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Growth of single wall carbon nanotubes from ^{13}C isotope labelled organic solvents inside single wall carbon nanotube hosts

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Abstract

We present the growth of single wall carbon nanotubes (SWCNTs) from organic solvents such as benzene and toluene inside a host SWCNT. The solvents encapsulated in SWCNTs are transformed to an inner tube when subject to a heat treatment under dynamic vacuum at 1270 °C. We used isotope labeling of the different carbon sources to prove that the source of the inner tubes is indeed the solvent. Our results put constraints on the models explaining the inner tube growth and provides a simple alternative for the fullerene based inner tube growth. It also provides the possibility to study a completely new field of in-the-tube chemistry.
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1. Introduction

Catalyst free growth of single wall carbon nanotubes (SWCNT) has been intensively attempted since their discovery in 1993 [1,2]. The efforts resulted in novel nanostructures such as, e.g. the nano-horns [3] but the metal catalyst-free synthesis remains elusive. Recently, catalyst free growth of SWCNTs was achieved from fullerenes encapsulated in SWCNTs, when these so-called peapods [4] are subject to a high temperature annealing at 1270 °C [5,6].

In this Letter, the synthesis of inner tubes is reported from ^{13}C isotope labeled organic solvents such as benzene and toluene encapsulated in SWCNTs. This is demonstrated to work when fullerenes are co-encapsulated preventing the solvents from evaporation. Isotope labeling proves unambiguously that the solvents contribute to the inner tubes and gives a measure on the yield. The current

result opens new perspectives for the catalyst free synthesis of SWCNTs in other confined environments such as zeolite [7] and allows further exploration of the in-the-tube chemistry.

2. Experimental

2.1. Sample preparation

Commercial SWCNT material (50 weight % purity, Nanocarblab), fullerenes (C_{60} and C_{70}) of natural carbon (Hoechst AG), benzene and toluene (Sigma–Aldrich) and isotope labeled benzene and toluene (Euriso-Top SA) were used. In the following, we denote these two latter compounds as solvents even though their primarily role is being precursors of a chemical process. The purification of the SWCNTs by the supplier in the form of repeated air oxidation at 400 °C and acid washing results in purified and opened SWCNTs. The tube diameter distribution was determined from Raman spectroscopy [8] and we obtained $d = 1.40$ nm and $\sigma = 0.10$ nm for the mean diameter and the variance of the Gaussian distribution, respectively. Vapor filling with fullerenes was performed by subjecting the SWCNT flakes to fullerene vapor in a sealed quartz ampoule at 650 °C following Ref. [9]. Non-encapsulated

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fullerenes were removed by a 650 °C dynamic vacuum treatment. Typically, 150 µg fullerenes in 100 µl solvent was sonicated for 1 h with 1 mg SWCNT in an Eppendorf tube for the solvent peapod preparation. The weight uptake of the SWCNT is ~15% [10] that is shared between the solvent and the fullerenes. The peapod was separated from the solvent by centrifuging and the peapod material was greased on a sapphire substrate. The vapor or solvent prepared peapods were treated in dynamic vacuum at 1270 °C for 2 h for the inner tube growth. The inner tube growth efficiency was found independent of the speed of warming.

2.2. Raman spectroscopy

Vibrational analysis was performed on a Dilor xy triple Raman spectrometer in the 1.64–2.54 eV (676–488 nm) energy range at ambient conditions.

3. Results and discussion

The growth of inner carbon nanotubes can be monitored by Raman spectroscopy. We use extensively the response from the overtone of the SWCNT D-line, known as the G′ mode [11], since this mode exhibits the largest absolute isotope shift. Fig. 1 shows the G′ mode for a SWCNT (a) and two DWCNT samples that were obtained by high temperature annealing from vapor prepared C_{60} peapods (b) and toluene + C_{60} peapods (c) by a 1270 °C heat treatment. The vapor method involves placing the SWCNT in a fullerene vapor in a sealed ampoule, while the solvent method involves sonicating the solvent + C_{60} solution together with the nanotubes which results in the encapsulation of both the fullerene and the solvent [12]. All results reported here are identical when C_{70} fullerenes were used. The G′ mode provides a convenient measure of the inner tube growth as the inner and outer tube response are separated in the DWCNT samples: the mode on the G′ component at lower Raman frequency comes from the inner tubes [13]. The ratio of the inner to outer tube mode intensities strongly depends on the exciting laser energy with a maximum around 2.41 eV [13], that is used in the current study.

The relative intensity of the inner tube mode in the vapor-C_{60} and solvent + C_{60} peapod based DWCNTs measures the inner tube content in the two samples. This can be quantified by deconvolution of the DWCNT signal into inner and outer tube components as shown in Fig. 1. The smaller inner tube signal in the solvent + C_{60} sample is the result of a partial evaporation of the solvent before the inner tubes are formed. It is known that encapsulation of the fullerene is energetically preferred and thus it cannot escape from the tubes [14]. However, a small molecule such as benzene and toluene can leave the tube at higher temperatures. We found that the yield of inner tubes grown from the benzene- (spectrum not shown) and toluene + C_{60} peapods is 44(1)% and 48(1)% of that from the vapor-C_{60} sample, respectively. To separate the contribution to the inner tubes from the solvents and C_{60}, the encapsulated C_{60} content can be determined in the solvent + C_{60} peapod samples. In Fig. 2, we show the spectral range that contains the C_{60} pentagonal pinch mode (PPM) at 1466 cm^{-1} [15]
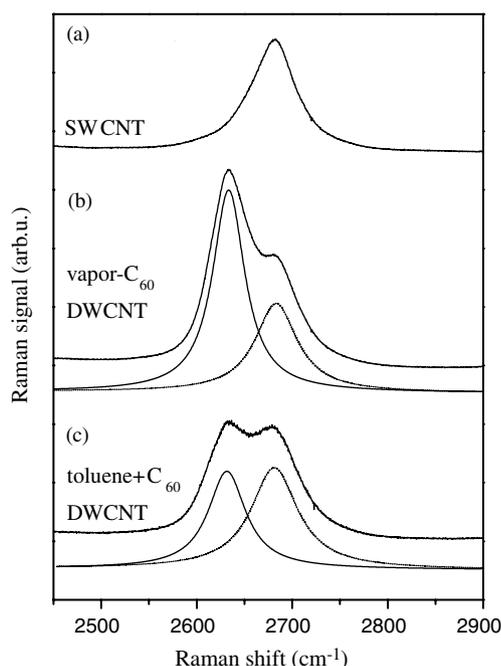

Fig. 1. The G′ Raman mode of: (a) SWCNTs, (b) vapor-C_{60} peapod and (c) toluene + C_{60} peapod based DWCNTs at $\lambda = 515$ nm laser excitation (2.41 eV). Smooth solid and dashed curves show the deconvolution to inner and outer tube modes, respectively.
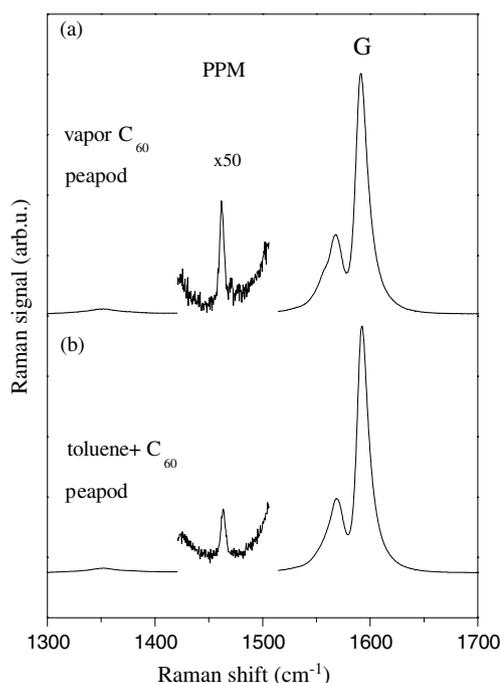

Fig. 2. The C_{60} PPM mode and the nanotube G mode in: (a) vapor-C_{60} peapod and (b) toluene + C_{60} peapod sample at $\lambda = 488$ nm laser excitation (2.54 eV). Note the 50 times magnified scale for the PPM range.

and the nanotube G modes around 1650 cm^{-1} [11] for the vapor-C_{60} and solvent + C_{60} peapod sample. It was demonstrated [16] that the encapsulated C_{60} content can be determined from the relative intensity of the PPM and G modes. Assuming 100% filling of the available volume with C_{60} for the vapor-C_{60} peapod sample [17], the results of Fig. 2 demonstrates only 40(1)% fullerene filling for the toluene + C_{60} sample. The same value was obtained for benzene as a solvent.

In summary, from the 44% inner tube content in the benzene + C_{60} peapod based sample, 91% of the carbon originates from C_{60}. Thus, benzene contributes only to approximately 9(4)% of the carbon. Similarly, toluene contributes to approximately 17(4)% fraction of the total carbon amount on the inner tubes. If we assume that solvents fill all available volume apart from that filled with C_{60}, the current result means that a significant portion, over 80%, is evaporated from both solvents without contributing to the inner tube growth.

Based on the current analysis, it cannot be ruled out that e.g. amorphous carbon is also inside the tubes or enters the tubes and thus contributes to the inner tube growth. Therefore, the crucial statement on the growth of inner tubes from organic solvents requires further reinforcement. To provide this, we studied the inner tube growth from solvent + C_{60} peapods, where the solvent was a mixture of ^{13}C isotope labeled and natural solvents with varying concentrations. Toluene was a mixture of ring ^{13}C labeled ($^{13}C_6H_6$–CH_3) and natural toluene (C_7H_8). Benzene was a mixture of ^{13}C enriched and natural benzene. The labeled site was >99% ^{13}C labeled for both types of molecules. The ^{13}C content, x, of the solvent mixtures was calculated from the concentration of the two types of solvents and by taking into account the presence of the naturally enriched methyl-group for the toluene. In Fig. 3a, we show the G′ modes of DWCNTs with varying ^{13}C labeled content in toluene–C_{60} based samples and in Fig. 3b, we show the same spectra after subtracting the outer SWCNT component. A shoulder appears for larger values of x on the low frequency side of the inner tube mode, whereas the outer tube mode is unchanged. Similar behavior was observed for the benzene + C_{60} based peapod samples (spectra not shown) although with a somewhat smaller spectral intensity of the shoulder. The appearance of this low frequency shoulder is evidence for the presence of a significant ^{13}C content in the inner tubes. This proves that the solvent indeed contributes to the inner tube formation as it is the only sizeable source of ^{13}C in the current samples. The appearance of the low frequency shoulder rather than the shift of the full mode indicates an inhomogeneous ^{13}C enrichment. A possible explanation is that smaller diameter nanotubes might be higher ^{13}C enriched as they retain the solvent better than larger tubes.

To quantify the ^{13}C enrichment of the inner tubes, the downshifted spectral weight of the inner tube G′ mode was determined from the subtracted spectra in Fig. 3b. The subtraction does not give a flat background above
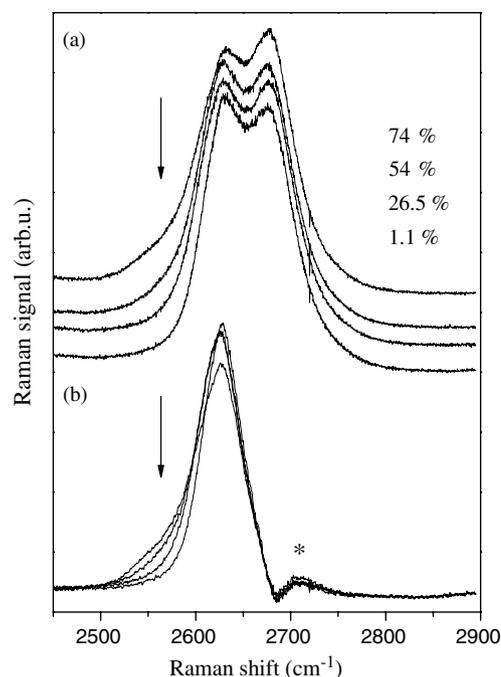

Fig. 3. (a) The G′ mode of toluene + C_{60} peapod based DWCNTs with varying ^{13}C enrichment at λ = 515 nm laser excitation (2.41 eV). From top to bottom: 74%, 54%, 26.5% and natural ^{13}C content. (b) The G′ mode of the inner tubes after subtracting the experimental SWCNT spectrum. Arrows indicate the spectral weight shifted toward lower frequencies. A small residual peak is observed around 2710 cm^{-1} (denoted by an asterisk) due to the imperfect subtraction.

2685 cm^{-1}, however it is the same for all samples and has a small spectral weight, thus it does not affect the current analysis. The line-shapes strongly deviate from an ideal Lorentzian profile. Therefore, the line positions cannot be determined by fitting, whereas the first moments are well defined quantities. The effective ^{13}C enrichment of the inner tubes, c, is calculated from $(v_0 - v)/v_0 = 1 - \sqrt{\frac{12+c_0}{12+c}}$, where v_0 and v are the first moments of the inner tube G′ mode in the natural carbon and enriched materials, respectively, and $c_0 = 0.011$ is the natural abundance of ^{13}C in carbon. The validity of this 'text-book formula' was previously verified by ab initio calculations for enriched inner tubes [10]. In Fig. 4, we show the effective ^{13}C content in the inner tubes as a function of the ^{13}C content in the starting solvents. The scaling of the ^{13}C content of the inner tubes with that in the starting solvents proves that the source of the ^{13}C is indeed the solvents. The highest value of the relative shift for the toluene based material $(v_0 - v)/v_0 = 0.0041(2)$, corresponds to about 11 cm^{-1} shift in the first moment of the inner tube mode. The shift in the radial breathing mode range (around 300 cm^{-1}) [11] would be only 1 cm^{-1}. This underlines why the high energy G' mode is convenient for the observation of the moderate ^{13}C enrichment of the inner tubes.

When fit with a linear curve with $c_0 + A*x$, the slope, A directly measures the carbon fraction in the inner tubes that originates from the solvents. The values,
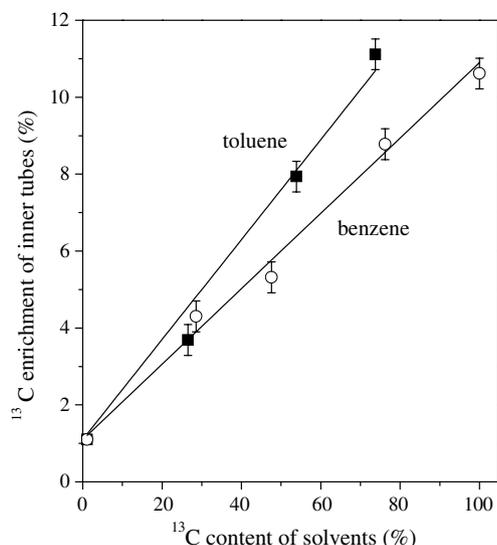
Fig. 4. ^{13}C content of inner tubes based on the first moment analysis as explained in the text as a function of ^{13}C enrichment of benzene and toluene. Lines are linear fits to the data as explained in the text.

$A = 0.098(5)$ and $A = 0.130(6)$ agree with the solvent related carbon fractions on the inner tubes of 9% and 17% as determined from the intensity of the inner tube modes for benzene and toluene, respectively.

The synthesis of inner tubes from organic solvent proves that any form of carbon that is encapsulated inside SWCNTs contributes to the growth of inner tubes. As mentioned above, inner tubes are not formed in the absence of fullerenes but whether the fullerene is C_{60} or C_{70} does not play a role. It suggests that fullerenes act only as a stopper to prevent the solvent from evaporating before the synthesis of the inner tube takes place. It also clarifies that the geometry of fullerenes do not play a distinguished role in the inner tube synthesis as it was originally suggested [18]. It also proves that inner tube growth can be achieved irrespective of the carbon source, which opens a new prospective to explore the in-the-tube chemistry with other organic materials.

Acknowledgements

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