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Abrasive immobilization of carbon nanotubes on a basal plane pyrolytic graphite electrode: application to the detection of epinephrine

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The performance of a basal plane pyrolytic graphite (bppg) electrode modified with carbon nanotubes is described. Abrasive immobilization of multiwall carbon nanotubes on a bppg electrode was achieved by gently rubbing the electrode surface on a filter paper supporting carbon nanotubes. The resulting electrode showed excellent mediation of epinephrine oxidation: a decrease in the overvoltage of the epinephrine electro-oxidation (200–500 mV) was observed as well as a dramatic increase in the peak current (4 times) compared to that seen at a bare bppg electrode. The oxidation peaks of epinephrine and ascorbic acid which overlap on bare bppg electrode were separated successfully (by *ca.* 220 mV) at the surface of the modified bppg electrode. The modified electrode showed good stability in comparison to most modified carbon nanotubes electrodes prepared by alternative methods.

Introduction

Since the discovery of carbon nanotubes in 1991 they have been the focus of intense interest.[1] Carbon nanotubes (CNTs) possess a high electrical conductivity, chemical stability and mechanical strength.[2] The properties of carbon nanotubes suggest that they have the ability to change electron transfer reactions when used as an electrode modifying material. The excellent electrocatalytic ability of carbon nanotubes in the redox behaviour of different compounds has been reported.[3–18] The first type of carbon nanotube electrode was constructed using multiwall carbon nanotubes (MWCNT) mixed with bromoform as a binder packed into a glass capillary. This modified electrode showed a dramatic improvement in respect of the electrochemical oxidation of dopamine.[3]

Glassy carbon electrodes modified with single and multiwall carbon nanotubes have been used for the electrocatalytic oxidation of 3,4-dihydroxyphenylacetic acid,[4] NADH,[5] norepinephrine,[6] 4-aminophenol,[7] 6-mercaptopurine,[8] nitric oxide,[9] ascorbic acid,[10] and cytochrome C.[11] The electrocatalytic activity of Pt[12,13] and Au[14] microelectrodes modified with nanotubes have also been investigated along with carbon nanotube paste electrodes[15,16] and carbon nanotube/teflon composites;[17] the effect of the surface state upon the electrode kinetics of modified carbon nanotubes electrodes has been explored.[18] Carbon nanotubes dispersed in *N*,*N*-dimethylformamide(DMF) were cast on a glassy carbon electrode to form a CNT film, which showed stable electrochemical behaviour and could be used for the electrochemical oxidation of some biomolcules such as dopamine, epinephrine, ascorbic acid and norepinephrine.[6,10] These CNT modified electrodes have shown interesting catalytic properties toward electrochemical processes, but the method of modification is difficult and irreproducible, requiring a substantial preparation time and there is clearly scope for the method of electrode preparation to be improved. Hence it is pertinent to explore and develop a simple and reliable method to fabricate electrode surfaces modified with carbon nanotubes.

In the present study multiwall carbon nanotubes were abrasively attached to the basal plane pyrolytic graphite (bppg) electrodes using the approach of Scholz developed for the study of solid electrocatalysts.[19] The resulting films showed very stable electrochemical behaviour and were used to mediate the electrochemical oxidation of epinephrine with the successful elimination of the interference by ascorbic acid in voltammetric detection of the latter.

Experimental

Reagents and equipment

Multiwall carbon nanotubes with a 95% purity (10–20 nm diameter and 1 μm length) were obtained from NanoLab (Brighton, MA). Epinephrine (4-[1-hydroxy-2-(methylamino)ethyl]-1,2-benzenediol, and all other reagents were obtained from Aldrich and used without further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm (Vivendi water systems, UK).

Electrochemical measurements were carried out in a conventional three electrode cell using an μ-Autolab 2 PGSTAT computer controlled potentiostat (ECO-Chemie, The Netherlands). A basal plane pyrolytic graphite electrode (Le Carbone, Ltd., Sussex, UK) was used as the working electrode; a platinum wire and saturated calomel electrode (SCE, Radiometer, Copenhagen) were used as the counter and reference electrodes respectively. The basal plane pyrolytic graphite electrode was housed in a Teflon mounting. The rotating disk electrode of bppg electrode (5 mm diameter in Teflon) was made in the workshop of Physical and Theoretical Chemistry Laboratory, Oxford. The bppg electrodes modified with carbon nanotube layers were characterized by scanning electron microscopy (SEM) using a Cambridge stereoscan electron microscope.

Immobilization of MWCNT on basal plane pyrolytic graphite electrode

First the purification of the supplied carbon nanotubes was accomplished by stirring the CNT in concentrated nitric acid at 60 °C for 12 h.[5] A basal plane pyrolytic graphite electrode was carefully polished with polish paper and then ultrasonically cleaned in distilled water. 2 mg of purified MWCNT was placed on a filter paper (Whatman no. 1001 110). The MWCNT were then abrasively immobilised onto the bppg electrode by gently rubbing the electrode surface on fine qualitative filter paper containing the carbon nanotubes for 1 min. The electrode was rinsed with distilled water before use.

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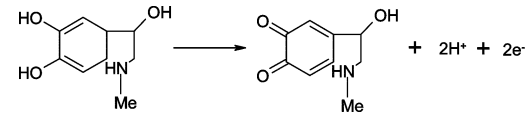
Results and discussion

Electrocatalytic oxidation of epinephrine at the MWCNT modified bppg electrode

Characterisation of the MWCNT film on a basal plane pyrolytic graphite electrode was investigated with SEM. As is shown in Fig. 1 many MWCNT bundles with a general diameter in the range 10–20 nm can be observed. The surface coverage by nanotubes can be estimated from such images.

Fig. 2 shows cyclic voltammograms of epinephrine at a bare bppg electrode (polished) and the electrode modified with carbon nanotubes in 0.1 M phosphate buffer solution (pH 7). With the unmodified electrode, the oxidation shows a broad peak, with a peak potential of 0.45 V *vs*. SCE. However at the nanotube modified electrode a clear anodic peak was observed at 0.18 V and the peak current was increased significantly in comparison with the unmodified electrode. The use of the nanotube layer to mediate the epinephrine oxidation is evident from the reduction of overpotential (250 mV) and three fold current increase compared with that of the bare electrode. These values are comparable or better than results for that reported at nanotube modified electrodes for the electrocatalytic oxidation of different neurotransmitters including the electrooxidation of norepinephrine and dopamine at a Au electrode modified with a single wall carbon nanotube film,[14] the voltammetry of dopamine, norepinephrine and epinephrine at the surface of glassy carbon electrode similarly modified.[6,10] Cyclic voltammograms of epinephrine in aqueous solution of different pH in the range 2 to 11 were recorded at the surface of a modified MWCNT electrode (Fig. 3). It was found that the peak potentials shifted negatively along with the increasing pH but that the peak currents are broadly similar. This is a consequence of the deprotonation involved in the oxidation process that is facilitated at higher pH values. The modified electrode shows stable electrocatalytic activity over the wide range of pH values studied (2–11). According to the literature reported,[20–22] the catalytic oxidation of epinephrine at the modified nanotube electrodes is described by the following equation.



A plot of peak potential *versus* pH was found to be linear over the pH range 2–8 with a gradient of 60 mV consistent with a 2 proton, 2 electron process.

The dependence of the voltammetric response of the modified CNT electrode to the addition of epinephrine concentration (0.4–1.6 mM) was investigated. With additions of epinephrine, the anodic peak currents were observed to increase with the dependence of the peak current response to the concentration of epinephrine found to be linear in the range 0.2–5 mM

The effect of scan rate on the electrooxidation of epinephrine at the modified electrode was investigated by cyclic voltammetry at pH 4 and 7. Fig. 4 shows the oxidation peak currents of epinephrine increased linearly with the square root of scan rates in the range 10–90 mV s^{-1}, with a correlation coefficient of 0.998. This suggests that the process of electrode reaction is controlled by diffusion, which is the ideal case for quantitative applications. At pH 4 the same behaviour was observed. The stability of modified electrode and its mediation for epinephrine oxidation was investi-

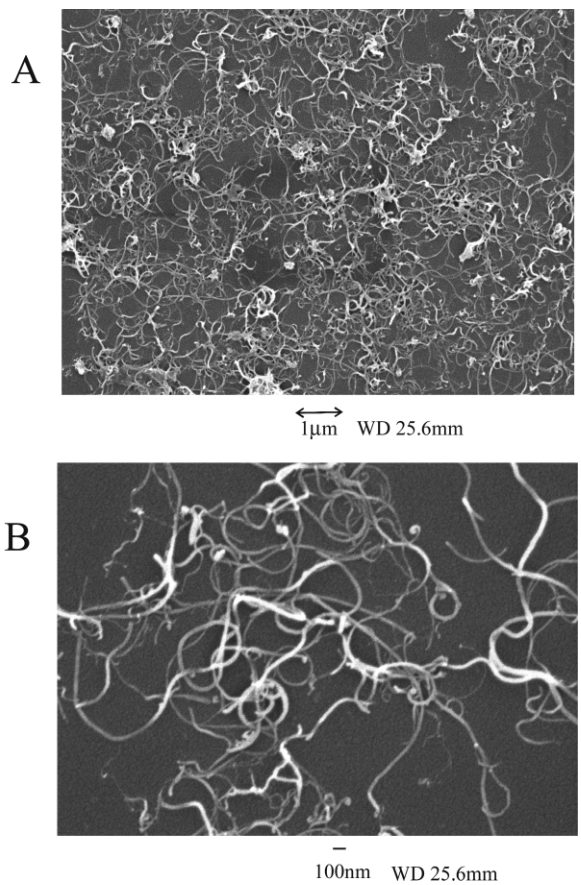


Fig. 1 SEM images of CNTs used to fabricate the CNT modified bppg electrode, magnification (A) 10000 and (B) 33000.

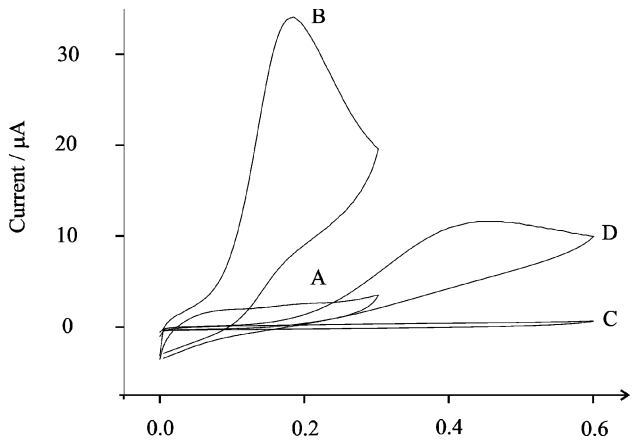


Fig. 2 Cyclic voltammograms at MWCNT film modified bppg electrode (A) and a bare bppg electrode (C) in the absence of epinephrine. The response of the modified (B) and unmodified (D) bppg electrode in the presence 0.4 mM of epinephrine in 0.1 M phosphate buffer solution pH 4.3, scan rate 20 mV s^{-1}.

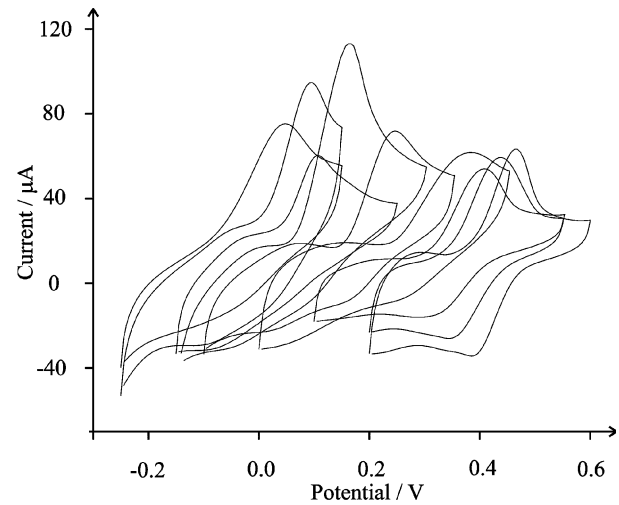


Fig. 3 Cyclic voltammograms of 0.4 mM epinephrine solution at a basal plane electrode modified with MWCNT film at different pH (from right to left 2, 3, 4, 5, 6, 7, 8, 10, and 11) scan rate 10 mV s^{-1}.

gated by recording the cyclic voltammograms of carbon nanotube modified bppg electrode before and after they were used in the presence of epinephrine. After cycling the potential for 50 cycles at scan rate 40 mV s^{-1} in solution containing 0.4 mM epinephrine, then rinsing the modified electrode and recording the cyclic voltammograms in the presence of epinephrine the peak potentials were unchanged to positive values and the currents were decreased by less than 2% but at bare bppg electrode the peak potential shifts to positive value (65 mV) and the peak current was decreased more than 12%. Thus the modified CNT electrode minimizes surface fouling and passivation effects. Also on using the electrodes after leaving them unused for period of one week the peak potential for epinephrine oxidation was again unchanged and the current signals showed only less than a *ca*. 3% decrease of the initial response. In reproducibility tests, it was found that the relative standard deviation (RSD) of the cyclic voltammogram currents of 0.4 mM epinephrine (pH 4.3) for eight replicate determinations was 2%.

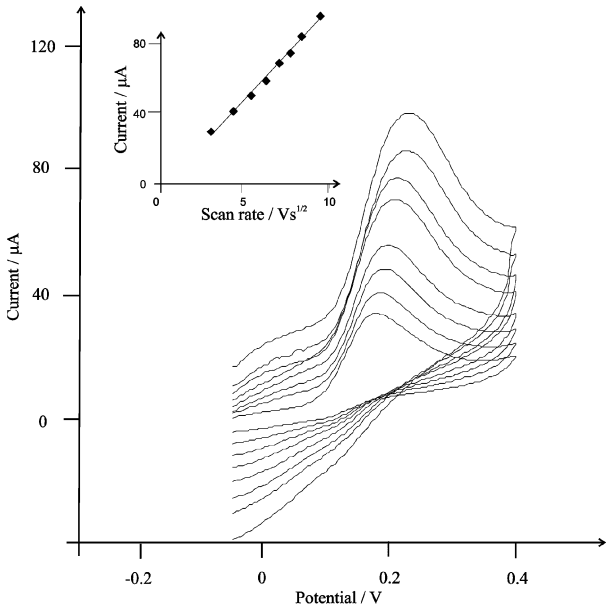


Fig. 4 Cyclic voltammograms of modified bppg electrode in phosphate buffer (0.1 M) solution pH 6 containing 0.4 mM epinephrine at different scan rates (from inner to outer) 10, 20, 30, 40, 50, 60, 70 and 90 mV s^{-1}. Inset, the variation of peak currents *vs*. square root of scan rate.

Amperometric detection of epinephrine at modified CNT electrode

As shown above the carbon nanotube modified bppg electrode has excellent and strong mediation properties and facilities the low potential amperometric measurement of epinephrine. Fig. 5 shows chronoamperograms recorded at a rotating modified bppg electrode (rotation speed 600 rpm), under conditions where the potential was kept at 0.25 V in phosphate buffer solution with pH 7. As shown during twelve successive additions of 0.5 μM a well-defined response is observed. For each addition of epinephrine, within a response time of *ca*. less than one second, a sharp rise in the current was observed. The plot of current *vs*. epinephrine concentration is shown inset in Fig. 5. The calibration plot was linear over the wide concentration range, 0.1 μM to 0.1 mM. Linear least squares calibration of the curve over the range 0.5–6.5 μM (13 points) had a slope of 420 nA μM^{-1} (sensitivity), a correlation coefficient of 0.999 and the detection limit was 0.02 μM. An extremely attractive feature of the carbon nanotube modified electrode is its highly stable amperometric response toward epinephrine. Fig. 6 shows the amperometric response of 40 μM epinephrine as recorded over a continuous 20 min period. Also the amperometric current of epinephrine remained unchanged after the CNT modified electrode was stored for three weeks in 0.1 M phosphate buffer solution (pH 7), indicating that it could be used as stable sensor for epinephrine detection.

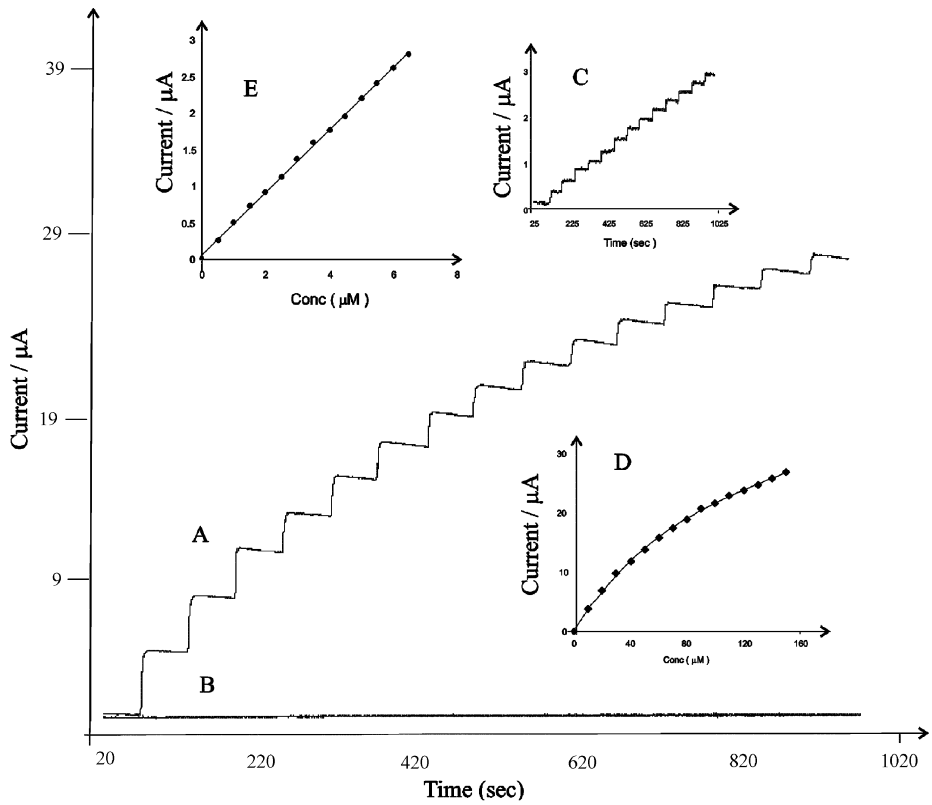


Fig. 5 Amperometric response at rotating modified bppg electrode (rotation speed 1200 rpm) held at 0.25 V in phosphate buffer solution (pH 7) for successive addition of (A) 10 μM and (C) 0.5 μM epinephrine. (B) is the response of additions to a bare bppg electrode. D and E are the plot of chronoamperometric currents *vs*. epinephrine concentrations from (A) and (C).

Analytical performance of the MWNT modified bppg electrode for the simultaneous measurement of epinephrine and ascorbic acid

The primary potential interfering agent in the electrochemical detection of neurotransmitters is ascorbic acid and various modified electrodes have been used for separation of the electrochemical responses of the neurotransmitters and that of ascorbic acid.[23–25] In the present study cyclic voltammetry was used to examine the simultaneous electrochemical response of ascorbic acid and epinephrine. Shown in Fig. 7, curve a is a cyclic voltammograms of a 0.4 mM solution of epinephrine containing 0.2 mM ascorbic acid in 0.1 M phosphate buffer solution (pH 4) at a bare bppg electrode. An overlapped smaller broad anodic peak corresponding to the oxidation of both epinephrine and ascorbic acid was observed at a bare electrode. However, the two oxidation peaks were clearly resolved at the MWCNT modified electrode (curve b) showing potential separation of 220 mV, which was large enough to allow the simultaneous determination of epinephrine and ascorbic acid in mixture. Fig. 8 shows the cyclic voltammograms of solutions containing ascorbic acid and different concentrations of epinephrine. As shown the peak currents for the oxidation of epinephrine increases with concentration.

Conclusions

A modified MWCNT electrode was successfully fabricated by abrasively attaching CNT to basal plane pyrolytic graphite electrode. A stable film with long stability and excellent reproducibility was achieved on the bppg electrode surface. Moreover the modified electrode could be used for the simultaneous determination of epinephrine and ascorbic acid. Compared with other types of CNT modified electrodes the preparation of the MWCNT modified bppg electrode is simple, fast and reproducible and the sensitivity, response time and selectivity of the modified electrodes are higher.

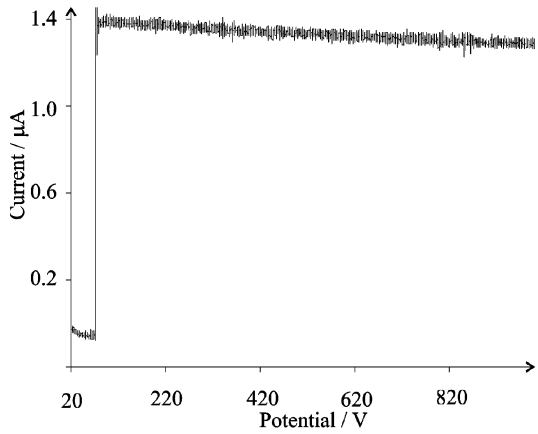


Fig. 6 Stability of the response of the modified electrode to 40 μM epinephrine, other conditions as in Fig. 5.

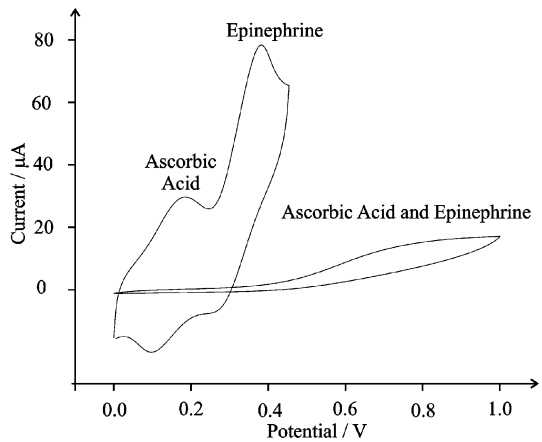


Fig. 7 Cyclic voltammograms of mixture of 0.4 mM epinephrine + 0.4 mM ascorbic acid in 0.1 M phosphate buffer solution (pH 9) at a bare bppg electrode (lower scan) and a MWCNT film modified electrode (upper scan), scan rate 20 mV s^{-1}.

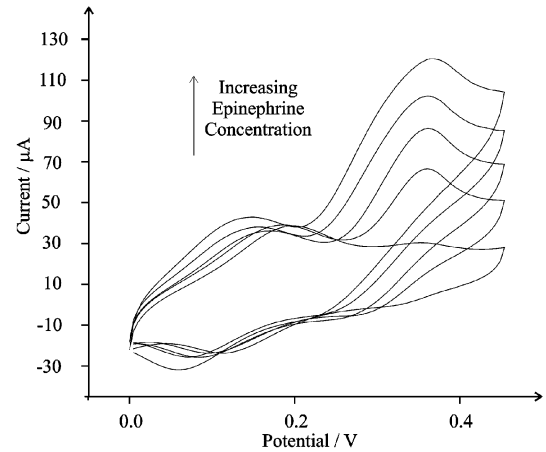


Fig. 8 Cyclic voltammograms of solution containing 1 mM ascorbic acid and different concentration of epinephrine (from inner to outer 0.2, 0.4, 0.6 and 0.8 mM epinephrine), scan rate 10 mV s^{-1}, pH 7.

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