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The effects of inhomogeneous isotope distribution on the vibrational properties of isotope enriched double walled carbon nanotubes

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1 Introduction

Recently, we prepared isotope engineered (IEd) carbon nanotubes which allowed Raman vibrational analysis [1] and NMR studies of the tube electronic properties [2]. The IEd nanotubes were produced by annealing from ^{13}C enriched fullerenes (C_{60}, C_{70}, . . .) encapsulated inside natural carbon single walled carbon nanotube (SWCNT) host outer tubes.

Open questions remain concerning the growth mechanism of inner tubes and the random distribution of ^{12}C and ^{13}C isotopes. Two mechanisms have been suggested for inner tube growth: (i) from di- or polymerized encapsulated fullerenes [3–5] through Stone–Wales transformations [6], (ii) from completely disintegrated fullerenes [7].

The random isotope distribution was found to induce an inhomogeneous broadening of the Raman modes, best observed for the radial breathing mode (RBM). Results on samples that were produced by using a *mixture* of enriched and non-enriched fullerenes as filling material yields a larger broadening

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than expected. This behavior can help to decide which of the two possible growth mechanisms is actually realized during synthesis.

Here we present calculations on the isotope distribution related inhomogeneous broadening for the RBM of ^{13}C enriched inner tubes using density functional theory within the local density approximation on SWCNT cell sizes which are sufficient for convergence of the data [10]. We synthesized two kinds of ^{13}C enriched inner tubes: made from ^{13}C enriched fullerenes (uniform enrichment) and from mixtures of natural and ^{13}C enriched fullerenes (mixed enrichment). We observed that the RBMs are a factor 3 more broadened for the mixed enrichment than for the uniform enrichment at the same overall enrichment levels. The relative difference is well reproduced by the calculations if inhomogeneous clustering of ^{13}C rich and poor regions are assumed along the inner tubes. A scaling of the data by a factor of 1.5–2 yields quantitatively accurate agreement between theory and experiment. The results presented here prove the absence of carbon diffusion along the tube axis during inner tube growth and are a strong support of inner tube growth through Stone–Wales transformations from preformed fullerene dimers or oligomers.

2 Method

We used the VASP density functional theory code [8] at the LDA level and PAW method to calculate the inhomogeneous broadening of the RBM mode for three experimentally relevant SWCNTs: (10,0), (7,4), and (5,5) (the inner tube diameter range is centered around 7 Å). Long range force constants were taken into account to ensure high accuracy of the frequencies: the length of the supercells used to calculate the Hessian matrices were 12.7 Å, 13.6 Å, and 14.7 Å for (10,0), (7,4), and (5,5), respectively.

In order to calculate the inhomogeneous broadening, the dynamical matrices of the tubes were constructed and diagonalized using a large number of different random distributions of ^{12}C and ^{13}C nuclei for the mass matrices. Once the RBM mode is obtained after the diagonalization, the inhomogeneous broadening is determined by calculating the standard deviation of RBM frequencies for all random isotope distributions.

Two grades of ^{13}C enriched fullerenes were used to prepare fullerene peapods, with enrichment levels of $c = 0.28$ and 0.82. We synthesized two different kinds of peapod materials: the so-called *uniform filling* sample (where the encapsulated fullerenes were alike, i.e. from one enrichment grade) and the so-called *mixed filling* sample (where $c = 0.28$ and natural C_{60} were mixed 1 : 1).

The peapods were transformed to double walled carbon nanotubes (DWCNTs) following Ref. [9]. DWCNTs based on uniformly filled peapods with different enrichment grades are denoted as $^{\mathrm{Nat}}$C, $^{13}C_{0.28}$ and $^{13}C_{0.82}$ DWCNT. The DWCNT based on the fullerene mixture is denoted as $^{13}C_{0.15\text{–}M}$ DWCNT, reflecting its average $c = 0.15$ enrichment.

Our calculations have shown [1] that the broadening follows a parabola-like function with a maximum at $c = 0.5$, suggesting that at $c = 0.15$ a smaller broadening is expected than at $c = 0.28$. However, a much larger broadening was observed for the former sample (see Ref. [10]). These findings clearly suggest the absence of carbon diffusion along the tube axis during inner tube growth and are a strong support of inner tube growth through Stone–Wales transformations from interconnected fullerenes.

3 Results

Using the method detailed above, we have calculated the inhomogeneous broadening of the RBM frequency of the (10,0), (7,4), and (5,5) SWCNTs.

In the case of the uniform filling method, the ^{13}C isotopes are uniformly distributed in the supercell along the tube axis: the ^{13}C nuclei are randomly placed within the entire supercell, with no predefined non-enriched regions. We have calculated the inhomogeneous Gaussian broadening for 10%, 30%, 50%, 70%, and 90% ^{13}C content for all three tubes (see Fig. 1). As expected, in all three cases the broadening increases with increasing level of enrichment until ^{13}C content reaches 50%, where the broadening has a maximum. We find a slight chirality dependence, and that the calculation underestimates the experimental broadening by about a factor of 1.5–2 (the underestimation is discussed in Ref. [10]).

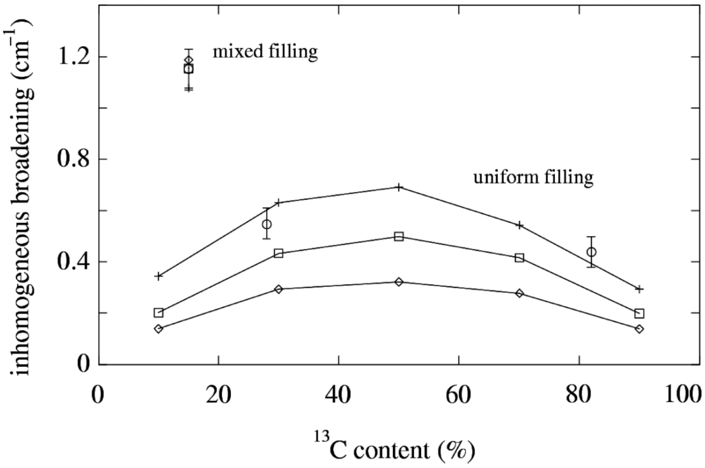

Fig. 1 Calculated inhomogeneous broadening of the RBM mode of the (10,0), (7,4), and (5,5) SWCNTs (diamonds, squares, and crosses, respectively), compared with measurements (circles). All values are FWHM. The calculated results are upscaled by a factor of 1.65 [10].

The mixed filling derived tubes were studied by performing calculations at an average enrichment level of 15%, but assuming that the nanotube is composed of enriched (30%) and non-enriched (0%) sections, which follow each other randomly in 1 : 1 ratio using the same section size as above.

The calculations are in very good qualitative agreement with the experiments: a significantly larger broadening is found than in the case of the uniform filling derived DWCNTs (see upper left corner of Fig. 1). We find no chirality dependence here, but the magnitude of the broadening is once again underestimated by a factor of 1.5–2.

If all of the calculated results are upscaled by a factor of 1.65, then all calculated values for the mixed filling derived DWCNTs fall within the errorbar around the experimentally obtained value. At the same time, the theoretical results on the uniform filling derived (5,5) inner tube also match the experimental results after this same upscaling, which shows that the relative increase of the inhomogeneous broadening for this tube is in excellent agreement with the experiments.

4 Discussion: Absence of carbon diffusion

The results detailed above are a clear indication that there is very little diffusion of carbon atoms along the tube axis during the creation of the inner tube in the peapod-to-DWCNT transformation process. An inner tube growth mechanism which satisfies this experimental observation was suggested in Refs. [3–5]: molecular dynamics calculations and transmission electron microscopy have shown that covalently bound fullerenes are formed as precursors; these structures can proceed toward short inner tube sections with low energy Stone–Wales transformations. This mechanism ensures that carbons do not diffuse along the tube axis, thus our results are a strong support for this kind of growth mechanism.

Alternative models considered the inner tube growth from completely disintegrated fullerenes into e.g. C_2 units [7]. However, in this model strong carbon diffusion along the tube axis would be expected. In contrast, our results show that there is practically no diffusion, which suggests that the growth of the inner tube does not occur by a complete disintegration of the fullerenes, but rather by a Stone–Wales type fusion mechanism.

5 Conclusions

We have performed first principles calculations on the inhomogeneous broadening of the Raman RBM lines of isotope engineered double walled carbon nanotubes, and compared the calculations to our experimental results. We have shown that the broadening grows monotonically with increasing enrichment, peaks at 50% ^{13}C content, then decreases monotonically and drops back to 0 at 100% ^{13}C content. We have found experimentally that if the filling of the peapod is performed with a mixture of enriched and non-enriched fullerenes, the Raman spectra of the resulting inner tubes show a much larger broadening than in the case of the uniform filling method. Our calculations have shown that this finding is consistent with the assumption that the local enrichment level of the double walled tube reflects the local enrichment level of the corresponding peapod material. The good agreement between our calculations and experiments clearly indicates that there is very little diffusion of carbon atoms along the tube axis, supporting the theory that the inner tubes are formed by Stone–Wales transformations from interconnected fullerenes.

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