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INTERACTION OF CARBON NANOTUBES WITH SACCHARIDES - A POSSIBLE ROUTE TO BIOCOMPATIBLE COMPOSITES

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ABSTRACT

Inclusion complexes of saccharides and HiPco Carbon Nanotubes (HCNT) were formed, resulting in water soluble complexes. These complexes were then characterised using a variety of spectroscopic techniques. Raman spectroscopy was used to probe changes in the vibrational character of both the host and guest species and also to assess if any selectivity of tube diameter occurred. UV-Vis-NIR and circular dichroic spectroscopies were used to assess the effect of inclusion on the electronic properties of the tubes. Spectroscopic analysis of these species showed clear evidence of an intermolecular interaction between the host material and the HCNT.

1 INTRODUCTION

The interaction of HCNT with saccharides has begun to emerge as an accepted route towards the purification and isolation of HCNT. Experiments using polymeric and surfactant based routes have proved successful, much of this work however employs harsh solvent based systems, thus limiting any potential biological applications. Most recently amylose a polymeric form of glucose and a constituent of starch has been proposed to weakly interact with HCNT via non-specific hydrophobic interactions [1]. In this study further spectroscopic analysis is carried out on starch and gamma cyclodextrin (γ -CD) systems to confirm their potential as dispersing agents for carbon nanotubes.

2 MATERIALS AND METHODS

2.1 Materials

HCNT were purchased from Carbon Nanotechnologies Incorporated. Starch (rice) was purchased from Sigma Aldrich.

2.2 Complex Preparation

A number of composite like systems were formed with HCNT and saccharides. The first complex of starch and nanotubes was created by dispersing HCNT (1mg) in 25ml of a starch solution (10g/l) followed by ultrasonication (4 minutes medium power). The second complex was prepared by saturating a solution of the starch (10g/l) with bromine, which resulted in an inclusion complex of the starch being formed prior to the addition of the HCNT the solution then under went a process involving sonication and centrifugation. The third complex was formed with γ -CD by grinding HCNT and γ -CD in a 30:1 ratio. The fourth composite was produced by refluxing 5mg HCNT in an aqueous (0.3M) solution of γ -CD.

2.3 Complex Characterisation

Vibrational analysis was carried out using an Instruments S.A Labram 1B Raman microscope and a Perkin Elmer Spectrum GX FTIR. Electronic analysis was carried out with a Perkin Elmer Lamada 900 UV/VIS/NIR spectrometer. Circular dichroism measurements were carried out using a Jasco J-810 spectropolarimeter

3 RESULTS AND DISCUSSION

Initially it was observed that the first 2 complexes of starch and HCNT were visually different. The complex of starch and HCNT resulted in a clear aqueous solution which held the HCNT in suspension for approximately 3 weeks. The complex formed with the bromine saturated starch retained the characteristic orange colour of the starch bromine inclusion complex (holding HCNT in suspension for upto 6 weeks). A previous study by Star et al [2] produced a similar complex using iodine opposed to bromine, this process yielded a clear solution of nanotubes indicating full displacement of the iodine. The remnant colour would therefore imply that not all bromine was removed in the complex formation. As a result it is postulated that a tertiary complex of starch-bromine-HCNT was produced. The ground sample of γ -CD and HCNT yielded a fine grey powder where as the refluxed sample of γ -CD (0.3M) and HCNT gave a yellowish solution, this colour was due to the presence of dissolved catalytic Fe^{+3} particles from the HCNT sample. Due to the nature of the complexes produced (differing colour) electronic analysis was carried out. The absorption spectrum of raw HCNT consists of 3 main features centred approximately at 1200, 800 and 270nm being attributed to optical transitions in the density of states and the π -plasma frequency of 5eV in carbon materials. Using electronic analysis a diameter range of the raw sample was found to be 0.8-1.36nm [3]. The absorption spectra of the complexes did show the presence of HCNT in the

NIR region, but did not give any definitive evidence as to the formation of a complex only verified their presence. Further electronic analysis was sought using circular dichroism, preliminary studies do indicate a shift in the predominant feature giving supportive evidence to the formation of an inclusion complex. However no clear insight to the exact nature of the complex could be ascertained.

Infrared absorption spectroscopy of the raw HCNT agreed with literature consisting of three main features at 1600cm^{-1} , 1400cm^{-1} and 1180cm^{-1} which have been attributed to the C-C and C=C stretching along the hexagonal array of the nanotube backbone. FTIR analysis of the complexes, showed mainly strong features of resulting from glucose with the exception of an extremely weak peak at 1180cm^{-1} in the bromine, starch, HCNT complex which could be attributed to the C-C stretching in the nanotube. This again indicates that HCNT were present but gave no clear insight into the formation of a complex.

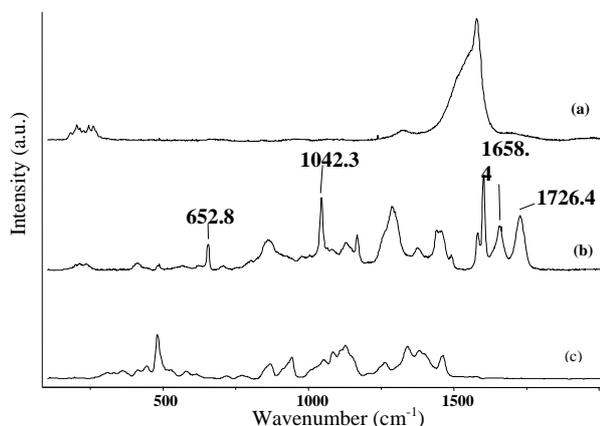


Fig.1. Raman Response for (a) Raw HCNT (b) Starch-Bromine-HCNT Complex (c) Raw Starch

Raman analysis was carried out on all samples produced at 514nm laser excitation. The Raman spectrum of pristine nanotubes (Fig.1.a) consists of three main features, the radial breathing mode (RBM), the D line and the G line. These modes are very sensitive to any perturbation to the local environment of the nanotube and therefore give good indication of complex formation. The results obtained for the γ -CD complexes agreed well with previous studies [4]. Analysis of the composite formed with starch and HCNT showed no discernible changes in the Raman signal with all modes present with their position similar to that of the raw HCNT as has been reported in literature [1]. Considerable changes were observed in the complex which used bromine saturated solution. As mentioned earlier not

all bromine was removed in the complex formation, as indicated by the final colour (orange). For this reason it is postulated that a tertiary complex was formed, supportive evidence for this can be seen in the Raman signal of the complex (Fig.1b.) by the appearance of four new features in the spectrum at 652.8cm^{-1} , 1042.2cm^{-1} , 1658.4cm^{-1} and 1726.4cm^{-1} . It is important to note that this spectrum is not a direct summation of the starch and HCNT spectra. The new feature present at 1042cm^{-1} may be due to IR active modes of the starch becoming Raman active due to changes in symmetry relaxing the normal selection rules. There are a number of candidate IR modes that could become Raman active in this region. The other three features appear to be new features and while their exact origin is still unknown, their presence undoubtedly indicates the formation of a new starch-bromine-Nanotube complex.

Finally there are also noticeable differences in the RBM region of the spectrum of the bromine based complex. The RBM's of pristine nanotubes are inversely related to the diameters of the nanotubes [5] using this relationship, a diameter range for the raw sample was calculated to be from 0.8nm-1.4nm. This was not the case in the complex formed involving bromine (Fig.3.b). In this spectral region starch is clear of features (Fig.1.c), facilitating the diameter range of the complex to be calculated in a similar fashion to the raw sample. The calculated range of the complex had decreased to 1.00nm -1.25nm.

4 Conclusion

It has been shown spectroscopically that saccharide systems can be used as dispersion agents for HCNT. The efficiency of the starch system was increased by the addition of the bromine (HCNT remained in suspension for longer). Vibration analysis verified the formation of a tertiary complex of Starch-Bromine-HCNT by the appearance of the new features in the spectrum. Indeed such saccharide based systems may provide a route for the integration of HCNT into biological environments, however questions are raised about the bio-compatibility of the Starch-Bromine-HCNT complex due to the insufficient removal of the bromine during the complex formation.

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