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Electronic structure of cyclodextrin–carbon nanotube composite films†

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The electronic structures of two kinds of cyclodextrin–carbon nanotube (α CD–CNT and γ CD–CNT) composite films are investigated by using (angular dependent) photoelectron spectroscopy to gain insight as to why the α CD–CNT and γ CD–CNT composite films show different performances in biosensor applications. The γ CD–CNT composite film is likely to have the CD localized on the surface rather than in the bulk of the film, while α CD–CNT has CD relatively more concentrated within the bulk of selvedge region of the film, rather than the surface. The results indicate that the CD, of the γ CD–CNT composite, may be more bioactive, and possibly a better sensor of biomolecules due to the favorable surface position compared with that of α CD–CNT. The valence band of α CD–CNT and γ CD–CNT show little difference from the CNT film except for a density of states, originating from CD, evident at a binding energy near 27 eV below Fermi level, meaning that there are few or no redox interactions between the CD and the CNT. The absence of a redox interaction between the CD and the CNT permits a clear electrochemical response to occur when guest biomolecules are captured on the composites, providing a route to biosensor applications.

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1. Introduction

Cyclodextrin (CD), with a toroidal shape, is hydrophobic on the inside radial edge, but hydrophilic on the outside perimeter, consists of six, seven, or eight glucoses named as α CD, β CD, or γ CD, respectively. α CD has the smallest inner diameter of 5.7 Å, while γ CD has the largest inner diameter of 9.5 Å. In a wider applications context, cyclodextrins and their derivatives are very important in drug delivery systems because they form inclusion complexes easily with guest molecules and improve the solubility, bioavailability, and stability of drugs.¹ It is, therefore, very important to investigate fundamental properties for the better design of further applications.

Various glucose bio anodes, with incorporation of carbon nanotubes (CNTs), are now being heavily investigated with an eye towards applications, such as enzymatic fuel cells, bio batteries, and biosensors.^{2–6} The hybrid glucose bio battery and supercapacitor have also been recently reported, where an efficient glucose bio-anode with carbon nanotubes or polymers was highlighted.⁵ The CNT may well lead to improve electron transfer from the enzymes to the electrodes as well as provide a good substrate for the immobilizing enzymes within designed CNT

networks. There is the potential that glucose or glucose oxidase could be immobilized efficiently on CNT electrodes, resulting in greatly enhanced stability of a fuel cell, due to an absence of diffusion of the enzyme to the cathode. There is also the possibility of enhanced performance of the cell because of more loading capability of enzymes on CNT networks.^{2–4} High supra-molecular recognition capabilities, from CD immobilized in CNT, have also been demonstrated for biosensor applications.⁶ Immobilized cyclodextrin and cyclodextrin derivatives have been shown to be effective in the detection of dopamine.^{7–11} Taken as a whole, this reinforces the need to investigate glucose or cyclodextrin based CNT electrodes at a fundamental level. We herein present the electronic structure of cyclodextrin–carbon nanotube composite films obtained by using the electron photoemission spectroscopy.

2. Experimental

The cyclodextrin (CD) incorporated CNT films were synthesized by a simple sol–gel method and compared, including electrochemical response to biomolecules, electronic structure and CD localization based on the core levels and valence band spectroscopies performed before and after annealing at 350 °C. The graphite (200 mesh) and multi-walled CNT (20 μ m of length, 10 nm of diameter) were purchased from Alfa Aesar and Hanwha Nanotech, respectively, and the three kinds of CD (α , β and γ CD) and biomolecules (dopamine and ascorbic acid) were purchased from Sigma-Aldrich and used without any pretreatment.

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The composites of α , β and γ CD–CNT were synthesized by mixing of each CD (200 mg) and CNT (20 mg) in deionized (DI) water of 20 mL. Then the mixture was sonicated for 180 min at room temperature, followed by vacuum filtration, using a cellulose paper (ADVANTEC, 0.45 μm of pore size, 47 mm of diameter). The resulting α , β and γ CD–CNT composite films were dried at 60 $^{\circ}\text{C}$ in a vacuum oven for overnight and then characterized.

The characteristic CD infrared absorption bands, belonging to the valence vibrations of the C–H bonds in the CH and CH₂ groups at 2926 cm^{-1} , absorption bands in the region of 1643 cm^{-1} related to distortions of the glucopyranoside ring, the deformation vibrations of the C–H bonds in the region 1400–1200 cm^{-1} as well deformation vibrations of the C–H bonds in the hydroxyl groups in the region 950–700 cm^{-1} were all observed (Fig. S1†). Typical X-ray diffraction (XRD) spectra of CNT were observed (Fig. S2†), and XRD spectra of the CD composites are very similar to those reported for CNT with β CD⁷ because of the general absence of CD crystallinity. The scanning electron microscopy (SEM) images (Fig. S3†) show fibers characteristic of the CNT structure clearly. Also the reduction of void volumes with the γ CD–CNT composite compared to the β CD– and α CD–CNT composites is evident in the SEM images. The SEM images, by themselves, are not conclusive indicators of the CD placement in the composites.

The potential for supramolecular recognition of the biomolecules was investigated by electrochemical differential pulse voltammetry (DPV) using an EC-Lab (Bio-Logic, sp-150, France) in a three-electrode cell. An Ag/AgCl electrode (BAS) was used as the reference electrode, and a platinum wire was employed as the counter electrode. The working electrode was prepared by the following method. Each sample of 0.5 mg was dispersed well in 1 mL of 2-propanol and then the mixture of 10 μg was drop casted onto a glassy carbon electrode (GCE) and dried completely. The pulse amplitude of 2.5 mV, pulse width of 100 ms, and scan rate of 10 mV s^{-1} were applied for the DPV measurements. Each 0.25 mL of biomolecule was mixed with 0.1 M phosphate buffer solution (PBS, $[\text{H}_2\text{PO}_4]^- / [\text{HPO}_4]^{2-}$, pH = 7.5) of 10 mL for the supramolecular recognition detection experiments. The thermogravimetric analysis (TGA, TGA Instruments, Q600, Ramp 10 $^{\circ}\text{C min}^{-1}$ to 900 $^{\circ}\text{C}$, N₂ gas) was also performed to measure components and its weight.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with a hemispherical electron analyzer (Thermo VG Scientific VG100AX), collecting a modest solid angle of photoelectrons, making angle resolved X-ray photoemission possible. The Mg K _{α} line of 1253.6 eV was used for the X-ray photoemission and provided by a dual anode X-ray lamp (SPECS). Both source and electron energy analyzer elements, as well as the samples, were placed inside an ultra-high vacuum chamber of about 10^{−10} Torr,^{12–14} to suppress impurity contributions to the photoemission spectra. The combined resolution of the detector and X-ray source, was 1.1 eV, contributing to the full width at half maximum (FWHM) of the C 1s peak, but the measured binding energies should be accurate to 0.2 eV or better. The annealing of all samples was performed under vacuum conditions to investigate stability of the samples, while

detering reactions with ambient. The ramping time, from the onset of increased temperature, for the annealing procedure, was 1 hour. Samples were held at elevated temperatures, about 350 $^{\circ}\text{C}$, for 3 hours, and allowed to cool for 12 hours back to room temperature. This means that any broadening that may be observed in either the valence band or core level photoemission spectra, must be the result of changes in the sample, and cannot be attributed to phonon effects. Binding energies are referenced to the Fermi level of gold, in intimate contact with the CD–CNT samples.

2.1. Biomolecule sensitivity

The electrochemical differential pulse voltammetry (DPV) responses of the α CD–CNT, β CD–CNT, and γ CD–CNT films to dopamine of 10 mmol L^{-1} are very different, as shown in Fig. 1a. The oxidation peaks of dopamine at 0.17 eV are observed in all samples, but the response obtained from γ CD–CNT is much higher relative to those of α CD–CNT and β CD–CNT. Similar behavior with ascorbic acid (30 mmol L^{-1}) was also found, as seen in Fig. 1b. A higher response to the ascorbic acid, in the region near -0.05 V, was obtained from γ CD–CNT, especially when compared to α CD–CNT and β CD–CNT. It is worth noting that the response of dopamine and ascorbic acid occurred at different potentials, opening up the possibility that these composites may be used to detect both simultaneously.

The amount of CD immobilized by the CNT host was similar in both types of CD–CNT samples. Fig. 1c and d show the results of thermogravimetric analysis (TGA), finding that α CD–CNT, β CD–CNT and γ CD–CNT have concentrations of 8.0, 5.0, and 8.9% of cyclodextrin (CD), respectively. The thermogravimetric analysis data are very similar to that reported reduced carbon nanotube composites with β -cyclodextrin,⁷ with most of the loss of mass occurring just below room temperature as observed here (Fig. 1c and d). More than twice higher DPV response of γ CD–CNT, to the biomolecules tested here, cannot be attributed to

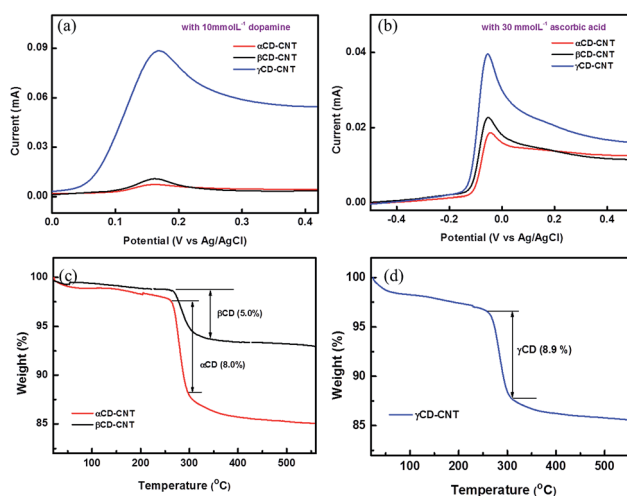


Fig. 1 Differential pulse voltammetry (DPV) responses of the samples to (a) dopamine and (b) ascorbic acid. Thermogravimetric analysis (TGA) results of (c) α CD–CNT and (d) γ CD–CNT.



the amount of CD, rather the differences may be due to the different cavity size of the CD or variations in the placement of the CD relative to the surface.

We note that the cyclic voltammetry (Fig. S4†) is qualitatively similar to that reported for the high pH,^{10,11} but far more significant in magnitude. The currents measured for γ CD-CNT are much higher than observed for α CD-CNT, suggesting better surface placement for the former.

The electronic structure may also have a significant contribution to the vastly different responses seen to the biomolecules and cannot be excluded *a priori*: the frontier orbital symmetries have not been determined by the measurements reported here.

2.2. The electronic structure and cyclodextrin stability

As seen in Fig. 2, there are no significant differences seen in the valence bands of the various samples: valence bands of α CD-CNT and γ CD-CNT resemble that of CNT, as shown in Fig. 2a. The one easily recognized difference between α CD-CNT and γ CD-CNT and that of CNT is the O 2s peak, with a binding energy near 27 eV relative to the top of the valence band. Such a shallow core level originates from the CD, and is an excellent signature of cyclodextrin as the carbon nanotubes used here are not heavily oxidized and contaminated with only a small amount of adventitious oxygen. With the addition of either α CD or γ CD to the CNT, there neither band shift nor Fermi level placement change were observed, with respect to the valence band of CNT. This implies that no redox interaction or charge transfer between CD and CNT occurred, providing favourable electrodes for biosensor application.

The shallow core level peak near 27 eV, that originates from the CD, is much diminished after the annealing at 350 °C, as

shown in Fig. 2b, where γ CD-CNT-a, α CD-CNT-a, and CNT-a refer to the spectra taken from the samples after the annealing. The valence bands before and after annealing are displayed in Fig. 2c for α CD-CNT and Fig. 2d for γ CD-CNT, not only confirming the presence of this 27 eV binding energy CD feature, below the bottom of the valence band, but also demonstrating that considerable shallow O 2s core level photoemission peak intensity is lost with the annealing. The latter suggests cyclodextrin decomposition occurs upon annealing. It was also found that higher intensity of the CD peak was obtained from γ CD-CNT, as is associated with increased numbers of -C=O moieties that exist in γ CD-CNT as compared to α CD-CNT, not vastly different CD concentrations, consistent with the TGA results.

The core level XPS spectra of α CD-CNT, are generally similar to that of the γ CD-CNT, as seen in Fig. 3. The precursor CNT has the typical sp² C 1s peak near 284.4 eV binding energy, the C 1s core level associated with an oxygen bond, near 285.5 eV, and the π - π^* satellite peak near 290 eV binding energy, as shown in Fig. 1a. α CD-CNT and γ CD-CNT have more oxygen, than the bare CNT film, compared in Fig. 3d. It is also evident in O 1s core level spectra intensities (Fig. 3e), all with binding energies in the region of 533 \pm 0.1 eV. The increased oxygen content in α CD-CNT and γ CD-CNT leads to a shift of the core level binding energies associated with the -C=O moieties from 285.5 eV (for the bare CNT film) to 285.9 \pm 0.1 eV, as seen in Fig. 3b and c. The more detailed comparison of the C 1s XPS spectra of the various samples is displayed in Fig. 3d. This too confirms that γ CD-CNT has the most intense oxygen to carbon C 1s peak (the C 1s component in the region of 286 eV) with α CD-CNT second.

The comparison of the XPS O 1s spectra in Fig. 3e and f also indicates that cyclodextrin degradation occurs upon the annealing, consistent with the changes in the valence band photoemission spectra, discussed above. The O 1s peak intensities decreased after the annealing although the oxygen γ CD-CNT remains more intense than that of α CD-CNT. Also key it the O 1s XPS core level feature has a much increased full width of half maximum: the full width of half maximum increases

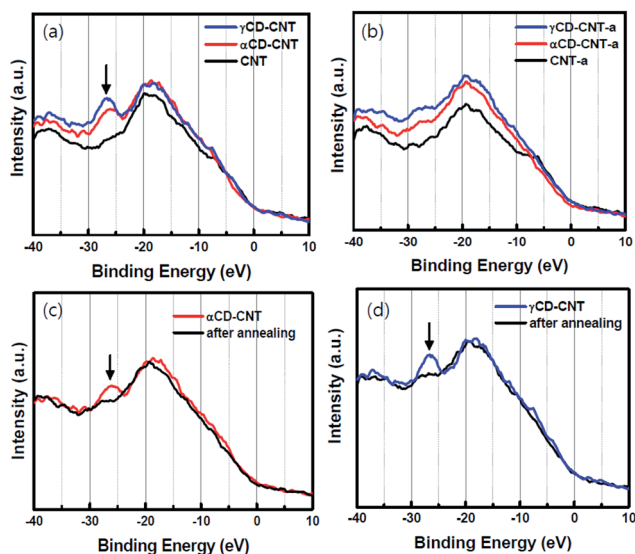


Fig. 2 Valence bands of (a) the fresh samples, (b) annealed samples, and before and after annealing of (c) α CD-CNT and (d) γ CD-CNT. α CD-CNT-a and γ CD-CNT-a refer to the samples after the annealing. Binding energies are reported here with respect to the top of the valence band.

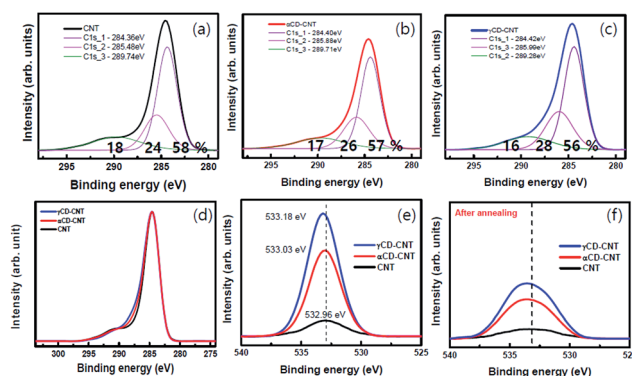


Fig. 3 XPS C 1s of (a) CNT, (b) α CD-CNT, (c) γ CD-CNT, and (d) all samples, and XPS O 1s of the all samples (e) before and (f) after the annealing at 350 °C. Binding energies are reported here in terms of $E_f - E$.



from roughly 3 eV to nearly 5 eV, indicating that the residual oxygen is in a much more heterogeneous environment after annealing, only possible if there is cyclodextrin decomposition.

Aside from the biomolecule sensitivity, the big difference between α CD-CNT and γ CD-CNT is in the π - π^* satellite peak near 290 eV binding energy, 289.7 ± 0.2 eV for α CD-CNT (Fig. 3b) and 289.3 ± 0.3 eV binding energy for γ CD-CNT (Fig. 3c). This feature is the result of a mixture of interband transitions from π to π^* (that occurs at the M point in graphene¹⁵) and a π band plasmonic excitation, commonly seen in the C 1s XPS spectra for graphene.¹⁶ The shift in this satellite feature suggests differences in the interband transition or differences in the screening of the two hole bound state.

2.3. The placement of the cyclodextrin

Since the top of the valence band and the core level spectra do not appear to differ significantly between γ CD-CNT as compared to α CD-CNT, differences in the γ CD placement, relative to α CD has been explored by angle dependent XPS. The oxygen to carbon ratio is mapped from XPS O 1s to C 1s peak intensity. Fig. 4a show the oxygen to carbon ratio obtained from α CD-CNT before (filled circles) and after (empty circles) annealing with respect to the angle, by using the angle dependent X-ray photoelectron spectroscopy. The O/C ratio for α CD-CNT decreases as the angle increases, meaning that less oxygen exists at the surface in α CD-CNT, compared to bulk or subsurface oxygen. Because of the limited electron mean free path (roughly 1–2 nm), increasing the photoelectron take-off angle means that the surface contributes more to the XPS signal than the subsurface, so as the O 1s signal is largely a result of the cyclodextrin, a decrease in the O 1s signal relative to the background carbon C 1s signal means there is less cyclodextrin at the surface than in the near subsurface region. The trend of the O/C XPS signal ratio, after annealing, remains very similar although, as discussed above, the oxygen content in α CD-CNT has diminished.

The O/C ratio obtained from γ CD-CNT, as shown in Fig. 4b, increases with increases in the photoemission take-off angle, implying that more of the γ CD is located on the surface. Basically, the signature of the cyclodextrin increases with the increased surface sensitivity that accompanies increasing the

photoemission take-off angle.¹⁷ The greater surface placement of γ CD is consistent with the larger size of γ CD compared to α CD. The greater surface localization of CD for the γ CD-CNT very likely contributes to the far greater activity as a biosensor, resulting in enhanced electrochemical responses to the biomolecules. Because greater surface localization more γ CD is available for direct charge transfer between CD and biomolecules. The higher response of γ CD-CNT compared to α CD-CNT is, therefore, due to not only large cavity size of the γ CD but also favorable surface position of CD in γ CD-CNT. A schematic to assist in clarifying the different placement of α CD and γ CD in the composites has been provided in the ESI (Fig. S5†).

3. Conclusions

The two kinds of cyclodextrin-carbon nanotube (α CD-CNT and γ CD-CNT) composite films studied here show vastly different performance as biosensors to ascorbic acid and dopamine. The valence bands of the different composite films are very similar to the CNT valence band except for the photoemission peak at binding energies near 27 eV below Fermi level, originating from cyclodextrin. We infer that there are no redox interactions between CD and CNT and the CD-CNT composite films are, therefore, good candidates of electrodes for the biosensor applications. The CD of γ CD-CNT is likely distributed to a significantly greater extent near the surface rather than in the bulk or subsurface region, while α CD-CNT has a CD placement relatively greater in the subsurface. It is not clear if differences in the electron structure of two different cyclodextrin species plays a role, but the placement of the larger cyclodextrin closer to the surface does imply that the cyclodextrin size is a significant factor in biosensor applications. Certainly, the CD of γ CD-CNT is more active with respect to the biomolecules studied here. We conclude that the γ CD-CNT film is the better electrode for biosensor applications compared to the α CD-CNT film due to the largest size of CD relative to other CDs and because of the more favourable surface placement of γ CD in the composite.

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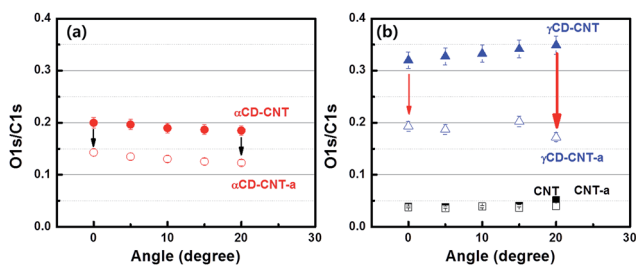


Fig. 4 The oxygen to carbon ratio of (a) α CD-CNT before (filled) and after (empty circles) annealing, plotted as a function of the photoemission take-off angle. (b) γ CD-CNT (before) and γ CD-CNT-a (after annealing) are marked with the triangles and the squares are for CNT before (filled) and after (empty squares) annealing.



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