Single wall carbon nanotube specific ^{13}C isotope enrichment

Ferenc Simon, Christian Kramberger, Rudolf Pfeiffer and Hans Kuzmany

Universität Wien, Institute für Materialphysik, Strudlhofgasse 4, 1090, Wien, Austria

Abstract. We report on the single wall carbon nanotube specific ^{13}C isotope enrichment. The high temperature annealing of isotope enriched fullerenes encapsulated in SWCNTs yields double wall carbon nanotubes with a high isotope enrichment of the inner wall. The methods helps to discriminate the Raman signal of the outer and inner tubes. The vibrational spectra evidences that no carbon exchange occurs between the two walls.

INTRODUCTION

The characterization of the electronic and structural properties of SWCNTs, that is neccessary for both fundamental and applied studies, can be conveniently performed with Raman spectroscopy. It yields a variety of information ranging from the SWCNT diameter distribution[1] to the electronic structure of SWCNTs due to the photoselectivness of the tube Raman response. However, the full identification of the large number of Raman active modes[2] is to date still not a completed task[3]. A simplifying approach for this task could be the synthesis of fullerene peapod based double-wall carbon nanotubes (DWCNTs). In DWCNT samples, the outer tubes are left intact and inner, smaller diameter tubes are grown. The comparison of the starting SWCNT and the final DWCNT samples could in principle greatly simplify the identification of the Raman active components. In addition, the study of the inner tubes in C_{60} peapod[4] based DWCNTs[5] enables the synthesis and study of small diameter tubes. This approach has been successfully applied for the identification of the inner tube radial breathing modes (RBMs)[6], which enabled refinement of the empirical constants relating the RBM frequencies with the tube diameters[7]. However, for other modes such as e.g. the tangential G mode, the diameter dependence of the Raman response is weaker thus separation of inner and outer tube Raman signals is difficult.

Here, we report a ^{13}C isotope enrichment method of single-wall carbon nanotubes that is selective for inner shell nanotubes only. We synthesized SWCNTs encapsulating ^{13}C enriched C_{60} and C_{70} fullerene molecules. A high temperature treatment transforms the fullerenes into a second smaller diameter inner tube that is isotope enriched reflecting the enrichement level of the fullerenes. The identification of inner tube vibrational modes is presented, based on different levels of ^{13}C enrichment using Raman spectroscopy.

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

EXPERIMENTAL

We prepared fullerene peapod C_{60},C_{70}@SWCNT based DWCNTs. Arc-discharge prepared commercial SWCNT material (Nanocarblab, Moscow, Russia), ^{13}C isotope enriched fullerenes (MER Corp., Tucson, USA), and natural carbon containing fullerenes (Hoechst AG, Frankfurt, Germany) were used for the synthesis. The SWCNT was purified by the supplier to 50 %. The tube diameter distribution was determined from Raman spectroscopy[1] and we obtained d = 1.40 nm, σ = 0.10 nm for the mean diameter and the variance of the distribution, respectively. We used two degrees of ^{13}C enrichment: 25 and 89 %. These enrichment factors were determined using mass spectroscopy by the supplier and are slightly refined according to our studies. The fullerenes used were C_{60}/C_{70}/higher fullerene mixtures containing 75%:20%:5% ($^{25\ \%,\ 13}C_{60}$ in the following) and 12%:88%:<1 % ($^{89\ \%,\ 13}C_{70}$ in the following) for the 25 and 89 % enriched materials, respectively. The fullerenes containing natural carbon ($^{\mathrm{Nat}}$C) had a purity of > 99 %. SWCNTs were sealed under vacuum in a quartz ampoule with the fullerene powder and annealed at 650 ^{o}C for 2 hours for the fullerene encapsulation[8]. Non-reacted fullerenes were removed by dynamic vacuum annealing at 650 ^{o}C. The peapod samples were transformed to DWCNT by a 2 h long dynamic vacuum treatment at 1250 ^{o}C following Ref. 5. Multi frequency Raman spectroscopy was used for the vibrational analysis on a Dilor xy triple axis spectrometer in the 1.64-2.54 eV (676-488 nm) energy range at 90 K. The spectral resolution as determined from the spectrometer response to the elastically scattered light was 0.5-2 cm^{-1} depending on the laser wavelength and the resolution mode used (high or normal resolution).

RESULTS AND DISCUSSION

In Fig. 1, we show the spectra of the DWCNTs based on the $^{\mathrm{Nat}}C_{60}$, $^{25\ \%,13}C_{60}$ and $^{89\ \%,\ 13}C_{70}$ for the radial breathing mode (RBM) (Fig.1a.) and the D and G mode spectral ranges Fig. 1b. at 676 nm excitation and 90 K. The narrow lines in Fig. 1a.) were previously identified as the RBMs of the inner tubes[6]. An overall down shift of the inner tube RBMs is observed for the ^{13}C enriched materials accompanied with a broadening. The down shift is a clear evidence for the effective ^{13}C enrichment of inner tubes. The magnitude of the enrichment and the origin of the broadening is discussed below.

The RBMs are well separated for inner and outer tubes due to the ν_{RBM} J $1/d$ reciprocal relation between the RBM frequency, ν_{RBM}, and the tube diameter, d. However, other vibrational modes such as the defect induced D and the tangential G modes are strongly overlapping for inner and outer tubes. Therefore, isotope substitution is a valuable too to separate the lines. This holds in particular for the D-line as shown in Fig. 1b. The broad line profile does not immediately allow to separate the response from the outer and inner tubes. The arrows in Fig. 1b. indicate a gradually downshifting component of the observed D and G modes. This mode is assigned to the D and G modes of the inner tubes. The sharper appearance of the inner tube G mode

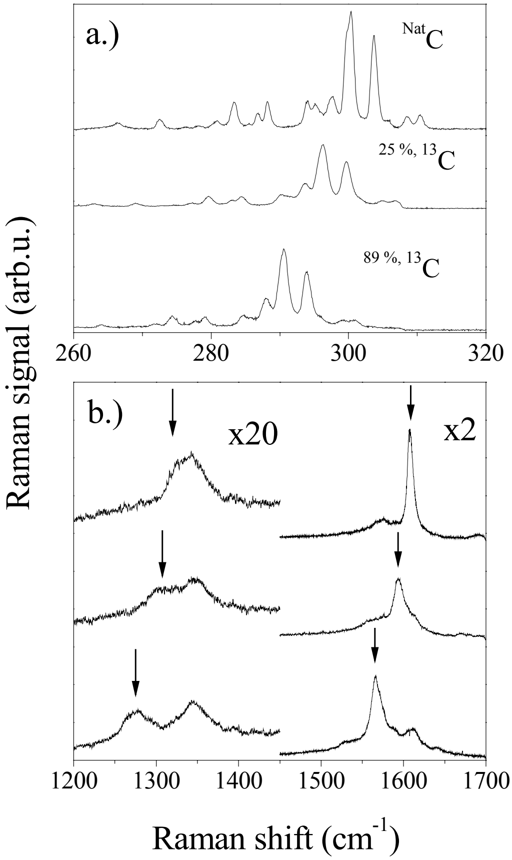

FIGURE 1. Raman spectra of DWCNT with ^{Nat}C and ^{13}C enriched inner walls at 676 nm laser excitation and 90 K. a.) RBM Raman shift range recorded with high resolution, (0.5 cm^{-1}), b.) D and G mode ranges recorded with normal resolution (1.5 cm^{-1}). Arrows indicate the D and G modes corresponding to the inner tubes.

as compared to the outer components is related to the excitation of semiconducting inner and the Fano lineshape broadened metallic outer tubes[6,9].

The relative magnitude of the inner and outer tube D modes are comparable as seen best for the $^{89\,\%,\,13}$C enriched sample. This is a surprising observation as the D mode is known to originate from a double resonance process and is related to the number of defects. However, the inner tubes were shown to contain significantly less defects than the outer ones as proven by the narrow RBM phonon linewidths[6]. The enhanced electron-phonon coupling in small diameter inner tubes can explain for the large D mode of inner tubes altough they contain less defects. The electron-phonon coupling was experimentally found to be roughly 10 times larger for inner than for the outer tubes[6,9]. The presence of superconductivity in 4 Å diameter tubes[10] is also thought to be related to a large electron-phonon coupling in smaller diameter tubes.

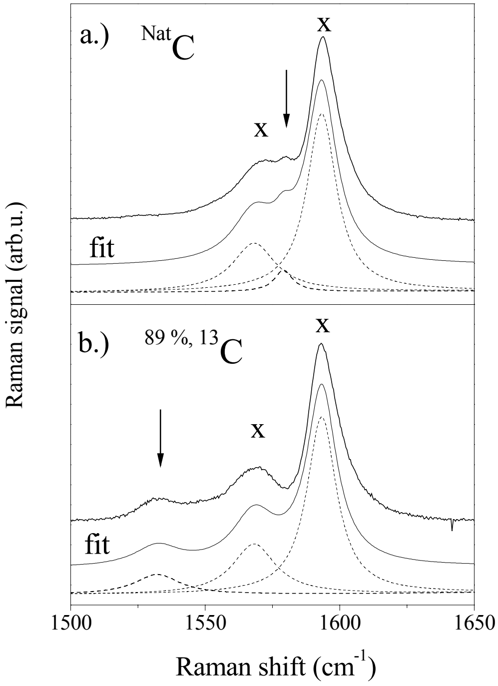

FIGURE 2. G modes of DWCNTs with a.) ^{Nat}C and $^{89\,\%,\,13}C$ enriched inner walls at 488 nm laser excitation and 90 K. Crosses indicate the non-shifting components of the outer tube G modes. Arrows show the only shifting componenent, identified as the inner tube G modes. Dashed curves show the deconvolution of the observed spectra.

Identification of the different signals also allows to address whether any carbon exchange between the inner and outer tubes occurs during the DWCNT synthesis. In Fig. 2. we compare the G mode spectra of ^{Nat}C and $^{89\,\%,\,13}C_{70}$ enriched DWCNTs at 488 nm excitation. For this excitation energy, the G mode of the outer tubes dominate the spectra[9]. Indeed, the only shifting component observed is very small (arrows in Fig. 2.) compared to the non-shifting components (crosses in Fig. 2.). A deconvolution using one Lorentzian line for the shifting and two for the non-shifting componenents allows to analyze whether any shift is observable for the outer tube G modes. We found that within the experimental uncertanity of our experiment the outer tube G modes are not shifting proving that no C exchange appears between the two walls at the 1250 °C of the inner tube synthesis. This, however, does not rule out the possibility of such exchange at even higher temperatures or at longer reaction times.

The shift of the RBM, D and G modes were analyzed for the two levels enrichment. We found that $(\upsilon_0-\upsilon)/\upsilon_0$ =0.0109±0.0003 and 0.0322±0.0003 for the 25 and 89 % samples, respectively. Here, ν_0-ν is the shift of the mode at ν_0 Raman shift in the material containing natural carbon only. Under the simplest assumption, the shift originates from the isotope effect such that $(\upsilon_0-\upsilon)/\upsilon_0=(c-0.011)*\left(\sqrt{13/12}-1\right)$, where c is the concentration of the ^{13}C enrichment on the inner tube. This formula also takes into account the 1.10 % natural abundance of ^{13}C in carbon. This gives 27.8±0.7 % and 80.0±0.7 % ^{13}C enrichement for the 25 and 89 % samples. The difference between the supplier provided values and those determined herein underlines the difficulties in estimating the nominal ^{13}C enrichment in the starting material.

CONCLUSIONS

We reported the synthesis of ^{13}C enriched SWCNTs. ^{13}C builds into the inner shell tube only without enriching the inevitable other carbon phases such as amorphous carbon or graphite. The method is based on the transformation of ^{13}C enriched fullerenes encapsulating SWCNTs into double wall carbon nanotubes. We showed that high levels of isotope enrichments can be achieved without significant carbon exchange between the two walls. The ^{13}C enriched inner tubes facilitate the identification of the vibrational modes of inner and outer tube components. The synthesis method opens the way for the controllabel isotope labelling of SWCNTs without labelling the non-wanted sideproducts. It is also hoped that the described isotope engineering may find application for the controllable doping of SWCNTs similar to the isotope engineering applied for Si in the semiconducting industry.

ACKNOWLEDGMENTS

This work was supported by the Austrian Science Funds (FWF) project Nr. 14893 and by the EU projects NANOTEMP BIN2-2001-00580 and PATONN Marie-Curie MEIF-CT-2003-501099 grants.

REFERENCES

1. H. Kuzmany, W. Plank, M. Hulman, C. Kramberger, A. Gruneis, T. Pichler, H. Peterlik, H. Kataura, Y. Achiba, Eur. Phys. J. B **22** (2001) 307.
2. M. Damnjanovic, I. Milosevic, T. Vukovic, and R. Sredanovic, Phys. Rev. B **60**, 2728 (1999).
3. M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza, G. G. Samsonidze, and R. Saito, J. Nanosci. and Nanotechn. **3**, 19 (2003).
4. B. W. Smith, M. Monthioux, and D. E. Luzzi, Nature **396**, 323 (1998).
5. S. Bandow *et al.*, Chem. Phys. Lett. **337**, 48 (2001).
6. R. Pfeiffer *et al.*, Phys. Rev. Lett. **90** 225501 (2003).
7. Ch. Kramberger *et al.*, Phys. Rev. B **68**, 235404 (2003).
8. H. Kataura *et al.*, Synth. Met. **121**, 1195 (2001).
9. F. Simon *et al.*, cond-mat/0404110.
10. Z. K. Tang, L. Y. Zhang, N. Wang, X. X. Zhang, G. H. Wen, G. D. Li, J. N. Wang, C. T. Chan, and P. Sheng, Science **292**, 2462 (2001).