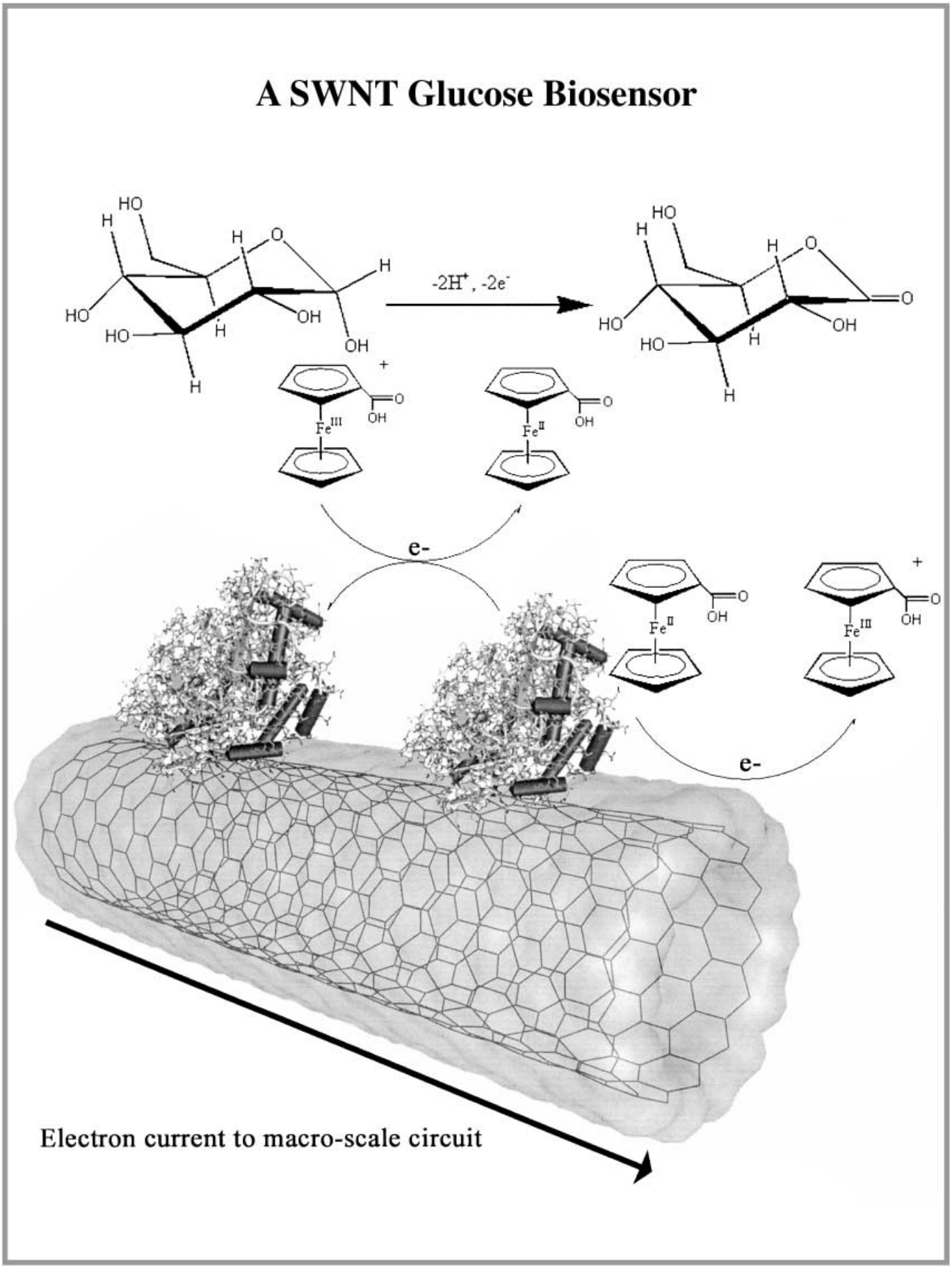
A SWNT Glucose Biosensor



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Chemical and Biochemical Sensing with Modified Single Walled Carbon Nanotubes

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Abstract: The nano dimensions, graphitic surface chemistry and electronic properties of single walled carbon nanotubes make such a material an ideal candidate for chemical or biochemical sensing. Carbon nanotubes can be nondestructively oxidized along their sidewalls or ends and subsequently covalently functionalized with colloidal particles or polyamine dendrimers via carboxylate chemistry. Proteins adsorb individually, strongly and noncovalently along nanotube lengths. These nanotube–protein conjugates are readily characterized at the molecular level by atomic force microscopy. Several metalloproteins and enzymes have been bound on both the sidewalls and termini of single walled carbon nanotubes. Though coupling can be controlled, to a degree, through variation of tube oxidative pre-activation chemistry, careful control experiments and observations made by atomic force microscopy suggest that immobilization is strong, physical and does not require covalent bonding. Importantly, in terms of possible device applications, protein attachment appears to occur with retention of native biological structure. Nanotube electrodes exhibit useful voltammetric properties with direct electrical communication possible between a redox-active biomolecule and the delocalized π system of its carbon nanotube support.

Keywords: biosensors · carbon nanotubes · electrochemistry · functionalization · metalloproteins

Introduction

The remarkable properties of single-walled carbon nanotubes (SWNTs), first observed in 1993,[1] have attracted interest and excitement across a broad spectrum of sciences and technologies including engineering, materials, chemistry, biology and medicine.[2] Such nanotubes have been found to be metallic or semiconducting depending on their structure. They are both immensely strong (a tensile strength similar to that of steel) and mechanically flexible. They are chemically inert to corrosion at standard temperatures and pressures and thermally stable to $>1000\,^{\circ}C$ under inert atmospheres. Traditionally SWNTs have been synthesised using electric arc[3] or laser ablation methods.[4] However, recently it has become apparent that a promising approach for producing SWNTs is via metal catalysed chemical vapour deposition (CVD) processes.[5] Much current research is focussed on finding reaction conditions that can yield high quality, high purity SWNTs with a low diameter distribution.

The broad potential of carbon nanotubes, and in particular single-wall nanotubes, in new generation materials has generated much interest. Their impressive mechanical and electronic properties have opened the way for the development of new nanotechnologies ranging from high-strength composite materials to field emission devices.[6, 7] Perhaps most striking in this respect are the electronic properties typified by these structures. To date, SWNTs have shown exceptional current-carrying capacity[8, 9] (electrical conductivity up to a 1000 times greater than copper)[7] and have recently been assembled into transistors,[10] diodes,[11] logic gates[12] and bits of memory.[13] However, in order for applications of such properties to be realized, reliable methods must be found for controlling chemical and physical properties of these materials. Chemical strategies such as selective functionalization of SWNTs (e.g. with thiol groups) and attachment to pre-organized surfaces (e.g. gold) presents one method by which it should be possible to assemble nanotubes in devices, tune nanotube electronic properties, and, importantly, provide low-resistance contacts of nanotubes to other electronic components. With such techniques in hand, nanotubes should see application in both the construction and use of novel nanoscale devices such as biosensors, fuel cells, and in molecular electronics. Though graphitic sidewall functionalisation will unavoidably lead to some modifications of the nanotube delocalised π system, this can offer a convenient and controllable means of tethering molecular species.[14]

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Molecular Modification of SWNTs

Though dissolution and manipulation remain problematic, a number of physical and chemical modifications of SWNTs have been performed to date. However, a key and as yet outstanding challenge is the "purification" of carbon nanotube electronic properties. External physical modifications of nanotubes have included interaction with polymers,[15] ionic functionalization,[16] and adsorption of gases.[17] The physisorption of gases by carbon nanotubes has also been shown to modify their electronic properties and thus may find use in new chemical sensing technology. Covalent functionalizations have employed two general strategies: amide bond formation at nanotube ends using carboxylate groups,[18] or nonselective attack of nanotube sidewalls by highly reactive species such as carbenes,[19] azomethine ylides[20] and aryl diazonium salts.[21] Characterization of functionalized samples have been performed mostly indirectly and in bulk, making difficult any interpretation of nanotube–reagent interactions and leaving in doubt the role of ever-present (metallic and carbonaceous) impurities in current carbon nanotube samples.

Recently, in Oxford we have achieved both physical modification and covalent attachment of quantum dots to SWNTs.[14] Silver colloids were deposited from a solution phase organometallic complex onto oxidized SWNT templates, and the reacted product assessed by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, and atomic force microscopy (AFM), see Figure 1.

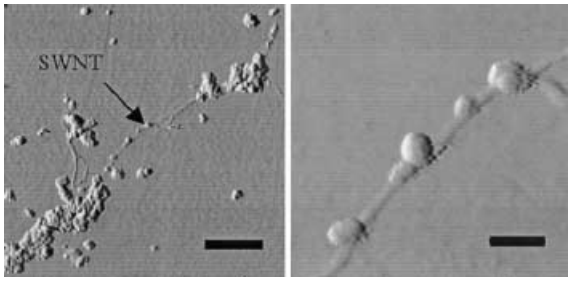


Figure 1. Amplitude (error) tapping AFM images of silver clusters grown on SWNTs by decomposition of (cycloocta-1,5-diene-) (hexafluoroacetylacetonato)silver(I). Scale bars 1 μm (left) and 200 nm (right).

Though comparisons between oxidized and native samples support the importance of oxygen-containing tube sites in nucleating the deposition of metal particles this is somewhat difficult to demonstrate unambiguously without the active, specific, utilization of carboxylate chemistry. To this end we devised a simple functionalization procedure, Scheme 1. We can controllably oxidize SWNTs along their lengths and utilize the carboxylates introduced to tether colloidal gold particles (ca. 3 nm) via 2-aminoethanethiol linkages. Imaging the *same* individual SWNTs before and after reaction proves chemical attachment to acid groups along SWNT sidewalls and provides a basis of comparison for a number of different oxidizing treatments. Before and after imaging of the same SWNTs also provides a reliable means for distinguishing colloids from any impurities (usually formed during their synthesis) present in the deposited SWNTs. Purified and vacuum annealed (1273 K) SWNTs, show no significant colloid attachment when subjected to the same reaction procedure. In order to verify that carboxylic acid groups were indeed responsible for the observed colloid labeling, control experiments were performed in which gold colloids were exposed to oxidised SWNTs without prior 2-aminoethanethiol functionalization. Colloid adsorption or attachment was not observed in this case, presenting strong evidence for the presence of carboxylic acid groups and their involvement in successful functionalization. Carrying out such experiments enables us to determine the location and degree of functionalization with the gold colloids acting as "visual" chemical markers as depicted Figure 2.

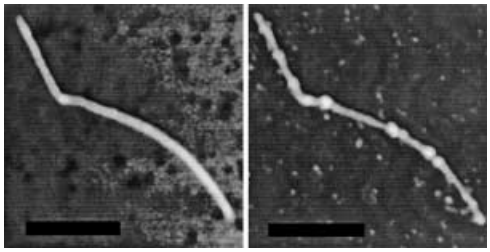
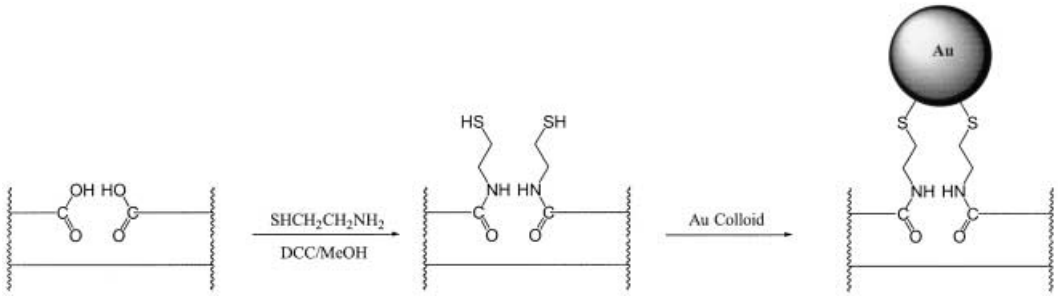
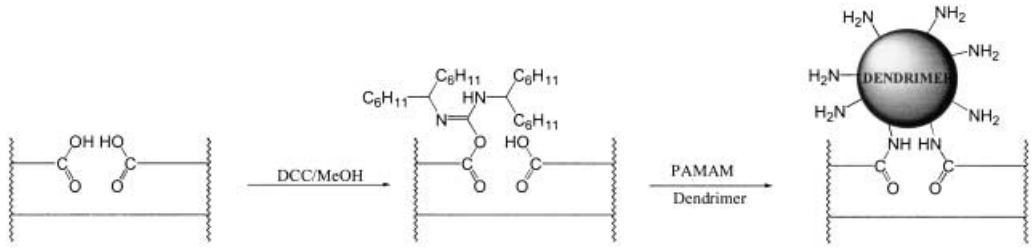


Figure 2. AFM height image of the same SWNT as imaged before (left) and after (right) exposure to DCC and 2-aminoethanethiol and 3 nm gold colloids. Scale bars 200 nm, z scale 0–4 nm.

Employing similar chemical and imaging strategies we have also been able to introduce starburst polyamideamine (PAMAM) dendrimers to the SWNT surface, Scheme 2, Figures 3 and 4. Dendrimers are of particular interest as they have a great many potential applications ranging from slow release agents for drug delivery to chemical sensors.[22, 23] Others have also studied the interaction of SWNTs with dendrimers and have formed "nanotube stars" with many tubes arranged



Scheme 1. Coupling chemistry (with carbodiimide) used to tether gold covalently to oxidized sites along SWNTs.



Scheme 2. Chemistry used to covalently attach PAMAM dendrimers to oxidized sites along SWNTs.

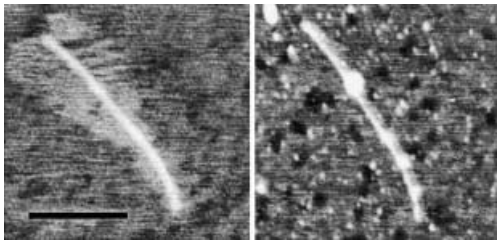


Figure 3. AFM height image of the same SWNT as imaged before (left) and after (right) exposure to DCC and a methanolic solution of a generation 4 PAMAM dendrimer. The light features clearly visible on the image on the right are not individual dendrimer molecules but 2–3 molecule (presumably H-bonded) aggregates. The expected diameter of a generation 4 PAMAM dendrimer is 4–5 nm. The nanotube in the left hand topograph is tip-broadened. Scale bar 350 nm, z scale 0–5 nm.

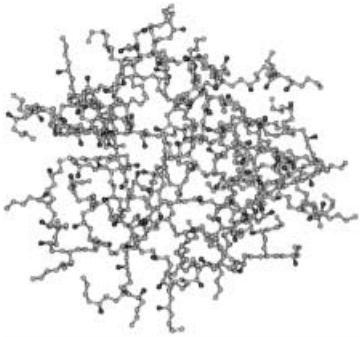


Figure 4. Ball and stick model of a G4 PAMAM dendrimer with hydrogen atoms omitted for clarity. Theoretical height ca. 4.5 nm.

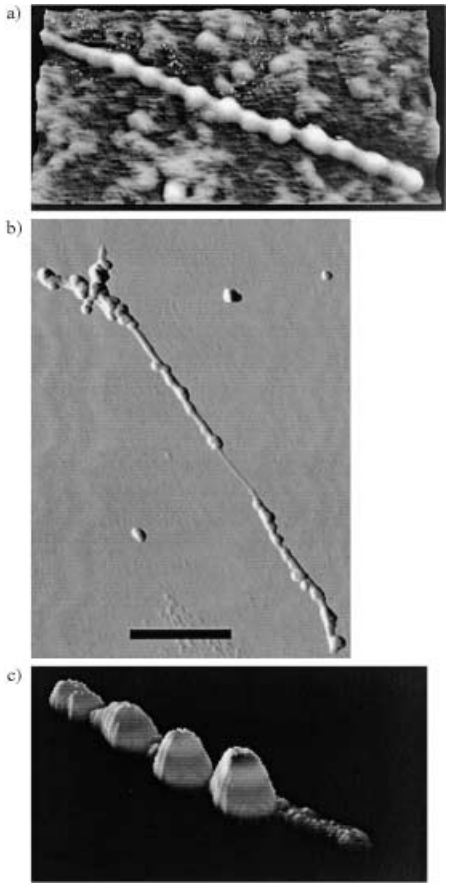


Figure 5. a) Cytochrome *c* molecules along an un-oxidized SWNT on a mica surface observed to be clean before protein exposure. b) Amplitude AFM image of ferritin molecules along a refluxed SWNT on silica, from a solution reaction of ferritin and SWNTs. Scale bar 400 nm, z scale 0–7 nm. c) Three-dimensional representation of ferritin molecules adsorbed along a single SWNT on SiO_2.

together in a "dandelion clock" formation joined at the core by a dendrimer molecule.[24]

Biomodification of SWNTs

Using similar (carbodiimide) coupling chemistry, the surface amine groups of biomacromolecules (DNA, proteins, enzymes) can be coupled to the carboxylate moieties of nanotubes in aqueous solution. In initial experiments, two robust metalloproteins, cytochrome c and ferritin, were examined. Cytochrome c is an electron transport protein found in the (inner) eukaryotic membranes of mitochondria where it plays an important role in respiration. The protein contains a redox-active *c*-type heam and is approximately 3 nm (~13 kDa) in size (Figure 5). Ferritin is a 24-subunit (~13 nm diameter) major, non-haem, iron storage protein found in animals, plants and microorganisms.

Through aqueous-phase incubation of suspended (oxidized) SWNTs with micromolar buffered protein solution, in the presence or absence of a chemical coupling reagent, robust adsorption of the biomolecule occurs. The biomolecular coverage attainable is observed to be a sensitive function of not only the protein concentration, but also the quality of nanotube suspension and incubation time. Figure 5a) shows an array of individual cytochrome c molecules, which can be resolved along the length of a SWNT. The adsorption of these proteins (and others including catalase, azurin and glucose

oxidase) is pH and ionic strength independent (to at least 1M KCl) and cannot be significantly alleviated through the addition of anionic or neutral surface-active agents (such as SDS or Triton X) to either the "reaction mixture" or to the nanotubes subsequent to "reaction".

Electroanalytical SWNTs

The electronic properties of carbon nanotubes have made them suitable candidates for the promotion of heterogeneous electron transfer studies. Promising voltammetric results have been obtained with both single-walled and multiwalled nanotubes in recent years.[25–27] The surface oxygen functionalities and high surface area of the structures give nanotube electrodes a characteristically high capacitance (indeed, they have been cited as possible components of "supercapacitors"[28]). In our experiments we have (predictably) determined the mass or surface area-specific capacitance to be greater with acid-refluxed SWNTs ($\sim 100\ F\,g^{-1}$ or $\sim 1\ F\,cm^{-2}$) than with vacuum annealed SWNTs (in which the oxygen functionalities have been largely lost) and more than one order of magnitude greater than a typical carbon macroelectrode. The redox response of functional groups present on oxidized nanotubes commonly give such electrodes a characteristic background "fingerprint". By modifying macro (typically 2–4 mm diameter) carbon electrodes (edge plane graphite or glassy carbon) with SWNTs (drop drying or spin coating), a high surface area sensor is generated which displays a greatly enhanced faradaic response to the presence of redox active (diffusive) solution species. In Figure 6 the comparative voltammetric responses

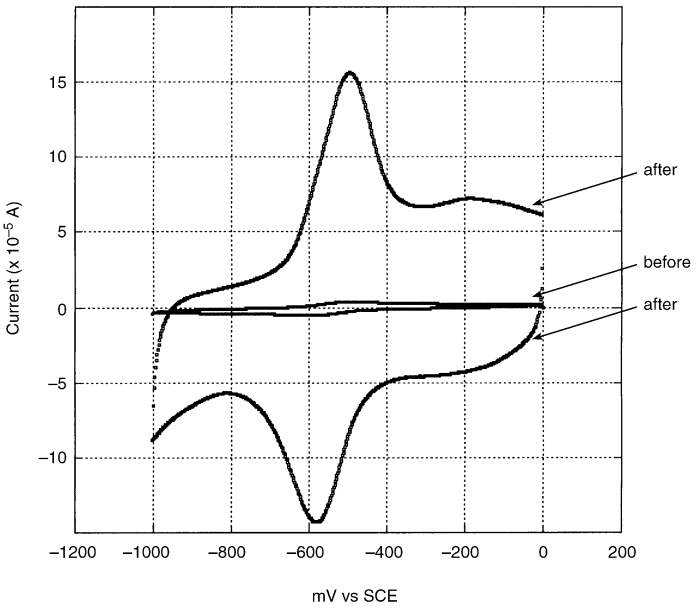
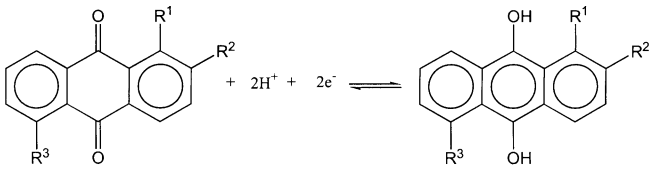


Figure 6. Comparative faradaic responses ($100\ mV\,s^{-1}$) of a glassy carbon macroelectrode to 2 mM 1,5-AQDS before and after modification with acid-refluxed SWNTs.

to a sulfonated anthraquinone (Scheme 3) of a glassy carbon electrode before (red) and after (blue) SWNT modification are shown. Such results are typical and observable with



AQMS: $R^2 = SO^{3-}$, $R^1 = R^3 = H$

1,5-AQDS: $R^1 = R^3 = SO^{3-}$, $R^2 = H$

Scheme 3. The structure and redox activity of water-soluble anthraquinones.

a variety of anionic, cationic and neutral redox species. With positively charged redox species, such as ruthenium hexamine, time and pH dependent electrostatic adsorption at the oxidised SWNT surface leads to voltammetry with both an adsorbed and diffusive component. It is worth noting that the electron transfer kinetics obtained at such nanotube electrodes are comparable (Table 1) to those at planar graphitic surfaces with the redox systems we have analysed.

Table 1. The kinetics of electron transfer of anthraquinones adsorbed on acid refluxed SWNT-coated electrodes (evaluated at $200\ mV\,s^{-1}$).[a]

Anthraquinone	Electrode	α	k_s [s^{-1}]
AQMS	EPG	0.40	0.52
		0.40	0.23
	SWNTs on GC	0.22	0.67
		0.76	0.63
	SWNTs on Au	0.11	0.36
		0.89	0.38
1,5-AQDS	SWNTs on EPG	0.14	0.76
		0.77	0.63

[a] SWNT-coated GC (glassy carbon) and EPG (edge plane graphite) were scanned in pH 7.5 100 mM phosphate buffer, and SWNT-coated gold and bare EPG in 100 mM $HClO_4$. α is the charge transfer coefficient and k_s denotes the heterogeneous electron transfer rate constant.

Bioelectrochemical studies, that is the analysis of the redox processes associated with a biological macromolecule, have led to a greatly improved understanding of fundamental electron and energy transducing pathways ubiquitous in nature and also to the development of biosensing devices. Central to these studies has been the development of procedures whereby delicate biomolecules "communicate" electrically with the interface of man-made circuitry. Much effort has been expended to refine both the generation of such interfaces and the analysis of responses subsequently obtained.[29, 30] Several years ago we suggested that MWNTs could act as conduits of electrical current between such electrochemical interfaces and metalloproteins/enzymes.[31] One can imagine that a pure SWNT represents the ultimate in terms of wiring a single protein/enzyme molecule (for example, one immobilized at a nanotube terminus) to a circuit. The nanometre size of the electrode and the combined sensitivity and facile substrate diffusion inherent in such a construction are significant in terms of the development of improved high-sensitivity molecular sensors.

Experiments have demonstrated that an oxidized SWNT electrode surface behaves largely (in terms of its communications with metalloproteins and enzymes) in the same way as polished (oxidized) glassy carbon or edge plane carbon surfaces. In this vein, for example, robust electrochemical responses, at comparable half-wave potentials, are obtainable from diffusive cytochrome c. Interestingly, these responses are typically weak unless the nanotube electrodes are electrochemically "pre-activated". This process (involving a prolonged anodic poise) presumably leads to increased surface functionalisation of the nanotube—in essence, making it "more biocompatable".[32, 33]

Amperometric biosensors are based on the ability of enzyme adlayer to transduce the turnover of substrate into a detectable, reliably quantifiable, current. This transduction is carried out either through monitoring the direct voltammetric response of the enzyme or, more commonly, by monitoring the catalytic enhancement in diffusive voltammetry of a suitable mediator (redox iron complexes, such as ferrocene have been popular in this context). Glucose oxidase (GOX) is a flavin enzyme used commercially on a massive scale to monitor the blood glucose levels in diabetics. Prolonged incubation of SWNTs (oxidized or otherwise) with glucose oxidase leads to an effective coating of the nanotube with enzyme[34] (Figure 7a). If biosensor applications, which may take advantage of the high biological loadings possible, are to be feasible, it is important that this robust immobilization can take place without gross loss of enzyme activity. The treatment of such "bio-SWNT" electrodes with both a diffusive mediator and equilibriated glucose substrate leads to the observation of a catalytic anodic wave (Figures 7b and 8). The magnitude of this catalytic response is more than one order of magnitude greater (for the same enzyme, substrate and mediator concentrations) than that observed at an activated macro carbon electrode and is aided not only by the high enzyme loading possible but also by the electrical transducing ability of the nanotube support itself. Knowing that metalloproteins in solution are able to communicate electrochemically with oxidized SWNTs at an electrode surface and that bioimmobilisation, at high loading, can occur with retention of activ-

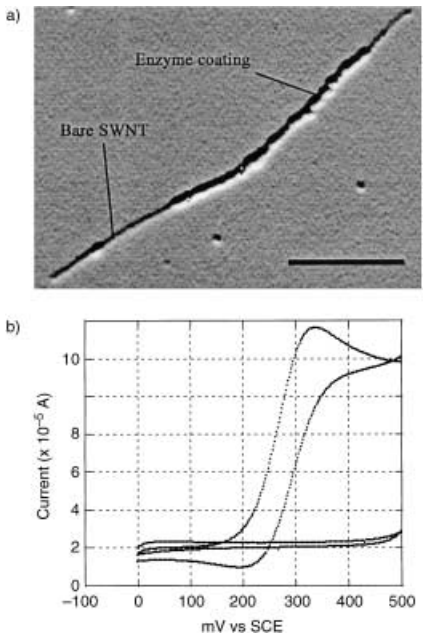


Figure 7. a) TMAFM amplitude micrograph of a GOX modified SWNT in which a high degree of enzyme loading is apparent. Scale bar 200 nm. b) Voltammetric response of such nanotubes in the absence (lower curves) and presence (upper curves) of substrate, β-D-glucose.

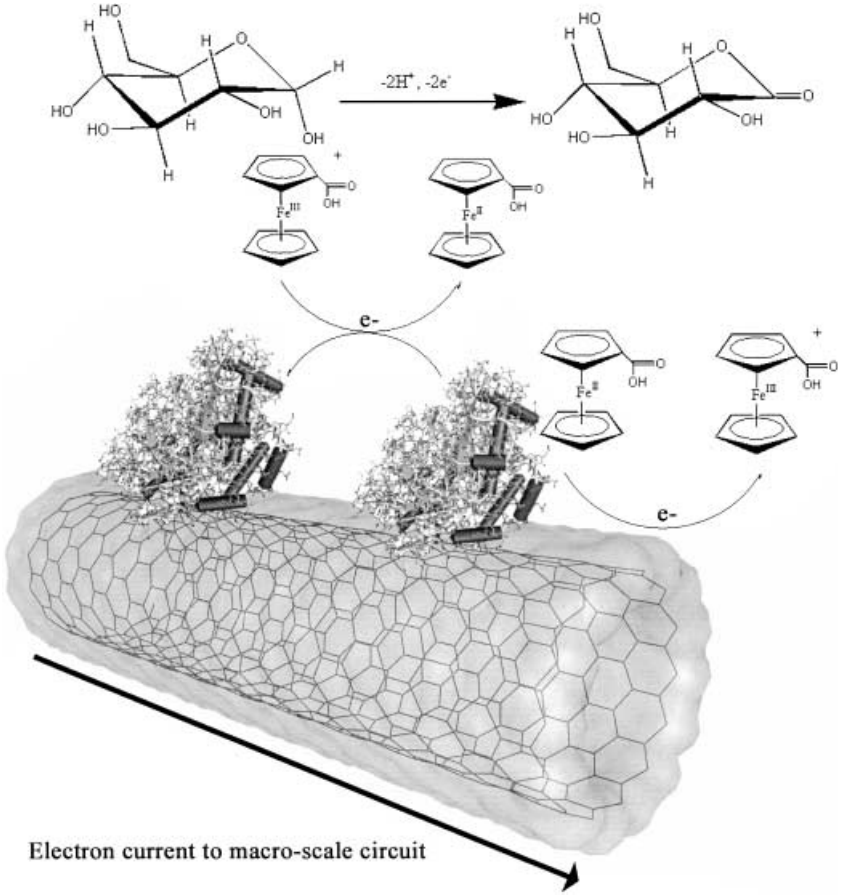


Figure 8. Schematic representation of the "SWNT Glucose Biosensor". Solution-phase D-glucopyranose is turned over by oxidase enzymes immobilized on the nanotubes. This redox process at the enzyme flavin moieties is "communicated" to the nanotube π system through the diffusive mediator ferrocene monocarboxylic acid. The redox action of the ferrocenes at the nanotube surface ultimately generates a quantifiable catalytic current characteristic of substrate detection and turnover.

ity, one naturally sets about investigating whether metalloproteins immobilized on a nanotube surface can communicate directly with the nanotube π system. It is worth noting here that direct electrochemical communication between the flavin active site of GOX immobilized in this way and the nanotube is not possible. As is characteristic with many similar enzyme systems, the tunnelling distance between the (redox) active site and any underlying support/electrode remains too great for this to be feasible. In cases where electrochemical responses have been observed, these, invariably, have been due to free flavin moieties lost from denatured enzyme. With cytochrome c it is known that the partial solvent exposure of the c-type haem aids not only its redox-communication with natural partners (such as cytochrome c oxidase) but also enables electrochemistry at graphitic or modified metal electrodes to be facile.[35] By physisorbing the cytochrome on oxidized SWNTs a faradaic response, indicative (in this case) of direct haem-nanotube (π – π) communication is, indeed, observable (Figure 9b).

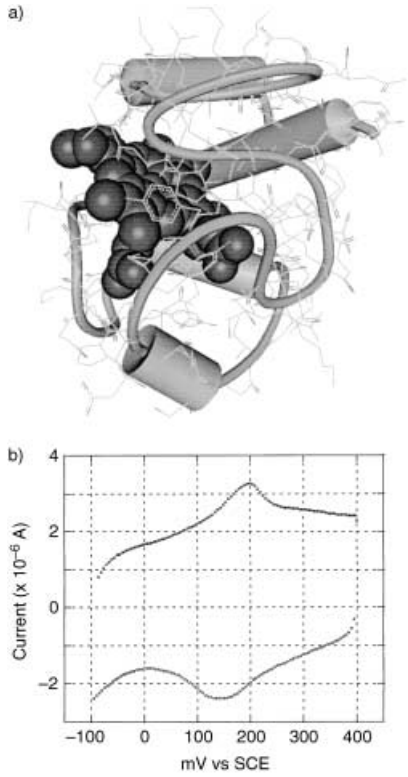


Figure 9. a) Schematic representation of the (~13 kDa) redox-active respiratory protein cytochrome c. The solvent-exposed haem moiety is highlighted. b) Redox activity (Fe^{II}/Fe^{III}) of a cytochrome c modified SWNT in 100 mM potassium phosphate buffer, pH 7.4, 100 mV s^{-1}.

Conclusion

By marrying the surface assembly and molecular recognition properties ubiquitous in proteins and enzymes with the molecular electronic properties of carbon nanotubes, it may be possible to generate unique sensing devices. More generally, the interactions between biomaterials and nanoscale structures lie central to the development/fabrication of miniature bio-devices. Key to this will be the ability to both understand and control interactions at the relevant surfaces and, in particular, to ensure that the biological support remains "biocompatible". We have herein reviewed the molecular and biomolecular SWNT functionalization experiments carried out in our laboratories in recent years. Though chemically quite inert, the graphitic walls on these molecules can be functionalised with a reasonable level of control. Though, for reasons of effective dispersion, the majority of this functionalization has been carried out in organic solvent, aqueous phase dispersion and modification can be used to controllably generate bio-functionalised carbon nanotubes. This work has progressed to the point where these interactions can be refined and analysed at a molecular level. These nanotubes exhibit electrical properties which can be utilised in voltammetric studies. The facile faradaic (electron transfer) kinetics (comparable to those observed at other carbonaceous electrodes) and the high surface areas generated at carbon nanotube electrodes makes them viable in electroanalytical devices. The SWNT surfaces provide a biocompatible and highly conductive support on which high levels of biological loading are attainable with comparative ease. This biofunctionalised surface can exchange electrons with solution-phase redox-active species or the redox-active prosthetic groups of immobilised metalloproteins. Either mechanism can be utilised in the generation of SWNT-based biosensing devices. If the chemical and physical manipulation of these structures can be refined to a sufficient extent one may fantasise about aligned arrays[36] of individually addressable enzyme-loaded nanotubes in simultaneous high-sensitivity multi-analyte detection.

Acknowledgement

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