscopy was performed on a Dilor xy triple axis spectrometer in the 1.83–2.54 eV (676–488 nm) energy range and in a Bruker FT-Raman spectrometer for the 1.16 eV (1064 nm) excitation at room temperature and at 90 K. The triple axis spectrometer can be operated in subtractive and additive mode allowing to take normal and high resolution spectra. The high resolution mode has a spectral resolution of 0.4 cm⁻¹ at 1.83 eV excitation as determined from the spectrometer response to the elastically scattered light.

3. Experimental results

In Fig. 1, we show the Raman spectra of the CVD grown material and the PEA-DWCNT samples for three laser excitations. Comparison of spectra taken with different laser excitation energies is required due to the strong photoselectivity of the nanotube Raman response. The radial breathing mode (RBM) of SWCNTs with \( d \approx 2.1–0.6 \text{ nm} \) dominates the Raman response for the displayed 120–400 cm⁻¹ spectral range. The spectral ranges of 120–220 and 240–400 cm⁻¹ were previously identified with the outer and inner tube Raman responses for the PEA-DWCNTs, respectively [6]. Surprisingly, the CVD grown material shows a similar pattern with higher and lower Raman shifted ranges and a gap in between. We also observed similar spectra for the two materials at other excitation energies (not shown). It is tempting to assume that in the CVD grown material the same spectral regions come from inner and outer tubes, too. This means that the current CVD sample contains a sizeable amount of DWCNTs rather than a broad distribution of SWCNTs as it was originally found for tubes from a similar preparation [22]. Below, we present other spectroscopic evidence which further supports that the lower and higher spectral ranges originate from outer and inner tubes in the CVD-DWCNT samples, respectively.

Although the inner and outer tube diameter distribution is very similar in the two materials, the Raman intensities are different: the inner tube modes Raman intensities are on average a factor two smaller for the inner tube modes Raman intensities of the corresponding DWCNTs in the earlier sample, however, an accurate determination based on the Raman intensities alone is not possible as it is affected by a number of sample dependent factors such as the surface morphology.

The determination of the phonon life-times in the inner tubes in CVD-DWCNTs is the important contribution of the current work. This parameter can be used to characterize the defect content on the tubes. Often, the intensity of the defect induced D-mode is used to estimate the defect concentration. However, it was shown recently that the D-modes of inner and outer tubes overlap, thus preventing a meaningful analysis.
unless $^{13}$C labelling of the inner tubes is used to separate their response [8]. Long phonon life-times in the inner tubes can be measured in high-resolution (HR) Raman experiments at 90 K and the corresponding spectra are shown in Fig. 2. For comparison, we show a spectrum taken on an SWCNT sample prepared with the HiPco process (lowest curve in Fig. 2). The HiPco sample contains tubes with similar diameters as the inner tubes in the DWCNT samples. Remarkably, the inner tubes have a very narrow line-width for both DWCNT materials whereas the line-width of the HiPco sample is significantly larger. The accurate Lorentzian line-widths, that measure the intrinsic phonon life-times, were determined by fitting the experimental spectra with Voigtian line-shapes whose Gaussian component is the spectrometer response for the elastically scattered light. The resulting deconvoluted spectrum is also shown for the CVD-DWCNTs in Fig. 2. Values for the FWHMs of the Lorentzian lines down to 0.8 cm$^{-1}$ were found for the CVD-DWCNTs which is almost as narrow as the FWHMs observed for the PEA-DWCNTs, down to 0.4 cm$^{-1}$ [6]. This is an order of magnitude smaller than the line-widths of 5–6 cm$^{-1}$ found for the HiPco sample, for the outer tubes in the current samples, or for individual SWCNTs [23] indicating the highly unperturbed nature of the inner tubes in both materials. The observable RBM modes agree in both materials within the 0.3 cm$^{-1}$ experimental precision of the line position measurement of the HR experiment. The reason for the larger number

Fig. 1. Comparison of CVD- (upper curves) and PEA-DWCNT (lower curves) samples at 1.16, 1.83, and 2.41 eV. The distinct lower and upper Raman shift ranges indicated by arrows correspond to the outer and inner tube RBM responses, respectively.

Fig. 2. High resolution Raman spectra taken at 1.83 eV excitation and 90 K on the CVD- and PEA-DWCNT and an SWCNT reference (HiPco) sample. The deconvoluted spectrum is also shown for the CVD-DWCNT sample. The narrow line-widths indicate the long radial breathing mode phonon lifetimes of the inner tubes in both DWCNT materials.
of RBMs in the DWCNT samples as compared to the HiPco sample was explained previously by the number of possible inner and outer tube pairs. It was shown that an inner tube can be grown in several outer ones and the corresponding RBMs are modified due to the inner–outer tube interaction [6,7]. The current result shows that the splitting is present irrespective of the DWCNT growth method. This confirms that the origin of the splitting is the inner–outer tube interaction as previously thought.

In Fig. 3, we show the temperature dependent Raman spectra for the two materials for the RBM ranges at the 1.83 eV excitation. The integrated intensity of the inner and outer tube RBMs follows a distinct temperature dependence for both compounds: it increases by a factor ~2 at lower temperatures for the inner and is constant for the outer tubes. Similar changes can be observed for the other laser excitations. The increase of integrated intensity proves that it is not caused by the lengthening of phonon life-times, i.e., narrowing of the modes, but it is due to an increasing life-time of the quasiparticle state which is excited during the Raman process. The details of this mechanism are studied and published separately [25]. In brief, the quasiparticle life-time is temperature independent and short for the outer tubes, whereas it is longer and further lengthens with decreasing temperatures for the inner tubes. In general, dirty and clean systems are characterized by temperature independent short and longer temperature dependent life-times, respectively. Analogous situations are encountered for the momentum relaxation time in dirty and clean conductors [26]. Therefore, the observed effect suggests that the outer and inner tubes behave as dirty and clean systems, respectively. The cleanliness of inner tubes is associated with the low concentration of lattice defects or impurities and that it is well protected from the environment.

4. Discussion

The similarity between the observed RBM patterns in the CVD- and PEA-DWCNT samples suggests that the 120–220 and 240–400 cm$^{-1}$ spectral ranges originate from outer and inner tubes in the two samples, respectively. The larger number of observed than geometrically allowed tubes for the latter range is a further evidence supporting the DWCNT nature of the CVD-DWCNT sample as it is characteristic for DWCNTs and originates from the interaction of inner and outer tubes [6,7]. In addition, RBMs in the two spectral ranges have very different properties for both samples. Line-widths of the RBMs in the 240–400 cm$^{-1}$ spectral range become narrower on lowering temperature, reaching an order of magnitude smaller line-widths than the temperature independent line-widths of the RBMs in the 120–220 cm$^{-1}$ spectral range. Similarly, Raman intensities of the RBMs in the 240–400 cm$^{-1}$ spectral range
increase on decreasing temperature whereas the Raman intensity of the 120–220 cm\(^{-1}\) spectral range modes is temperature independent. This proves that the two spectral ranges come from tubes with distinct properties and further supports the above assignment. This also shows that inner tubes have long phonon and quasiparticle life-times indicating that they are highly defect free and are well protected from the environment.

The observation of long phonon- and quasiparticle life-times, and the concomitant high perfectness of inner tubes in non peapod-grown DWCNTs is surprising. The high perfectness of inner tubes in the PEA-DWCNT sample was associated with the catalyst-free growth conditions and the perfectness of the growth conditions as the inside of the host tubes can be considered as a nano clean-room [6,24]. As a result, only inner tubes in PEA-DWCNTs were thought to be highly perfect. This paradigm appears to be violated by the current CCVD-DWCNTs. Previous results have considered large diameter inner tubes with \(d = 1.52\) nm where the inner tubes had a large linewidth [14]. Interestingly, the inner and outer tube diameters in the currently described CCVD-DWCNTs are very similar to the PEA-DWCNTs. Similar diameter inner tubes as those used here were reported, however the temperature dependent effects were not studied [17–21]. Therefore, it cannot be ruled out that perfectness of small diameter inner tubes is a general feature.

Unfortunately, the dominant contribution to the SWCNT RBM phonon and quasiparticle life-times is not fully understood. It has been speculated that SWCNTs strongly interact with attached impurities as well as contain a number of defects, partly produced during synthesis or during purification. Inner tubes are well protected from attached impurities. The effect of attached impurities can also give rise to an inhomogeneous broadening. This would explain why the similarly small diameter tubes in the HiPco samples show significantly broader RBMs. Concerning lattice defects during growth, it can only be speculated that the ensemble of the two shells of a growing DWCNT energetically prefers the formation of a highly perfect inner tube. Alternatively, it is also possible that the inner tubes are grown in the CVD-DWCNT material only when the outer tube has been pre-formed. Then, the outer tube provides a host template similarly as in the case of PEA-DWCNTs, which enables the growth of highly defect-free inner tubes. Clearly, more theoretical work is required to understand the growth processes of both peapod based and CVD grown DWCNTs.

5. Conclusion

In conclusion, we reported the CCVD synthesis of DWCNTs with highly unperturbed inner tubes similar to the inner tubes in peapod based DWCNTs. This is a surprising result as for the latter material the inner tubes are grown in a catalyst free nano clean-room environment. The diameter distributions of the inner tubes are similar for both kinds of materials and we suggested that the diameter of the inner tubes plays an important role for their defect-free nature. The currently synthesized material is expected to have improved properties compared to other DWCNTs and it is a potential candidate for applications such as conducting wires with increased ballistic transport length or reinforcing element with improved mechanical properties.

Acknowledgments

We thank Dóra Mén for her assistance in the nanotube synthesis. This work was supported by FWF Project P17345, by EU Projects BIN2-2001-00580, MEIF-CT-2003-501099 and by OTKA T046491 and F046361. Á.K. and F.S. acknowledge support from a Zoltán Magyary and Z.K. acknowledges support from a János Bolyai fellowship.

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