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Graphene electrochemistry: Fabricating amperometric biosensors

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The electrochemical sensing of hydrogen peroxide is of substantial interest to the operation of oxidase-based amperometric biosensors. We explore the fabrication of a novel and highly sensitive electroanalytical biosensor using well characterised commercially available graphene and compare and contrast responses using Nafion -graphene and -graphite modified electrodes. Interestingly we observe that graphite exhibits a superior electrochemical response due to its enhanced percentage of edge plane sites when compared to graphene. However, when Nafion, routinely used in amperometric biosensors, is introduced onto graphene and graphite modified electrodes, re-orientation occurs in both cases which is beneficial in the former and detrimental in the latter; insights into this contrasting behaviour are consequently presented providing acuity into sensor design and development where graphene is utilised in biosensors.

Introduction

Since the free-standing form of graphene, a 2D nanomaterial one-atom-thick that possesses spectacular physical, chemical, and electrical properties, was isolated in 2004 there has been enormous interest from many scientific communities concerning the exploration and exploitation of its unique properties.[1–5] One area where graphene is currently making an impact is the field of electrochemistry,[2,4] particularly its use as a sensor substrate where, despite its relatively young age, it has already been shown as domineering over other fullerene allotropic dimensionalities such as graphite and carbon nanotubes[1,4,5] and has the potential for cost effective, sensitive, and selective electrochemical sensors to be derived.

The electro-catalysis of graphene has been widely reported, for example, towards the sensing of dopamine,[6] glucose,[7,8] hydrazine,[9] nitric oxide,[10] β-nicotinamide adenine dinucleotide (NADH)[11] and paracetamol.[12] These studies report that graphene based materials are beginning to revolutionise sensing, and have been demonstrated to exhibit improved sensitivity and selectivity, facilitating lower limits of detection and offering quick response times over other analytical methods.[2,12] Recently we have demonstrated that the reported electro-catalytic responses and enhanced electron transfer of graphene occur at its edge, as opposed to the side of the graphene, where the former acts electrochemically akin to edge plane sites and the latter to that of basal plane sites;[3] a conceptual picture of this for both graphene and graphite is presented in Fig. 1.

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One analyte of great significance in chemistry, biology, clinical control, and environmental protection[13,14] is hydrogen peroxide, which is of considerable interest due to its use in oxidase-based amperometric biosensors.[15–17] Additionally, Nafion films, because of their unique ion-exchange, discriminative, and biocompatibility properties, have been used extensively for the modification of electrode surfaces and for the construction of amperometric biosensors.[18,19] For example, graphene modified electrodes have been shown to boast superior bio-sensing performance over carbon nanotube counterparts towards adenine and guanine[20] when using a graphene based Nafion composite film modified glassy carbon electrode, and the same is true for the sensing of lead and cadmium using a graphene nanosheet-Nafion (Nafion-G) composite film.[18]

In this paper we explore the electro-catalytic behaviour of graphene based electrodes for the sensing of hydrogen peroxide and contrast observed electrochemical responses with graphite

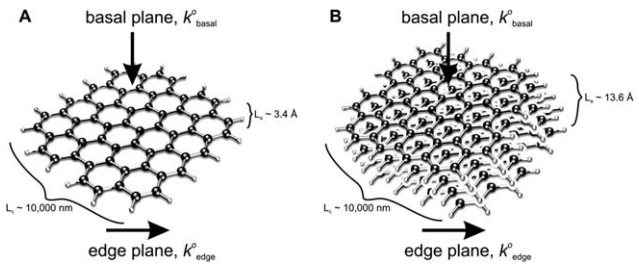

Fig. 1 Schematic representation of graphene **(A)** and graphite **(B)** indicating the edge and basal sites, where the heterogeneous electron transfer rate of the former (k^o_{edge}) is anomalously faster over that of the latter (k^o_{basal}). Also shown are the relative sizes as indicated by the intraplanar microcrystallite size, L_a, and interplanar microcrystallite size, L_c.

based electrodes, performed under identical conditions, and demonstrate that the electrochemical properties of graphite for use as a sensor substrate towards the selected target analyte are far superior to those of graphene. Additionally, because of the lack of understanding behind the enhanced electro-catalytic responses observed when utilising Nafion based composites, we explore the effects of Nafion upon the same electro-catalytic responses using appropriate control experiments,[2] and show that the *opposite is observed* in that the Nafion modified graphene exhibits a superior response over that of Nafion modified graphite. This report allows insights into sensor design and development where graphene is utilised in biosensors.

Experimental section

All chemicals (analytical grade or higher) were used as received from Sigma-Aldrich without any further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm and were vigorously degassed prior to electrochemical measurements with high purity, oxygen free nitrogen. Voltammetric measurements were carried out using a μ-Autolab III (ECO-Chemie, The Netherlands) potentiostat. All measurements were conducted using a three electrode system.

Screen-printed carbon electrodes (SPEs) were fabricated in-house with appropriate stencil designs using a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK). A carbon-graphite ink formulation was first screen printed onto a polyester flexible film (Autostat, 250 μm thickness) defining the carbon contacts, counter and working electrodes. This layer was cured in a fan oven at 60 degrees for 30 min. Next a silver/silver chloride reference electrode was included by screen printing Ag/AgCl paste (Gwent Electronic Materials Ltd, UK) on to the plastic substrate, which again was cured at 60 degrees for 30 min. Last a dielectric paste ink (Gwent Electronic Materials Ltd, UK) was printed to cover the connections and define the 3 mm diameter graphite working electrode. After curing at 60 degrees for 30 min the screen printed electrode is ready to use. These electrodes have been characterised electrochemically in a prior paper and have heterogeneous rate constants of $\sim 1.7 \times 10^{-3}$ cm^2 s^{-1}.[21]

Graphene was commercially obtained from NanoIntegris (Illinois, USA), in a form known as 'PureSheets'™ (research grade) which are comprised entirely of pristine graphene platelets that have not been oxidised, reduced, or chemically modified in anyway.[22] The graphene is produced *via* density gradient ultracentrifugation and the methodology has been reported and characterised previously.[23] The process involves the bile salt sodium cholate which promotes graphite exfoliation resulting in graphene-surfactant complexes having buoyant densities that vary with graphene thickness. This results in a 'sorting' of the graphene and hence different fractions are observed meaning that graphite and multi-layer graphene is not inadvertently incorporated into the graphene samples. The graphene is in an aqueous solution (0.5 mg per 10 mL) with an ionic surfactant, sodium cholate hydrate (2% w/v), and consists of a mean flake area of 10,000 nm^2.[22,23] XPS chemical analyses were performed with a VG-Microtech Multilab electron spectrometer. This reveals the presence of 74.66% atomic carbon, 16.43% atomic oxygen, 4.12% atomic nitrogen, 2.63% atomic sodium and 2.13% atomic sulfur. Interpretation of the XPS spectra for the case of the oxygenated species reveals the presence of hydroxyl, carbonyl, epoxy and ether functional groups. Identification of nitrogen *via* XPS likely indicated pyridone type functionalisation which is likely due to an acid treatment performed prior to the density gradient ultracentrifugation process. We however note that this information is not easily de-convoluted from the contribution of the sodium cholate surfactant which is present. Additionally the presence of sulfur, sodium and nitrogen suggests the presence of additional anionic and cationic surfactants added by the company following production of the graphene (see above).

The graphene consists of: 27% single layer, 48% double layer, 20% triple layer and 5% 4+ layer, and due to the fabrication approach is free from graphite impurities (see above). Aliquots of the graphene (10 μL) were carefully pipetted onto the electrode surface using a micro-pipette and allowed to dry at room temperature under nitrogen flow in order to eliminate oxidation of the graphene by the presence of atmospheric oxygen, following which the electrode can either be further modified, or is ready to use. All comparison and control measurements using graphite (0.5 mg per 10 mL, with the same ionic surfactant (2% w/v)) were conducted within the exact manner as with graphene (aliquots of 10 μL were utilised). Where Nafion was employed in the presence of graphene, graphite, or surfactant, the underlying (graphene/graphite) layer was first deposited using the above procedure, and when dry 40 μL of 0.05% Nafion (in ethanol) was added and dried using the same procedure; when Nafion alone was used, it was deposited directly upon the unmodified electrode surface and dried under nitrogen flow. During amperometric experiments a magnetic stirrer was used to provide convection, rotating at 200 rpm.

Results and discussion

We first consider the electrochemical sensing of 5 mM hydrogen peroxide in a phosphate buffer solution (pH 7.4) using a graphene modified SPE. Fig. 2 reveals that the use of graphene significantly increases charge transfer leading to a greatly increased signal response in comparison to the bare underlying graphene free electrode. A similar voltammetric response has been previously observed using carbon nanotubes.[19] Next, attention was turned to the amperometric response of the graphene/Nafion modified electrode towards the sensing of hydrogen peroxide. Fig. 3 depicts the amperometric response showing successive additions of hydrogen peroxide over the range 0.5 to 7.5 mM into a pH 7.4 phosphate buffer solution, with the inset of Fig. 3 also showing the response from smaller additions of hydrogen peroxide over the range 50 to 500 μM. Analysis of the current as a function of increasing concentration is depicted in Fig. 4 where a highly linear response is observed over the range 50 to 750 μM with further information presented in Table 1. When considering the response of the graphene modified electrode (in the absence of Nafion) (Fig. 4; Ge/S) it is apparent that the modification of the electrode surface with graphene causes an immense increase in sensitivity over the bare electrode, where in the latter a negligible response towards hydrogen peroxide is observed (see Fig. 2), with an increase in the sensitivity from 0.1 to 32.8 μA mM^{-1} observed for the bare

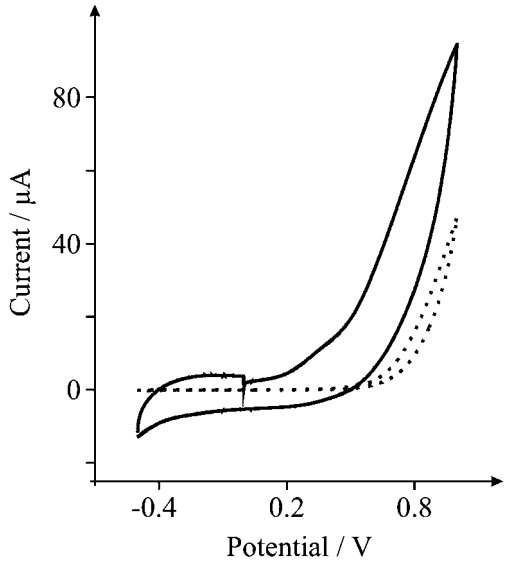

Fig. 2 Cyclic voltammetric profiles recorded for 5 mM hydrogen peroxide in a pH 7.4 phosphate buffer solution using a SPE (dotted line) and a graphene modified SPE (solid line). Scan rate: 50 mV s^{-1} (*vs.* Ag/AgCl).

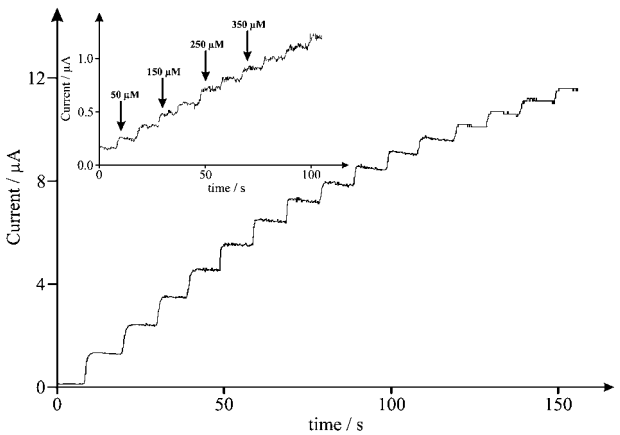

Fig. 3 Amperometric response of graphene/Nafion modified SPE for successive additions of 0.5 mM hydrogen peroxide into (pH 7.4) phosphate buffer. Operating potential: +0.4 V. **Inset**: successive additions of 50 μM hydrogen peroxide under identical conditions.

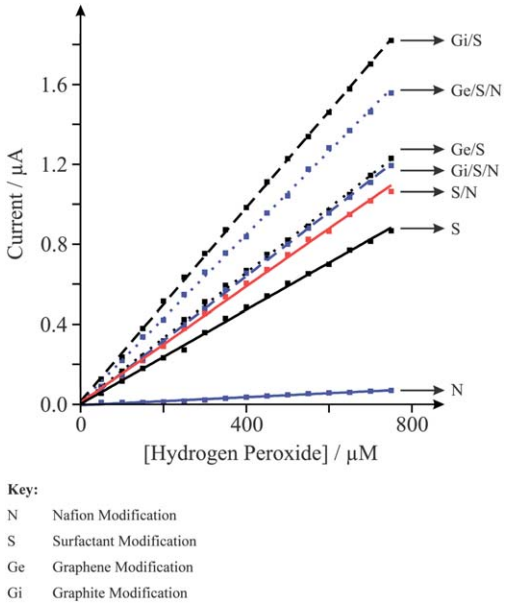

Fig. 4 Analysis of amperometric data from additions of hydrogen peroxide into a (pH 7.4) phosphate buffer solution using a SPE modified with; 40 μL Nafion (blue solid line); 10 μL graphite/surfactant and 40 μL Nafion (blue dashed line); 10 μL graphene/surfactant and 40 μL Nafion (blue dotted line); 10 μL surfactant (black solid line); 10 μL graphite/surfactant (black dashed line); 10 μL graphene/surfactant (black dotted line); and 10 μL surfactant and 40 μL Nafion (red solid line). Operating potential: +0.4 V.

Table 1 Comparison of the sensitivities of various electrode modifications proposed for the fabrication of an amperometric hydrogen peroxide biosensor recorded in pH 7.4 phosphate buffer solution; Operating potential: +0.4 V

Electrode modification	Sensitivity (μA mM^{-1})
Unmodified	0.1
Graphene	32.8
Graphite	49.0
Graphene and Nafion	42.2
Graphite and Nafion	32.0
Nafion	1.8
Surfactant	23.6
Surfactant and Nafion	29.4

electrode and the graphene modified electrode respectively. This response is likely due to the greater proportion of edge plane sites from the addition of graphene in comparison to the underlying bare electrode surface which has been characterised previously and exhibits slow electron transfer rates.[3]

For comparative purposes we performed a control experiment using graphite (Fig. 4; Gi/S) where it can be observed that the graphite produces a greater response, 49.0 μA mM^{-1}, over that observed for graphene, 32.8 μA mM^{-1}. To understand this response, consider the surface area ratio of basal plane, S_{basal}, to edge plane (perimetrical boundary carbon atoms), S_{edge}, for the case of increasing layers of graphene. We know that the mean flake/sheet area of graphene is 10,000 nm^2, and using $S_{basal} = \pi r^2$ the surface area of the basal contribution for a single piece of graphene may be deduced. The S_{edge} is considered to be the perimetrical surface area consisting of the boundary of carbon atoms of the graphene layer. The perimetrical surface area is considered to be a round strip or band, the same as the length of the perimeter of a circular disk; $L = 2\pi r$, r is the radius, and the width is the height of this stripe (h). The surface area of the edge plane is therefore, $S_{edge} = 2\pi rh$, where for a single layer of graphene the height of the stripe is equal to the thickness of the graphitic monolayer sheet which is 3.4 Å,[24,25] and each layer of graphene added contributes to an increase to the height of the circular stripe by 3.4 Å. Fig. 5 compares the ratio of S_{basal}/S_{edge} on increasing the number of graphene layers where it is evident that as more layers are introduced, the amount of edge, *viz* edge plane sites is increased. This is also related to the theoretical current that would be expected as the amount of edge plane is increased, assuming the S_{edge} to be a 'band type' electrode. As

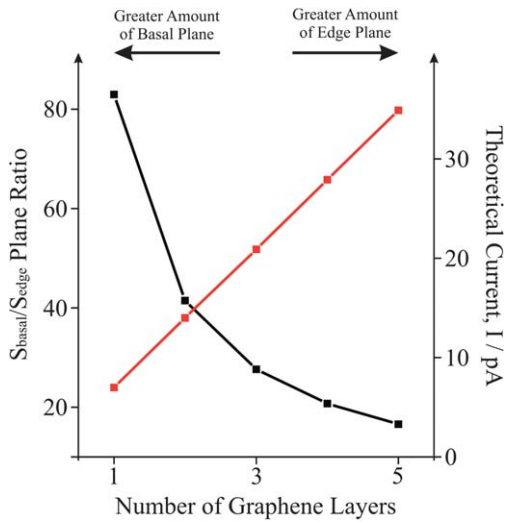

Fig. 5 The effect of increasing the number of graphene layers upon the ratio of basal/edge plane sites for a single piece of graphene (black line) and the effect on the theoretical observed current (red line). Note that this is for a single piece of graphene.

a consequence of increasing the amount of edge plane, which is the origin of electron transfer, an increase in the current is expected (from increasing layer numbers) and thus as we move from single layer graphene to multi-layer graphene which is approaching that of graphite, the observed voltammetric responses will theoretically surpass that of graphene. Note that for representation this considers a single piece of graphene when in reality this will have to be multiplied, as best can be, for the number of graphene pieces on the electrode surface where also orientation might have to be taken into consideration. Additionally, the contribution from the change in mass transport, when immobilised upon an electrode surface is yet to be fully understood.

Aligning these insights with the response observed above, where graphite outperforms graphene towards the sensing of hydrogen peroxide (Fig. 4), this can be attributed to a greater proportion of edge plane as depicted in Fig. 1, where the percentage of edge to basal plane ratio in graphite is greater than that of graphene and as a consequence a superior electrochemical response is observed.

We now turn to exploring the role of introducing Nafion which is widely used in fabricating biosensors. We observe that the addition of Nafion upon a graphene modified electrode (Fig. 4; Ge/S/N) increases the sensitivity for the amperometric sensing of hydrogen peroxide from 32.8 μA mM^{-1} (Fig. 4; Ge/S) to 42.2 μA mM^{-1}. Such an improvement in the voltammetric response from the addition of Nafion to graphene is in agreement with previous literature reports.[18] If we compare the response of the Nafion solely (Fig. 4; N), in the absence of graphene, to that of Nafion in the presence of graphene (Fig. 4; Ge/S/N) as shown in Fig. 4, we find that the Nafion alone is not responsible for the observed increase in sensitivity towards hydrogen peroxide sensing, though Nafion exhibits a small contributory effect upon the response of the bare electrode; it may be inferred that the increased sensitivity is resultant of the effect that Nafion has upon the graphene sheets present. When considering the impact of Nafion on graphite within the same manner as above (graphite/Nafion modified electrode: Fig. 4; Gi/S/N), as depicted in Table 1 and Fig. 4, a completely different effect is apparent; the addition of Nafion to a graphite modified electrode has an overall detrimental effect and causes a decrease in the observed sensitivity from 49.0 to 32.0 μA mM^{-1} respectively. Note that this effect has not been reported in the literature.

It is well known that the voltammetric response of graphite electrodes depends on the proportion of edge plane like-sites/defects where a low and high proportion result in slow and fast electron transfer respectively,[24,25] which has also recently been shown to be the case for graphene.[3] We also note above that Nafion itself is not responsible for the improvements in the

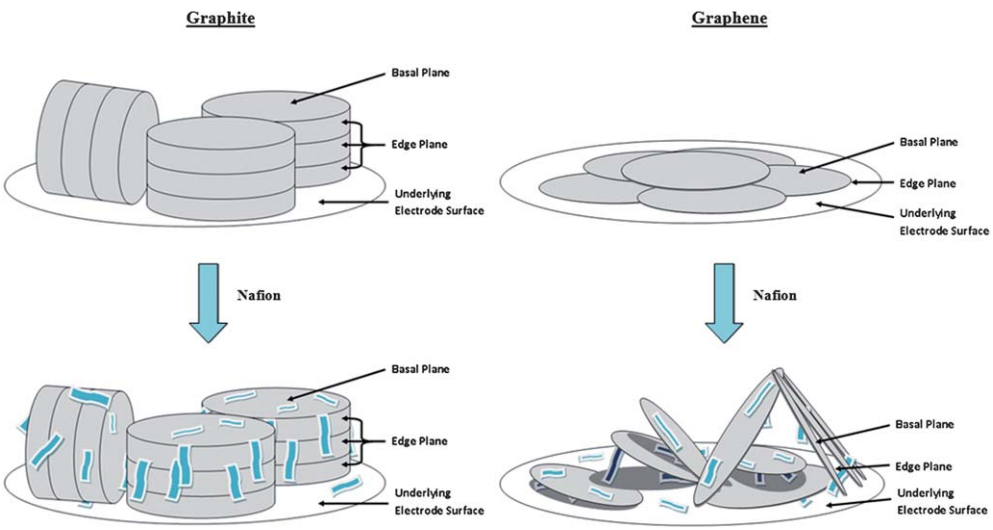

Fig. 6 Schematic representation for the detrimental effects observed (inhibition of edge plane like sites) with the addition of Nafion to a graphite modified electrode **(A)** and the schematic representation for the enhanced edge plane effects observed (through the re-orientation of graphene layers) with the addition of Nafion to a graphene modified electrode **(B)**.

sensing of hydrogen peroxide (see above). We therefore infer that when graphene is deposited on an electrode surface it lays relatively flat, with some layers even stacking on top of one-another, but with the overall edge plane percentage of the modified layer relatively low; this is consistent with recent work by Pumera *et al.*[26] With the introduction of Nafion the graphene layer is re-dissolved into the Nafion solution which adsorbs onto edge plane like sites causing graphene to become consequentially re-orientated upon the electrode surface when the solution has evaporated, forming a jagged and highly disordered surface, as depicted in Fig. 6; and as a result the edge plane percentage of the graphene-Nafion layer is now greatly increased, due to a greater disorder, leading to an increased number of exposed electron transfer sites and thus exhibits an enhanced sensitivity towards hydrogen peroxide as observed in Fig. 4. Note that a control experiment was performed where ethanol was cast upon the graphene without Nafion to see if this was the origin but it did not result in any improvements in the electroanalytical response.

To gain further insights, Fig. 7 depicts SEM images of bare, graphene modified, and graphene/Nafion modified electrodes. While we cannot resolve the individual graphene sheets the dramatic change in surface morphology is visually useful, confirming our inference as shown in Fig. 6. It is likely in the case of graphite that Nafion adsorbs onto hydrophobic edge plane sites resulting in attraction of graphite pieces which has the overall effect of blocking electron transfer due to a change in orientation and resultant decrease in the percentage of edge sites available as depicted in Fig. 6. The overall effect is that less electron transfer can occur which results in an overall reduced electrochemical response and consequently a reduced sensitivity towards hydrogen peroxide, as is evident from inspection of Table 1 where a decrease in sensitivity is observed.

Comparison of data within Table 1 and Fig. 4 reveals that the graphene/Nafion modified electrode produced the most sensitive response for the detection of hydrogen peroxide when compared against the graphene modified and bare SPEs. However, contrary to current literature,[13,14] the most electro-catalytic electrode modification observed is graphite, raising the question: why use graphene for the sensing of hydrogen peroxide? This is of course in model solutions and when applied to complex real solutions, the discriminator effects of Nafion to reduce interferents might become useful with the insights presented in this paper helping in the design and development of such sensors involving these components.

The observations presented above, particularly in the case of graphene, are further complicated due to the presence of the surfactant, sodium cholate hydrate, an intrinsic property of the graphene used in its fabrication and also to stop the coalescing of the graphene layers which is absorbed onto the basal plane sites of the graphene; we next consider whether this has a contributable effect on the electrochemistry of graphene. Table 1 demonstrates that the surfactant modified electrode (Fig. 4; S) results in an increased sensitivity over that of the bare electrode towards hydrogen peroxide, additionally, Fig. 8 depicts that increments in the amount of surfactant deposited on the electrode surface also lead to further increased sensitivities. Thus it is apparent that the surfactant has a catalytic activity for the detection of hydrogen peroxide and therefore contributes to the overall sensitivities observed when it is present. When observing

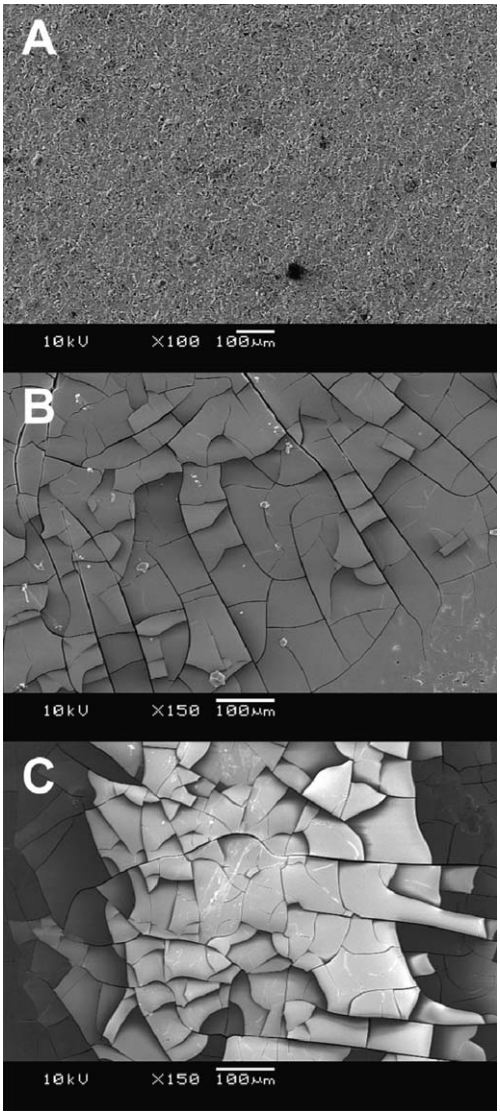

Fig. 7 SEM images of a SPE (A) modified with 0.5 µg graphene (B) and 0.5 µg graphene with 0.02 µg Nafion (C).

the response of a surfactant/Nafion modified electrode (Fig. 4; S/N) it is evident that Nafion contributes marginally to the electrochemical response. With this in mind we suggest that when considering the effect observed within the presence of the surfactant discussed here, it must be considered that the resultant electrochemical response is from a combination of effects, namely the underlying electrode, graphene, surfactant, and Nafion.

When comparing the response of the graphene modified electrode, which is present with surfactant at the same concentrations and deposition quantities, with that of the surfactant modified electrode apparent within Table 1 and Fig. 8, we are able to de-convolute the effect of graphene upon the electrochemical response towards hydrogen peroxide. It is clear that the graphene only contributes a small degree to the overall effect and that it is in fact the surfactant that increases the sensitivity by the majority over the bare electrode. Until graphene can be obtained without the presence of a surfactant this

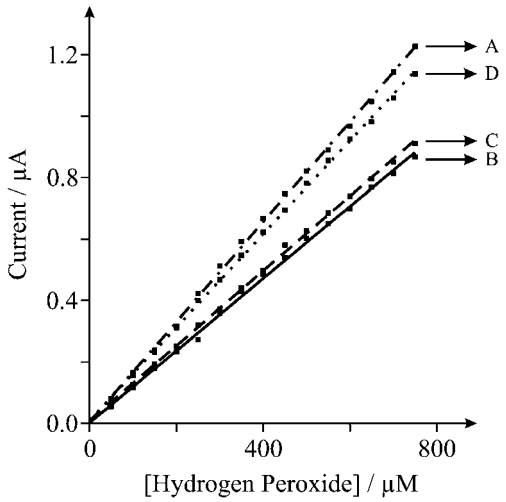

Fig. 8 Calibration plots from amperometric experiments using SPEs modified with; 10 μL graphene/surfactant (dot-dashed line: A); 10 μL surfactant (solid line: B); 20 μL surfactant (dashed line: C); and 40 μL surfactant (dotted line: D). Operating potential: +0.4 V; phosphate buffer (pH 7.4).

'combined effect' will always be apparent and will need to be diligently explored.

Conclusions

We have demonstrated that in fabricating amperometric biosensors using carbon based materials, graphite based electrodes provide greatly enhanced electro-catalytic activity over graphene, which is attributed to an increased percentage of edge plane sites in model solutions. This at first sight suggests that graphene is not such a 'hot material' as first thought; this has also been reported for uric acid,[27] cadmium,[28] NADH,[29] and acetaminophen.[29]

However when Nafion is introduced, as is the case in biosensors due to its potential discriminator effects from interferents, this is reversed and graphene is superior over graphite which we infer to be due to substantial re-orientation and disorder of the graphene. We also show that the surfactant used in the fabrication of the graphene, an intrinsic property, contributes towards the electroanalytical response of the target analyte. Based upon our findings we suggest the following when graphene is used within the areas of electrochemical sensing:

i. The electrochemical response is compared and contrasted to that of structurally related carbons under identical conditions.[2]

ii. The effect upon the percentage of edge plane sites available for electro-catalytic reactions to occur due to the addition of external compounds (such as Nafion), which may be beneficial or detrimental, needs to be considered.

iii. The role of surfactants used to reduce graphene coalescing and used in the fabrication process needs to be considered.[2,3]

iv. The orientation of the graphene sheets in composite materials is crucial in the design of new graphene based electrochemical sensors.

Graphene, as we have utilised so far from a commercial source, does not perform as the current literature would suggest; further work in this area is underway.

References

1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
2 D. A. C. Brownson and C. E. Banks, *Analyst*, 2010, **135**, 2768.
3 D. K. Kampouris and C. E. Banks, *Chem. Commun.*, 2010, **46**, 8986.
4 M. Pumera, *Chem. Rec.*, 2009, **9**, 211.
5 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
6 Y.-R. Kim, S. Bong, Y.-J. Kang, Y. Yang, R. K. Mahajan, J. S. Kim and H. Kim, *Biosens. Bioelectron.*, 2010, **25**, 2366.
7 X. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu and Y. Lin, *Biosens. Bioelectron.*, 2009, **25**, 901.
8 Y. Liu, D. Yu, C. Zeng, Z. Miao and L. Dai, *Langmuir*, 2010, **26**, 6158.
9 Y. Wang, Y. Wan and D. Zhang, *Electrochem. Commun.*, 2010, **12**, 187.
10 J.-F. Wu, M.-Q. Xu and G. C. Zhao, *Electrochem. Commun.*, 2010, **12**, 175.
11 W.-J. Lin, C.-S. Liao, J.-H. Jhang and Y.-C. Tsai, *Electrochem. Commun.*, 2009, **11**, 2153.
12 X. Kang, J. Wang, H. Wu, J. Liu, I. A. Aksay and Y. Lin, *Talanta*, 2010, **81**, 754.
13 K. Zhou, Y. Zhu, X. Yang, J. Luo, C. Li and S. Luan, *Electrochim. Acta*, 2010, **55**, 3055.
14 Y. Fang, S. Guo, C. Zhu, Y. Zhai and E. Wang, *Langmuir*, 2010, **26**, 11277.
15 Y. Lin, F. Lu, Y. Tu and Z. Ren, *Nano Lett.*, 2004, **4**, 191.
16 A. L. Brioukhanov and A. I. Netrusov, *Appl. Biochem. Microbiol.*, 2007, **43**, 567.
17 T. Li, Z. Yao and L. Ding, *Sens. Actuators, B*, 2004, **101**, 155.
18 J. Li, S. Guo, Y. Zhai and E. Wang, *Anal. Chim. Acta*, 2009, **649**, 196.
19 J. Wang, M. Musameh and Y. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 2408.
20 H. Yin, Y. Zhou, Q. Ma, S. Ai, P. Ju, L. Zhu and L. Lu, *Process Biochem.*, 2010, **45**, 1707.
21 P. M. Hallam, D. K. Kampouris, R. O. Kadara and C. E. Banks, *Analyst*, 2010, **135**, 1947.
22 http://www.nanointegris.com.
23 A. A. Green and M. C. Hersam, *Nano Lett.*, 2009, **9**, 4031.
24 R. L. McCreery, *Chem. Rev.*, 2008, **108**, 2646.
25 C. E. Banks, T. J. Davies, G. G. Wildgoose and R. G. Compton, *Chem. Commun.*, 2005, 829.
26 M. S. Goh and M. Pumera, *Electrochem. Commun.*, 2010, **12**, 1375.
27 M. S. Goh and M. Pumera, *Anal. Chem.*, 2010, **82**, 8367.
28 D. A. C. Brownson and C. E. Banks, *Electrochem. Commun.*, 2011, **13**, 111.
29 D. A. C. Brownson, J. P. Metters, D. K. Kampouris and C. E. Banks, *Electroanalysis*, 2011, DOI: 10.1002/elan.201000708.