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ABSTRACT

In this study a number of composite-like samples of ç-cyclodextrin and HiPco carbon nanotubes were prepared. The first sample was prepared by a simple grinding procedure, which has been reported to cut HiPco carbon nanotubes. The other samples were obtained via a refluxing procedure analogous to similar studies on other fullerenes and ç-cyclodextrin. The samples were analyzed using absorption and Raman spectroscopy, and differential scanning calorimetry. The results presented show clear evidence of an intermolecular interaction between ç-cyclodextrin and single-walled carbon nanotubes.

The production of small diameter and high purity singlewalled carbon nanotubes (SWNTs) by Smalley et al.[1] using a gas-phase catalytic approach called HiPco has aroused considerable interest in the physical and chemical properties of these unique materials. Most recently it has been proposed that SWNTs produced by this process can be cut by simply grinding the tubes in soft organic material such as cyclodextrins (CD). [2] 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. [3] There are three main types of cyclodextrin; however, only ç-cyclodextrin, which has an inner cavity diameter of 0.75-0.83 nm, was used in this study. One of the key chemical properties of cyclodextrins is there ability to form inclusion complexes with a wide variety of molecules that is to accommodate a guest molecule into their inner cavity. The results reported on the aforementioned "soft" cutting techniques using CD, however, concentrated upon microscopy thereby limiting the degree of information that can be deduced about the type of interaction between the two materials. In this study electronic and vibrational spectroscopy as well as thermal analysis has been performed upon ç-cyclodextrin and SWNT (HiPco) composites produced by two different methods. The first sample, a ground mixture of SWNT (HiPco batch HPR-86 obtained form Carbon Nanotechnologies Inc.) and ç-cyclodextrin (obtained form Wacker-Chemie) was prepared in accordance with the procedure outlined by Chen. et al. [2] in which a mixture of çCD and SWNT (in a 30:1 ratio) was ground in an agate mortar and pestle for approximately 2 h with the dropwise addition of ethanol (1 mL) over the first 10 minutes. This procedure resulted in a fine homogeneous black powder. The interaction of fullerene-based materials with cyclodextrins has been reported previously

with the formation of ç-cyclodextrin-C60 inclusion complexes. [4] However, these complexes were formed via a refluxing procedure. [3] As a result, the second sample analyzed in this study was produced in a similar fashion. SWNTs (5 mg) were refluxed in an aqueous çCD solution (0.3 M) for 100 h at 100 °C under constant stirring. It was seen that a yellow solution began to form after about 72 h, from which a number of crystals were formed and analyzed in order to asses the effect that such a process would have on the degree of interaction. It is well established that C60 can form an inclusion complex with çCD.4 However, it was suggested by Chen et al. [2] that it was unlikely that individual SWNTs could form inclusion complexes with çCD since the inner cavity size [3] is comparable to the diameter size of SWNT (HiPco). [5] Instead it was suggested that the CD are absorbed at the surface of nanotube ropes by van der Waals forces. [2] Indeed there is evidence from the absorption spectra shown in Figure 1 of an intermolecular interaction between the two species. The absorption spectra were obtained for films drop cast from DMF using a PerkinElmer Lambda 900 spectrophotometer.

Figure 1a shows the optical absorption spectrum of the çCD in the region 0.5-6 eV. It can be seen that the spectrum contains few features in the visible and near-IR region; however, at 5.1 eV the characteristic çCD band is observed. [3] In comparison the absorption spectrum of the pristine SWNT shown in Figure 1d appears extremely rich.This spectrum agrees well with literature [5,6] having a broad absorption centered at approximately 0.9 eV. This broad absorption consists of a number of absorption peaks, which have been attributed to optical transitions between mirror image spikes in density of states of semiconducting tubes. [6] In addition the position of each peak is also sensitive to the tube diameter, allowing an estimate of the diameter distribution of the SWNT used in this study to be obtained as 0.7-1.3 nm [5]. Indeed the average tube diameter determined using electron microscopy was 1.1 nm [7]. This diameter distribution supports the notion that SWNTs and çCD cannot form an inclusion complex since the diameter size of the SWNT and the inner cavity size of çCD are comparable. [3,5] The final feature in the SWNT spectrum is the peak at 4.7 eV which is associated with the ∂-plasmon background. [6] By comparing the spectra for both the pristine samples to that of the çCDSWNT mixture shown in Figure 1b, a number of differences can be observed. Upon initial inspection the çCD-SWNT mixture spectrum seems to resemble closely that of the pristine çCD; however, it can be seen that the feature in the UV region is positioned at 4.9 eV a shift of 0.2 eV from that of the çCD band. Indeed the shifts in the characteristic çCD band have in the past been associated with the formation of substituted çCD complexes although the shifts observed are usually of a greater magnitude. [3] As a result it is unlikely that the çCD and the SWNT are forming a covalent couple; nevertheless, it may suggest a weak electronic interaction between the two species. It must also be noted that the SWNTs also contain an absorption band within this narrow region of the spectrum. However, as can be seen from the inset in Figure 1, the SWNT bands in the ground mixture appear extremely weak, and weighted summations of boththe pristine samples does not yield a spectrum with the corresponding shift in the UV band. This suggests that the observed shift is not simply the result of combined bands. In contrast to the ground mixture, the absorption spectra of the crystals produced from the refluxing procedure, seen in Figure 1c, seem to resembled more closely the pristine SWNT due to its large background. There is however little evidence

from the inset in Figure 1 to suggest that this background is in fact due to the SWNTs as the nanotube features appear extremely weak and are comparable to the noise. Although as in the ground mixture the feature in the UV region is also centered around 4.9 eV. An absorption spectrum was also taken of the solution produced by the reflux process after it had settled; however, it showed no evidence of any interaction, i.e., there is no discernible shiftin the UV band from that of the çCD band. In fact there was little evidence to suggest that any SWNTs were present at all in the solution. Nevertheless it should be noted thatthe solution had a "yellow" tint reminiscent of C60-çCD inclusion complexes produced in a similar fashion. [3] It is unlikely however that this coloration is due to the formation of an inclusion complex between the SWNT and çCD. A more likely explanation for the coloration is the presence of dissolved $Fe3+$ produced from catalytic iron particles. [5] The evidence presented for an intermolecular interaction between the çCD and the SWNT based upon the absorption spectra is not entirely convincing and at most suggests only a very weak interaction in the ground mixture. Further spectroscopic evidence however of an intermolecular interaction can be obtained from Raman spectroscopy. The Raman spectrum for SWNT soot obtained using an Instruments S. A. Labram 1B spectroscopic microscope operating at 633 nm is shown in Figure 2a. As in the absorption spectra, the diameter distribution can be estimated from the radial breathing modes (RBMs) to be in the range 0.7 nm to 1.3 nm. [6] Raman scattering of the RBMs (positioned between 150 cm-1 and 300 cm-1) and the tangential displacement mode (TDM positioned at 1580 cm-1) of SWNT have been intensively studied in recent years [8,9] 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 SWNT as the sample preparation moves from the ground mixture through to the recrystallized material produced after refluxing, spectra (b) and (c) Figure 2, respectively. It is seen that the RBMs and the TDM undergo considerable changes in position and relativeintensity.

Figure 3 highlights the changes observed in the RBM region of the Raman spectra for the çCD-SWNT samples, It can be seen that for the pristine SWNT sample Figure 3a that the dominant RBM is positioned at 254.7 cm-1 (corresponding to a tube diameter of 0.9 nm), whereas in the ground sample, Figure 3b, a slight upshift in the RBMs position toward smaller diameters is observed. In particular the dominant RBM is positioned at 257.6 cm-1 for the çCDSWNT ground mixture. Additionally a new RBM appears in the ground sample at 197 cm-1 which is not discernible in the pristine SWNT Raman spectrum. Nevertheless, the overall shape of the çCD-SWNT ground sample is comparable to that observed for the pristine sample with only a slight shift in the main RBMs. The recrystallized material produced from the refluxed solution, however, shows considerable changes in the RBMs. It can be seen from Figure 3c 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 then the specific selection of larger diameter tubes. Nevertheless, the changes suggest that the refluxing method results in a stronger interaction between the SWNT and the çCD. Further changes are observed for the tangential displacement mode (TDM) positioned at 1580 cm-1, Figure 4. This mode involves tangential C-C bond stretching motions and stems from the E2 g mode at 1580 cm-1 in graphite. [6,9] In contrast to the RBMs, the graphite-like TDM exhibits a

definite upward shift of 7 cm-1 after the nanotubes were ground with ςCD and an even further upshift of 10 cm-1 for the recrystallized material. Similar upshifts in this mode have been reported before in SWNT bundles and SWNT/epoxy resin composites. [8] In terms of the SWNT/epoxy resin composites, [8] it was reported that the TDM upshifted by approximately 3 cm-1 when the SWNTs were embedded in Shell epoxy resin 862/EPI-CURE W¢. [8] However, no discernible change in the RBM frequencies were reported on going from the pristine SWNT to the composite-based material. The apparent absence of shifts in the RBM regions led to the suggestion that a direct coupling of the SWNT/ropes to the epoxy matrix was responsible rather than a van der Waals type mechanism. [8,9] In the case of the ςCD-SWNT ground mixture there are, however, clear shifts in the RBM region (Figure 3B), suggesting in the light of the SWNT/epoxy resin composites that the observed shifts are not the result of a direct coupling of the SWNT/ropes to the ςCD but rather a weaker interaction. Indeed this agrees well with the small shifts observed for the characteristic ςCD band in the absorption spectra. The notion that the type of interaction between the ςCD and SWNT may be the result of a weak interaction similar to a van der Waals type mechanism is supported by pressure dependent studies on the Raman active modes of SWNT bundles. [9] In such studies it was noted that changes in both the RBMs and the TDM were observed with changes in pressure, and significantly shifts of 14 cm-1 were observed in the TDM with respect to increasing pressure. It was further suggested that these shifts under the influence of hydrostatic pressure are in fact governed by van der Waals type interactions and that observed losses in intensity similar to those shown in Figure 4, may be the result of a lowering of the cylindrical symmetry of the tubes. [9] The observation of upshifts in Raman active TDM and RBMs in this study for the ςCD-SWNT samples may thus be due to strains induced by adsorbed cyclodextrins at the surface of nanotube ropes, thereby stiffening the bonds and hence constricting the molecular vibrations. It is unlikely that pressures comparable to those used in the aforementioned study can be induced by such an absorption process; however, the reduction in tube symmetry due to the absorbed cyclodextrins may also play a significant role in determining the mode frequencies in question. [9] Indeed, Chen et al. [2] did propose that cyclodextrins could be adsorbed onto the surface of nanotube ropes by van der Waals forces. Nevertheless, the shifts in the TDM observed in this study are among the first spectroscopic evidence to support the notion that SWNT can readily interact with ς-cyclodextrin. In addition to the spectroscopic evidence suggesting that the cyclodextrins may be adsorbed onto the surface of nanotube ropes, differential scanning calorimetry (DSC) shows clearly the presence of two species in the SWNT and ςCD samples. The DSC measurements in this study were all performed in closed aluminum crucibles using a RheometricScientific DSC. Figure 5c shows the DSC scan obtained for the ςCD-SWNT ground mixture. It can be clearly seen that two exothermic features are present in the scan. The first is positioned at 154 °C, the second at 170 °C. This second feature is clear evidence of an intermolecular interaction between the ςCD and the SWNT, in which the ςCD absorbs onto the surface of the nanotubes/ropes and is thermally stabilized, shifting the phase transition to a higher temperature. The retention of the original ςCD peak at 154 °C may indicate the presence of excess ςCD with respect to ςCD absorbed onto the SWNT (i.e., the "composite-like species"). Finally, the recrystallized material produced from the reflux suspension also shows significant changes in the DSC (Figure 5c), giving rise to

quite a complex scan. As in the çCD-SWNT ground mixture, two main features can be identified positioned at 150 °C and 180 °C. It should be noted, however, that the position of these features varied depending upon the crystal. The two sharp peaks below 130°C have been attributed to trapped water retained within the crystal as it formed in the aqueous solution and were seen to disappear on subsequent cycles. It is tempting to conclude that the two broad peaks are the same features seen in the çCD-SWNT ground mixture merely broadened due to the harsher refluxing process. Indeed, an obvious explanation for the broadening is the elevated temperature (i.e. 100 °C for 100 h) at which both species where maintained. It is unlikely that the nanotubes would be affected in any way by this temperature as their oxidizing temperature is considerably higher; [5] however, the same cannot be said about the çCD which is evident from the DSC can undergo significant changes as low as 150 °C. [3] As a result, further analysis is required on the temperature dependence of the observed changes reported in this study if the true nature and extent of the intermolecular interaction between SWNT and çCD is to be fully understood. Nevertheless the DSC measurements reported here show evidence of two species in the SWNT-çCD mixtures. The first has been attributed to simply excess çCD, while the second species can be speculated to be a "composite-like" species in which the çCD is absorbed on to the surface of the nanotubes/ropes via van der Waals forces as proposed by Chen et al. [2] In summary, this work has both confirmed and shown conclusively that çCDs and SWNTs do interact with each other in a fashion similar to that originally suggested by Chen *et al.*,[2] who proposed that the CDs were absorbed at the surface of nanotube ropes by van der Waals forces. Indeed evidence from absorption spectroscopy did indicate a weak electronic interaction with shifts of the order of 0.2 eV from the pristine çCD feature in the UV. Further analysis using Raman spectroscopy as a probe of the degree and extent of the interaction showed significant changes in the RBM and TDM regions of the nanotube spectra. It was seen that for the SWNT-çCD ground mixture shifts of the order of 3 cm-1 to higher frequencies were observed in the RBM region while the TDM was seen to upshift by 7 cm-1. Further upshifts in these modes were observed for the crystals formed via the refluxing process. These shifts were attributed to the absorption of çCD via van der Waals forces along the length of the tube, inducing compressive strains and hence constricting the molecular vibrations in accordance with pressure dependent studies of SWNT bundles. [8] In addition, it was noted that the reduction in symmetry due to the absorption of the çCD may also play an important role in determining the relative mode positioning. Evidence of this adsorption process was, however, shown by the presence of two distinct features in the DSC. While the first feature was attributed to excess çCD, the second feature position at 170 °C was speculated to be a "composite-like" species of the absorbed çCD and SWNT/ropes. In conclusion, the verification of the interaction of SWNT (HiPco) with çCD may point the way toward the use of other supramolecular molecules for the chemical manipulation and processing of SWNT. Work has already been reported on the solubilization of SWNT using such molecules.11 As a result, it is essential that a true understanding of the degree and nature of such interactions on the unique properties of SWNTs been obtained in order to take full advantage of such composites.

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