Deuterium Attachment to Carbon Nanotubes in Deuterated Water

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Abstract: A systematic investigation on the unusual attachment of labile deuterium to carbon nanotubes in deuterated water and alcohols is reported. The carbon nanotubes were solubilized through the established functionalization of the nanotube-bound carboxylic acids to allow solution-phase reaction and characterization. The deuterium attachment was found under several experimental conditions, including the use of deuterated ethanol as a co-reactant in the nanotube functionalization reaction and the refluxing of functionalized or simply purified carbon nanotubes in deuterated water and alcohols. The solubility of the functionalized carbon nanotube samples in common organic solvents and water allowed unambiguous ^{2}H NMR characterization. The reproducible broad ^{2}H NMR signal at ~6.5 ppm is assigned to carbon nanotube-attached deuterium species. The assignment is supported by the results from FT-IR measurements. The carbon−deuterium interaction is so strong that the corresponding vibration resembles the typical C−D stretching mode in the characteristic frequency region. The FT-IR peak intensities also correlate well with the ^{2}H NMR signal integrations in a series of samples. Mechanistic implications of the results are discussed.

Introduction

The functionalization and solubilization of carbon nanotubes have made it possible to study their properties and chemical reactivities in solution.[1−5] In particular, carbon nanotubes may be functionalized at the defect sites, typically through the use of the nanotube-bound carboxylic acids for attaching oligomeric or polymeric functional groups.[1,2a] The functionalization reactions with the acids include amidation, esterification, and carboxylate−ammonium salt ionic interactions, and the functionalities include long alkyl chains, lipophilic and hydrophilic dendra, and polymers. The approach is applicable to both shortened and as-prepared single-walled (SWNT) and multiple-walled (MWNT) carbon nanotubes. These functionalized carbon nanotubes retain the graphitic surface structure for further addition-like reactions.

Several addition reactions of carbon nanotubes have been reported.[3−11] Of particular interest and importance is the hydrogenation of carbon nanotubes[10,11] because it not only represents the most basic addition to the nanotube graphitic surface but also is highly relevant to applications such as hydrogen storage.[12−14] According to Pekker et al.,[10] the addition of hydrogens to nanotubes could be achieved in the Birch reduction reaction, with the hydrogenated derivatives being thermally stable up to 400 °C and the estimated coverage of hydrogen atoms on the nanotube surface being ~9% for both SWNTs and MWNTs. Khare et al. reported the hydrogenation and deuteration of SWNTs using the atomic hydrogen and deuterium generated in cold plasma.[11] Their characterization of the hydrogenated and deuterated SWNTs was based primarily on FT-IR measurements, with the observation of absorptions corresponding to the C−H and C−D stretching vibrational

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modes.[11] Recently, we found that deuterium could be attached to carbon nanotubes in the functionalization reactions using deuterated alcohol as a reactant.[15] The labile deuterium was identified as the deuterium source by comparing the results from the reactions with selectively deuterated alcohols. The functionalized carbon nanotube samples were characterized by solution-phase ^{2}H NMR, with the spectra exhibiting a reproducible broad signal in the aromatic region (centered at $6.5-6.7$ ppm). The NMR and corresponding FT-IR results have been explained in terms of the attachment of deuterons to the carbon nanotube surface.[15]

The observed facile attachment of labile deuterium is an indication for unusual surface properties of carbon nanotubes, which may have broad implications. For example, this is highly relevant to the widespread interest in the use of carbon nanotubes for hydrogen storage and the ongoing debate on the hydrogen adsorption mechanism related to the storage applications.[14] In an effort to achieve a better understanding of the unique phenomenon, we have carried out a systematic study by using deuterated water as a labile deuterium source for the strong interactions with carbon nanotubes in solution. Practically, carbon nanotubes are often processed in aqueous suspensions for purification and other purposes. The similar hydrogen attachment may affect some investigations of the carbon nanotubes thus processed and should be taken into consideration in those experiments and data interpretations.

Reported here are results of the deuterium attachment to carbon nanotubes in aqueous solution and a comparison to those in the alcohols. These results were from the characterization of the deuterium-attached-functionalized SWNTs and MWNTs by using NMR, FT-IR, and other optical spectroscopy and electron microscopy techniques, the correlation of different characterization methods, and the determination of deuterium contents in the carbon nanotube samples and their dependence on reaction conditions.

Experimental Section

Materials. Thionyl chloride (99%) was purchased from Acros. Deuterated compounds and solvents were obtained from Cambridge Isotope Laboratories. Organic solvents were either of spectrophotometry/HPLC grade or purified via simple distillation. Dialysis tubing of various cutoff molecular weights was supplied by Sigma.

SWNT and MWNT samples were produced in Prof. A. M. Rao's laboratory (Physics Department, Clemson University) by using the arc discharge and the chemical vapor deposition (CVD) methods, respectively.[16–18] A small quantity of SWNT sample was also produced by using the laser ablation method for comparison.[19] The samples were purified by using the literature procedure based on the nitric acid treatment.[20] Typically, a carbon nanotube sample (1 g) was suspended in an aqueous HNO_3 solution (2.6 M, 200 mL) and refluxed for 48 h. Upon centrifuging to remove the supernatant, the remaining solids were washed repeatedly with deionized water until neutral pH and then dried under vacuum. For comparison, some of the purified SWNTs were further purified via cross-flow filtration, as was already reported in the literature.[21,22]

Measurements. NMR spectra were obtained on a JEOL Eclipse +500 NMR spectrometer. FT-IR measurements were carried out in solution (carbon tetrachloride as solvent, which is well known for use in the concerned frequency region) in an optical cell of KBr windows and a fixed 1-mm optical path-length. The spectra were recorded on a Nicolet Magna-IR 550 spectrometer. The solvent background (not so significant) was corrected. Scanning electron microscopy (SEM) analysis was conducted on a Hitachi S4700 field-emission SEM system. Transmission electron microscopy (TEM) images were obtained on a Hitachi HF-2000 TEM system equipped with a Gatan Multi-Scan CCD camera for digital imaging.

Deuterium Attachment. The synthetic procedures and characterization results have already been reported for the functional group I_{PEG}[23] and the functionalized carbon nanotube samples I_N-SWNT,[23] I_N-MWNT,[23] PEG_{1500N}-SWNT,[24] and PPEI-EI-SWNT[25] (Figure 1).

Deuterated alcohols and water were used in reactions either for the functionalization of carbon nanotubes (I_{PEG}-SWNT-ethanol-d_6) or with the functionalized carbon nanotube samples (all other deuterium-attached compounds).

I_{PEG}-**SWNT-ethanol-d_6.** In a typical experiment, a purified SWNT sample (15 mg) was refluxed in thionyl chloride for 24 h. After complete removal of residual thionyl chloride on a rotary evaporator with a vacuum pump, the sample was well mixed with I_{PEG} (300 mg, 0.69 mmol) and ethanol-d_6 (36 mg, 0.69 mmol) in a flask, heated to 70 °C, and vigorously stirred for 48 h under nitrogen protection. After being cooled, the mixture was dissolved in chloroform and centrifuged at a high speed ($\sim$3100g). The remaining sample in the solution was further purified via dialysis against fresh deionized water in a membrane tubing with a cutoff molecular weight of 2000 for 3 days, yielding I_{PEG}-SWNT-ethanol-d_6. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.3 (br), 3.4–4.2 (br), 4.5 (br), 6.2–6.8 (br) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 15.7–16.4, 55.6–55.9, 59.5, 67.3, 67.8, 69.4, 69.7, 69.9, 70.1, 70.5, 70.6, 70.9, 71.7, 97–102, 103–109, 143–144, 159–160 ppm. ^{2}H NMR (77 MHz, CHCl$_3$): δ = 1.3–1.6 (br), 3.3–4.0 (br), 6.1–6.8 (br) ppm.

I_N-**MWNT-ethanol-d_6.** A I_N-MWNT sample (30 mg) was suspended in ethanol-d_6 (0.5 mL) via sonication for $\sim$5 min. The suspension was heated with vigorous stirring and refluxed for 48 h. After being cooled, the mixture was centrifuged at a high speed ($\sim$3100g) to remove any residual solids, followed by Soxhlet extraction with acetone for 24 h to obtain I_N-MWNT-ethanol-d_6. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.7–0.9 (br), 1.1–1.5 (br), 1.7–1.8 (br), 3.2–4.0 (br), 4.6–5.3 (br), 6.0–7.2 (br) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 14.1, 22.9, 26.0, 29.4, 29.5, 29.8, 31.9, 68.1, 71–72, 97–100, 103–106, 112–116, 135–137, 158–161 ppm. ^{2}H NMR (77 MHz, CHCl$_3$): δ = 0.7–1.5 (br), 3.3–3.8 (br), 6.0–7.7 (br) ppm.

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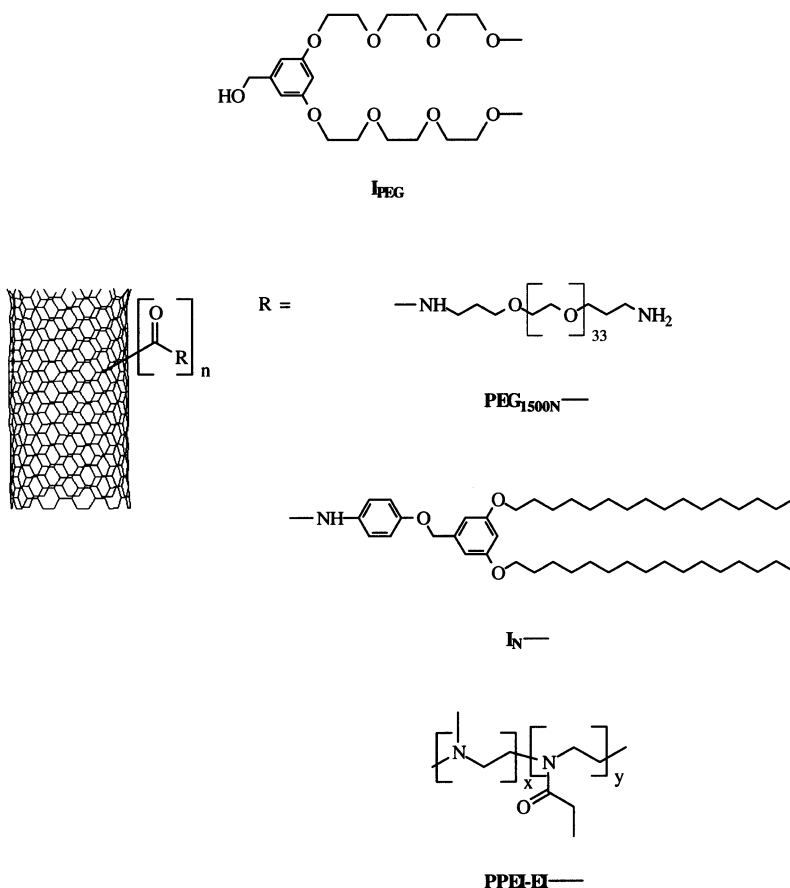(25) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879.

Figure 1. The compound I_{PEG} and the functionalized carbon nanotube samples used in this investigation.

PEG$_{1500N}$-SWNT-D$_2$O, I$_N$-SWNT-D$_2$O, I$_N$-MWNT-D$_2$O, and PPEI-EI-SWNT-D$_2$O. A water-soluble PEG$_{1500N}$-SWNT sample (20 mg) was dissolved in D$_2$O (0.5 mL). The solution was refluxed with stirring for 48 h. Upon cooling, the mixture was centrifuged at a high speed (~3100g). The remaining sample in solution was purified via dialysis against fresh deionized water in a membrane tubing with a cutoff molecular weight of 12 000 for 3 days, yielding PEG$_{1500N}$-SWNT-D$_2$O. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.6 (br) ppm. ^{2}H NMR (77 MHz, CHCl$_3$): δ = 6.2−6.9 (br) ppm.

The same reaction procedure was applied to the preparation of I$_N$-SWNT-D$_2$O and I$_N$-MWNT-D$_2$O, except that the sample purification was carried out via Soxhlet extraction with acetone for 24 h. For the SWNT sample, ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.83 (t, J = 6.5 Hz), 1.1−1.5 (br), 1.7−1.8 (br), 3.2−3.9 (br), 4.6−5.2 (br), 6.1−7.2 (br) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 14.1, 22.7, 26.4, 29.4, 29.6, 29.8, 32.0, 68.1, 71−72, 97−100, 104−106, 113−116, 135−137, 157−160 ppm. ^{2}H NMR (77 MHz, CHCl$_3$): δ = 5.7−7.7 (br) ppm. For the MWNT sample, ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.85 (t, J = 6.5 Hz), 1.1−1.5 (br), 1.7−1.8 (br), 3.2−4.1 (br), 4.6−5.2 (br), 6.1−7.1 (br) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 14.1, 22.5, 26.5, 29.3, 29.6, 29.8, 32.2, 68.1, 71−72, 97−100, 104−106, 113−116, 135−137, 157−160 ppm. ^{2}H NMR (77 MHz, CHCl$_3$): δ = 5.6−7.2 (br) ppm. The I$_N$-MWNT-D$_2$O samples of different deuterium contents were also prepared by using the same reaction conditions but different reaction times.

Both low ($M_W \approx$ 2800) and high ($M_W \approx$ 200 000) molecular weight PPEI-EI-functionalized SWNT samples were reacted with D$_2$O under the same experimental conditions. However, only the former resulted in the deuterium attachment, yielding PPEI-EI-SWNT-D$_2$O. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.7−1.5 (br), 1.9−2.5 (br), 2.7−2.9 (br), 3.2−4.2 (br) ppm. ^{2}H NMR (77 MHz, CHCl$_3$): δ = 6.1−7.1 (br) ppm.

Results and Discussion

We reported recently that when the functionalization of SWNTs with the dendron 3,5-dihexadecanoxybenzyl alcohol (**I**) was carried out in an esterification reaction in the presence of deuterated ethanol, there was essentially the "addition" of deuterium to the carbon nanotube.[15] Selectively deuterated alcohols including CD$_3$CD$_2$OD, CH$_3$CD$_2$OH, and CH$_3$CH$_2$OD were used under the same reaction conditions. The results suggested that the labile deuterium was responsible for the unusually strong interactions with the carbon nanotube.[15] In an effort to examine the deuterium attachment under other reaction conditions, ethanol-d_6 was used as a co-reactant in the functionalization of SWNTs with **I$_{PEG}$** via acylation-esterification. The soluble sample thus obtained, **I$_{PEG}$**-SWNT-ethanol-d_6, allowed solution-phase ^{2}H NMR characterization. The ^{2}H NMR spectrum is similar to that of the soluble **I**-SWNT-ethanol-d_6 sample reported previously, which are compared in Figure 2.

The deuterium attachment is not limited to the use of the labile deuterium source as a co-reactant in functionalization reactions. It is also readily accomplished by reacting functionalized carbon nanotube samples with ethanol-d_6 or ethanol-d_1. A typical reaction condition is to reflux the functionalized carbon nanotube sample with the alcohol. Thus, to maintain the chemical stability of the sample, the functionalized carbon nanotubes in which the functionalization is through amide linkages are preferred in the reaction for deuterium attachment. For example, the soluble **I$_N$**-MWNT sample was used as the starting material to be refluxed with ethanol-d_6. The amide linkages for the functional groups are stable under the refluxing
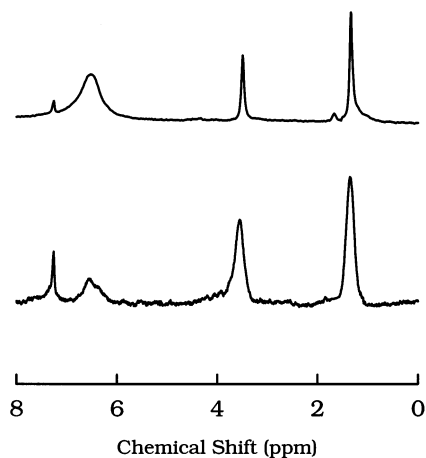
Figure 2. The ^{2}H NMR spectra of **I**-SWNT-ethanol-d_6 (top) and **I$_{PEG}$**-SWNT-ethanol-d_6 (bottom) samples in room-temperature chloroform solution. The samples were obtained from the cofunctionalization.
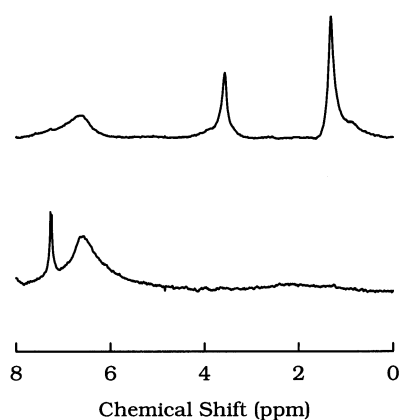

Figure 3. The ^{2}H NMR spectra of **I$_N$**-MWNT-ethanol-d_6 (top) and **I$_N$**-SWNT-D$_2$O (bottom) samples in room-temperature chloroform solution. The samples were obtained from refluxing the functionalized carbon nanotubes in ethanol-d_6 and D$_2$O.

condition, thus minimizing the possibility for any transesterification (ethanol replacing the functional group) that might reduce the sample solubility. The reaction product thus obtained, denoted as **I$_N$**-MWNT-ethanol-d_6, was characterized by ^{2}H NMR. The spectrum exhibits the characteristic broad signal at ~6.5 ppm (Figure 3), assignable to the deuterium attached to the carbon nanotube. Apparently, the deuterium attachment to the carbon nanotube is not hindered by the oligomeric functional groups on the nanotube surface.

The deuterium attachment to functionalized carbon nanotubes requires the presence of a labile deuterium in the alcohol, ethanol-d_6 or ethanol-d_1 but not ethanol-d_2.[15] It prompted the idea that deuterated water could also serve as a labile deuterium source. Indeed, refluxing the functionalized carbon nanotubes in D$_2$O also resulted in the same deuterium attachment. For example, the water-soluble sample PEG$_{1500N}$-SWNT was refluxed with D$_2$O for 48 h. The resulting sample PEG$_{1500N}$-SWNT-D$_2$O was characterized in solution-phase ^{2}H NMR measurements. The same broad signal around 6.5 ppm in the ^{2}H NMR spectrum is again assignable to the deuterium attached to the carbon nanotube.

In addition to PEG$_{1500N}$-SWNT, other functionalized carbon nanotube samples including **I$_N$**-SWNT and **I$_N$**-MWNT were used in the reaction with labile deuterium. The same deuterium
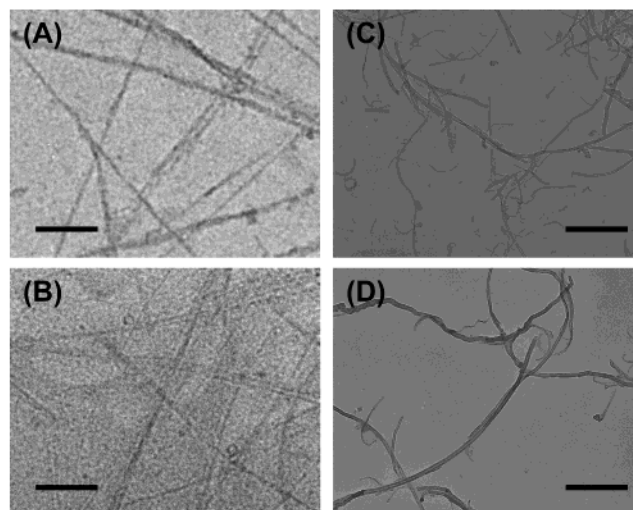
Figure 4. TEM images of the PEG$_{1500N}$-SWNT sample before (A) and after (B) and the **I$_N$**-MWNT sample before (C) and after (D) the reaction with D$_2$O. The scale bars represent 100 nm for (A) and (B) and 500 nm for (C) and (D).

attachment was found in the soluble sample **I$_N$**-SWNT following its being refluxed in D$_2$O. The primary experimental evidence is again the characteristic broad signal at ~6.5 ppm in the ^{2}H NMR spectrum of the **I$_N$**-SWNT-D$_2$O sample (Figure 3). The results suggest that the deuterium attachment is not hindered by a change of the functional groups on the nanotube surface from hydrophilic PEG$_{1500N}$ to hydrophobic **I$_N$**. However, the amide linkages of the functional groups to the nanotubes are essential to the success of the subsequent D$_2$O treatment and the solution-phase characterization. If the functionalized carbon nanotube samples were based on ester linkages, the reaction with refluxing in D$_2$O would result in a partial precipitation of the carbon nanotubes, resembling the situation found in the chemical defunctionalization of functionalized carbon nanotube samples.[23]

The deuterium attachment is not associated with the purity of the carbon nanotube sample. In a comparison, a SWNT sample that had been purified by the nitric acid treatment was further purified via the cross-flow filtration procedure. According to the SEM characterization, the sample obtained from the cross-flow filtration contained considerably less impurities. However, the SWNT samples of the different purity yielded similar deuterium attachment results. Separately, we experimented with the SWNT samples from different preparation methods, arc discharge versus laser ablation, and found that the deuterium attachment results were again similar.

No similar deuterium attachment to carbon nanotubes was found in deuterated solvents containing no labile deuterium, such as ethanol-d_2 and acetone-d_6, under the same experimental conditions.

There is little effect of the deuterium attachment on the physical properties of the functionalized carbon nanotube samples, such as their solubilities in common organic solvents or water and their ^{1}H and ^{13}C NMR results. In addition, the homogeneous solutions of the PEG$_{1500N}$-SWNT and **I$_N$**-MWNT samples before and after the reaction with D$_2$O were used to prepare specimen for TEM analyses. The images thus obtained show that the functionalized carbon nanotubes are similarly well dispersed (Figure 4).
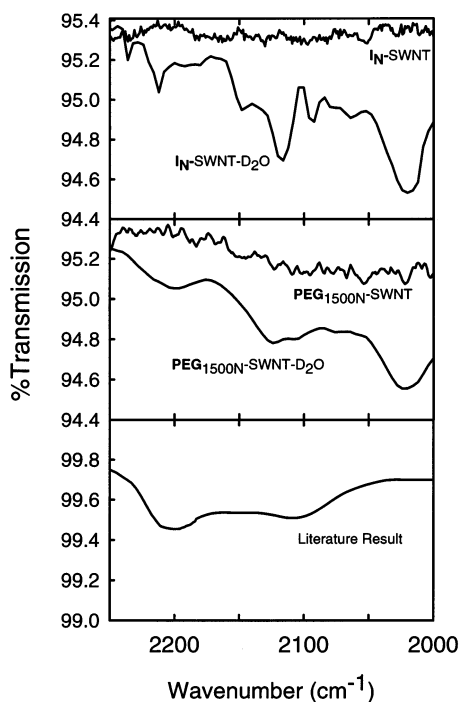
Figure 5. FT-IR spectra of $\mathbf{I_N}$-SWNT (top) and PEG$_{1500N}$-SWNT (middle) samples before and after the deuterium attachment are compared to that of the deuterated SWNTs in the literature (ref 11).

Table 1. FT-IR Results of the Functionalized Carbon Nanotubes after Deuterium Attachment

sample	major FT-IR peaks in the C–D region (cm^{-1})[a]		
$\mathbf{I_N}$-MWNT-ethanol-d_6	2021	2117 (0.4)	broad shoulder
PEG$_{1500N}$-SWNT-D$_2$O	2024	2123 (0.76)	broad shoulder
$\mathbf{I_N}$-SWNT-D$_2$O	2020	2116 (0.82)	2147 (0.49)
$\mathbf{I_N}$-MWNT-D$_2$O	2021	2114 (0.63)	2147 (0.33)
PPEI-EI-SWNT-D$_2$O	2026	2113 (0.66)	2143 (0.47)

[a] The number in parentheses is the intensity relative to that of the first peak.

The assignment of the broad ^{2}H NMR signal at ∼6.5 ppm to the nanotube-attached deuterium is supported by the FT-IR results. The deuterium attachment is so strong that it is detectable as a C−D vibration in the FT-IR spectrum. The C−D stretching mode is generally in the 1900−2300 cm^{-1} region, where there are hardly any contributions from the vibrational modes associated with the C−H and C−O bonds. In fact, the C−D vibration in deuterated fullerenes was studied extensively by using FT-IR.[26] It was concluded that the C−D vibrational frequency in those compounds was generally 2100−2200 cm^{-1}, with the exact position of the absorption band dependent on the deuterium location, number, and sample symmetry.[26] Recent reports on deuterated carbon nanotubes also put the C−D stretching mode in a similar frequency region.[11] For the deuterium-attached carbon nanotube samples in this study, the FT-IR spectra were measured in carbon tetrachloride solutions in an IR cell with KBr windows (1 mm optical path-length). There are a number of absorption peaks in the 1900−2300 cm^{-1} region (Figure 5), with major peaks around 2022, 2117, and 2147 cm^{-1} (Table 1). These peaks may be assigned to the vibrational mode of the C−D stretching under a different molecular environment and/or with different structural configu-
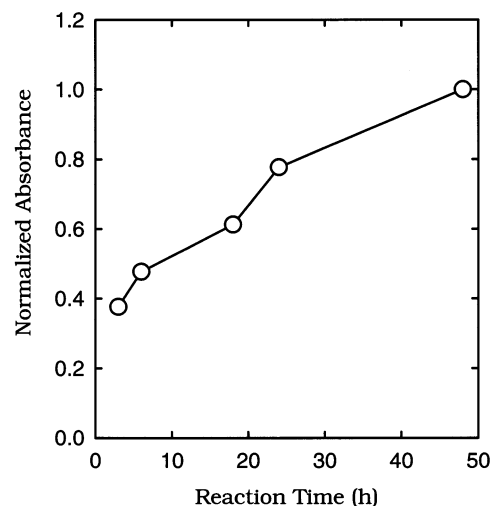
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Figure 6. A series of $\mathbf{I_N}$-MWNT-D$_2$O samples were obtained by refluxing $\mathbf{I_N}$-MWNT in D$_2$O for different lengths of time. Plotted here is a dependence of the IR absorbance at the 2021 cm^{-1} peak on the reaction time.
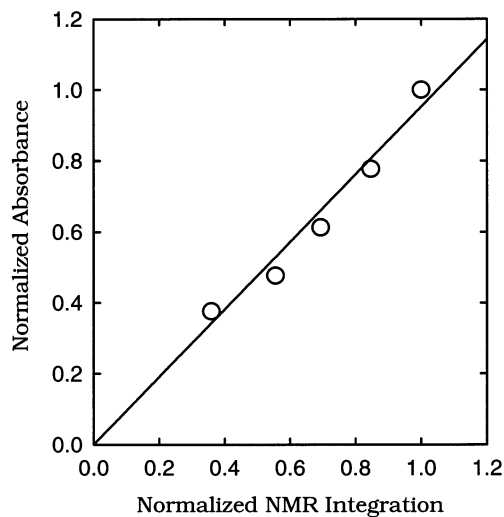

Figure 7. The results in Figure 6 are correlated with the ^{2}H NMR signal (centered at ∼6.5 ppm) integrations for the same series of samples.

rations. The FT-IR results of these samples are comparable to those of the deuterated carbon nanotube samples reported by Khare et al. (Figure 5).[11]

The $\mathbf{I_N}$-MWNT-D$_2$O samples with different degrees of the deuterium attachment were used in the FT-IR study. The samples were obtained by varying the time of refluxing a $\mathbf{I_N}$-MWNT sample in D$_2$O from 3 to 48 h, corresponding to an increasing amount of deuterium attachment. The FT-IR measurements of the samples were again in carbon tetrachloride solutions. As the amount of deuterium in the samples increases, the FT-IR spectra exhibit consistently higher absorbances in all of the C−D vibrational bands. Shown in Figure 6 are the FT-IR results (the 2021 cm^{-1} peak) of the $\mathbf{I_N}$-MWNT-D$_2$O samples obtained with different reaction times. The absorbance clearly increases monotonically with the increase in reaction time. The same series of samples were studied by ^{2}H NMR in a quantitative fashion. The signal at ∼6.5 ppm due to the deuterium attachment exhibits a higher intensity with the increasing reaction time in the sample series. Shown in Figure 7 is a correlation between the ^{2}H NMR signal integration and the FT-IR peak intensity for the series of $\mathbf{I_N}$-MWNT-D$_2$O

Table 2. Deuterium Contents and Deuterium/Carbon (D/C) Ratios in the Functionalized Carbon Nanotube Samples after Deuterium Attachment

sample	deuterium content (wt %/wt)	D/C ratio	
		weight	molarity
I_{PEG}-SWNT-ethanol-d_6	0.12		
I_N-MWNT-ethanol-d_6	0.14	0.014	0.08
PEG_{1500N}-SWNT-D_2O	0.03	0.006	0.035
I_N-SWNT-D_2O	0.17	0.034	0.2
I_N-MWNT-D_2O	0.12	0.012	0.07
PPEI-EI-SWNT-D_2O	0.09	0.018	0.11

samples with different degrees of the deuterium attachment. The obviously well-correlated results suggest that the ^2H NMR signal at ~6.5 ppm is most likely due to the nanotube-bound deuterium species with defined C−D vibrations.

The deuterium attachment to the functionalized carbon nanotubes was quantified by determining the deuterium contents in the samples. The determination was based on the NMR signal integration by using multiple internal standards simultaneously in a chloroform solution, including the natural deuterium abundance in chloroform, CH_3CD_2OH (20 $\mu L/mL$), and DMSO-d_6 (20 $\mu L/mL$). The internal standards were calibrated against each other for consistency. The measurements were repeated at least three times for the reproducibility. The results thus obtained for various samples are shown in Table 2. While the average deuterium contents in the samples appear low, the results should be evaluated in reference to the carbon nanotube contents in the solubilized samples. On the basis of UV/vis absorption and thermal gravimetric analysis results, the nanotube contents in the solubilized SWNT and MWNT samples used in this work are on the order of 5 and 10 wt %, respectively. Thus, the estimated ratio of deuterium to nanotube carbon (D/C) is in the range of 0.6−3.4% in weight or 3.5−20% in molarity.

The deuterium attachment is hindered by the presence of polymeric species on the carbon nanotube surface. For example, when the high molecular weight ($M_W \approx 200\,000$) PPEI-EI-functionalized SWNT sample was refluxed in D_2O for 48 h, no deuterium attachment was observed according to ^2H NMR characterization (Figure 8). However, when the low molecular weight ($M_W \approx 2800$) PPEI-EI-functionalized SWNT sample was used under the same reaction conditions, the ^2H NMR spectrum of the resulting sample exhibits the characteristic deuterium signal at ~6.5 ppm (Figure 8). The experiments were repeated several times, yielding reproducible results. A logical explanation is that the polymeric PPEI-EI provides more effective wrapping of the nanotube, leaving behind a much reduced accessible area on the nanotube surface.[2a,25,27] On the other hand, the nanotube surface coverage by low molecular weight PPEI-EI or other oligomeric functional groups may be less significant, making the deuterium attachment possible.

The experimental evidence presented above apparently points to a rather unusual phenomenon that there is essentially the "addition" of labile deuterium to both SWNTs and MWNTs,[28] with the C−D interactions as strong as in a chemical bond responsible for the vibrations in the characteristic IR frequency
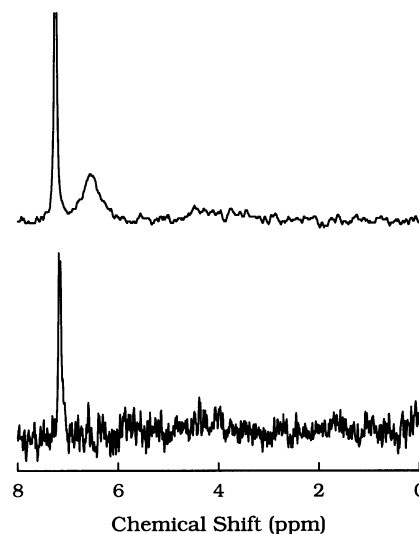
Figure 8. The ^2H NMR spectra of the PPEI-EI-SWNT samples with PPEI-EI molecular weights of 2800 (top) and 200 000 (bottom) after being refluxed in D_2O under the same experimental conditions.

region (Figure 5).[11,15] The structural and mechanistic details on the deuterium attachment remain unclear. However, during the preparation of this manuscript, Dai and co-workers reported that there was charge trapping by water molecules surrounding carbon nanotubes.[29] Their results are consistent with what Ajayan and co-workers found, that the water adsorption on carbon nanotubes decreased the conductance of the nanotubes probably through water−nanotube charge-transfer interactions.[30] We suspect that a similar charge-transfer mechanism might be responsible for the deuterium attachment to functionalized carbon nanotubes in deuterated water and alcohols. We speculate that some part of the nanotube surface is polarized due to the presence of defects and/or a polar solvent environment, with some of the same characteristics as those found in organic ion radicals. Thus, the deuterium attachment is possibly a result of deuteron transfer from the labile source to the ion radical-like nanotube surface carbons.[28] Recently, Hayashi and co-workers reported that there were both ionic and covalent bondings between C and F atoms in the fluorination of MWNTs and that atomic fluorine covers not only the full length of the outer layer but also the inner layer of MWNTs.[31] These reported findings might have a significant implication in the understanding of the seemingly unusual interactions of the labile deuterium with both SWNTs and MWNTs.

The functionalization is not a prerequisite of the deuterium attachment to carbon nanotubes, rather the solubilization as a result of the functionalization makes it possible to detect the deuterium attachment in solution. In fact, there is also deuterium attachment to purified carbon nanotubes before any functionalization. For example, a purified SWNT sample was suspended in D_2O via brief sonication. The suspension was heated with stirring and then refluxed for an extended period of time (typically 48 h). The D_2O-treated SWNT sample was recovered and used in the functionalization reaction with an oligomeric species such as PEG_{1500N}. The functionalized SWNT sample

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(28) We use the word "attachment" instead of addition (C−D binding) because there is no sufficient evidence for the association of a deuterium with only one carbon atom of the nanotube.

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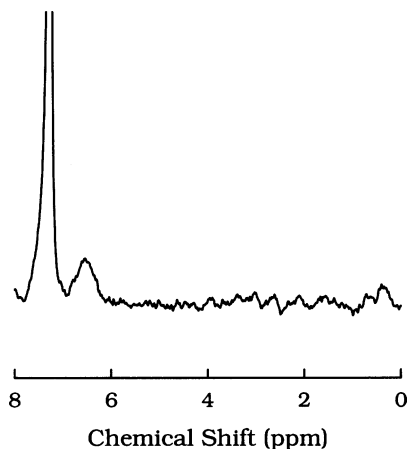
Figure 9. The ^{2}H NMR spectrum of the PEG$_{1500N}$-SWNT-D$_2$O sample obtained by first refluxing the purified SWNTs in D$_2$O and then functionalizing them with PEG$_{1500N}$.

thus obtained from the common reaction and purification procedures was similarly characterized by ^{2}H NMR in solution. The spectrum again exhibits the characteristic broad signal at ~6.5 ppm, indicating the deuterium attachment (Figure 9). Preliminary results also seem to suggest that the deuterium contents are relatively lower in the functionalized carbon nanotube samples obtained with deuterium attachment before the functionalization reaction. This could be due to several factors, including the possibly lower efficiency for the deuterium attachment to the suspended carbon nanotubes (significantly bundled) and the fact that only a portion of the deuterium-attached carbon nanotube sample is solubilized in the functionalization reaction for the ^{2}H NMR characterization in solution. Further investigations are required.

Conclusion

The experimental results provide unambiguous evidence for the conclusion that carbon nanotubes interact strongly with labile deuterium in deuterated water and alcohols under relatively mild reaction conditions. The strong interactions result in deuterium attachment to carbon nanotubes, which is phenomenologically similar to the deuteration to form carbon–deuterium bonds. Such deuteration is not available to fullerenes. The involvement of only labile deuterium in the addition-like reaction suggests unique surface properties of carbon nanotubes, consistent with the notion that the addition reactions widely used in the derivatization of fullerenes may not be applicable to the nanotube functionalization. Specifically, the observed facile attachment of labile deuterium to carbon nanotubes serves as a reminder that chemisorption deserves special attention in the use of carbon nanotubes for hydrogen adsorption and storage applications. The seemingly unusual surface properties of carbon nanotubes have broad implications. One example is that the difference in surface properties between semiconducting and metallic SWNTs is likely responsible for their separation in noncovalent interactions with selected functionalization reagents.[32–34] It is hoped that the reported work will stimulate the interest of the research community to take a closer look, both experimentally and theoretically, at the apparently different surface reactivities of carbon nanotubes from those of fullerenes and graphite and to explore their relevant applications.

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