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The Generation of a Carbon Nanotube- Cyclodextrin Complex.

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ABSTRACT

In this study the intermolecular interactions of small diameter (~0.7nm) carbon nanotubes and γ -cyclodextrin were examined. Four samples of γ cyclodextrin and HiPco carbon nanotubes were prepared. The first, by grinding the tubes and the cyclodextrin (1:30 ratio) together in a dry mixture, the second was prepared in a similar fashion but was ground in the presence of water (1ml). Finally an aqueous solution of γ -cyclodextrin (0.3M) and HiPco carbon nanotubes (5mg) was prepared by refluxing for ~100 hours, forming a pale yellow solution from which a number of crystals were produced, both the solution and the recrystallised material were analysed. The samples were analysed using UV-Vis-NIR and Raman spectroscopy. The results presented are the first spectroscopic evidence of an intermolecular interaction between γ -cyclodextrin and single wall nanotubes.

INTRODUCTION

Since the discovery [1] of carbon nanotubes there has been considerable interest in the development of fullerene based nanotechnology. Theory predicts that carbon nanotubes have extraordinary electrical properties [2] and can behave as a one-dimensional conductor making them ideal candidates for interconnects in molecular electronic devices. Experimental confirmation of these predictions however has been hampered by the difficulty in purifying, processing and manipulating the carbon nanotubes. Several methods for processing and purifying both multi-walled carbon nanotubes (MWNT) and single walled carbon nanotubes (SWNT) have been reported using conjugated polymer systems [3] and chromatographic approaches [4]. However reports on the chemical manipulation of the tubes have been slow to emerge. The recent production of small diameter (0.7-0.8nm) and high purity single walled carbon nanotubes (SWNTs) by Smalley et al. [5] using a gas-phase catalytic approach called HiPco (high pressure CO disproportionation) has resolved to some degree the question of purity, with current purities of >90% atomic percent SWNT carbon [6]. The dominant impurities begin metal catalyst particles of Iron [6]. The purity of HiPco nanotubes has aroused considerable interest in the chemistry of this unique material [7,8] and significantly the interaction of these tubes with supra-macromolecules, bio-molecules and polymeric material. Recently it has been demonstrated that SWNTs (HiPco) can be cut by simply grinding the tubes in soft organic

material such as cyclodextrins [7] (CD). The results reported on such cutting techniques however concentrated upon microscopy thereby limiting the degree of information that can be deduced about the type of interaction between the two materials.

Cyclodextrins are crystalline, water soluble, cyclic oligosaccharides built up of glucopyranose units (Glucose units) and contain a relatively hydrophobic central cavity and hydrophilic outer surface. There are three main types of cyclodextrin α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin, which have inner cavity diameters of 0.47-0.53nm, 0.6-0.65nm and 0.75-0.83nm respectively [9]. One of the key chemical properties of cyclodextrins is their ability to form inclusion complexes with a wide variety of molecules that is to accommodate a guest molecule into their inner cavity. It is well known for example that C_{60} can readily form an inclusion complex with γ -cyclodextrin (γ -CD) [10]. The question then is can similar electronic interactions occur with the HiPco SWNTs? It was suggested by Chen et al. [7] that it was unlikely that individual SWNTs could form inclusion complexes with γ -CD since the inner cavity size [9] is comparable to the diameter size of the HiPco tubes. Instead it was suggested that the CD is adsorbed at the surface of nanotube ropes by van der Waals forces and can cut the tubes [7].

In this study UV-Vis-NIR spectroscopy and Raman microscopy have been performed upon a set of ground mixtures of SWNTs (HiPco) and γ -Cyclodextrin to help elucidate the nature and extent of any electronic interactions between the two species. In addition an aqueous solution of γ -CD and SWNT (HiPco) refluxed together in a similar manner to early experiments with γ -CD and C_{60} was also analysed.

EXPERIMENTAL

In total there were four samples considered throughout this study. The first was a dry ground material produced by grinding in an agate mortar and pestle γ -CD and SWNT (HiPco) in a 30:1 ratio. The mixture was ground for approximately 1 hour resulting in a fine light grey powder. A second mixture again in a 30:1 ratio was then ground but this time it was ground in 1ml of deionised water resulting in a fine dark grey powder (which retained its dark grey colour after heating). The third sample was produced by refluxing a suspension of SWNTs (5mg) in an aqueous γ -CD solution (0.3M) for <100hrs at 100°C under constant stirring. It was seen that a yellow solution began to form after about ~72 hours from which a number of crystals were formed. The subsequent solution was allowed to rest for two days (allowing excess tubes to settle out) before it was decanted off and analysed. The final and fourth samples were simply the recrystallised material produced from the refluxed solution. The material, which settled out after the reflux time, was also analysed and found to be simply carbon nanotubes.

The samples were analysed using Raman microscopy and UV-Vis-NIR spectroscopy. The Raman spectra were obtained using an Instruments S.A. Labram 1B spectroscopic microscope operating at 633nm while the UV-Vis-NIR spectra were obtained using a PerkinElmer Lambda 900 spectrophotometer. All samples for the UV-Vis-NIR spectra were dissolved in de-ionised water.

RESULTS AND DISSCUSSION

The solution produced by refluxing a suspension of SWNTs (5mg) in an aqueous γ -CD solution (0.3M) for ~100hrs at 100°C had a 'yellow' tint reminiscent of C₆₀- γ -CD inclusion complexes produced in a similar fashion [10]. It is unlikely however that this coloration is due to the formation of an inclusion complex between the SWNT and γ -CD a more likely explanation is the presence of dissolved Fe⁺³ produced from catalytic iron particles [6]. There is evidence from the absorption spectra shown in figure 1 that the γ -CD interacts electronically with either the SWNTs or the catalyst iron particles, however identification of exactly which species it interacts with at this stage is difficult. Figure 1 (a) shows the optical absorption spectrum of the HiPco SWNTs, obtained in SDS, which agrees well with literature [6, 11] having two broad absorption peaks centered at approximately 1200nm and 1000nm. These peaks have been attributed to optical transition between mirror image spikes in density of states of semiconducting tubes [11]. In addition the peak position is also very sensitive to the tube diameter [11], allowing an estimate of the diameter distribution of the HiPco tubes used in this study to be obtained as 0.7-1.0nm. Indeed the average tube diameter obtained from TEM images was ~0.8nm. This diameter distribution further supports the notion that HiPco SWNTs and γ -CD cannot form an inclusion complex together since the diameter size of the HiPco tubes and the inner cavity size of γ -CD [9] are comparable. Spectrum (b) in figure 1 highlights the absorption spectrum of γ -CD in aqueous solution, it can be seen that this absorption has few features in the NIR region however there is a strong feature at ~260nm. By comparing the wet and dry ground sample spectra (obtained from aqueous solution) (d) and (e) respectively to the pristine samples (a) and (b) we can see a number of distinct changes.

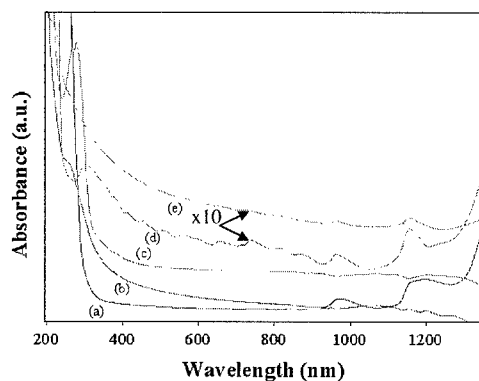


Figure 1. NIR-UV-Vis of (a) HiPco SWNTs raw sample in SDS solution, (b) γ -Cyclodextrin in aqueous solution, (c) aqueous solution produced from reflux. (d) wet ground mixture of γ -CD and HiPco SWNTs (30:1 ratio), (e) dry ground mixture of γ -CD and HiPco SWNTs (30:1 ratio). Both (d) and (e) are in aqueous solution.

Firstly the dry ground sample, spectrum (e) shows only weak SWNTs peaks in the NIR region with little or no positional changes with respect to the pristine SWNT sample. In

comparison to the γ -CD spectrum the feature at $\sim 260\text{nm}$ appears to be smeared out making any conclusion about an electronic interaction difficult. However for the wet ground sample, spectrum (d) figure 1 clear differences exist. Significantly the feature at $\sim 260\text{nm}$ in the absorption spectrum of the γ -CD is seen to under go a shift of $\sim 40\text{nm}$ towards the red for the wet ground mixture. Indicating a change in the electronic structure of the γ -CD. Furthermore the characteristic SWNT peaks in the NIR region also appear to become more defined and sharper with peak maximum at $\sim 960\text{nm}$ and $\sim 1150\text{nm}$ suggesting that SWNTs of diameter $\sim 0.76\text{nm}$ and 0.92nm are retained in the wet ground sample. In contrast spectrum (c) obtained for the yellow solution produced from the reflux shows no evidence of any tubes, supporting the suggestion that the yellow tint is in fact due to Fe^{+3} ions. It should be noted however that the feature at 260nm for γ -CD appears to be enhanced in this solution. In general the evidence for an intermolecular interaction between the γ -CD and the HiPco SWNTs from the absorption spectra is weak.

More convincing spectroscopic evidence of an intermolecular interaction can be obtained from Raman spectroscopy. The Raman spectrum for HiPco SWNTs is shown in figure 2 (a). As in the absorption spectra the diameter distribution can be estimated from the radial breathing modes (RBMs) to be in the range 0.7nm to 1nm . Raman scattering of the RBMs (positioned between 150cm^{-1} and 300cm^{-1}) and the tangential displacement mode (TDM positioned at $\sim 1580\text{cm}^{-1}$) of SWNT have been intensively studied in recent years [12,13] and are known to be sensitive to perturbations in the local environment of the tube. This is evident in the spectra shown in figure 2, which shows changes in the Raman scattering of the HiPco SWNTs as the sample preparation moves from the dry ground mixture through to the recrystallised material produced after the reflux. It is seen that the RBMs and the TDM undergo considerable changes in position and to some degree intensity.

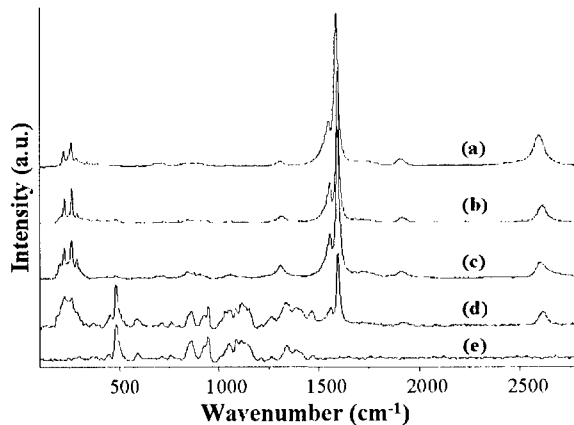


Figure 2. Raman spectra for (a) raw HiPco SWNTs (b) dry ground mixture, (c) wet ground mixture, (d) the recrystallised material produced from the refluxed suspension and (e) γ -CD.

Figure 3A highlights the changes observed in the RBM region of the spectrum, it can be seen that for the pristine sample the dominant RBM is positioned at 254.7cm^{-1} (corresponding to a tube diameter of $\sim 0.9\text{nm}$). Whereas in the ground samples (both the dry ground and the wet ground mixtures) a slight up shift in the RBMs position towards smaller diameters is observed.

In particular the dominant RBM is positioned at 257.0cm^{-1} for the dry ground mixture and 257.6cm^{-1} for the wet ground mixture which is a shift of 2.3cm^{-1} and 2.9cm^{-1} respectively from the pristine sample. Additionally a new RBMs appears for both the ground samples at $\sim 197\text{cm}^{-1}$ which is not discernable in the pristine HiPco SWNTs Raman spectrum. Nevertheless the

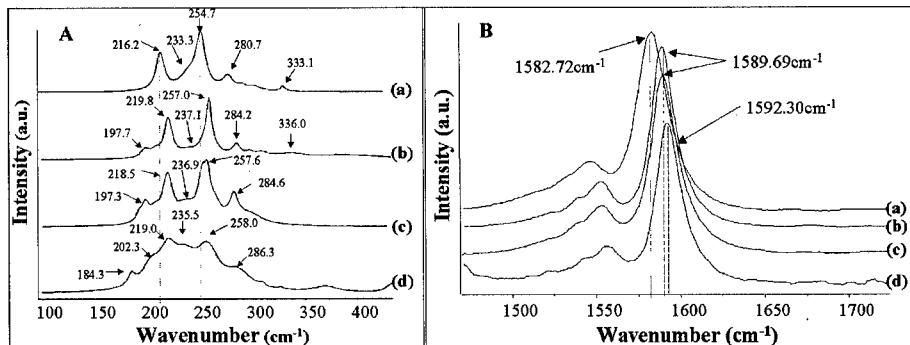


Figure 3. Raman spectra of (A) radial breathing modes and (B) tangential displacement mode spectra shown are (a) raw HiPco SWNTs (b) dry ground mixture, (c) wet ground mixture, and (d) the recrystallised material produced from the refluxed suspension. Peak positions were obtained from Lorentzian/Gaussian fits.

overall shape of the dry and wet ground samples are comparable to that observed for the pristine sample with only a slight shift in the main RBMs. The recrystallised material produced from the refluxed solution, however shows considerable changes in the RBMs. It can be seen from figure 3A spectrum (d), that the RBMs broaden considerably resulting in what appears to be a more even diameter distribution. This broadening may be the result of a decrease of the dominant RBMs rather than the specific selection of larger diameter tubes. Nevertheless the changes suggest that the refluxing method results in a stronger interaction between the HiPco nanotubes and the γ CD.

Further changes are observed for the Tangential displacement mode (TDM) positioned at $\sim 1580\text{cm}^{-1}$ figure 3B. This mode involves tangential C–C bond stretching motions and stems from the E_{2g} mode at 1580cm^{-1} in graphite [2]. In contrast to the RBMs the graphite-like TDM exhibits a definite upward shift of $\sim 7\text{cm}^{-1}$ after the nanotubes were ground with γ CD and an even further up shift of $\sim 10\text{cm}^{-1}$ for the recrystallised material. Similar up shifts in this mode have been reported before in SWNT bundles and SWNT/epoxy [12,13] composites in which it was seen that the TDM can shift up in frequency due to compressive strains induced along the length of the nanotubes. The compressive strains were attributed to van der Waals interactions between the individual SWNTs in bundles (or the epoxy and SWNTs in the composite) thereby stiffening the bond and hence constricting the molecular vibrations [12,13]. This observation of an up shift in this study may thus be due to strains induced by adsorbed cyclodextrins at the surface of nanotube ropes. Indeed Chen et.al. [7] proposed that cyclodextrins could be adsorbed onto the surface of nanotube ropes by van der Waals forces. The shifts in the TDM are thus the first spectroscopic evidence to support the notion the HiPco SWNTs can readily interact with γ cyclodextrin.

The true nature and extent of the intermolecular interaction between SWNTs and γ CD however has still to be elucidated. Leaving many questions about the potential use of supramacromolecules, such as cyclodextrins, calixerenes and other soft organic materials, in the development of molecular self assembly techniques.

CONCLUSION

Reported is the first spectroscopic evidence of an intermolecular interaction between HiPco SWNTs and γ CD. It was seen that by grinding or refluxing the SWNTs with the soft organic material considerable changes to the electronic and vibrational structure of both materials can be induced. Evidence from Raman spectroscopy, in particular up shifts in the TDM at $\sim 1580\text{cm}^{-1}$, seem to indicate that the cyclodextrins can absorb via van der Waal forces along the length of the tube inducing a compressive strain. The interaction of SWNT with organic materials has been proposed as a possible route towards self assembly techniques, however before such techniques can be utilised a true understanding of the nature and extent of the interaction of SWNTs with such molecules must be obtained.

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