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A detailed comparison of CVD grown and precursor based DWCNTs

R. Pfeiffer[1,*], H. Peterlik[1], H. Kuzmany[1], F. Simon[2], K. Pressl[3], P. Knoll[3], M. H. Rümmeli[4], H. Shiozawa[5], H. Muramatsu[6], Y. A. Kim[6], T. Hayashi[6], and M. Endo[6]

[1] Faculty of Physics, University of Vienna, Austria
[2] Budapest University of Technology and Economics, Hungary
[3] Karl-Franzens University, Graz, Austria
[4] IFW Dresden, Germany
[5] University of Surrey, UK
[6] Shinshu University, Japan

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* Corresponding author: e-mail rudolf.pfeiffer@univie.ac.at, Phone: +43-1-4277-51378, Fax: +43-1-4277-51375

Double-wall carbon nanotubes (DWCNTs) grown directly via a CVD method and DWCNTs produced by annealing C_{60} and ferrocene filled single-wall carbon nanotubes were studied with X-ray diffraction (XRD) and Raman spectroscopy. The samples showed the typical XRD patterns of hexagonally bundled tubes. The frequencies and linewidths of the inner tube radial breathing modes (RBMs) were (within experimental precision) equal in all three samples only the intensities differed. Finally, all samples showed the typical clustering of the inner tube RBMs due to the distribution of inner-outer tube pairs. The only difference was the population of specific inner-outer tube pairs where the CVD and ferrocene based DWCNTs were rather similar and both differed from the C_{60} based DWCNTs.

1 Introduction Double-wall carbon nanotubes (DWCNTs) can either be grown directly (e.g., in a CVD process) or they can be produced by annealing SWCNTs filled with carbon rich precursors [1]. In the former case, outer and inner tubes are growing at the same time and more or less under the same conditions. In the latter case, the inner tubes grow inside an already existing shielded environment [2]. Growing the inner tubes from precursor materials allows a detailed study of the involved growth processes [3] and could be used to enhance our understanding of carbon nanotube growth processes in general. Furthermore, by using different precursors one can study the growth with and without additional catalysts. On the other hand, growing DWCNTs directly has advantages for immediate technological applications.

The radial breathing mode (RBM) Raman response of the inner tubes is rather peculiar. A certain inner tube type can grow in various outer tube types with different diameters. Depending on the wall-to-wall (WtW) distance the interaction between the concentric tubes can vary and thus the RBM frequency of the inner tube depends on the outer tube type. The smaller the WtW distance the larger the interaction and thus the upshift of the RBM. Due to the distribution of outer tube types in macroscopic samples every inner tube gives rise to a whole cluster of RBMs where each line corresponds to a well-defined inner-outer tube pair [4].

In a recent paper, we demonstrated that annealing SWCNTs filled with C_{60} fullerenes and ferrocene ($FeCp_2$) gives rise to two different growth processes of the inner tubes [5]. The non-catalytic growth of the inner tubes from the C_{60} fullerenes takes about 1 hour at 1250 °C (the inner tubes can be grown at temperatures as low as 800 °C but the transformation takes literally weeks in this case [6]). On the other hand, the catalytic growth of the inner tubes from $FeCp_2$ can be done in 1 hour at 600 °C. Additionally, even for the same starting SWCNT material the result-

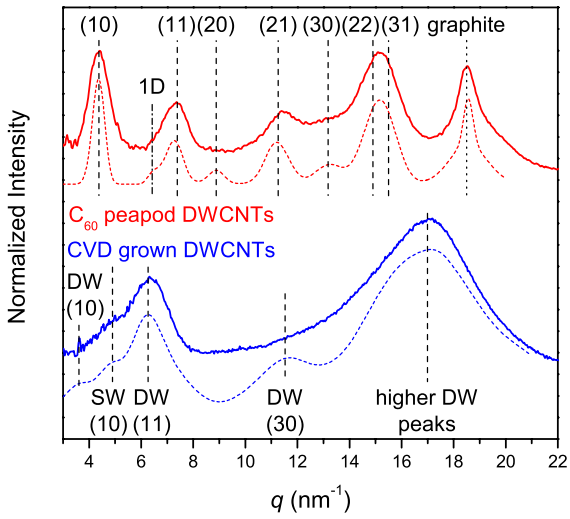

Figure 1 XRD patterns of DWCNTs produced by annealing C_{60} peapods to 1250 °C for 45 minutes (top) and of directly grown CVD DWCNTs (bottom). The dashed lines are simulations of the measured patterns. The orders of the Bragg peaks are given in brackets. 1D indicates a small contribution from the 1D chain of not yet transformed C_{60} fullerenes. SW and DW in the pattern of the CVD grown DWCNTs indicate peaks from SWCNTs and from DWCNTs, respectively.

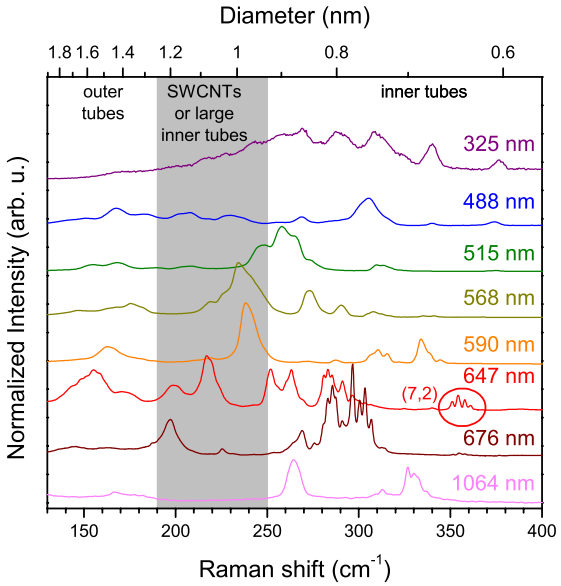

Figure 2 RBM Raman spectra of the directly grown CVD DWCNTs for various excitation energies at 80 K (325 and 1064 nm: room temperature). For the RBM frequency-diameter relation we used $\omega_{\mathrm{RBM}} = 217.8/d_t + 15.7$ from Ref. [8]. In the 647 nm spectrum, the cluster of the $(7, 2)$ inner tubes is circled.

ing inner-outer tube pair populations are different. Since $FeCp_2$ is also used as a catalyst in CVD growth processes it is interesting to compare CVD grown with $FeCp_2$ based DWCNTs.

In this contribution, we give a detailed comparison of DWCNTs grown directly via a CVD process [7] with DWCNTs produced by high-temperature annealing of SWCNTs filled either with C_{60} or $FeCp_2$ molecules. Indeed it turned out that CVD grown and $FeCp_2$ based DWCNTs are more similar to each other than to the C_{60} based DWCNTs.

2 Experimental The CVD DWCNTs were produced as described in Ref. [7]. The mean diameter of the empty starting SWCNT material was 1.39 nm. The opened SWCNTs were filled with C_{60} or $FeCp_2$ from the vapor phase. The C_{60} based DWCNTs were produced by annealing the peapods in a dynamic vacuum either at 1250 °C for 45 minutes or at 1150 °C for 24 hours. The $FeCp_2$ based DWCNTs were produced by annealing to 1150 °C for 1 hour.

The samples were characterized with X-ray diffraction (XRD) at room temperature with Cu K_α radiation and by Raman spectroscopy at 80 K.

3 Results and discussion Figure 1 depicts the XRD patterns of DWCNTs produced by annealing C_{60} peapods to 1250 °C for 45 minutes (top) and of directly grown CVD DWCNTs (bottom). The dashed lines represent simulations of the respective patterns (using Bessel functions J_0 for the form factor of the tubes — arranged in a hexagonal lattice — and Gaussian functions for the lattice terms [3]). For both types of DWCNTs the simulated patterns agree very well with the measured ones, although some weak peaks appear in the simulations which were not observed experimentally. In the case of the C_{60} based DWCNTs, the simulation revealed a mean outer tube diameter of about 1.4 nm and a mean inner tube diameter of about 0.7 nm. The so obtained outer tube diameter is in very good agreement of the mean diameter of the starting SWCNTs as determined from Raman. Additionally, a very small reminiscence of the 1D fullerene chain peak is visible. In the case of the directly grown CVD DWCNTs the simulation yielded a mean outer tube diameter of about 1.6 nm and a mean inner tube diameter of about 0.9 nm. Additionally, a fraction of about 25% empty SWCNTs with a mean diameter of 1.2 nm had to be added to the simulated pattern. The small graphite peak in the C_{60} based DWCNTs is completely absent in the CVD grown DWCNTs. The higher order DWCNT peaks in the CVD sample extend to larger q values than in the peapod based sample. This implies that the typical bundle size in the samples is less than 10×10 tubes/bundle.

Figure 2 depicts the radial breathing mode (RBM) Raman response of the CVD grown DWCNTs for several excitation energies. In order to calculate the tube diameter from the RBM frequency, we used the relation $\omega_{\mathrm{RBM}} = 217.8/d_t + 15.7$ from Ref. [8]. In the range 130–190 cm^{-1} we see the response of the outer tubes while the inner tubes can be seen in the range 250–400 cm^{-1}. In between is a

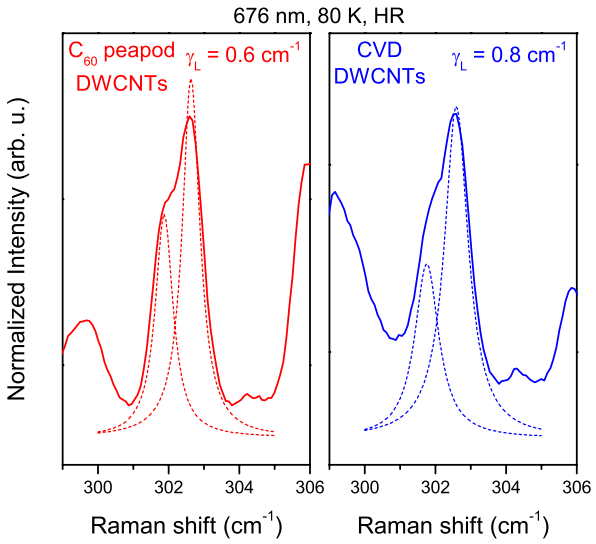

Figure 3 High resolution inner tube Raman response of C_{60} based (left; 1250 °C, 45 minutes) and CVD grown (right) DWCNTs. The dashed lines are deconvolutions with the spectrometer response [2].

region where a discrimination of the empty SWCNTs in the sample and large diameter inner tubes was not possible from our measurements. Especially in the 647 and 676 nm spectra one can see the clustering of the inner tube RBMs. E.g., the circled set of lines in the figure originates solely from $(7,2)$ inner tubes in various outer tubes.

Figure 3 compares the high resolution inner tube Raman spectra of the peapod and CVD DWCNTs. One of the most intriguing features of the inner tube RBMs is their very small linewidth with intrinsic FWHMs as small as $0.4\,\mathrm{cm}^{-1}$ [2]. This small linewidth indicates rather long phonon lifetimes and thus high quality inner tubes. However, despite the narrow RBMs one can also observe a defect induced D mode of the inner tubes. It was thus ventured that the fusion of the fullerene molecules forms inner tubes which are in fact rather short pieces of well-defined chiralities connected by segments with undefined chirality. The left and right parts of the figure depict the response of the same RBM from the C_{60} based and the CVD DWCNTs, respectively. Fitting the spectra with Voigtian lines, where the Gaussian part was fixed at a value obtained from the elastically scattered light, gives a deconvolution with the spectrometer response. The Lorentzian part of the Voigtian is then the natural line of the mode [9]. The dashed lines in the figure are such deconvoluted natural lines with intrinsic linewidths of 0.6 and $0.8\,\mathrm{cm}^{-1}$ for peapod and CVD DWCNTs, respectively. Similar qualitative results—although without fitting—were discussed in Ref. [10] for different CVD grown DWCNTs. In all DWCNTs studied so far (directly grown or precursor based) the inner tube linewidths are essentially equally small. This evidences against the idea of merely short tube segments.

Figure 4 compares the high resolution RBM Raman response of the $(6,5)$ and$(6,4)$ inner tube clusters of the C_{60} and $FeCp_2$ based DWCNTs and the CVD DWCNTs. All spectra were normalized to the peak indicated by the arrow. As mentioned in the Introduction, each peak in the cluster stems from a definite inner-outer tube pair and the higher the frequency the smaller the WtW distance. For the C_{60} based inner tubes, the $(6,4)$ cluster extends between 330 and $360\,\mathrm{cm}^{-1}$, with a maximum around $345\,\mathrm{cm}^{-1}$. In comparison, the $(6,4)$ clusters of the $FeCp_2$ based and the CVD DWCNTs extend only up to $350\,\mathrm{cm}^{-1}$, with a maximum around $335\,\mathrm{cm}^{-1}$. This means that the inner-outer tube WtW distance can be much smaller in the fullerene based DWCNTs than in the other two samples. For the CVD DWCNTs this could partly be explained by the larger mean outer tube diameter, although the spectra evidence that even in this sample there are enough small diameter outer tubes available. However, the peapod and $FeCp_2$ based DWCNTs were grown from the same SWCNT starting material and thus the outer tube diameter distribution is identical. The $(6,5)$ cluster is qualitatively similar to the $(6,4)$ cluster although in this case the intensity especially of the CVD DWCNTs is located at even lower wave numbers within the cluster and thus there are relatively more DWCNTs with larger WtW distances.

In order to make the different WtW distributions more visible we fitted the RBM frequency dependence on the WtW distance $\Delta d/2$ of the clusters in Fig. 2 of Ref. [11] with $\omega_{\mathrm{RBM}} = (A/\Delta d)^B + C$. As fitting parameters we got $A = 0.798$, $B = 14.2$, and $C = 301.9$ for the $(6,5)$ cluster and $A = 0.794$, $B = 14.2$, and $C = 330.0$ for the $(6,4)$ cluster. Finally, we transformed the frequency range 302–330 cm^{-1} and the range 330–365 cm^{-1} of the spectra in Fig. 4 via $\Delta d = A/(\omega_{\mathrm{RBM}} - C)^{1/B}$. The results are depicted in Fig. 5. Since we neglected the slightly different resonances of the various peaks [4], the lines in Fig. 5 are not exactly inner-outer tube pair populations but a good approximation. They show that for the C_{60} based inner tubes the most probable WtW distance is around 0.65 nm while for the other two DWCNT types the average WtW distance is about 0.68 nm for the $(6,5)$ inner tubes and about 0.7 nm for the $(6,4)$ inner tubes. The rather large intensity at large WtW distances in the $(6,4)$ cluster of the $FeCp_2$ based DWCNTs is at least partly an artifact of the used transformation procedure. The vertical lines at the bottom of the figure indicate the possible outer tubes with the corresponding WtW distances. The deviations at large WtW distances stem from the fact that the above fitting procedure was only based on an assignment at small WtW distances.

4 Summary In summary, we studied DWCNTs grown directly via a CVD process and DWCNTs produced by annealing precursor (C_{60} and $FeCp_2$) filled SWCNTs with XRD and Raman spectroscopy. All samples show the same clustering of the inner tube Raman modes caused by the fact that one inner tube type can grow in several

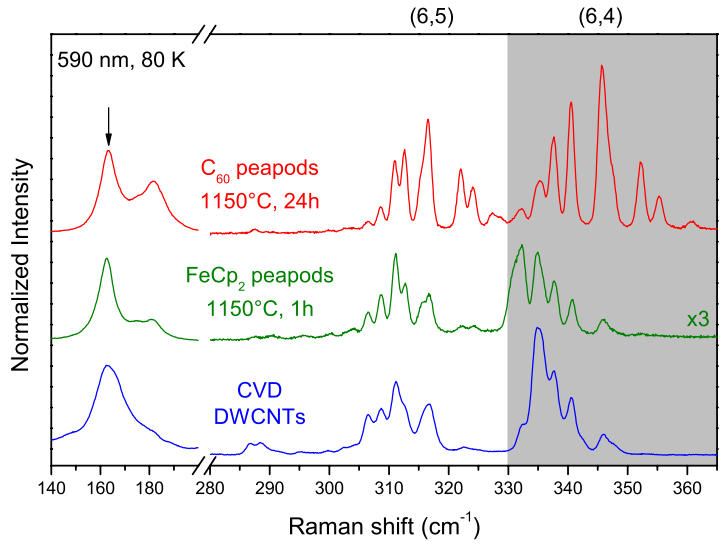

Figure 4 Detailed comparison of the Raman response of C_{60} based, $FeCp_2$ based, and CVD grown DWCNTs. For the chosen excitation of 590 nm the clusters of the $(6,5)$ and $(6,4)$ inner tubes are close to resonance. The arrow indicates the peak to which all spectra were normalized.

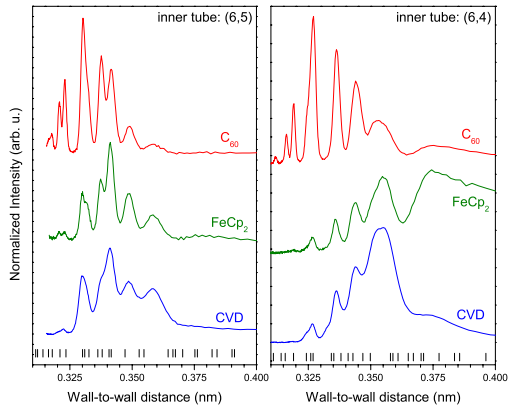

Figure 5 Distributions of inner-outer tube pairs for the $(6,5)$ (left) and $(6,4)$ (right) inner tubes as a function of wall-to-wall distance. The vertical lines at the bottom indicate the possible outer tubes with the corresponding WtW distance.

different outer tube types. Within experimental precision, the frequencies of all lines in the clusters are equal between the three samples, i.e., the same inner-outer tube pairs are present. Similarly, all samples have almost the same narrow inner tube RBMs indicative of long phonon lifetimes. The only difference between the samples lies in the population of the different inner-outer tube pairs where in the case of C_{60} based inner tubes significantly smaller wall-to-wall distances are obtained.

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