

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7450883>

# Edge Plane Pyrolytic Graphite Electrodes in Electroanalysis: An Overview

Article in *Analytical Sciences* · December 2005

DOI: 10.2116/analsci.21.1263 · Source: PubMed

---

CITATIONS

144

READS

1,863

2 authors, including:



**Craig E Banks**

Manchester Metropolitan University

623 PUBLICATIONS 30,851 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



3D printed ceramic substrate for catalytic applications [View project](#)



Chemistry Conference Survey [View project](#)

# Edge Plane Pyrolytic Graphite Electrodes in Electroanalysis: An Overview

Craig E. BANKS and Richard G. COMPTON<sup>†</sup>

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QX, UK

The recent development, behavior and scope of edge plane pyrolytic graphite electrodes in electroanalysis are overviewed. Similarities to, and advantages, over multi-walled CNT modified electrodes are noted and the wide scope of applications, ranging through gas sensing, stripping voltammetry and biosensing, illustrated.

(Received June 28, 2005; Accepted September 21, 2005)

1 Introduction and Background	1263	6 Direct Oxidation of Ascorbic Acid Facilitated at Bare Edge Plane Pyrolytic Graphite Electrodes	1267
2 Electroanalytical Detection of Thiols	1264	7 Edge plane and Basal Plane Electrodes Allow the Electrocatalytic Sites of Carbon Nanotubes to Be Determined: NADH Detection	1267
3 Optimising Gas Sensors which Utilise Carbon Based Electrodes	1265	8 Conclusions	1268
4 Stripping Performance of Edge Plane Pyrolytic Graphite Electrodes	1266	9 References	1268
5 Halide Detection	1266		

## 1 Introduction and Background

In 2004 we questioned the electrocatalytic properties of carbon nanotubes (CNTs) while studying model systems using carbon nanotubes- and graphite powder-modified basal plane pyrolytic graphite electrodes (bpgg).<sup>1</sup> These electrodes were formed *via* film and abrasive attachment; in the former case graphite powder or carbon nanotubes were dispersed in an organic solvent, pipetted onto a polished bpgg electrode, and allowed to volatilise leaving a carbon 'film' on the electrode surface. In the latter case we pioneered abrasive attachment of CNTs onto bpgg electrodes by gently rubbing a polished bpgg electrode on a fine quality filter paper containing either graphite powder or nanotubes. Using these electrodes modified with either graphite powder or CNTs we explored the electro-reduction of ferricyanide and the oxidations of NADH, epinephrine and norepinephrine. While observing enhanced voltammetric currents with reduced peak-to-peak separations at the CNT modified electrodes in comparison with the naked bpgg electrode, similar catalytic behaviour was also seen at the graphite powder modified electrodes.<sup>1</sup> We therefore advocated the need for caution in attributing special catalytic or electrocatalytic properties to CNTs without conducting the appropriate control experiments.<sup>1</sup> The vast majority of studies employ glassy carbon electrodes as supports and we suggested that in the future, nanotube catalytic activity be additionally compared against that of graphite powder where the latter is conveniently studied *via* immobilization on a bpgg electrode.<sup>1</sup>

The above observations aroused our suspicion as to what is

responsible for the observed electrocatalytic properties of CNTs. Shortly after our first paper in this area,<sup>1</sup> we provided definitive evidence for the electrocatalytic properties of CNTs.<sup>2</sup> The reduction of ferricyanide was explored at CNT film modified bpgg electrodes and compared directly with a bare bpgg electrode and an edge plane pyrolytic graphite electrode (epg). The basal plane electrode was fabricated from a high quality piece of highly ordered pyrolytic graphite surface, which consists of graphite layers which lie parallel to the surface and are separated from each other by 3.35 angstroms (see Fig. 1). In comparison, epg electrodes are fabricated from highly ordered pyrolytic graphite (hopg) by cutting the desired electrode surface geometry such that the layers of graphite lie perpendicular to the surface. Note that it is well documented that the electrode kinetics at edpg are at least three orders of

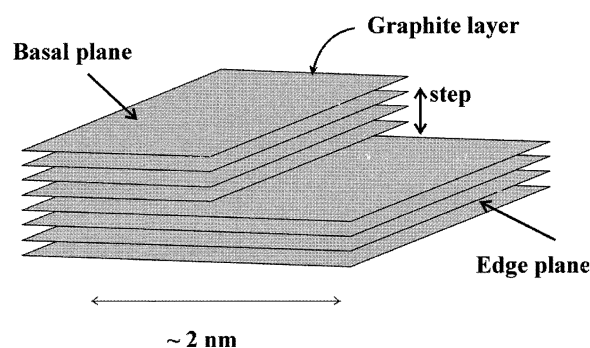


Fig. 1 Schematic representation of a step edge on a hopg surface. The steps are multiples of 3.35 angstroms deep and typically range between 1 - 20 layers for hopg.

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: richard.compton@chem.ox.ac.uk

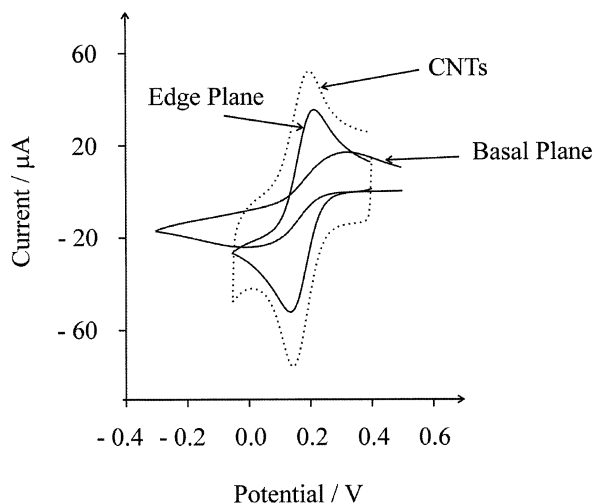


Fig. 2 Cyclic voltammograms for the reduction of 1 mM ferricyanide at CNT film-modified bppg electrodes compared with an epg electrode and a bare bppg electrode showing definitive evidence that the electron transfer kinetic of the ferricyanide reduction are similar on epg and CNT modified electrodes. All scans recorded at  $100 \text{ mV s}^{-1}$ .

magnitude faster than at basal plane graphite.<sup>3</sup>

Returning to the comparison of the reduction of ferricyanide at the CNT film modified electrodes with the edge plane and bppg electrodes, a peak-to-peak separation of 58 mV was observed whereas for the edge plane and basal plane pyrolytic graphite electrodes separations of 78 mV and 350 mV were seen;<sup>2</sup> these responses are depicted in Fig. 2. The similar peak-to-peak separations observed at the CNTs and epg supports that there is little significant difference between the two hinting that the reactive sites are due to edge plane sites which occur at the open ends of the nanotubes or at defects along the tube axis. The small differences in the peak-to-peak separations of the CNT and the epg electrode may reflect the slight basal plane impurities in the epg electrodes. Note that the bppg used to record the data in Fig. 2 is hopg which provides basal plane surface with fewest edge plane like defects. On other grades of bppg with a much higher step density more nearly reversible voltammograms can be recorded.

The role of edge plane sites/defects was further explored by examining the response of the reduction of ferricyanide at a bare bppg electrode modified *via* film and abrasive attachment of  $\text{C}_{60}$ . The bare bppg electrode and  $\text{C}_{60}$  film modified bppg electrode exhibited peak-to-peak separations of 315 mV and 340 mV while at the abrasive  $\text{C}_{60}$  modified bppg electrode peak-to-peak separation of 134 mV was observed suggesting fast heterogeneous electron transfer in the case of the abrasively modified case. It was demonstrated that in the preparation of the abrasively modified electrode the abrasive nature of the  $\text{C}_{60}$  crystals served to 'roughen' the bppg electrode which is well known to introduce edge plane sites/defects on the bppg electrode surface and hence the observed electrocatalysis. As will be shown later, comparison of CNTs with edge plane and basal plane pyrolytic graphite electrodes allow a greater understanding of the electrochemical reactivity of CNTs.

Definitive evidence for the role of edge plane sites in the electrochemistry of graphite surfaces was provided by two conclusive experiments using hopg where the distance between the step site is unusually large and can be as much as 5 to 10 microns on carefully handled samples.

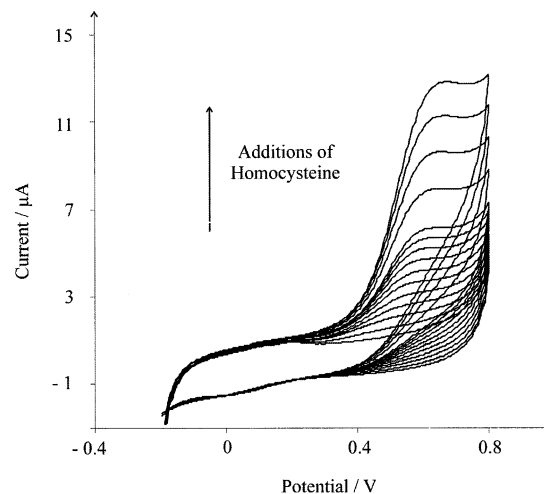


Fig. 3 Cyclic voltammetric response of increasing additions of homocysteine in a pH 7 buffer solution using an epg electrode. Scan rate used was  $55 \text{ mV s}^{-1}$ .

First the cyclic voltammetry response<sup>3</sup> of simple, nominally outer sphere redox couples was shown to be inconsistent with that predicted for simple linear diffusion. Rather the characteristic and unusual wave shapes were only consistent with a diffusional model in which the substrates effectively acted as an "array of microband electrodes" with the edge plane step sites acting as the electrochemically active "microbands" and the basal plane terraces as voltammetrically inert material.

A second key experiment<sup>4</sup> in defining the role of the edge plane sites as the site of electron transfer and the basal plane terraces as voltammetrically inert was carried out using AFM in parallel with the voltammetry of modified hopg surfaces. In particular the cyclic voltammetric response of hopg to various model redox couple was essentially unchanged when the basal plane terraces, but not the edge plane steps, were covered with a thick layer of polymer. This confirmed that the terraces were effectively voltammetrically inert and that measurable levels of electron transfer were confined to the edge plane steps defects.

Given the fast electrode kinetics seen at pure edge plane graphite, and the identical response seen at the CNTs, this led us propose the use of epg as an electrode substrate for electroanalysis. It is this we next discuss.

## 2 Electroanalytical Detection of Thiols

A first example of using epg electrodes in electroanalysis was in the detection of thiols.<sup>5</sup> The quantification of thiol moieties are biomarkers for a wide range of diseases with high levels associated with early pregnancy loss, depression and mental disorders. Typical electroanalysis utilises chemically modified electrodes since the direct oxidation occurs at high overpotentials leading to uncertainty or quantitative error arising from discriminating the analytical signals from solvent breakdown.

Exploring the oxidations of homocysteine, *N*-acetylcysteine, cysteine and glutathione at epg electrodes, well defined voltammetric currents were observed to occur at *ca.* +0.6 V (*vs.* SCE) at the edge plane electrode, which were hard to distinguish from the background current at bppg, glassy carbon, boron-doped diamond and CNT 'film' modified bppg electrodes. Given the voltammetric responses seen over the range of electrode materials commonly used in electroanalysis,

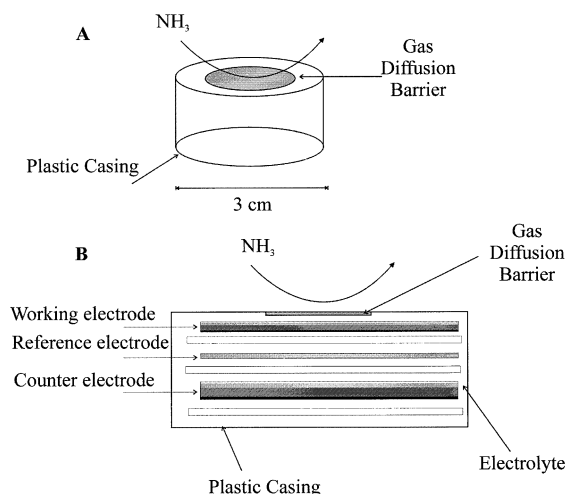


Fig. 4 Schematic representation of a typical Clark-type configuration which is commonly used in gas sensing.

it was concluded that for the direct electroanalysis of thiols, the epg electrode is superior due to its enhanced signal-to-noise ratio and electrocatalytic activity.

Subsequently the response of additions of homocysteine at the edge plane electrode was examined; these are shown in Fig. 3. A large linear range was observed with enhanced signal-to-noise characteristics allowing low micro-molar levels to be analysed for all the thiol moieties. The method was tested for the detection of cysteine in growth tissue media containing a high number of biological electrochemical interferences, which was found to be in excellent agreement with the manufacturers quoted value.<sup>5</sup> This electrochemical methodology represents the best direct electrochemical sensing to date for thiols due to the reduction in overpotential while having enhanced signal to noise characteristics facilitating low detection limits<sup>5</sup> in comparison to both direct and indirect electrochemical methodologies.

### 3 Optimising Gas Sensors which Utilise Carbon Based Electrodes

Commercial gas phase sensors employ a Clark-type configuration which consists of a sensor unit that houses both electrodes and electrolyte, as depicted in Fig. 4, with a gas-permeable membrane hydrophobic membrane separating the electrolyte from the gaseous sample.<sup>6,7</sup> Contained within the electrolyte is an optimised working electrode for the detection of the toxic gas to be measured. In these amperometric sensors the sensing electrode can employ either noble metals, bare carbon based- or modified-working electrodes with improvements in the performance of such amperometric sensors best achieved by understanding the chemical and physical process.

We have reported the first example of gas sensing utilising edge plane electrodes for the detection of nitrogen dioxide comparing the response with boron-doped diamond, basal plane and glassy carbon electrodes, thus allowing a greater understanding for optimal sensing performance.<sup>8</sup>

The reduction of nitrogen dioxide in 5 M sulphuric acid was explored where a well-defined redox couple starting at  $-0.2$  V (vs. graphite reference), as shown in Fig. 5 was observed. Also a large anodic wave at  $+0.48$  V was seen. These observations are in contrast to previous work on the amperometric detection of nitrogen dioxide using gold film electrodes where an oxidation wave at  $+0.2$  V (vs. platinum) was observed but with

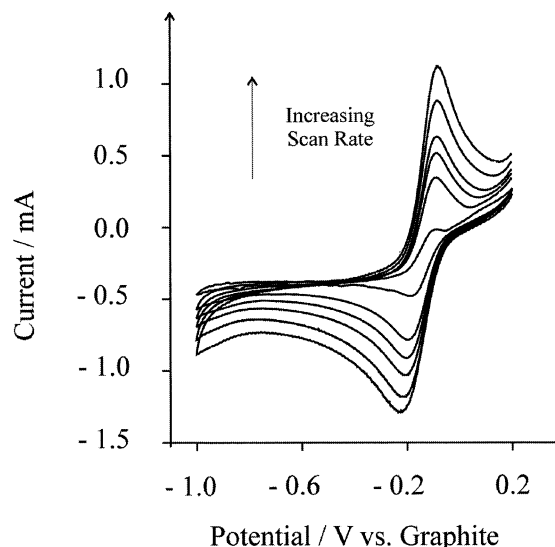


Fig. 5 Cyclic voltammograms of nitrogen dioxide recorded over a range of scan rates ( $10-200$   $\text{mV s}^{-1}$ ) at an epg electrode (vs. graphite) in 5 M sulphuric acid.

no corresponding reduction wave. It was demonstrated that the electrochemical reduction of nitrogen dioxide was sensitive to pH; only in 2.5 M or more concentrated sulphuric acid was a reduction wave observed.<sup>8</sup> It was demonstrated that for the low level sensing of nitrogen dioxide, edge plane electrode were superior in comparison to bppg, glassy carbon and boron-doped diamond, which are commercially available electrode substrates to the analytical chemist. For these three electrodes no Faradaic waves were observed in contrast to the well-defined signal seen at the epg electrode.<sup>8</sup>

We have extended the gas sensing capability of edge plane electrodes by exploring the electrochemical reduction of chlorine in nitric acid solutions.<sup>9</sup> As shown in Fig. 6, the reduction of chlorine to chloride occurs with lowest overvoltage in the case of epg in comparison to glassy carbon, basal plane or boron-doped diamond electrodes. One can infer from this that it is the edge plane sites that are responsible for the reduction in overpotential; this is quite easy to confirm *via* the use of bppg electrodes.

The bppg electrode used throughout all our work is prepared *via* the 'cellotape method'.<sup>1</sup> This involves polishing the bppg electrode on carborundum paper and then pressing cellotape on to the cleaned bppg surface before removing along with general attached graphite layers. This is repeated several times with the electrode being cleaned in acetone prior to use to remove any adhesive. This results in an electrochemical response, which is at high overpotentials in comparison to that seen at the epg. The electrode is then polished on a soft-lapping pad with 0.1 micron sized alumina for 30 and 60 s with the electrochemical response shown in Fig. 7. Clearly the effect of polishing is to reduce the overpotential for the electroreduction of chlorine. This is because when the electrode is initially prepared *via* the cellotape method the electrode consists of a low level of edge plane sites/defects which is typically between 1 - 10%.<sup>3</sup> In fact it has been shown through comparison of numerical simulations and experiment that the basal plane is effectively electrochemically inert. These defects are substantially increased when the surface is abrasively modified, for example, *via* rubbing with micron-sized alumina on a soft-lapping pad. Thus the electrochemical response reflects the increment in edge planes on the bppg electrode confirming that the observed

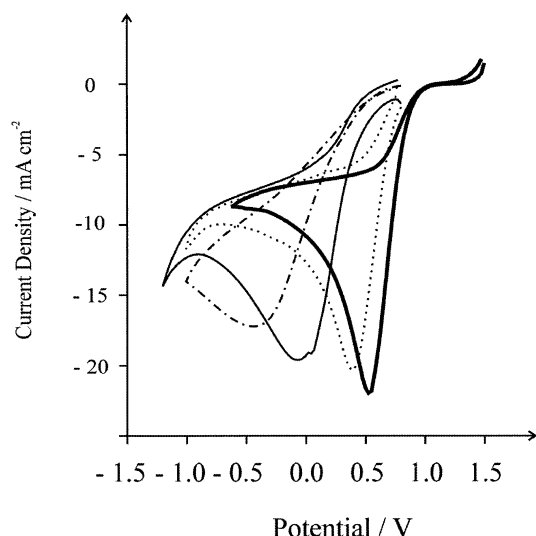


Fig. 6 Cyclic voltammograms for reduction of chlorine in 0.1 M nitric acid solution using eppg (thick line), which is compared with a glassy carbon (dotted), bpgg (thin line) and boron-doped diamond (dotted and dashed line) electrodes. All scans recorded at 100 mV s<sup>-1</sup> vs. SCE.

electrocatalytic active sites for chlorine reduction are edge like defects. The electroanalytical utility of edge plane electrodes was examined in a solution containing a low concentration of chlorine and compared with the other electrode substrates which revealed that the only the edge plane exhibited a voltammetric reduction wave. In the above two examples the use of edge plane and basal plane has allowed us to understand the active sites for gas sensing allowing us to show that gas sensors built using graphite based electrode depend critically on the presence of a high edge plane content for optimal or even adequate sensing performance.<sup>8,9</sup>

#### 4 Stripping Performance of Edge Plane Pyrolytic Graphite Electrodes

We have provided the first examples of using eppg electrodes in the anodic and cathodic stripping voltammetric analysis. Specifically we have studied silver and manganese for anodic stripping and cathodic stripping voltammetry respectively.<sup>10</sup> The accessible potential window of the edge plane electrode was examined and found to be *ca.* 3.3 V in 0.1 M nitric acid which is comparable to boron-doped diamond (*ca.* 3.7 V) and glassy carbon (*ca.* 3.2 V) electrodes, which is shown in Fig. 8. The edge plane, boron doped diamond and glassy carbon have similar anodic limits while boron-doped diamond and basal plane have similar cathodic limits which is closely followed by edge plane and finally glassy carbon. These anodic and cathodic limits suggest that the edge plane could be of use in electroanalysis. This was further explored by considering the anodic stripping voltammetry of silver *via* using square wave-anodic stripping voltammetry in 0.1 M nitric acid solution containing 14 mM KCl; the addition of latter results in a well-defined stripping signal due to the stabilisation of the silver ion as AgCl<sub>2</sub><sup>-</sup> and has been reported previously.<sup>11</sup> At the edge plane electrode large voltammetric responses were observed facilitating a detection limit of 8 nM for a 120 s deposition at -0.5 V (vs. SCE) which was reduced to 0.2 nM using a 300 s deposition period. These limits are superior to that seen at glassy carbon and basal plane electrodes. Furthermore the edge

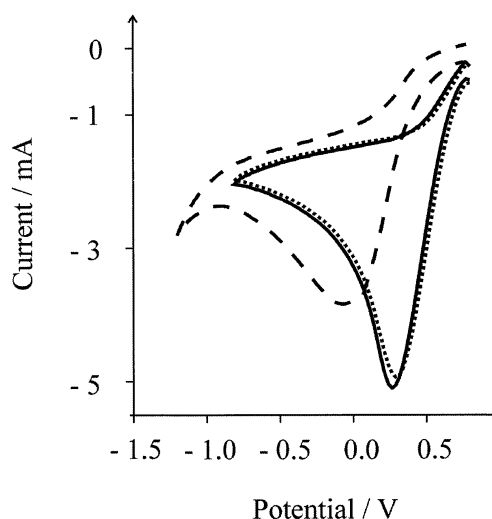


Fig. 7 Cyclic voltammograms of bpgg electrode in 0.1 M nitric acid solution after cellotape preparation (dashed line) and then polishing on micron sized alumina for 30 s (line) and 60 s (dotted line).

plane response towards silver deposition found to be comparable to that reported at boron-doped diamond electrodes under insonation, where a detection limit of 0.4 nM was achieved using a 300 s acoustically assisted accumulation protocol.<sup>11</sup>

The cathodic stripping voltammetry of manganese has also been examined at edge plane electrodes and was compared directly with commonly used electrode substrates.<sup>10</sup> The method is based on manganese(II) being oxidised on the electrode surface forming manganese(IV) dioxide by holding the potential at a sufficiently positive potential. The potential is then swept negative which produces a stripping peak corresponding to the reduction of manganese dioxide(IV) back to soluble manganese(II). It was demonstrated that a detection limit for manganese of 0.29 μM was possible which was comparable with that achievable with a boron-doped diamond electrode but with the edge plane exhibiting a 3 times higher sensitivity.

We have extended this work and have examined the possible determination of manganese in environmental analysis.<sup>12</sup> Low nano-molar detection limits were observed, with a stirred deposition protocol permitting high sensitivities with the efficacy of the protocol assessed in the determination of manganese in a certified seawater reference material, which was found to be in excellent agreement with the independently verified sample.<sup>12</sup>

It was inferred from the above examples and improvement in performance, that edge plane graphite may offer far more nucleation sites for the growth of the solid silver or manganese dioxide nuclei, while noting the cost and performance of the edge plane electrode with that of the boron-doped diamond, it was suggested that in the context of stripping analysis the edge plane can conveniently replace boron-doped diamond electrodes. Promising prospects for stripping measurements of other trace metals are envisaged.

#### 5 Halide Detection

We have explored the oxidations of chloride, bromide and iodide at edge plane electrodes and directly compared these with basal plane, glassy carbon or boron-doped diamond electrodes.<sup>13</sup> The oxidation of chloride in 0.1 M nitric acid was

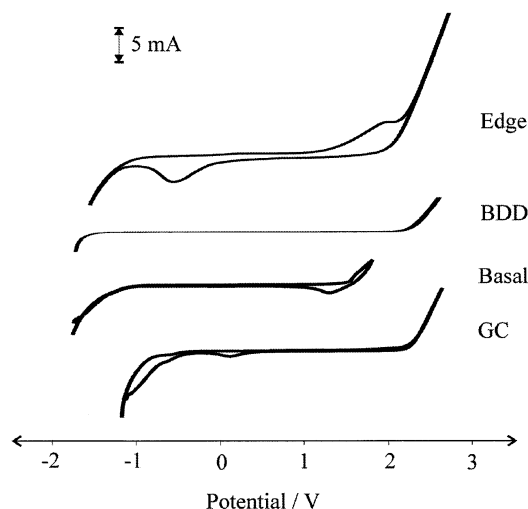


Fig. 8 Accessible potential windows recorded at  $100 \text{ mV s}^{-1}$  in  $0.1 \text{ M}$  nitric acid.

investigated where it was found that no voltammetric waves corresponding to the oxidation of chloride to chlorine was observable suggesting a high overpotential is required which are outside the electrochemical window of the edge plane electrode.

In the oxidation of bromide in  $0.1 \text{ M}$  nitric acid was explored with edge plane electrodes where it was observed to exhibit a peak-to-peak separation of  $154 \text{ mV}$  exhibiting the most electrochemically reversible signal in comparison to  $590 \text{ mV}$  separations at a basal plane electrode and  $230 \text{ mV}$  at a glassy carbon with the boron-doped diamond exhibiting an electrochemically irreversible wave. It was found that the electroanalytical detection of bromide could be facilitated *via* the back-peak allowing, *via* cyclic voltammetry, low micromolar levels of bromide to be detected. The protocol was explored in river water where an identical sensitivity and detection limit were observed as that found in nitric acid.

The oxidation of iodide was also explored using the range of electrode substrates where the peak-to-peak separation were found to be  $74 \text{ mV}$  for glassy carbon,  $84 \text{ mV}$  for basal plane and  $62 \text{ mV}$  for eppg while the boron-doped diamond displayed an electrochemically irreversible oxidation wave.<sup>13</sup> It was observed that at slow scan rates ( $>100 \text{ mV s}^{-1}$ ) the voltammograms deviated from diffusion control such that the reduction peak looked similar to a stripping peak. It was found that iodine is adsorbed onto the electrode surface on the anodic scan which is stripped on the cathodic sweep. It was found that low micro-molar levels of iodide could be detected using either the reduction wave or from cyclic voltammetry or *via* accumulation of iodide by holding the potential at  $+0.8 \text{ V}$  for  $30 \text{ s}$  followed by a cathodic sweep to strip the accumulated iodine back to iodide.<sup>13</sup>

## 6 Direct Oxidation of Ascorbic Acid Facilitated at Bare Edge Plane Pyrolytic Graphite Electrodes

The clean direct oxidation of ascorbic acid (AA) is almost impossible to perform electrochemically on conventional electrodes due to large overpotentials required and to electrode fouling by the oxidation products.<sup>14</sup> However, we have demonstrated that the oxidation of AA is possible with a significantly higher degree of electrochemical reversibility that seen at glassy carbon, boron-doped diamond and bppg

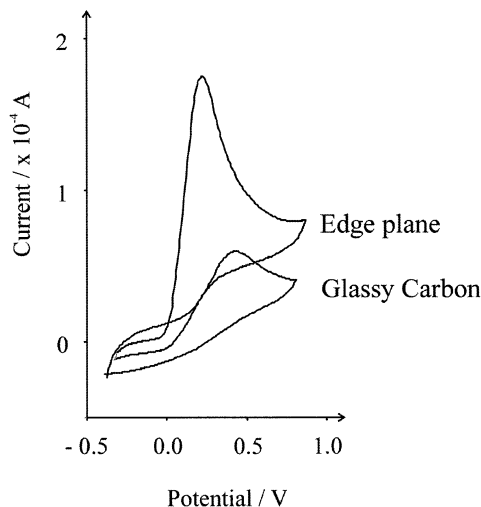


Fig. 9 The electrochemical oxidation of  $2.8 \text{ mM}$  AA in  $\text{pH } 7$  phosphate buffer solution using an eppg and a glassy carbon electrode.

electrodes.<sup>15</sup> This is exemplified in Fig. 9 where the response of the edge plane electrode is directly compared with a glassy carbon substrate in a  $\text{pH } 7$  phosphate buffer solution. The direct electroanalytical response to additions of AA was found to produce a detection limit of  $71 \mu\text{M}$  which is similar to indirect electrochemical methodologies. Furthermore no electrode passivation was observed at the edge plane electrode which usually limits the sensing of AA at bare electrode substrates. Note that Kuwana, McCreery, Adams and Wightman<sup>16-19</sup> all have separately studied the oxidation of AA at carbon based electrodes but that the electrode used do not consist completely of either pure edge plane or pure basal plane, but rather a mixture of the two depending on the grade of HOPG purchased and constructed and modification of the electrode.<sup>15</sup>

The protocol was assessed in the commercial drink Ribena<sup>®</sup> which contains high levels of sugars, natural flavouring and colorants making it notoriously difficult to analyse *via* classical electrochemical techniques. However, simple 1:1 dilution of the sample with  $\text{pH } 7$  phosphate buffer allowed the concentration of AA to be successfully and quantitatively determined.<sup>15</sup>

## 7 Edge Plane and Basal Plane Electrodes Allow the Electrocatalytic Sites of Carbon Nanotubes to Be Determined: NADH Detection

The electrochemical oxidation of nicotinamide adenine dinucleotide (NADH) receives great interest since approximately 300 dehydrogenases are known to be dependant on the coenzyme, NADH and its oxidised form and is therefore required in a whole diversity of dehydrogenase-based biosensors. However the direct oxidation at electrode substrates produces a signal at high overpotentials with electrode deactivation due to electrode fouling from the oxidation product of NADH; electrode materials which oxidise NADH at low potentials and which do not lose sensitivity are increasingly sought.

Representing 'state of the art' electrochemical methodologies are CNT modified electrodes<sup>20-26</sup> with many more sensing methodologies for NADH oxidation employing CNTs are likely to be conceived. However, in these reports utilising CNTs, the observed improvement in the overpotential and low

susceptibility to electrode fouling has never been explained.

We have examined the bio-sensing applications of edge plane pyrolytic graphite electrodes in the example of the electro-analytical detection of NADH. An oxidation wave was seen at a low overpotential, in comparison to conventional electrode substrates, coupled with easily quantifiable signals facilitating a detection limit of 5  $\mu\text{M}$  *via* cyclic voltammetry. Alternatively, and if desired, amperometry can be used providing a limit of detection of 0.3  $\mu\text{M}$ . However, most importantly we examined the electrochemical oxidation of NADH at CNT modified electrodes and compared these responses directly with the response of edge plane and basal plane pyrolytic graphite electrodes.<sup>27</sup> In comparison oxidation waves at +0.4 V and 0.3 V (both *vs.* SCE) were observed at the edge plane and CNT modified electrodes respectively. The slight deviation is likely due to the higher number per square centimetre of edge plane sites on the CNTs than in comparison to the eppg electrode.

The direct comparison allowed insights into the electrocatalytic sites for NADH oxidation which not would otherwise be elucidated. By studying the electrochemical oxidation of NADH at the edge plane and CNT modified electrodes with that of a bppg which had been first prepared by the cellotape method and then abrasively modified on alumina, we demonstrated that the electro-catalytic properties of CNT modified electrodes toward the oxidation of NADH to be solely due to edge plane sites/defects which occur along the tube axis or at the open ends of the tubes.<sup>27</sup> Note that the abrasive rubbing of the bppg with alumina on a soft-lapping pad introduces edge plane defects on the electrode surface which results in a shift of the oxidation wave to less negative potentials because the kinetics on the edge plane sites are considerably faster. We note that Lawrence *et al.*,<sup>28</sup> explored a range of commercially available CNTs obtained from different sources. It was observed that Nanolab CVD (chemical vapour deposition) produced CNTs were the most electrochemically reactive in comparison with those made using an ARC methodology. The authors speculated this to be due to the higher density of edge plane defects occurring on the CVD fabricated CNTs in comparison to the ARC produced CNTs, but critically no experimental comparisons were made with either edge plane or basal plane pyrolytic graphite electrodes.

Exploration of the electrochemical response at nanotube modified electrodes with edge plane and basal plane electrodes also allowed a better understanding of the adsorption of NADH at CNTs and edge plane electrodes. It was inferred that adsorption occurs at edge plane sites and due to the high density of edge plane sites on CNTs and eppg electrodes meaning that they are unsusceptible to electrode passivation. This of course allows a better understanding of the requirement of electrochemical sensors which should ideally be graphite based having a large proportion of edge plane sites for the best detection limits. Last, eppg electrodes can conveniently replace CNT modified electrode for the routine sensing of NADH due to their simplicity of preparation, low susceptibility to electrode fouling, low detection limit and insensitivity to interference from AA.<sup>27</sup>

## 8 Conclusions

Edge plane pyrolytic graphite electrodes are advantageous for use as electrode substrates in electroanalysis due to the highly reactive edge plane sites which allow low detection limits, high sensitivities, improved signal to noise characteristics and low overpotentials. We have shown that in many cases the edge

plane electrode can conveniently replaced CNT modified electrodes in this area due to their simplicity of preparation, cost and relative advantages of reactivity.

We also advocate, in all studies where CNT modified electrodes are used, the routine comparative examination of edge plane and basal plane pyrolytic graphite electrodes should be enforced before assigning "electrocatalytic properties".

## 9 References

1. R. R. Moore, C. E. Banks, and R. G. Compton, *Anal. Chem.*, **2004**, *76*, 2677.
2. C. E. Banks, R. R. Moore, T. J. Davies, and R. G. Compton, *Chem. Commun.*, **2004**, *16*, 1804.
3. C. E. Banks, T. J. Davies, G. G. Wildgoose, and R. G. Compton, *Chem. Commun.*, **2005**, *7*, 829.
4. T. J. Davies, M. E. Hyde, and R. G. Compton, *Angew. Chem.*, **2005**, *44*, 5121.
5. R. R. Moore, C. E. Banks, and R. G. Compton, *Analyst*, **2004**, *129*, 755.
6. L. C. Clark, *Trans. Am. Soc. Artif. Intern. Organs*, **1956**, *2*, 41.
7. M. C. Buzzeo, C. Hardacre, and R. G. Compton, *Anal. Chem.*, **2004**, *76*, 4583.
8. C. E. Banks, A. Goodwin, C. G. R. Heald, and R. G. Compton, *Analyst*, **2005**, *130*, 280.
9. E. R. Lowe, C. E. Banks, and R. G. Compton, *Anal. Bioanal. Chem.*, **2005**, *382*, 1169.
10. F. Wantz, C. E. Banks, and R. G. Compton, *Electroanalysis*, **2005**, *17*, 655.
11. A. J. Saterlay, F. Marken, J. S. Foord, and R. G. Compton, *Talanta*, **2000**, *53*, 403.
12. C. M. Welch, C. E. Banks, S. Komorsky-Lovric, and R. G. Compton, *Croat. Chem. Acta*, in press.
13. E. R. Lowe, C. E. Banks, and R. G. Compton, *Electroanalysis*, **2005**, *17*, 1627.
14. J.-B. Raoof, R. Ojani, and A. J. Kiani, *Electroanal. Chem.*, **2001**, *515*, 45.
15. F. Wantz, C. E. Banks, and R. G. Compton, *Electroanalysis*, **2005**, *17*, 1524.
16. I.-F. Hu and T. Kuwana, *Anal. Chem.*, **1986**, *58*, 3235.
17. R. J. Rice, N. M. Pontikos, and R. L. McCreery, *J. Am. Chem. Soc.*, **1990**, *112*, 4617.
18. J. O. Schenk, E. Miller, and R. N. Adams, *Anal. Chem.*, **1982**, *54*, 1452.
19. K. J. Stutts and R. M. Wightman, *Anal. Chem.*, **1983**, *55*, 1576.
20. M. Musameh, J. Wang, and A. Merkoci, Y. Lin, *Electrochem. Commun.*, **2002**, *4*, 743.
21. J. Chen, J. Bao, C. Cai, T. Lu, *Anal. Chim. Acta*, **2004**, *516*, 29.
22. F. Valentini, S. Orlanducci, M. L. Terranova, A. Amine, and G. Paleschi, *Sens. Actuators, B*, **2004**, *100*, 117.
23. F. Valentini, A. Salis, A. Curulli, and G. Paleschi, *Anal. Chem.*, **2004**, *76*, 3244.
24. J. Liu, S. Tian, and W. Knoll, *Langmuir*, **2005**, *21*, 5596.
25. M. D. Rubianes and G. A. Rivas, *Electroanalysis*, **2005**, *17*, 73.
26. R. Antiochia, I. Lavagnini, and F. Mago, *Anal. Bioanal. Chem.*, **2005**, *381*, 1355.
27. C. E. Banks and R. G. Compton, *Analyst*, **2005**, *130*, 1232.
28. N. S. Lawrence, R. P. Deo, and J. Wang, *Electroanalysis*, **2005**, *17*, 65.