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Electrolysis of Ammonium Carbamate: A Voltammetric and X-ray Photoelectron Spectroscopic Investigation into the Modification of Carbon Electrodes

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Uchiyama *et al*. (*J. Electrochem. Soc.*, 154, F31 (2007)) report that a glassy carbon (GC) electrode modified with surface amino groups via the electrochemical oxidation of ammonium carbamate can react with catechol in a 1,4-Michael addition through the surface amino groups. This was deduced from XPS data and the observation of a new reversible couple at less positive potentials than the catechol redox couple, which was attributed to a quinone-imine-like adduct. In this paper we demonstrate that identical voltammetry is observed at an unmodified GC electrode that has been oxidatively pre-treated in an identical fashion to that reported by Uchiyama *et al.* but in the absence of ammonium carbamate and any other sources of nitrogen. XPS characterisation of a graphite electrode before and after electrolysis in ammonium carbamate solution suggests that the nitrogen species on the carbon surface may not be in the form of amino groups, but may due to adsorbed ammonium ions or the formation of amides. This indicates that it is not the surface amino groups that are reacting with catechol, and alternative explanations are discussed.

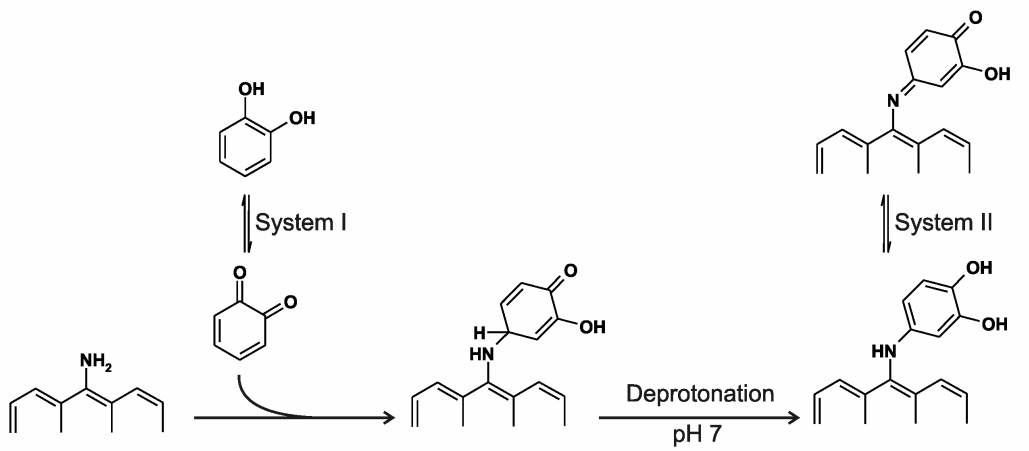
Keywords: Glassy carbon, catechol, *o*-benzoquinone, surface modification, electropolymerisation

1. INTRODUCTION

Graphitic carbon electrodes have found widespread use in a range of electrochemical applications, in part due to their relative chemical inertness in a range of common electrolytes and wide potential window, typically +1 to -1 V in aqueous solutions[1-3]. But it is the relative ease in

which carbon surfaces can be chemically modified to tailor the properties of the electrode which is currently attracting a great deal of interest amongst electrochemists[4-8]. Several reviews have covered the topic of chemically modified carbon and carbon nanotube electrode substrates: see for example references 6 and 8 and references contained therein.

One method of chemically modifying the surface of a glassy carbon (GC) electrode was recently reported by Uchiyama *et al.*[9] who claimed that amino groups could be grafted onto the electrode surface with a high coverage simply by repeatedly cycling the electrode potential beyond 0.9 V vs. Ag/AgCl in a 0.1 M solution of ammonium carbamate ($NH_2CO_2^-NH_4^+$). The presence of surface amino groups was supposedly confirmed by carrying out cyclic voltammetry in the presence of catechol, the oxidised *o*-quinone derivative of which is reported in their earlier work to react with primary and secondary amines such as aniline and dialkylamines[10, 11], and is widely known to undergo 1,4-Michael additions with a variety of amine species[12-15]. Two quasi-reversible redox processes were observed which Uchiyama *et al.* attributed to physisorbed catechol at *ca.* 0.1 V vs. Ag/AgCl and the purported adduct of surface amino groups with the catechol at *ca.* -0.05 V (scheme 1), which we will refer to as system I and II respectively[9].



Scheme 1. The mechanism proposed by Uchiyama *et al.* to explain the observed voltammetry corresponding to system I and system II, adapted from reference 1.

Diligently Uchiyama *et al.* performed several control experiments such as electrolyzing in ammonium carbonate solution and used X-ray photoelectron spectroscopy (XPS) to further confirm that the presence of nitrogen-containing groups on the electrode surface was only due to electrolysis of the ammonium carbamate. The XPS results presented provide compelling evidence that nitrogen atoms are incorporated onto the GC surface using this procedure[9].

The work by Uchiyama *et al.* prompted us to extend their derivatisation technique to modify other forms of graphitic carbon including graphite and carbon nanotubes (CNTs) as part of a separate research project to that reported herein. To test for the presence of surface bound amino groups we too utilised the reported method whereby the "modified" graphite or CNT electrodes were cycled in a solution of 1mM catechol and then the electrode was washed and immersed into a pH 7 buffer solution and subsequently cyclic voltammetry was used to look for systems I and II. However, we also performed a control experiment in which the graphite or CNT electrode was first subjected to repeated

cycling up to potentials beyond 0.9 V (0.9-1.4 V see below) in phosphate buffer in the absence of any carbamate or other nitrogen containing species and then the test with catechol was performed as described in reference 9. The results of these simple control experiments are not the subject of this report. However what we can say is that, disturbingly, in these control experiments systems I and II were always observed even though the graphitic surface could not have been modified with any amino or other nitrogen containing species, in contrast to the results reported by Uchiyama *et al*[9].

This result led us to repeat the experiments of Uchiyama *et al.*, this time using a GC electrode as used in their original work, but in addition we performed the control experiments where electrolysis of the GC electrode was performed in the absence of carbamate. It is the results of these experiments that are reported here, in addition to some comparative experiments on the surface of a graphite electrode. Our results suggest that an alternative mechanism to that proposed by Uchiyama *et al.* must be responsible for the observed voltammetry, and that the nitrogen-containing species incorporated onto the electrode surface by oxidation of ammonium carbamate may not necessarily be reactive amino groups.

2. EXPERIMENTAL PART

2.1. Reagents and Equipment

All reagents were purchased from Aldrich (Gillingham, UK) with the exception of potassium chloride (Reidel de Haën, Seelze, Germany), and were of the highest grade available and used without further purification. Aqueous solutions of 0.1 M ammonium carbamate (pH 8.9) were freshly prepared in de-ionised water (minimum resistivity 18.2 MΩ cm at 25°C) immediately prior to performing any voltammetry. A buffer solution of pH 7 was prepared using 0.25 M KH_2PO_4 + 0.25 M Na_2HPO_4. These solutions contained in addition 0.1 M KCl as supporting electrolyte.

Electrochemical measurements were carried out using a μAutolab computer controlled potentiostat (Ecochemie, Utrecht, Netherlands) in a cell of volume 10 cm^3 using a three-electrode configuration. Either a glassy carbon electrode (GC; 3mm diameter, BAS, Indiana, USA) or a basal-plane pyrolytic graphite electrode (bppg; 5 mm diameter, Le Carbone, Sussex, UK) acted as the working electrode with a bright platinum wire coil acting as the counter electrode. A saturated calomel reference electrode (SCE, Radiometer, Copenhagen, Denmark) completed the cell assembly. The GC electrode was successively polished using diamond lapping sprays (Kemet) of decreasing particle size from 3 micron to 1/10 micron. The electrode was sonicated and finally rinsed in ethanol between polishing. All solutions were thoroughly degassed with pure N_2 for 15 minutes prior to performing any voltammetric measurements. Unless stated otherwise all cyclic voltammetry was performed at a scan rate of 100 mVs^{-1} step potential 2 mV.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Clam 4 MCD analyzer system at the OCMS Begbroke Science Park, University of Oxford, UK, using X-ray radiation from the Mg Kα band (hν = 1253 eV). All XPS experiments were recorded using an analyzer energy of 100 eV for survey scans and 20 eV for detailed scans over the N_{1s} region with a take-off angle of 90°. The base pressure in the analysis chamber was maintained at not more than 2.0×10^{-9} mbar. The bppg

electrode was mounted on a metal stub using double sided adhesive tape and then placed in the ultra-high vacuum analysis chamber of the spectrometer. Analysis of the resulting spectra was performed using Origin 6.0. Assignment of spectral peaks was determined using the UKSAF[16] and NIST[17] databases.

3. RESULTS

3.1. Cyclic voltammetry of catechol

Cyclic voltammetry of a 1 mM solution of catechol in pH 7 buffer was recorded at a clean GC electrode which had not been pre-treated in anyway. As shown in figure 1a a quasi-reversible system can be observed at *ca.* 0.2 V vs. SCE corresponding to the two-electron, two-proton catechol / *o*-benzoquinone redox couple labelled system I[18-25]. The electron transfer kinetics are sluggish, with

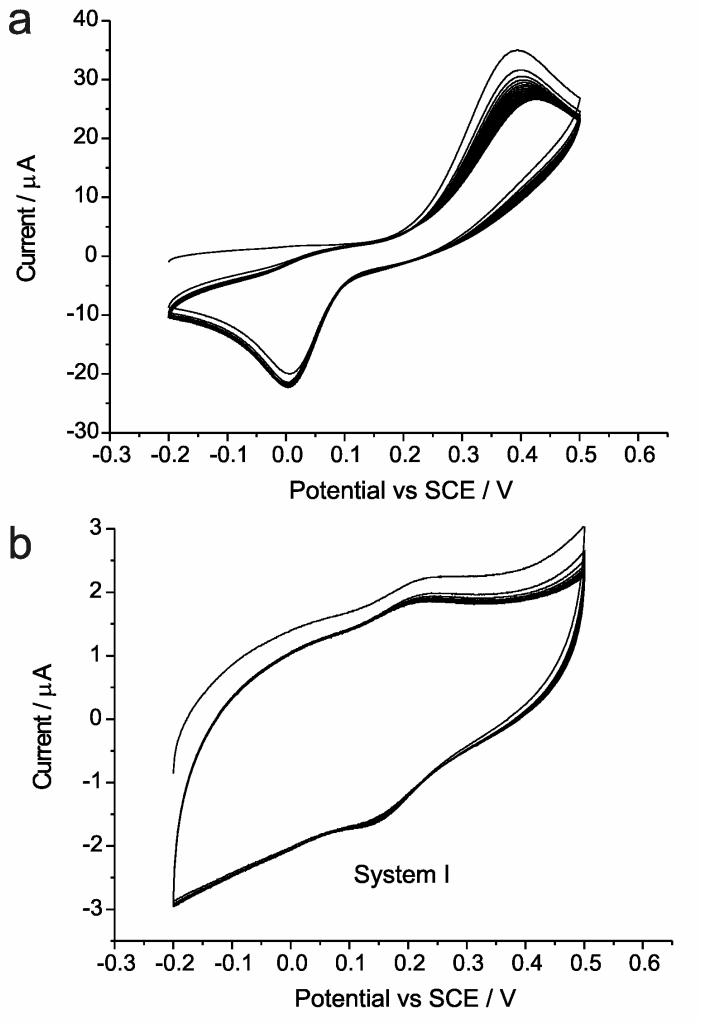


Figure 1. Twenty overlaid cyclic voltammograms of a GC electrode (no pre-treatment in **a)** 1 mM catechol solution in pH 7 buffer and **b)** in pH 7 buffer (no catechol) after cycling in catechol solution and then rinsing in water.

a large peak-to-peak separation of *ca.* 400 mV similar to the behaviour reported by Nabi *et al*[25]. Interestingly, Nabi *et al.* also reported the presence of a more reversible redox couple that developed after scanning anodically up to +0.85 V which they attributed to the adsorbed catechol species, and was always present regardless of the solution pH[25]. In our experiments no such signal corresponding to system II which might be attributed to this "adsorbed oxidised species" as Nabi *et al.* described it or as an "adduct" as Uchiyama *et al.* describe it was observed but it must be noted that we were not scanning to such positive potentials as Nabi (see below). After 20 scans had been recorded the GC electrode was removed from the catechol solution and rinsed in water. Next the electrode was placed into a fresh pH 7 buffer solution containing no catechol and a further twenty scans were recorded. As shown in figure 1b only a small poorly resolved quasi-reversible couple could be observed corresponding to residual physisorbed catechol (system I) on the electrode surface.

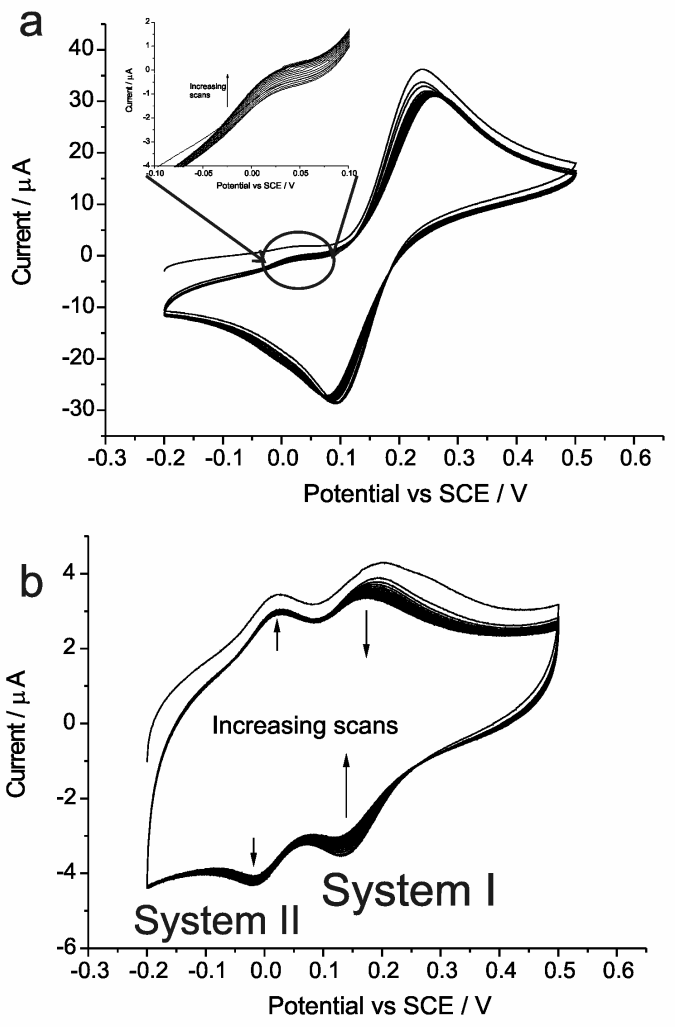


Figure 2. Twenty overlaid cyclic voltammograms of a GC electrode (after oxidative pre-treatment by cycling up to +1.4 V in pH 7 buffer) in **a)** 1 mM catechol solution in pH 7 buffer; **Inset:** an exploded view of the system II and **b)** in pH 7 buffer (no catechol) after cycling in catechol solution and then rinsing in water.

The electrode was then cleaned and polished before undergoing an oxidative pre-treatment whereby the GC electrode was cycled ten times between -0.2 V and +1.4 V in the pH 7 phosphate buffer. The experiments described above were then repeated in pH 7 buffer both with and then without the presence of 1 mM catechol as shown in figure 2a and b. From figure 2a it is apparent that oxidative pre-treatment has activated the electrode surface towards the catechol / *o*-benzoquinone couple. The voltammetry still exhibits a quasi-reversible wave centred at *ca.* 0.2 V vs. SCE but the electron transfer kinetics are now faster which is manifested by the reduction in peak-to-peak separation (*ca.* 180 mV). McCreery *et al.* have investigated the effects of various electrode pre-treatments on the voltammetry of catechol derivatives at a glassy carbon electrode and determined that these can have significant effects on the observed electrode kinetics[26], as indeed can physisorption of catechols which can "self-catalyse" the heterogeneous electron transfer to solution phase catechol[24].

What is more interesting is that on repetitive cycling in catechol solution with a pre-oxidised GC electrode a small pre-wave can be observed when the potential is scanned oxidatively at *ca*. 0.05 V vs. SCE. The process may be reversible (see below) as reported by Nabi *et al*.[25] but the corresponding reduction peak is obscured by the reduction wave of system I. It is also apparent from the inset in figure 2a that this wave grows with successive cycling between -0.2 and 0.5 V. Again the electrode was rinsed in water and placed in a fresh pH 7 buffer solution not containing any catechol. Figure 2b shows the corresponding voltammetry. Two redox systems can now be observed; system I at 0.15 V corresponding to physisorbed catechol and a new system, labelled system II at 0 V vs. SCE. This is exactly identical voltammetry to that reported by Uchiyama *et al.*[9] with identical peak potentials (after correction for the difference between the SCE and Ag/AgCl reference electrodes) and identical peak currents. On repetitive cycles the peak current of system I was found to slowly decrease whilst that of system II slightly increased apparently as the physisorbed catechol is converted into the adduct via reaction of surface groups with the oxidised form of catechol[9].

Next the effect of varying the oxidative pre-treatment potential was investigated. Uchiyama *et al.* reported that the introduction of amino groups occurred when ammonium carbamate was oxidised above 0.9 V[9]. Therefore the above experiments were repeated but with a different oxidative pre-treatment involving cycling the electrode in pH 7 buffer (without catechol) ten times from -0.2 V up to either 0.9, 1.1, or 1.4 V vs. SCE. When the oxidative potential was cycled up to 0.9 V vs. SCE system I and II were both observed in phosphate buffer after the electrode was previously cycled in catechol (see above) but system II was less well defined. Above 1.1 V however system II was very well defined. This slight difference in potential before the onset of electrode oxidation probably reflects the change in pH between cycling in pH 8.9 ammonium carbamate and pH 7 phosphate buffer solution.

Note that certain kinds of glassy carbon substrates have nitrogen atoms incorporated during the manufacturing process, which may possibly act as the active site. Although no evidence from either the voltammetric or spectroscopic experimental results suggests that the glassy carbon material used to make our electrodes contains any nitrogen surface groups we carried out one further experiment to verify this. The experiments described above were repeated using a basal-plane pyrolytic graphite electrode (bppg) as the working electrode which is constructed form very high purity synthetic graphite and which does not contain any surface nitrogen impurities. Identical voltammetry was

observed to that described above, thus precluding nitrogen incorporated into the GC electrode during manufacture as a possible explanation for observed voltammetry (figure 3a and b).

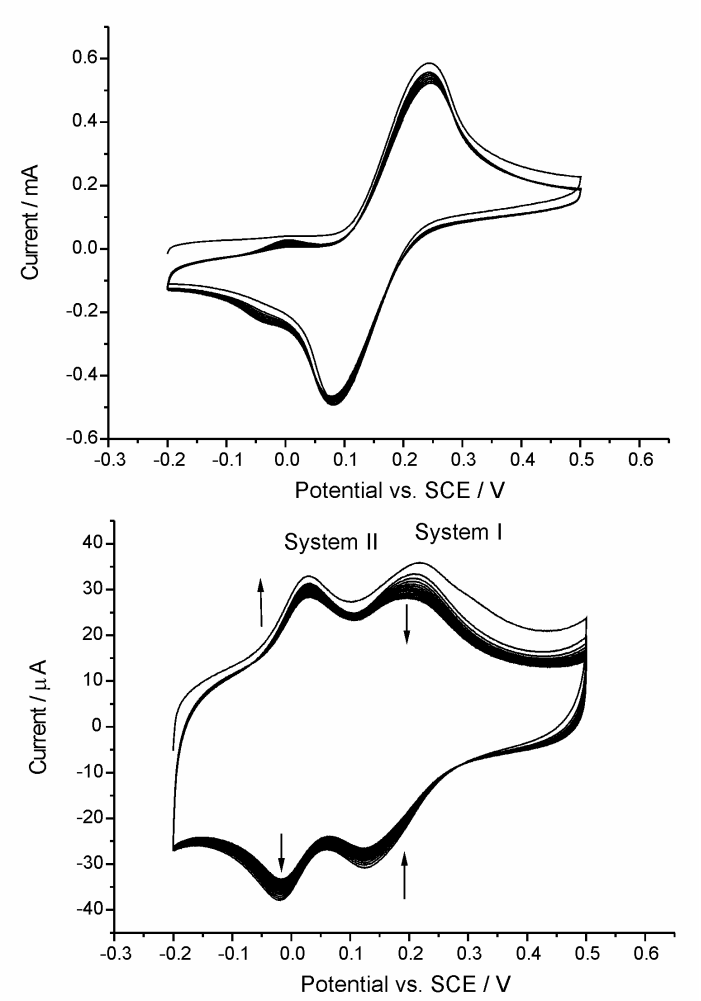


Figure 3. Twenty overlaid cyclic voltammograms of a graphite electrode (after oxidative pre-treatment by cycling up to +1.4 V in pH 7 buffer) in **a)** 1 mM catechol solution in pH 7 buffer; **b)** in pH 7 buffer (no catechol) after cycling in catechol solution and then rinsing in water.

3.2. XPS characterisation of a carbon surface after electrolysis in ammonium carbamate solution

As the voltammetric behaviour of the GC and bppg electrodes is identical in all cases the surface modification is likely identical. Therefore, for convenience, a bppg electrode that had been designed for use in the XPS spectrometer in previous studies was examined using XPS before and after performing the electrolysis of 0.1 M ammonium carbamate. One wide scan was performed on the blank bppg electrode from 0-1100 eV. Only two principle spectral peaks could be observed at 286 eV and 533 eV for the bppg prior to modification, corresponding to emission from the C_{1s} and O_{1s} levels, with corresponding Auger emissions at higher energies. No peaks could be observed above the background noise in the N_{1s} region around 400 eV. After electrolysis in 0.1 M ammonium carbamate, a small peak could also be observed at *ca.* 400 eV, corresponding to surface nitrogen atoms, in

agreement with the spectra reported by Uchiyama *et al*[9]. Next, ten cumulative scans were performed over the N_{1s} region of the modified bppg electrode a shown in figure 4. A single spectral peak is observed at 402.1 eV. Comparison with spectral assignments in both the UKSAF[16] and NIST[17] databases reveal that emission from aromatic or aliphatic amino groups are usually located between 398-400 eV, with emission from amido nitrogen atoms being found over a similar range of binding energies at 400-402 eV. Interestingly, the spectral assignment using the NIST database strongly matches that of nitrogen in the form of the ammonium ion. Considering the fact that such high concentrations of ammonium carbamate are used, this assignment may tentatively identify the nature of the nitrogen species on the surface.

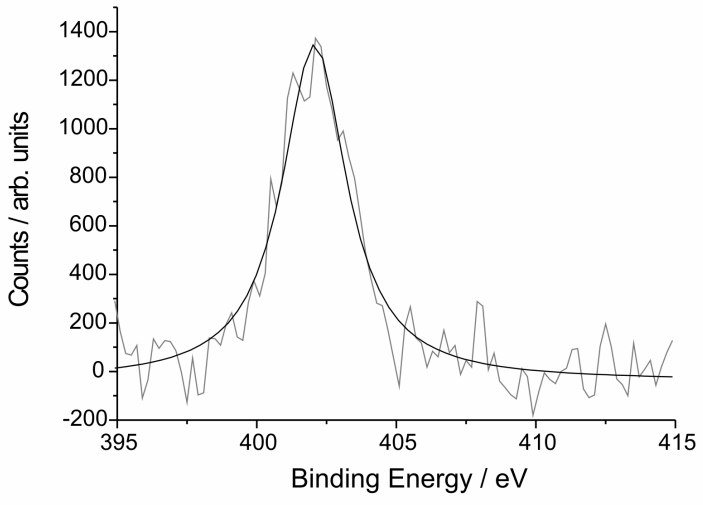


Figure 4. The baseline corrected XPS spectrum of a bppg electrode after electrolysis in 0.1 M ammonium carbamate solution, recorded over the N_{1s} region (grey line = raw data, black line = the result of fitting a Lorentzian curve to the data).

4. DISCUSSION

As mentioned in the introduction, the XPS data presented by Uchiyama shows, convincingly, that significant incorporation of nitrogen atoms into the electrode surface occurs when the GC electrode is cycled in ammonium carbamate solution[9]. However, after pre-treating either GC or bppg electrodes in the absence of any carbamate groups or other sources of nitrogen, we can still reproduce the peak current and potential of a supposed adduct of surface amino groups and *o*-benzoquinone. This suggests that the nitrogen-containing surface groups introduced by Uchiyama are not amino groups, or that if they are, they are not reacting with catechol via a 1,4-Michael addition as claimed. Closer inspection of the XPS data provided by Uchiyama *et al.* reveals that in addition to incorporating nitrogen atoms onto the electrode surface, the atom percentage (relative to the intensity of the C_{1s} spectral line) of oxygen-containing species also increases significantly. This is well known behaviour for graphitic electrodes such as GC pre-treated with either an electrochemical or chemical oxidation step[27-29]. Oxidative pre-treatment and subsequent introduction of oxygen-containing surface groups

can, in certain cases, given rise to enhanced electron transfer kinetics, which may explain the improved reversibility observed in figure 2a[30]. We note that McCreery *et al.* claim that the degree of surface oxidation does not have a significant effect on either the degree of adsorption or the electrode kinetics of catechol derivatives[26]. However, in their work the degree of surface oxidation was limited to between 2-12 atom percent whilst using Uchiyama's method oxidation of the GC surface accounts for between 12-19 atom percent of the surface. In light of our results it would appear that the adduct between the reactive surface groups on the GC electrode and catechol oxidation products can not be attributed to the presence of surface amino groups and the voltammetric evidence of Uchiyama *et al.* can not be interpreted as confirming the presence of such groups. This leaves two questions unanswered: i) what is the species giving rise to the voltammetry observed as system II and what is the mechanism of its formation? ii) what is the nature of the nitrogen-containing functional groups incorporated onto the GC electrode surface in when the electrode is oxidised in the presence of ammonium carbamate?

The first question can be answered by the work of Davis *et al*[31]. *o*-benzoquinone and its derivatives are known to be much more reactive than the 1,4-analogues[32-34] and can undergo a variety of addition reactions and polymerisation reactions[35]. Davis *et al.* have studied the electropolymerisation of a variety of *o*-benzoquinone derivatives formed by the electrooxidation of the corresponding catechol species on carbon electrodes[31]. Under similar conditions to those used herein and in Uchiyama's work they observed almost identical voltammetric features which were attributed to the formation of polymeric films of electropolymerised *o*-benzoquinone adsorbed on the carbon electrode surface[31]. Similar behaviour has also been reported in the literature for the electrooxidation of other catechols and related species[36-39]. Based on these reports, and the results of our own experiments, it is likely that system II corresponds to surface bound polymeric forms of *o*-benzoquinone which have either reacted with the parent molecule in solution and/or with *o*-quinone-like groups on the surface of the GC electrode introduced during the oxidative pre-treatment.

In the absence of any other characterisation the nature of the nitrogen species introduced onto the electrode by Uchiyama *et al.* can only be speculated upon. However, ammonium carbamate solutions form complex equilibria, principally between carbamate ions, ammonia, carbon dioxide, carbamic acid, carbonate ions, bicarbonate ions, carbonic acid, ammonium ions, hydroxonium ions and hydroxide ions. One can also envisage the possible formation of trace amounts of other reactive nitrogen-containing species in the vicinity of the electrode surface such as isocyanic acid (H-N=C=O) and the corresponding anion. Oxidation of these species might then generate reactive intermediates which might result in the attachment of unreactive amido groups ($CONH_2$) to the GC surface. Alternatively, the surface nitrogen-containing groups might also be in the form of ammonium cations which also exhibit spectral peaks at similar binding energies to those observed in section 3.2. We speculate that these might remain on the carbon surface, despite thorough washing, if they are ion-paired to carboxylate groups. These carboxyl groups, which are also known to decorate the graphitic surface, may indeed be further introduced during the process of electrolysis, as demonstrated by the percentage increase in the elemental percentage of oxygen on the carbon surface.

5. CONCLUSIONS

In the absence of oxidative pre-treatment, only a single voltammetric wave is observed in the voltammetry of catechol, corresponding to the two-electron, two-proton quasi-reversible catechol / *o*-benzoquinone couple, as is widely reported in the literature at other graphitic electrodes. If a GC electrode is oxidatively pre-treated by cycling to potentials more positive than 0.9 V vs. SCE in aqueous buffer solution (pH 7), then a second redox quasi-reversible redox couple can be observed. The observed voltammetry is identical to that used by Uchiyama *et al.* to demonstrate that amino groups had been grafted to a GC surface by oxidative pre-treatment in 0.1 M ammonium carbamate solution[9]. Our control experiments preclude this as a possibility. Instead we propose an alternative explanation involving the electropolymerisation of *o*-benzoquinone formed by oxidation of catechol and or polymerisation of *o*-benzoquinone with *o*-quinone-like species formed on the GC surface during the oxidative pre-treatment step. We emphasise that whilst the electrolysis of ammonium carbamate solutions does incorporate nitrogen-containing functional groups onto a carbon electrode surface, the voltammetric evidence provided in reference 9 can not, in light of our experimental results, be used to support the claim that these are in the form of amino groups. Furthermore, we have provided additional experimental using XPS that indicate that the majority of the incorporated nitrogen-containing functional groups are in fact in a form other than amino groups and may be in the form of amido groups or residual ammonium ions.

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