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Confined adamantane molecules assembled to one dimension in carbon nanotubes

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Abstract

We have encapsulated adamantane ($C_{10}H_{16}$) in single- and multi walled carbon nanotubes. Adamantane is a high symmetry cage like molecule with point group symmetry, T_d and can be considered as a hydrogen-terminated diamond fragment. We confirmed and identified

the successful filling by high resolution transmission electron microscopy, ^{13}C nuclear magnetic resonance, and infrared and Raman spectroscopy. ^{13}C nuclear magnetic resonance of the adamantane filled nanotubes reveals that the adamantane molecules stop rotating after encapsulation. A blue-shift of the Raman active radial breathing modes of the carbon nanotubes supports this and suggests a significant interaction between encapsulated adamantane molecules and the single wall nanotubes. The encapsulated adamantane molecules exhibit red shifted infrared C-H vibration modes which we assign to a slight elongation of the C-H bonds. We observe both a nanotube diameter dependence of the adamantane fill ratio and a release rate of adamantane from the CNTs that depends on the CNT diameters.

1. Introduction

Diamondoids is an attractive class of hydrocarbon that are fully sp^3 hybridized and can be visualized as hydrogen-terminated nanosized diamond fragments[1]. Diamondoids are well known for their outstanding thermal stability, light weight, and rigidity[1-3]. Few experimental studies have been reported on the diamondoids due to the difficulty to synthesize them[4]. Recently 11 different diamondoids could however be extracted from sludge formed in oil industry[1]. The smallest diamondoid is adamantane (Figure 1). It consists of 10 carbon atoms arranged as a single diamond cage surrounded by 16 hydrogen atoms[5, 6] with point group symmetry, T_d . The C-C distance is 1.53 Å which is very close to the C-C distance in diamond, 1.54 Å. The melting point is 269 °C but adamantane sublimates readily already at room temperature due to its high vapor pressure.

Figure 1. Molecular structure of adamantane. Blue spheres represent hydrogens and white spheres represent carbons.

The unique structures of diamondoids together with their chemical and physical stability make them to promising candidates as building blocks for self assembled processes.

Nanoscale electromechanical systems (NEMS) represent one of the most attractive fields

of nanotechnology. In order to construct functional elements of diamondoid-based NEMS devices a controllable method to arrange and possibly connect the diamondoids with strong bonds is desirable. An intriguing possibility is to use carbon nanotubes (CNT) as vessels in the same way as for fullerenes[7-14], polymers[15] and other organic[13, 16-18] and inorganic materials[19-22]. Very soon after their discovery the nanotubes were proposed as possible nano sized vessels for chemical reactions [23, 24]. Although this progress has been partly hindered due to difficulties to probe the reactions inside the single walled carbon nanotubes (SWCNTs) some experimental studies in this direction have been reported lately [15, 25-28]. As suggested by McIntosh et al the nanotubes encapsulating the diamondoids may both guide the molecules into an ordered arrangement and in particular suppress the free rotation of the diamondoids[3]. We report here a study of single- and multi-walled carbon nanotubes filled by adamantane, the smallest of the diamondoids. Our focus is to understand the filling and release mechanism, the interactions between the encapsulated adamantane molecules and the nanotube walls, the mutual interactions between the adamantane molecules and their dynamical properties in their confined state. We show that the filling of the molecules can be achieved at relatively low temperature in the gas phase (190 °C) and that the filling depends on nanotube diameters. From nuclear magnetic resonance (NMR) measurements we conclude that the interaction between the adamantane molecules and the nanotubes hinders the normally free rotation of the adamantane molecules. This is different from C₆₀ encapsulated inside SWCNTs which retain their free rotation to lower temperatures compared to their normal bulk crystalline state[29]. Consistent with the NMR results we observe a blue shift in the radial breathing Raman modes which also indicate some interaction between adamantane molecules and

the interior wall of SWCNTs. For large diameter tubes the adamantane can be released with time even at room temperature. To confirm a successful filling and to study the nanotubes and the encapsulated adamantane molecules, we have employed a large set of techniques including Raman spectroscopy, infrared spectroscopy (IR), high resolution transmission electron microscopy (HRTEM), and ^{13}C nuclear magnetic resonance (NMR).

2. Experimental

Three different types of nanotubes were used for filling experiments; i) MWCNT-1 (Nanocyl Inc., Belgium) with a distribution of internal diameters of 1.0–3.0 nm and a length in the range of several to tenths of micrometers, ii) HP-SWCNTs (Nanostructured & Amorphous Materials Inc, USA) produced by HiPCO process with diameters of 0.8–1.2 nm, and iii) Arc-SWCNTs (Carbon Solutions, Inc. (Batch #AP265) and Fr-SWCNTs (Nanoledge Inc., Montpellier, France)) produced by arc-discharge with diameter 1.3-1.6 nm. The lengths of the single walled nanotubes were not specified from the manufacturer but are usually several micrometers long estimated from TEM observations. The two arc discharge samples are very similar both in their characteristics and the results for the filling. Therefore the results for these are generalized and referred to as Arc-SWCNTs. The HP-SWCNTs and the MWCNTs are purified already when received and were only treated in the opening process whereas the arc-discharge SWCNTs are purified in our lab before filling experiments. In brief, the SWCNTs samples were heated at 290 °C for 12 hours in a furnace, followed by an acid-treatment (HCl, 37%) for an hour at 80 °C in an ultrasonication bath. After filtration and washing with deionized water and a drying process, the purified samples form a paper-like morphology. To open the nanotube caps all

samples were heated in air for one hour (425 °C for SWCNTs and 450 °C for MWCNTs). Prior to use, the CNT samples were degassed at 220 °C for 6 hours under dynamic vacuum (10^{-6} torr), and then transferred into an Argon-filled glove-box without contact to air. Stoichiometric amounts (usually 2:1 in weight) of adamantane and CNTs were inserted into separate parts of U-shaped glass tubes and sealed in a dynamic vacuum (10^{-6} torr). We have tested a range of temperatures for the filling, from 450 to 150 °C and found that the optimum temperature is 190 °C. The samples were heated at 190 °C for 72 hours. Before and after filling the samples were characterized by Raman spectroscopy (Renishaw 1000 single grating spectrometer), IR spectroscopy (Perkin Elmer II) working in dry N₂ atmosphere, transmission electron microscopy (JEM-2010F, Japan) with working voltage of 200 KeV and ¹³C solid state magic angle spinning nuclear magnetic resonance (NMR MAS). Infrared spectroscopy was conducted on solid samples pressed by an ATR crystal. NMR was conducted on a Bruker AMX2 500 spectrometer operating at 125.77 MHz in a 4 mm rotor at room temperature and spinning rates about 10 kHz. The powder samples, typically around 10 mg, were filled into the NMR rotors inside an argon filled glove box. All spectra were recorded using a Hahn echo pulse sequence ($\pi/2$ pulses of 4 micro seconds) synchronized with the spinning rate which is particularly adapted to detect broad lines generally observed in CNT materials and to carefully determine the baseline. Sampling time between pulses, τ , was 30 s.

Figure 2. HRTEM image of (a) the end and (b) the middle section of MWCNTs filled with adamantane; (c) pristine, empty SWCNTs; (d) filled SWCNTs (Arc-SWCNTs) and (e) the end of the filled SWCNTs.

3. Results and discussion

Figure 2 shows HRTEM pictures of filled MWCNTs (a), (b), empty Arc-SWCNTs (c) and filled Arc-SWCNTs (d), (e). Both the open end (tip) and the middle part of the nanotubes can be seen. Picturing the encapsulated adamantane molecules with HRTEM is very challenging due to the low contrast between adamantane and the nanotubes and the non spherical shape of adamantane (as opposed to for example C_{60} molecules). Nevertheless the HRTEM pictures for the adamantane filled samples do reveal features that indicate a successful filling. For the untreated samples these features could not be observed. In figure 2e we have “highlighted” the positions of eight encapsulated adamantane molecules at the end of an opened SWCNT by pointing arrows. We have modeled this by inserting eight adamantane molecule with a structure obtained from molecular mechanics simulations into a (10, 10) SWCNT with a diameter of 1.38 nm (see inset 2e). The average intermolecular distance determined from HRTEM for the eight molecules is 9.3 Å. This is slightly lower than the corresponding intermolecular distance between C_{60} molecules (about 10 Å)[30]

and agrees well with the smaller molecular diameter of adamantane (6.4 Å) [31] compared to C₆₀ (7.0) Å. Different from fullerene peapods where the fullerenes have been shown to be packed in ordered arrangements[10], no ordering can be distinguished for adamantane molecules inside the nanotubes by HRTEM. This could partly come from the low contrast making it hard to distinguish the individual molecules inside of the HRTEM. In the MWNTs we also see some signs of degradation of the adamantane molecules under the electron beam. Due to the contrast problem between the adamantane molecules and the nanotubes it is rather difficult to estimate the filling factor. We have tried to do this by comparing the contrast between filled and unfilled nanotubes and by this way we estimate that roughly 70-80 % of the MWCNT:s are filled. For the SWCNTs the situation is even more difficult and we cannot give any reliable filling ratio. In conclusion we find that the NMR pictures do support the successful filling of adamantane but that other characterization techniques are necessary to confirm this. Below we present Raman, infrared and NMR spectroscopy measurements of our treated samples which all give strong support for a successful encapsulation of adamantane in the carbon nanotubes.

3. 1. Infrared spectroscopy

Figure 3. IR spectra of I), crystalline adamantane II), adamantane treated HP-SWCNTs III) filled MWCNTs, IV) filled Arc-SWCNTs and V) empty HP-SWCNTs.

Figure 3 shows the IR spectra of the empty SWCNTs (HP-SWCNTs and Arc-SWCNTs are identical and therefore only the HP-SWCNTs are shown), three different kinds of filled CNTs and a crystalline adamantane sample for comparison. Carbon nanotubes exhibit a broad absorption over the whole range from 600 cm^{-1} to 4000 cm^{-1} due to a strong optical density in the infrared region. Adamantane has its most intense IR bands around 2900 cm^{-1} , assigned to the C-H vibrations in adamantane. In this region the interference from CNTs is lower and in all the spectra of the filled samples, the C-H vibrations are clearly visible while it is absent in the spectrum of the empty SWCNTs. Analyzing the IR spectra more in detail reveals that the C-H vibrations of the adamantane molecules are red-shifted when encapsulated in the Arc-SWCNTs and in the MWCNTs (see figure 3). No red shift can be observed for the adamantane molecules in the HP-SWCNTs and the reason for this will be

discussed later. The red shift of the C-H vibrations is about 11 cm^{-1} (to lower wave numbers) compared to crystalline adamantane. A comparable ($15\text{-}19\text{ cm}^{-1}$) red shift was observed for Si-H vibrations in $\text{H}_8\text{Si}_8\text{O}_{12}$ molecules encapsulated inside single and multiwalled carbon nanotubes with similar diameters as in our study[32]. Probable explanations for the lower red shift for encapsulated adamantane compared to $\text{H}_8\text{Si}_8\text{O}_{12}$ are the slightly smaller size of the adamantane molecules ($6.36\text{ \AA}$) compared to the $\text{H}_8\text{Si}_8\text{O}_{12}$ molecule ($6.6\text{ \AA}$) and the different bond structure. In the study by Wang et al[32] the red shift was rationalized by an elongation of Si-H bonds due to the interaction between the molecules and CNTs walls.

3. 2. Raman spectroscopy

Figure 4. a) Raman spectra showing the regions around the G-mode, D-mode and the RBM mode of empty Arc-SWCNTs (I) and adamantane filled Arc-SWCNTs (II). The RBM region has been multiplied by a factor 10 for clarity; b) Raman spectra of

empty Arc-SWCNTs (I), adamantane filled Arc-SWCNTs (II) and adamantane (III).

Figure 4a shows the Raman spectra for the pristine Arc-SWCNTs (I) and the filled Arc-SWCNTs (II). In figure 4b we show the same spectra again in an expanded region and have also added a spectrum for crystalline adamantane (III). The empty pristine nanotubes (I) reveal a typical Raman spectra with lines in three characteristic regions; i) a high frequency tangential G-band with a peak at 1590 cm^{-1} and shoulder peaks around 1567 and 1551 cm^{-1} , ii) low frequency radial breathing modes(RBM) at $100\text{-}300\text{ cm}^{-1}$, and iii) a defect-induced D-band at 1350 cm^{-1} . The low intensity of the D-band indicates a low defect concentration in the SWCNTs. In addition to these Raman modes some weaker lines assigned to SWCNT vibrations are also observed[33]. Comparing the pristine (I) and the filled SWCNTs (II), we observe no new peaks in the spectrum of the filled SWCNTs but a clear change in the RBM region. Analyzing our data with a peak fit program (PeakFit 4.12) reveals that the pristine SWCNTs have RBM peaks at 149.3 , 164.8 , 174.9 and 184.2 cm^{-1} , corresponding to the SWCNTs with diameters of about 1.65 , 1.48 , 1.39 and 1.31 nm , respectively[33]. In the Raman spectrum of the filled SWCNT sample these RBM peaks are blue-shifted to 154.1 , 168.0 , 180.0 and 186.6 cm^{-1} after encapsulation of adamantane (see inset figure 4a. In addition to the shift in RBM frequency also a change in the RBM peak intensity is observed. A shift of the RBM modes in the SWCNTs can reveal important information about the interaction of the encapsulated molecules and the SWCNT walls. The observed blue shift for our filled SWCNT samples agrees well with earlier reports of SWCNTs filled with similar organic molecules such as hexamethylelamine[34] (HMM) and $\text{C}_{60}\text{-C}_3\text{NH}_7$ [35]. Encapsulation of both these molecules induces a similar blue shift for the SWCNT RBM modes as do the adamantane molecules. This differs from the induced

red shift of SWCNTs filled with ordinary C_{60} [9] and C_{70} [36] molecules and points out that the interaction between the two classes of molecules are different. The very low rotational transition temperature from free rotation to a ratcheted motion of encapsulated C_{60} (< 100 K)[29, 37] compared to the significantly higher (260 K) transition of C_{60} s in crystals agrees well with this interpretation. This is also further discussed in the NMR section.

In figure 4a we see further that the G-band of the filled Arc-SWCNTs is unaffected by inserting the adamantane molecules. This is different from the effect on the G-band of the HP-SWCNT (not shown) which is discussed below. The G-band has been shown to be affected by a charge transfer to the SWCNTs[38] as well as by a wrapping of SWCNTs by molecules on the outside of the tubes[39]. The unaffected G-mode thus indicates that neither of these effects is present in the Arc-SWCNTs. It should be noted however that both these effects give relatively weak effects on the G-band and to observe a possible p-doping from the adamantane as predicted theoretically[3] direct electrical measurements are probably necessary. The Raman spectrum of the filled SWCNTs reveals only very weak signals from the adamantane. Considering the earlier discussion together with the strong support of encapsulated adamantane from the infrared measurements and the nuclear magnetic resonance data (as discussed below) this rather indicates that the adamantane signal is suppressed due to a screening effect from the CNTs. Such significant weakening of the Raman signal of encapsulated molecules in carbon nanotubes is also observed in earlier reports[12, 34].

For the filled MWCNTs, we find no obvious difference between the Raman spectra before and after filling (not shown). Since the differences for the SWCNTs can only be observed in the RBM modes and MWCNTs usually do not show any such modes, the Raman data

cannot be used to gain information about the adamantane filling for this system. The Raman spectrum of the “adamantane treated HPSWCNTs” also reveals a much weaker effect (not shown). Only for the RBM modes representing the larger diameter tubes we could observe a slight blue shift. For the G-band there is however a slight up shift in the G-band frequency and an increase in the D-band intensity. We rationalize this by that the adamantane in this type of nanotube sample probably are positioned outside the nanotubes explaining the effect on the G-band up shift by a wrapping effect. This is also consistent with the absent red shift in the adamantane infrared vibrations. The diameter of adamantane in solution has been determined to be 6.36 Å[31] and taking into account that the radii of C and H atoms are 0.15 nm and 0.12 nm, CNTs should have a diameter larger than 1.18nm ($0.636 + 0.12 \times 2 + 0.15 \times 2$) to host the model molecules. The much lower diameter ~1nm of the HP-SWCNT than the Arc-SWCNTs (1.3-1.6 nm) thus explains the low success in filling these tubes.

3. 3. Nuclear Magnetic Resonance

Figure 5 shows the NMR MAS spectra of pristine adamantane (I), empty Arc-SWCNTs (II), filled Arc-SWCNTs (III), empty MWCNTs (IV) and filled MWCNTs (V). The ^{13}C signal of adamantane (I) contains two sharp signals located at 38.5 and 28.5. The sharp signals are consistent with the orientational disorder of adamantane molecules in crystal form similar to the C_{60} molecules in crystalline C_{60} . The NMR signal of purified and opened but empty SWCNTs (II) show the expected relatively broad signal centered at 124 ppm assigned to the carbons in the SWCNTs. A weak shoulder at the right is assigned to graphitic flakes not removed by the purification. The NMR spectrum of the empty MWCNTs (IV) shows an even larger broadening as expected for a MWCNT sample[40].

The NMR signal of the filled SWCNTs (III) and the filled MWCNTs (V) show in addition to the signal assigned to SWCNT and MWCNT carbons also a broad distribution downshifted with respect to the signal of pristine adamantane.

Figure 5. ^{13}C NMR of I) adamantane, II) empty Arc-SWCNTs, III) adamantane filled Arc-SWCNTs, IV) empty MWCNTs, and V) adamantane filled MWCNTs

We can draw two important conclusions from these results; i) the down field shift of the adamantane carbons unambiguously show that the adamantane is located on the inside of the nanotubes and thus experience a diamagnetic shift due to ring currents at the nanotubes envelope[26, 41], ii) the adamantane molecules are now static manifested by a significant broadening of the signal. Similar observations have been reported for fullerenes[29, 37] and hydrogenated fullerenes[26] encapsulated in carbon nanotubes. It is likely that the change in the dynamics of the adamantane molecules after encapsulation probably comes from the interaction with the SWCNT walls. Especially the similarity in behavior with hydrogenated fullerenes encapsulated in SWCNTs supports this assumption[26]. The

broadening of the adamantane signal could of course also stem from decomposition of adamantane molecules inside SWCNTs and thereby give rise to a broader distribution of NMR signals. The IR spectra of the filled materials however do not support such decomposition as the relative intensity of the adamantane IR bands from the filled samples keeps their original ratio as in the adamantane crystal. The shift to lower field of the signal representing encapsulated adamantane molecules inside MWCNTs compared to the corresponding signal of the adamantane molecules in SWCNTs (spectrum III and V) is also in excellent agreement with the stronger diamagnetic shielding due to the encapsulation inside multi walled carbon nanotubes (larger screening) compared to in single walled nanotubes^[42].

The NMR spectrum of the filled SWCNTs also contains a signal at 143 ppm. Currently we have no explanation for this signal. It is well known that a signal at this position can be assigned to C_{60} . We have made systematic studies of the pristine SWCNT samples and we have not been able to find any signs of C_{60} in the raw samples which has been shown to be a possible “impurity” in arc discharge synthesized SWCNTs^[43] (note the absence in the NMR spectrum of the empty SWCNTs). In contrast we have observed this signal in two adamantane filled Arc-SWCNT samples. Intuitively some of the encapsulated adamantane could dissociate and form new compounds. The interior space of the nanotubes has been shown to facilitate the transformation from C_{60} peapod structures to double walled nanotubes^[44, 45] but we believe that the temperature is too low for similar processes to occur in our samples. Also the signal at 143 ppm rather indicates that the signal can be assigned to small fractions of C_{60} outside the CNTs, since we can see no diamagnetic shift of the C_{60} line due to ring currents at the nanotube envelopes. We are investigating this

further to find an explanation.

3. 4. *Releasing of Adamantane*

Infrared spectroscopy was found to be the best technique to probe the state of the adamantane molecules and therefore we used this technique to further probe the adamantane filled samples. A mixture of adamantane and Arc-SWCNTs was prepared for comparison by grinding for long time. This is expected to produce a sample where the adamantane is located outside the SWCNTs. For this sample the IR signal of adamantane is very strong even at very low concentrations as 1:20, and no shift in the infrared bands can be observed.

Figure 6. IR spectra of (I) as-prepared adamantane-SWCNTs mixture and the samples after heating at 100 C for 1 hour (II) filled arc-SWCNT; (III) filled MWCNT; (IV) adamantane-SWCNTs mixture; (V) adamantane treated HP-SWCNTs. The position marked with triangle is showing the position of the band assigned to adamantane and the two peaks marked with asterisk are from new C-H vibrations.

To test the stability of our adamantane filled carbon nanotubes we have performed a heat treatment of the samples in ambient atmosphere. It is expected that the thermal stability of encapsulated molecules inside a nanotube (especially for a suitable cavity size) is higher than those outside. Figure 6 shows that after heating at 100 °C for 1 hour, we can hardly detect the IR vibration signal of adamantane in MWCNTs, HP-SWCNTs and the mixture sample while the IR signal of adamantane is still present in the filled arc-SWCNTs. The remaining peak to the right and left in the spectra (marked by asterisk) we assign to new C-H bonds in the nanotubes, probably by reaction of moisture or air (or dissociated adamantane) with defect radicals on the nanotube. Similar results with a decrease in the adamantane signal in the MWCNTs were obtained also at lower temperatures and after long time storage in room temperature (not shown). In the Arc-SWCNTs however the signal was still present after six months of storage. These results indicate that adamantane located on the outside of the nanotubes or inside large cavity tubes can be released by temperature treatment. This mechanism could potentially be used in drug delivery systems^[46], especially since diamondoid derivatives where hydrogen atoms have been replaced by NO_3^- , Cl^- , Br^- have shown potential as cancer treatment medicine^[47].

4. Conclusions

We have demonstrated that adamantane, an interesting form of caged hydrocarbons, can be efficiently inserted into SWCNTs with diameters of 1.3–1.6 nm (arc-SWCNT) and MWCNTs with internal diameters of 1.0–3.0 nm but that the filling of nanotubes with diameters of 0.8–1.2 nm is unsuccessful. This is consistent with an estimated minimum diameter of 1.18 nm required for insertion of adamantane. Similar diameter selectivity has been observed for metallocenes[17].

All our results consistently indicate that the interaction between the adamantane molecules and the carbons in the nanotube walls is different from that, for example, between C₆₀ and SWNTs. This is first of all manifested by ¹³C NMR Magic Angle Spinning experiments which reveal that the adamantane molecules become static after encapsulation. Both infrared measurements and Raman measurements support these results. The possibility to fill nanotubes with adamantane open up new roads to perform further reactions on these molecules as pointed out in earlier theoretical studies[3]. We note that polymerization of the adamantane inside the nanotubes by for example applying high pressure and high temperature could be of particular interest. A similar molecule cubane, C₈H₈, has been shown to form polymer bonds between the carbon dices after release of hydrogen at high pressure and high temperature[48]. The formation of low dimensional diamonds inside carbon nanotubes would be an important contribution to the field of nanostructured carbons and could probably be probed by in situ resistance measurements^[49].

The release of adamantane from carbon nanotubes is observed with a rate depending on temperature and the diameter of CNTs, in which faster release in MWCNTs could be related to its bigger cavity and thus weaker interaction between adamantane and nanotube wall. We note however that the adamantane signal is similar in the filled Arc-SWCNTs as in the filled MWCNTs. This either indicate that although the adamantane molecules can be released from MWCNTs they are still static on the NMR time scale, giving a broad ¹³C-signal or that the sharp signal representing “free” adamantane molecules is drowning in the broad envelope of the signal representing molecules that are static.

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