Highly Diameter Selective ^{13}C Enrichment in Carbon Nanotubes

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Abstract. We performed vapor phase filling of SWCNTs with various kinds of fullerenes. C_{60}, C_{70}, ^{13}C enriched C_{60} and mixtures of these were used. The resulting peapods as well as the DWCNTs obtained by annealing were characterized with multi frequency Raman spectroscopy. Simultaneous filling with C_{60} and C_{70} was found to take place with the same efficiency. When using the ^{13}C enriched C_{60} for DWCNT synthesis, mode softening for all inner shell lines was observed, while the outer shell response remained unchanged. The yield of inner shell CNTs is almost the same for C_{60} and C_{70} except that C_{70} is very inefficient in forming mid diameter inner CNTs with RBM frequencies close to 365 cm^{-1}. If inner CNTs are grown from mixed peapods of C_{70} and ^{13}C enriched C_{60} these particular CNTs are mainly built from C_{60}. This is confirmed by the observation of distinct line shifts in the inner shell RBM.

INTRODUCTION

Raman spectroscopy is a convenient and widely used technique in the investigation of different nano structured phases of carbon. Especially multi frequency Raman spectroscopy was demonstrated to be applicable for the observation of distinct inner shell CNTs in DWCNTs [1]. So far this was demonstrated for the strongly diameter dependent RBM, whereas the high frequency modes are on top of each other. By using ^{13}C enriched fullerenes and turning the obtained peapods into DWCNTs all inner shell modes are down shifted. This technique allows a clear separation of the outer and inner shell response throughout the whole spectrum. Furthermore, ^{13}C marked fullerenes in combination with Raman spectroscopy can be used to monitor the diameter dependency of the filling efficiency for different fullerenes in a mixture of these. This contribution is focused on an observed unusual behavior of the diameter dependence of the filling efficiency for C_{70}. This anomaly can be exploited to prepare very special DWCNT samples. The outer shell CNTs as well as any other carbonic impurities have the natural abundance (~1%) of ^{13}C. Only the inner shell CNTs are ^{13}C enriched. This enrichment is the same for almost all inner tubes, but in a very narrow diameter range corresponding to $\nu_{RBM} = 365cm^{-1}$ it is twice as high compared to all other very thin CNTs. The general spectroscopic benefit of ^{13}C enriched inner shell CNTs in the high frequency domain (D,G and D* Band) is reported in detail later [2]

CP723, *Electronic Properties of Synthetic Nanostructures*, edited by H. Kuzmany et al.

EXPERIMENTAL

Peapods were obtained through the vapor phase filling method. Fullerenes and SWCNTs material purified by oxidation and prepared as bucky paper were sealed in an evacuated quartz ampoule and heated at 650 °C for 2h. Excess fullerenes were removed by heating the peapods at 800 °C for 30 min in dynamic vacuum. Transformation to DWCNTs was performed by 1 h annealing at 1270 °C in dynamic vacuum. Raman spectra were recorded with a xy triple monochromator spectrometer from Dilor. The 180° backscattered light was analyzed. An ArKr laser was used for excitation at different laser lines.

RESULTS AND DISCUSSION

The above described vapor filling method for preparation of peapods works for either C_{60} or C_{70}. Figure 1 depicts Raman spectra of C_{60} and C_{70} peapods at 488 nm. In both cases the characteristic lines of the fullerenes are observed together with the D-band of the hosting SWCNTs. If a 50%:50% mass ratio mixture of C_{60} and C_{70} is subject to peapod preparation a superposition of the Raman spectra from Fig. 1 is observed, as shown in Fig. 2a. As expected this spectrum can be simulated by superimposing the two spectra of Fig. 1. Best agreement for this simulation is obtained for a 45% to 55% ratio of C_{70} and C_{60}. The resulting spectrum is shown in Fig. 2b.

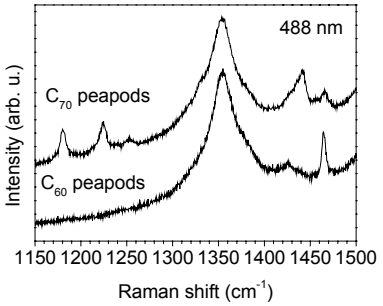

FIGURE 1. Raman spectra of vapor phase prepared C_{60} and C_{70} peapods at 488 nm.

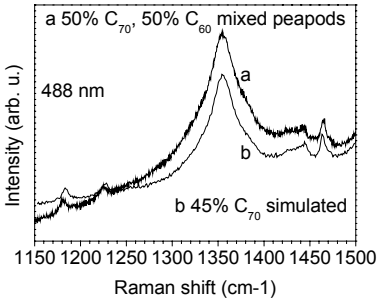

FIGURE 2. Raman spectrum of C_{60}/C_{70} mixed peapods at 488 nm (a) and best fitting superposition of the spectra from Fig. 1 (b).

Thus, when the vapor filling method is applied to prepare mixed peapods from C_{60}/C_{70} mixtures, the initial mass ratio is almost retained.

When annealing C_{60} and C_{70} peapods and investigating the resulting DWCNTs by multi frequency Raman spectroscopy, it is found that both kinds of peapods have the same yield of inner shell CNTs, except for a very narrow spectral range around 365

cm^{-1}. In this range C_{70} peapod material exhibits a significantly lower yield of inner shell CNTs [3].

Figure 3 shows Raman spectra of the RBM of C_{60} and C_{70} based inner shell CNTs. While the spectra at 676 nm clearly show the suppressed signal around 365 cm^{-1} in C_{70} based DWCNTs, the spectra at 502 nm show that there is again a compareable yield at higher frequencies and even thinner inner shell CNTs. All spectra are normalized to the response of the outer shell RBM. Therefore the suppressed RBM signal at 365 cm^{-1} is not related to different minimum filling or transformation diameters of C_{60} and C_{70}. In both samples transformation and therefore filling is observed at higher and lower frequencies corresponding to smaller and bigger diameters. By now there are two possible scenarios explaining this anomaly, either the transformation of C_{70} into inner shell CNTs is hindered in the corresponding diameter range, or even more exciting, there are almost no C_{70} peapods in this diameter range. The crucial experiment to decide between these two scenarios is to prepare mixed peapods from ^{13}C enriched C_{60} and standard C_{70} and transform them to DWCNTs. Figure 4 depicts a compilation of the RBM of standard C_{60}, pure ^{13}C enriched C_{60} and of a mixture of ^{13}C enriched C_{60} and standard C_{70} based inner shell CNTs recorded at 647 nm.

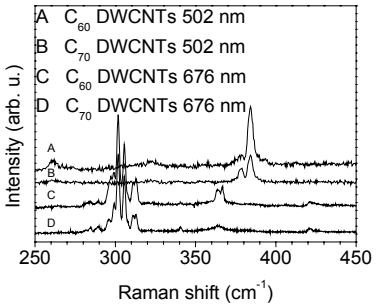

FIGURE 3. Raman spectra of the RBM of C_{60} and C_{70} based inner shell CNTs at 502 and 676 nm.

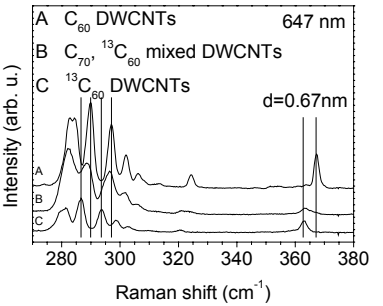

FIGURE 4. Raman spectra of the RBM of C_{60}, $^{13}C_{60}/C_{70}$ mixed and $^{13}C_{60}$ based inner shell CNTs at 647 nm.

Obviously the transformation of mixed peapods to DWCNTs works as well as the transformation of either pure C_{60} or C_{70} peapods. As expected the lower frequency RBM lines of the mixed material exhibit line positions only slightly down shifted as compared to the standard C_{60} based inner shell CNTs. In contrast the RBM line at 365 cm^{-1} shows almost the full downshift as compared to the pure $^{13}C_{60}$ material. Therefore, this particular CNTs are mainly built from the ^{13}C marked C_{60}. This proves that C_{70} is inefficient in filling the corresponding outer diameter CNTs. Taking into account the experimental wall to wall distance in DWCNTs obtained from X-ray diffraction [4] of 0.36 nm and different relationships of the RBM frequency and inverse diameter [5, 6, 7] the corresponding outer tube diameter is found in the range from 1.35 nm to 1.40 nm. This experimental result matches to the reported theoretical

borderline between the preference of lying and standing, e.g. the longer axis either parallel or standing with respect to the CNT axis, arrangements in C_{70} peapods[8].

SUMMARY

^{13}C marked fullerenes can be used to prepare DWCNTs where the very thin inner shell CNTs are ^{13}C labeled. This selective labeling allows for a clear discrimination between these very thin CNTs from any other material in the samples. When using different kinds of fullerenes it is possible to determine which fullerenes contribute to which inner shell CNTs. In this way we have confirmed an anomalous filling behavior of the asymmetrically shaped C_{70} molecule. The latter is inefficient in filling CNTs with diameters very close to the borderline of standing and lying arrangements. Similar effects may be expected for other well defined asymmetric nano particles and thus provide a way to highly diameter selective reactions. This can open a new route to separation of SWCNTs.

ACKNOWLEDGEMENTS

This work was supported by the Austrian Science Foundation, project 14893 and the EU PATONN Marie-Curie MEIF-CTC2003-501099 grants.

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