

The Effects of Thin Layer Diffusion at Glassy Carbon Electrodes Modified with Porous Films of Single-Walled Carbon Nanotubes

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Due to their small size and remarkable electrical properties, carbon nanotubes have been used to modify electrode surfaces to create sensors for a range of important analytes. In this study, glassy carbon (GC) electrodes modified with films of HiPCo[®] single-walled carbon nanotubes (SWCNTs) were prepared by drop-coating dispersions of the nanotubes. A number of different solvents were evaluated for this purpose. Atomic force microscopy was used to show the porous nature of the nanotube assemblies. The modified electrodes were used in the determination of dopamine and epinephrine, and compelling evidence of thin-layer mass transport regimes within the porous films was observed using cyclic voltammetry. The work described here exposes some potentially flawed arguments commonly made in the literature regarding the ‘catalytic’ properties of nanotubes. We believe that the issues raised must be addressed if the much-promised applications of nanotubes in sensor devices are to become a reality.

Keywords: Carbon nanotube modified electrodes ; finite diffusion ; amperometric detection of dopamine.

1. INTRODUCTION

Carbon electrodes are used widely in electroanalysis due to their low background currents, wide potential windows, chemical inertness and low cost [1]. Since their identification by Iijima [2] in 1991, carbon nanotubes have been the subject of a vast number of studies in a multitude of disciplines within the physical sciences. Broadly speaking, CNTs may be classified as either single-walled or

multi-walled. The former are single, hollow tubes with diameters between 0.4 and 2 nm, while the latter are concentric tubes, 0.34 nm apart [3,4]. The average diameter of a multi-walled carbon nanotube (MWCNT) is around fifteen nanometers. Purification of HiPCo[®] nanotubes is done by treatment with strong acid, which introduces oxides to the nanotube surfaces at defect sites [5]. It has been shown [6,7] that the electrochemistry of nanotube-modified electrodes and the rate of electron transfer are greatly influenced by these functionalities.

Despite the presence of oxygenated species at defect sites, the vast majority of the mass of a nanotube is composed of hydrophobic basal-plane graphitic regions. This means that it is difficult to disperse carbon nanotubes uniformly in most solvents, and represents a considerable challenge when it comes to the controlled modification of electrode surfaces. Nanotubes have been traditionally dispersed in non-polar organic solvents such as dimethyl formamide [8-12]. In 2000, Ausman *et al.* [13] showed that carbon nanotubes may be dispersed in *N*-methyl-2-pyrrolidone (NMP). This solvent is now widely regarded as the most suitable for nanotube dispersion, following a very thorough study by Giordani and co-workers [14]. However, in electrochemical studies it has not been used to our knowledge. The reasons for it being overlooked have never been given. The present work explains why this solvent is not totally suitable as an agent for electrode modification.

The first application of nanotubes in electrochemistry was reported in 1996 by Britto *et al.* [15], who, using bromoform as a binder, packed a paste of nanotubes into a glass tube in order to study the redox reaction of dopamine. The process was found to occur at a much faster rate than observed using other catalytic surfaces. Subsequently, many other groups have attributed electro-catalytic properties to carbon nanotubes [8,16-24]. Britto's pioneering method for the fabrication of nanotube electrodes spawned several others, including the use of NT paper as the electrode [17,25] and abrasion onto the basal planes of pyrolytic graphite [19]. However, the most common approach has been the simple drop-coating [16,26-28] technique employed in the present work.

A considerable body of research has been carried out on the incorporation of nanotubes into sensors for a range of bio-molecules, including dopamine [15,16,20,23,24], ascorbic acid [16,20-24], uric acid [21,22,29], NADH [1,12,19,26,30], norepinephrine [19,22-24] and epinephrine [16,19,23,24]. Commonly it is shown that nanotube modification decreases peak separations (or oxidation potentials in the case of irreversible processes) and increases peak currents for the various species. The lowering of detection potentials by simple modification procedures involving nanotubes is easily achieved, perhaps so much so that precious few reports have taken the time to mention complications such as the possible adsorption of certain analytes onto nanotubes during electrochemical experiments, or differences in mass transport regimes between the modified electrodes and the underlying substrates against which they are so favorably compared.

Recently, Huang and co-workers [31] have noticed voltammetric evidence of the parasitic adsorption of species when using GC/MWCNT electrodes to study the drugs haloperidol and hydroxyzine. They suggested that before every scan, the modified electrode should be renewed by repeated cycles in background electrolyte until the unwanted peaks disappeared, and that only the first cycle should be analysed. Another recent paper by Streeter *et al.* [32] has questioned the common application of the semi-infinite planar diffusion model to electrodes modified with carbon nanotubes. These workers warned against the use of smaller voltammetric peak separations to infer enhanced

electro-catalysis of the standard ferro/ferricyanide redox reaction at GC/SWCNT electrodes. They pointed out that the lower values might not necessarily be entirely due to enhanced electron transfer kinetics, but might contain a significant contribution from thin layer mass transport within the porous nanotube assemblies. The present work extends this idea to two important analytes in sensor research, namely dopamine and epinephrine. Dopamine, epinephrine and norepinephrine are very important catecholamine neurotransmitters in the mammalian central nervous system and are often monitored electrochemically *in vivo* with microfibre electrodes. The oxidation of these compounds occurs in the human body. Catecholamine drugs are used to treat many ailments including heart disease and asthma. An understanding of the electrochemical reactions of these three structurally similar compounds is necessary in the development of methods for studying their physiological function, and to aid in the diagnosis of some diseases.

2. EXPERIMENTAL PART

2.1. Reagents and equipment

All chemicals in this study were of analytical grade and were used as received (from *Aldrich*) without any further purification. These were potassium ferrocyanide (99.0 %), potassium chloride (99.0 %), dopamine hydrochloride (>98 %) and epinephrine (>98 %). Potassium chloride solutions were prepared with water (18.2 M Ω) from an Elix[®] Millipore system. A 50 mM pH 7.0 phosphate buffer solution was purchased from *Aldrich* and used as background electrolyte for experiments involving dopamine and epinephrine. Purified single-walled carbon nanotubes (HiPCo[®]) were purchased from Carbon Nanotechnologies, Inc., and used as supplied (lot no. P0289).

A CH Instruments 440 potentiostat was used to perform all voltammetric measurements. These were conducted using a three-electrode configuration. Glassy carbon working electrodes (model CHI104, radius 1 mm), Ag / AgCl reference electrodes (CHI111) and platinum wire counter electrodes (CHI115) were supplied by IJ Cambria.

2.2. Electrode preparation

Glassy carbon electrodes were initially polished on Nylon pads covered with a paste of 1.0 micron alumina in deionised water. After thorough rinsing with the latter, they were polished using 0.3 micron alumina on Nylon pads. Finally, after more rinsing, they were polished using 0.05 micron alumina on Microcloth pads. When performing measurements using bare glassy carbon, the electrodes were placed immediately in the electrochemical cell after polishing. When further modification was required, they were blown dry using a stream of nitrogen and promptly modified.

Suspensions of carbon nanotubes were prepared by adding SWCNTs (1 mg) to 10 cm³ of the required solvent and agitating the mixture using a high-frequency sonicating tip. In order to fabricate GC/SWCNT electrodes, these suspensions were dropped (4 μ L) on inverted glassy carbon electrodes. The latter were then covered using clamped sample tubes and the solvents were evaporated by

exposure to a fan heater at 40 °C. The resulting films were clearly visible to the naked eye. We have previously published AFM images of these [28], which show randomly orientated, porous assemblies of nanotube bundles. The modified electrodes were rinsed sequentially with deionised water and working electrolyte before being placed in the cell. They were activated before measurements by cycling in background electrolyte until reproducible scans were obtained. Three or four cycles were usually found to be sufficient to achieve this.

3. RESULTS AND DISCUSSION

3.1. Solvent issues

We begin with investigations into the suitability of a number of different solvents as agents for nanotube dispersion prior to electrode modification. Giordani and co-workers [14] have noted that a desirable situation would be to develop a solvent in which nanotubes are thermodynamically soluble which corresponds to the situation where the Gibbs energy of mixing is negative. On a less definite but more practical level, it would be advantageous if a solvent could be identified in which nanotubes could be dispersed down to the level of individual strands or small diameter bundles for a reasonable period of time. Nitrogen containing solvents have been identified by many workers as being useful candidates for nanotube de-bundling. But why one may ask is this so? Recent work has suggested that the attributes of a good solvent for nanotube dispersion is the property of high electron pair donicity denoted β (the latter describing the ability of the solvent to donate a pair of non-bonding electrons to a suitable acceptor molecule to form a coordinate bond), a low hydrogen bond donation parameter α and a high solvatochromic parameter [33]. We are very far however from being able to quantitatively predict, in an ab-initio manner, the capability of a particular solvent to de-bundle single wall carbon nanotube ropes, due to the inherently complex nature of the problem. Giordani and co-workers discuss this topic in some detail in their seminal publication [14]. They utilized ideas from the theory of macromolecule solvation [34]. The Gibbs energy of mixing consists of an enthalpic component ΔH_m and an entropic component ΔS_m , the relevant relation being given by $\Delta G_m = \Delta H_m - T\Delta S_m$. Both the magnitude and sign of the enthalpy of mixing will determine whether the Gibbs energy of mixing is negative. The enthalpy of mixing is a measure of the relative strengths of solute-solute interactions versus solvent-solvent interactions versus solute-solvent interactions. In a true solution ΔH_m tends to be slightly positive or even negative reflecting a favourable solute-solvent interaction. Hence to successfully disperse carbon nanotubes in any solvent the solvent-nanotube interaction must be as strong as possible. The solvent molecule may not only interact with the hexagonal carbon lattice of the nanotube but also with the various oxygenated defects and polar functionalities present due to nanotube preparation protocols. It is also important that the solvent not be very ordered in the interfacial region near the nanotube wall since this ordering reduces the configurational entropy of mixing which generates an extra positive enthalpy contribution over and above that of mixing. If appreciable solvent ordering is present at the nanotube/solvent interface it costs more and more energy to create the interface as debundling proceeds.

Given the paucity of quantitative indicators for nanotube salvation in a given solvent it was decided to adopt a pragmatic approach with respect to solvent choice for modified electrode fabrication. In short a fast dispersal time coupled with significant stability when dispersed was set as the gold standard for solvent adoption. The use of acetone (dielectric constant, 20.7 at 298 K) was precluded by its volatility (b.p. 56.2 °C). It was found to readily evaporate due to the heat generated by the sonicating tip. Acetonitrile (dielectric constant, 37.5 (293 K), b.p. 81.6 °C) was also eliminated because the nanotubes were found to take a relatively long time (twenty minutes) to disperse in the solvent. Furthermore, the resulting suspensions were stable for no more than one day. In contrast, N,N-Dimethyl formamide (DMF) with a boiling point of 153 °C and a dielectric constant having a value of 36.7 at 298 K, showed promising results, forming very stable suspensions within five minutes of sonication. N-methyl-2-pyrrolidone (NMP) with a still higher boiling point of 202 °C, and a dielectric constant of 32 at 293 K, proved even more promising, with sonication producing stable dispersions within one minute. Hence our studies focused mainly on DMF and NMP as target solvents for nanotube debundling.

However, when it came to attempts at electrode modification, NMP showed itself to be quite obtuse when compared with DMF. NMP typically took far longer than DMF to desorb from the electrode surface (one day compared with 15 minutes) on application of a fan heater to the latter at a temperature of 40°C. As well as these obvious practical concerns, the final decision to choose DMF as the working solvent was reached on the basis of voltammetric measurements involving potassium ferrocyanide. Figure 1(a) shows a comparison between voltammograms obtained for the ferrocyanide redox reaction at electrodes modified using suspensions which were identical in every way except the solvent in which the nanotubes were dispersed. It is clear from Figure 1(a) that the voltammetric profiles recorded for the oxidation of ferrocyanide at nanotube modified glassy carbon electrode in which NMP and DMF were used as dispersal solvents was quite different. At any given sweep rate peak separations were greater and peak current value much smaller for the SWNT modified electrode using NMP as dispersion solvent (termed the NMP electrode) as compared to the modified electrode formed using DMF (the DMF electrode). The thermodynamics of the ferrocyanide/ferricyanide redox couple was independent of the choice of dispersal/debundling solvent since the standard potential for the redox couple was relatively unchanged when the dispersion solvent was varied from DMF to NMP. For the ‘NMP electrode’ $E^0 = 223$ mV whereas for the ‘DMF electrode’ $E^0 = 227$ mV when both measurements were performed at a sweep rate of 10 mV/s. Figure 1(b) shows the manner in which the voltammetric peak separations varied with scan rate. For the NMP electrode, they were observed to be larger and increased more steeply with increasing sweep rate than those determined for the DMF electrode. If peak separation is interpreted in terms of the Nicholson model based on finite reaction kinetics coupled with semi-infinite planar diffusion [35] then peak separation should be related to a theoretical Ψ parameter which in turn is related to the heterogeneous electron transfer rate constant k^0 according to

$$\Psi = \frac{(D_o/D_R)^{\alpha/2} k^0}{\sqrt{\pi D_o F v / RT}} = \frac{k^0}{\sqrt{\pi D_o F v / RT}} \quad (1)$$

where it has been assumed for simplicity that the diffusion coefficients of the oxidized and reduced forms of the redox couple (ferrocyanide and ferricyanide respectively) are equal which is a good assumption in the present case, and that the transfer coefficient α is 0.5. The theoretical Ψ parameter can be evaluated from the experimentally determined peak separation ΔE_p value at a given sweep rate value v using a working curve [36]. We have shown [36] that for $n\Delta E_p > 140$ mV the plot of $\log Y$ versus $n\Delta E_p$ is essentially linear and the variation is expressed by the following $\log \Psi = -K_1 n\Delta E_p + K_2$ where $K_1 = 5.36 \times 10^{-3}$ and $K_2 = 0.15$. It is worth noting that the variation of Ψ with peak separation is virtually independent of the value assumed for the transfer coefficient α for scan rate values at which the redox couple exhibits quasi-reversible kinetic behaviour [37]. If we assume a value for the ferrocyanide diffusion coefficient at 293 K as $8.12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 0.1 M KCl solution [38] then use of eqn.1 produces the result that $k^0 = \kappa \Psi \sqrt{v}$ where the constant $\kappa = 0.032$ and the sweep rate is expressed in units of V/s. Heterogeneous rate constants were calculated for both types of SWNT modified electrodes at typical sweep rates of 10, 20, 50, 70, 100 and 200 mV/s. The average values of heterogeneous rate constant obtained were $8.1 \times 10^{-4} \text{ cm s}^{-1}$ and $1.9 \times 10^{-2} \text{ cm s}^{-1}$ respectively for SWNT modified electrodes dispersed with NMP and DMF solvents respectively.

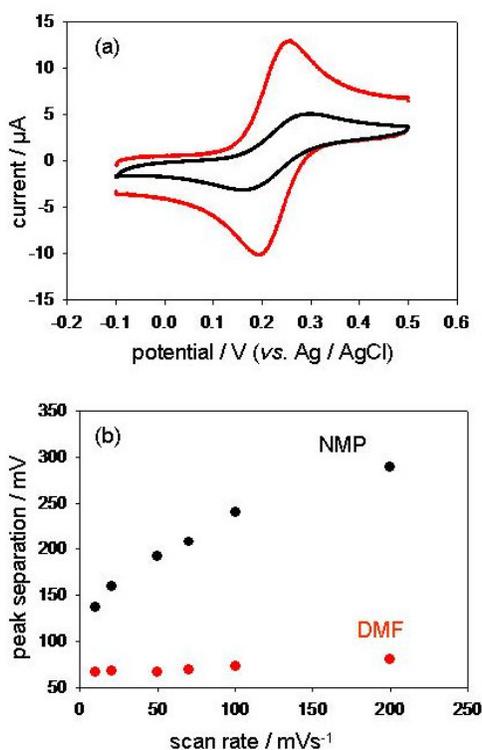


Figure 1. (a) Cyclic voltammograms for 1 mM potassium ferrocyanide in 0.1 M KCl at glassy carbon electrodes modified using suspensions of SWCNTs in both DMF and NMP. The scan rate employed was 10 mV s^{-1} . (b) The variation of peak separation with scan rate for the two electrodes.

These findings using a semi-infinite diffusion model, indicate that the use of NMP creates a kinetic sluggishness compared with DMF. It is difficult however to say with any great certainty why

this is so. It could be suggested that some NMP remains within the nanotube films, despite the application of heat until the electrodes are visibly dry. Hence we may expect that the nanotube is coated with an organic film of low dielectric constant solvent which may well inhibit electron transfer between the redox probe molecule and the nanotube strand. Furthermore diffusion of the probe molecule through pores containing significant quantities of immobilized NMP may be inhibited significantly compared with diffusion through a purely aqueous medium. If present within the film, it is likely that NMP is held there by strong interactions with surface oxides present on the nanotubes. These are the sites at which electron transfer occurs [6,7], so it is conceivable that the redox probe would have greater difficulty reacting at these functionalities. The smaller background currents found for the NMP electrode would certainly support the view that ferrocyanide has access to a smaller surface area or indeed that probe molecule diffusion is inhibited.

It should be noted that care should be taken when interpreting the cyclic voltammetry of solution phase redox couples at electrode surfaces modified with dispersed carbon nanotube meshes. Streeter and co-workers [32] have recently discussed the cyclic voltammetry of such systems. They suggested that the observed current response should be interpreted in terms of semi-infinite planar diffusion towards the macroelectrode surface and in terms of a finite diffusion model describing the redox reaction of the electroactive species trapped in solvent pockets in between the immobilized nanotubes, a situation which can be described using a diffusion model developed to describe voltammetry in a thin layer cell of a specific diffusion layer thickness L [39]. Hence the observed voltammetric behaviour of solution phase redox couples at SWNT modified electrode surfaces reflects a combination of semi-infinite and thin layer finite diffusion effects which may, to a first approximation, be additive .

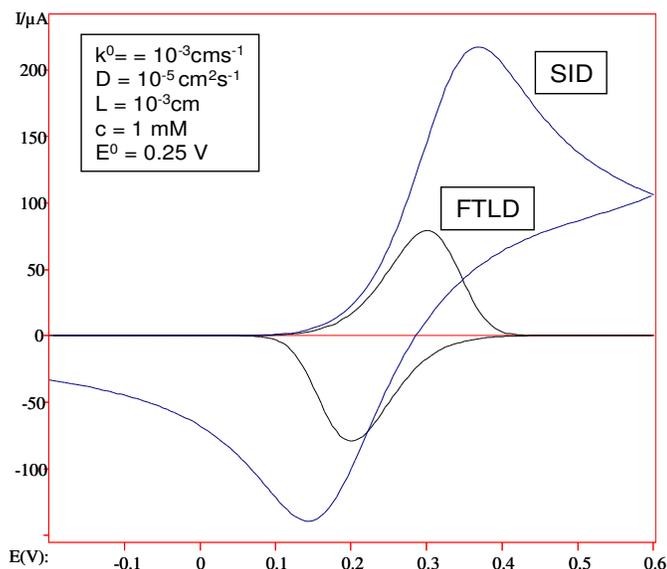


Figure 2. Typical voltammetric profiles computed using the commercial software package DIGISIM, for a simple solution phase redox couple reacting under semi-infinite diffusion conditions and within a thin layer cell. In both cases double layer capacitance and solution resistance effects were neglected and quasi-reversible kinetic behaviour is assumed.

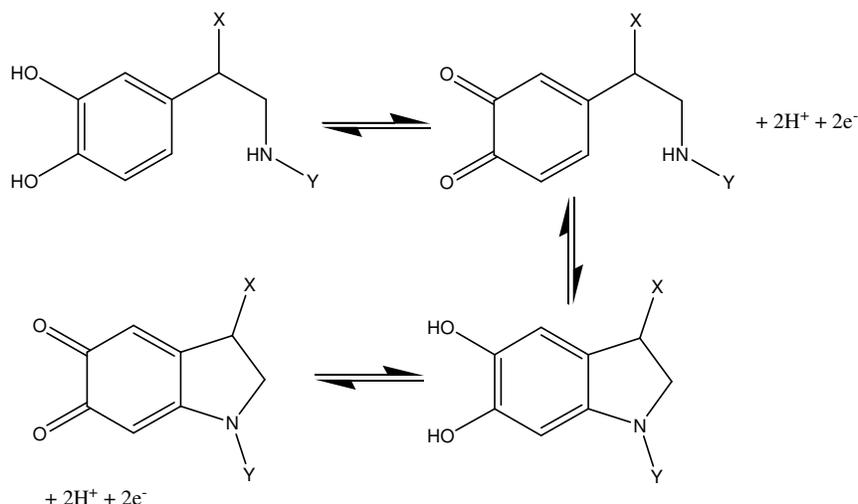
To further explore this idea we have performed a simulation of the cyclic voltammetric response of the transport and kinetics of a simple redox reaction such as ferrocyanide oxidation both under standard semi-infinite diffusion conditions and under conditions of finite thin layer diffusion. It is assumed that the electrode kinetics are quasi-reversible with a heterogeneous rate constant of $10^{-3} \text{ cm s}^{-1}$. The diffusion layer thickness is set at $L = 10^{-3} \text{ cm}$. We have used the commercial software package DIGISIM 3.0 developed by Feldberg and Rudolph and supplied by BAS [40] which is based on the fast implicit finite difference method [41]. The results are presented in figure 2. It is clear that adoption of a thin layer geometry results both in a marked lowering of the peak currents and a marked reduction in the peak to peak separation as compared with the corresponding quantities computed assuming semi-infinite diffusion. Indeed Streeter and co-workers [32] have extended this type of analysis and used DIGISIM to compute the variation of the peak to peak separation with assumed diffusion layer thickness L for a number of typical values for the heterogeneous rate constant k^0 (fig.4 of reference 32). The key result presented in this work was that for a given value of k^0 , inter-peak separation increases steadily with increasing diffusion layer thickness, until a threshold value of the latter is attained, typically 10^{-2} cm , after which ΔE_p remains invariant. This general trend is observed for all values of k^0 examined over the range $10^{-6} - 10^{-3} \text{ cm s}^{-1}$. Also when L gets very small and close to 10^{-6} cm , ΔE_p approaches zero. Hence figure 2 and the results presented in fig.4 of reference 29 suggest that the solvent effect behaviour presented in fig.1 of the present paper should be interpreted both in terms of thin layer finite diffusive effects resulting in a decrease in current intensity and kinetic inhibition effects resulting in an increase in inter-peak separation.

Whatever the explanation, it is now clear that DMF is the most suitable of the solvents investigated, and we may now address the interesting effects observed when nanotube-modified glassy carbon electrodes prepared in this way are used in the detection of dopamine and epinephrine.

3.2. Nanotube modified electrodes for dopamine determination

The redox chemistry of the structurally similar biomolecules dopamine, epinephrine and norepinephrine is well established and is outlined in scheme 1 below. In neutral aqueous solution these oxidations include two sequential electron transfer processes. In the first of these the compound is oxidized to an open-chain quinone (cyclic diketone) which then is transformed to a leucochrome. Finally, the latter is oxidised to form the cyclisation product.

Voltammetry was performed using a $50 \mu\text{M}$ solution of dopamine in phosphate buffer (pH 7.0). Figure 3 shows a comparison between voltammograms obtained using a bare (fig.3(a)) and nanotube-modified (fig.3(b)) glassy carbon electrode. Pairs of peaks corresponding to the redox reaction of dopamine were observed, with a standard redox potential of $+0.17 \text{ V}$ (*vs.* Ag / AgCl). Note the larger peak currents for the modified electrode, which are attributed to the large surface area of the nanotubes.



Scheme 1. Proposed scheme for the oxidation of epinephrine (X = OH, Y = CH₃), norepinephrine (X = OH, Y = H) and dopamine (X = H, Y = H).

The shape of the dopamine oxidation peak at the modified electrode indicated that comparison between the two electrodes might not be as straightforward as they have been commonly portrayed in the literature. The peak is considerably more symmetrical than that observed at the bare electrode. While the characteristic diffusive tail remains evident at the modified electrode (figure 3(b)), it is suggested that this peak might be the aggregate of contributions from up to *three* different processes. These are the expected oxidation of dopamine diffusing from bulk, dopamine diffusing through thin layers of solution within the porous NT film, and perhaps even dopamine adsorbed onto the surface of the nanotubes. While the large capacitive background current of the modified electrode¹ contributed to the symmetry of the peaks [42], it was felt that this possibility merited further investigation. With this in mind, a freshly-prepared GC/SWCNT electrode was scanned in phosphate buffer. After immersion in 50 μM dopamine for five minutes followed by thorough rinsing using deionised water, the electrode was again scanned in buffer. The result is presented in Figure 4.

Undeniably, the electrode had been modified during its immersion in dopamine solution. Redox peaks were observed, which are attributed to dopamine either adsorbed onto the nanotube surface, or present within thin layers of electrolyte trapped within the film. Comparison with Figure 3(b) also shows that these peaks were significantly smaller than those obtained when 50 μM dopamine was present in solution. Clearly, a greater quantity of charge is transferred when dopamine is present in solution, which might explain the survival of the diffusive tail. However, the point is that when an electrode modified in this way is exposed to dopamine, one must be aware that the response obtained in the subsequent determination of the latter is likely to contain a contribution from at least one ‘parasitic’ process. To our knowledge, such complications have not been pointed out widely in the literature.

¹ Typically we have measured for SWNT meshes in phosphate buffer solution pH 7 a double layer capacitance of 0.13 mF and a calculated surface area of $(9.76 \pm 0.98) \times 10^{-2} \text{ cm}^2$ yielding a surface specific capacitance of 1.4 mF cm^{-2} .

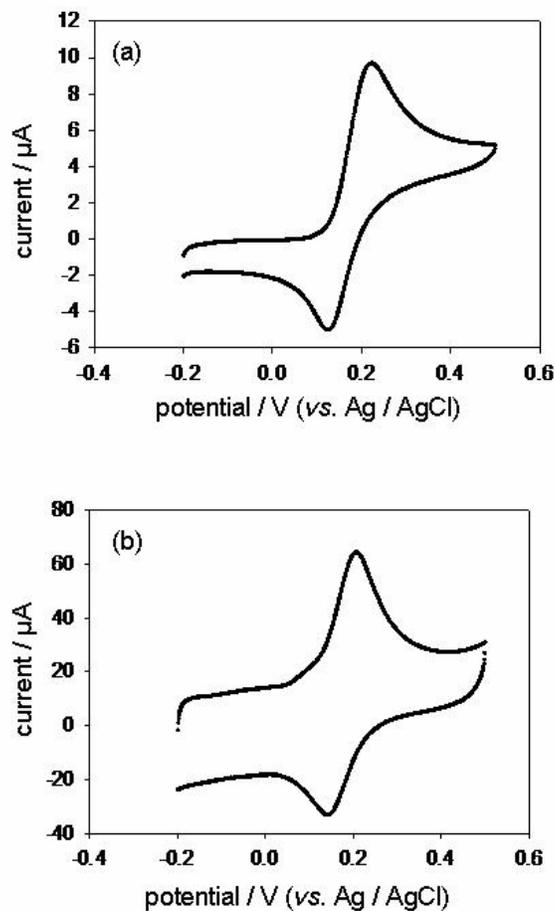


Figure 3. (a) Voltammogram for 50 μM dopamine in 50 mM phosphate buffer solution (pH 7.0) at a bare glassy carbon electrode. (b) Same for a SWCNT-modified glassy carbon electrode.

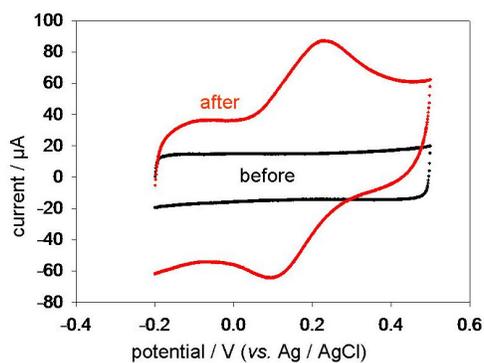


Figure 4. Voltammograms obtained using a SWCNT-modified GC electrode in pH 7.0 PBS before and after the electrode had been immersed in 50 μM dopamine for five minutes. No dopamine was present in the electrolyte in either of the experiments shown. The scan rate employed was 100 mV s^{-1} .

In publications concerning the use of modified electrodes to determine dopamine and other biomolecules, it is common to simply show that the modified electrode gives rise to smaller peak separations and therefore conclude that it has superior electro-catalytic properties when compared with the bare electrode. Figure 5 shows that in the present case, however, the data do not adhere to such a facile interpretation. If this figure is viewed purely on the basis of a semi-infinite planar diffusion model, it suggests that the modified electrode exhibits a superior electro-catalytic response at low scan rates, but the opposite situation prevails at high scan rates!

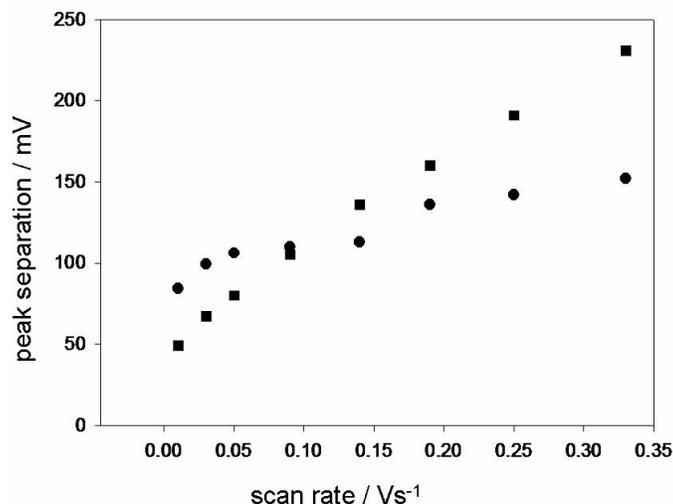


Figure 5. Comparison of peak separations obtained for bare (●) and SWCNT-modified (■) glassy carbon electrodes in 50 μM dopamine in 50 mM pH 7.0 phosphate buffer at various sweep rates.

Reasons for this are debatable but it is suggested that, at high sweep rates, there is not enough time for diffusion through the narrow pores in the film and therefore no significant contribution from thin layer behaviour. At low scan rates, however, there is sufficient time for the nanotube film to behave as a three-dimensional electrode, with significant contributions from species diffusing within thin layers. It is envisaged that the reaction occurs not only at the outer surface of the nanotubes but also at reactive sites within the adsorbed assembly. Like adsorbed species, thin layer species give rise to smaller peak separations and more symmetrical peaks³³. It is therefore conceivable that the observed separations at the modified electrode are deceptively low. This suggestion is supported by the 'more diffusive' appearance of the peaks at higher scan rates. Figure 6 shows a comparison between scans obtained using a GC/SWCNT electrode in dopamine solution at high and low sweep rates. Of course, peak currents and separations are higher for larger scan rates, but the difference in the *shape* of the peaks is noted with particular interest. Caution is urged, therefore, when assigning 'catalytic' properties to nanotubes on the basis of voltammetric peak separations before contributions from thin layer and/or adsorbed species are ruled out.

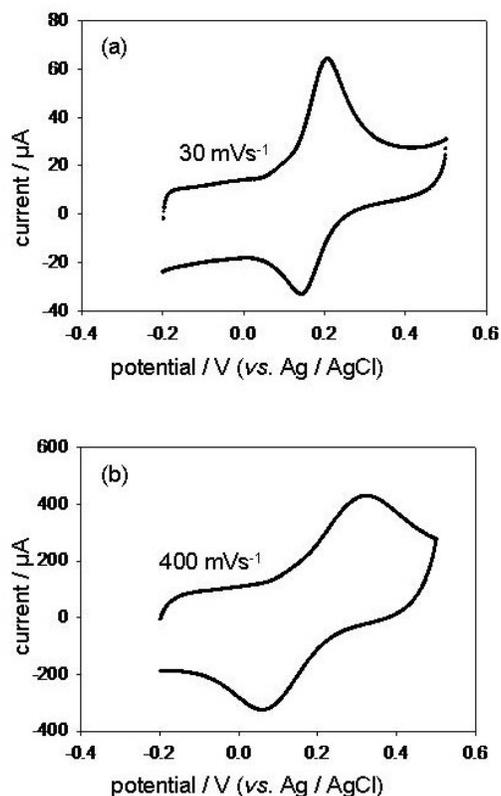


Figure 6. (a) Cyclic voltammogram obtained at 30 mV s^{-1} using a GC/SWCNT electrode in $50 \mu\text{M}$ dopamine in pH 7.0 phosphate buffer solution. (b) Same at a scan rate of 400 mV s^{-1} .

Further evidence for the possible operation of thin layer finite diffusion behaviour was found from potential step chronoamperometric experiments. In these experiments, the potential was held at 0 V for 25 seconds to ensure only the reduced form of dopamine was present near the electrode surface. The potential was then stepped to $+0.3 \text{ V}$ (vs. Ag / AgCl) and the current response was recorded. The pulse width was four seconds, which was found to be sufficient to allow currents to decay to steady-state values, as shown by the raw data in Figure 7(a). Currents recorded for dopamine oxidation at the nanotube mesh modified electrode are higher than those recorded at the unmodified glassy carbon electrode. This is as expected due to differences in surface area. What is more interesting is the data presented in figure 7(b) where the current response is plotted as a function of inverse square root of time. This is the so called Cottrell format. For a simple redox reaction where mass transport occurs via semi-infinite diffusion the current should be directly proportional to the inverse square root of time (the Cottrell relationship). The simple Cottrell linearity is observed for dopamine diffusion and reaction at the unmodified glassy carbon electrode. However, the GC/SWCNT data deviate drastically from the semi-infinite Cottrell model. Indeed the specific form of the Cottrell plot is characteristic of finite diffusion coupled with electron transfer where the expected Cottrell linearity is observed at short times whereas a marked deviation from linearity is observed at longer times. It can be shown that

solution of the potential step problem under conditions of finite diffusion yields the following expression for the current transient [43] :

$$i = \left(\frac{D}{\pi t}\right)^{1/2} \frac{\Delta Q}{L} \left\{ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp\left[-\frac{j^2 L^2}{Dt}\right] \right\}$$

$$= \left(\frac{D}{\pi t}\right)^{1/2} \frac{\Delta Q}{L} \sum_{j=0}^{\infty} \left\{ \exp\left[-\frac{jL^2}{Dt}\right] - \exp\left[-\frac{(1+j)^2 L^2}{Dt}\right] \right\} \quad (2)$$

Where we note that ΔQ denotes the charge passed under the current transient and L denotes the diffusion layer thickness.

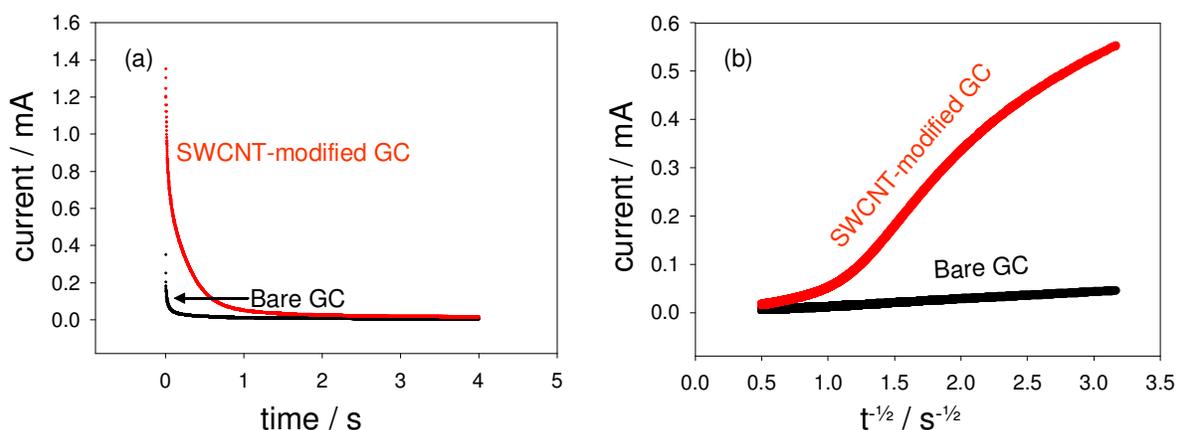


Figure 7. (a) Chronoamperometric responses of 50 μM dopamine at bare and SWCNT-modified glassy carbon electrodes to a potential step from 0 to +0.3 V after poisoning the electrodes at 0 V for 25 seconds. Pulse widths were four seconds. (b) The resulting Cottrell plots.

We note that at short times when $t \ll D/L^2$ the concentration polarization within the finite region between the nanotube strands does not reach the boundary of the diffusion space and eqn.2 reduces to the well known Cottrell equation for semi-infinite diffusion:

$$i = \left(\frac{D}{\pi t}\right)^{1/2} \frac{\Delta Q}{L} \quad (3)$$

At longer times when $t \cong D/L^2$ the concentration polarization in the interstrand pore reaches the surface of the diffusion space and the diffusion limited current falls below that predicted by eqn.2. This can be seen in the experimental data presented in fig.7(b) where the current is less than that

predicted by the linear Cottrell response at longer times when the exponential terms in eqn.2 become significant.

3.3. Nanotube modified electrodes for epinephrine determination

At the bare glassy carbon electrode, the oxidation of this bio-molecule was found to occur at a potential of +0.31 V (*vs.* Ag / AgCl). When the nanotube-modified electrode was used, this peak shifted negatively to +0.20 V, and the oxidation peak current increased dramatically (see Figure 8). This oxidative peak shift of 110 mV is considerably larger than the 70 mV reported by Luo *et al.* [16] and the 50 mV reported by Wang and co-workers [23] for SWCNTs immobilised on a glassy carbon electrode.

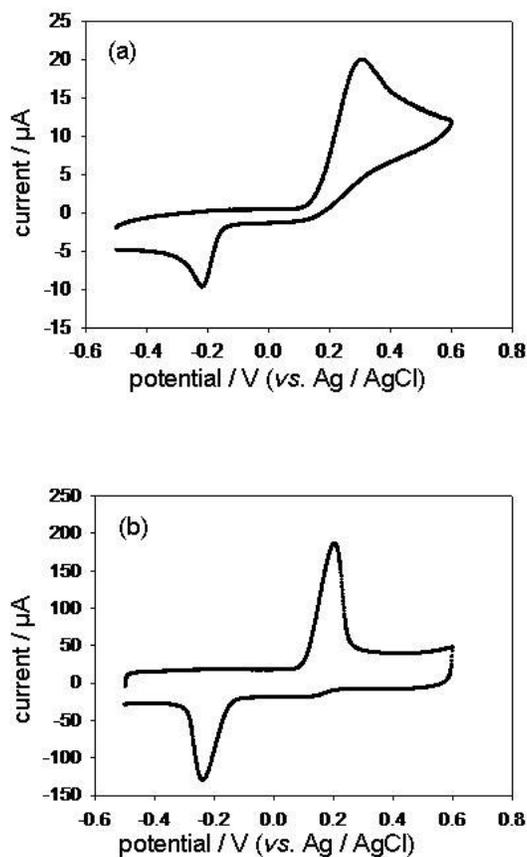


Figure 8. (a) Cyclic voltammogram for 0.4 mM epinephrine in phosphate buffer (pH 7.0) at a bare glassy carbon electrode. The scan rate was 100 mV s^{-1} . (b) Same for a SWCNT-modified GC electrode.

It is our view that it is naïve to attribute these effects definitively to the superior electrocatalytic properties of the nanotube mesh. The striking symmetry of the oxidation peak at the modified electrode leads us to propose that thin layer diffusive conditions coupled with reactant adsorption must

be considered in this case. The marked separation between the oxidation and reduction peaks is also of note. We will return to this interesting system in a subsequent paper.

4. CONCLUSIONS

We have shown for the first time that, despite its excellence as a solvent, *N*-methyl-2-pyrrolidone is not suitable as an agent for the modification of electrode surfaces with carbon nanotubes. Using the bio-molecules dopamine and epinephrine, we have provided evidence of thin-layer behaviour at GC/SWCNT electrodes. We have therefore concluded that it may be foolhardy to attribute the observed peak shifts exclusively to enhanced reaction kinetics. The three-dimensional characteristics of electrodes fabricated in this way mean that comparisons between bare and modified electrodes are not as straightforward as they have been portrayed until now. We have pointed out that, during voltammetric measurements, the prevailing mass transport regime at a nanotube-modified electrode depends on the sweep rate chosen, and this has serious implications for research into the applications of nanotubes in sensors. In particular, standard electrochemical tests based on the planar diffusion model such as the variation of peak currents with scan rate are undermined, since the problem of thin-layer behaviour effectively means that the electrode does not have a constant active surface area as sweep rate changes.

Despite the vast number of publications extolling the 'electro-catalytic' properties of carbon nanotubes, their true value as sensors may not be fully understood until this issue is resolved. In the future, we recommend that this problem should be approached from both practical and theoretical perspectives. The fabrication of robust, aligned arrays of thin nanotubes on electrode surfaces will perhaps lead to non-porous nanotube assemblies whose mass transport regimes may justifiably be treated using the semi-infinite planar diffusion model. As regards theory, the work presented here exposes the need for the development of an alternative model of mass transport which can satisfactorily incorporate contributions from both planar and thin-layer diffusion to an electrode surface.

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