DISCUSSIONS

Role of surface contaminants, functionalities, defects and electronic structure: general discussion

Richard McCreery, Chi-Chang Hu, Julie Macpherson, Matěj Velický, John Foord, Matteo Duca, Katherine Holt, Manuel Alvarez-Guerra, Robert Dryfe, Surbhi Sharma, Patrick R. Unwin, Jingping Hu, George Zheng Chen, Fulian Qiu, Robert Hamers, Mark Newton, Andrew N. J. Rodgers, Philip A. Ash, Deborah Lomax, Keith Stevenson, Aleix Güell, Thomas Varley, Stephen Hodge and Fernanda Juarez

Richard McCreery opened the discussion of the paper by Robert Dryfe: You stated that Ru(hexamine) shows a depression of the outer sphere ET rate, on graphene, possibly due to the proximity of its redox potential to the Dirac point. If so, then other redox systems with different E^os should show an increasing kinetic trend as the potential moves from the Dirac point. Has anyone observed such a trend?

Robert Dryfe answered: This has not been explicitly investigated, to the best of my knowledge. We have plotted this data for the limited number of redox couples (four) we have investigated, *i.e.* the FcTMA and $Ru(NH_3)_6{}^{3+}$ couples reported in this manuscript, as well as ferricyanide and hexachloroiridate; the latter pair from data that is currently unpublished. Plotting the decadic logarithm of the standard rate constant on monolayer graphene (using the 'sample 1' preparation) as a function of the standard reduction potential yields the graph shown (Fig. 1), which does give an approximate correlation. This does support the density of states argument advocated by the questioner – given that the Dirac point of graphene is reported[1] to be close to the reduction potential of the $Ru(NH_3)_6{}^{3+}$ complex, the complex displaying the slowest kinetics. However, given the limited dataset, we have also taken the liberty of attempting this kinetic correlation with redox potential for a wider set of data, namely the rate constants reported on CVD-prepared monolayer graphene by Prof. Abrūna and co-workers.[2] This plot revealed no strong correlation, so the best we can say is that the question is still open.

1 Q. H. Wang *et al.*, *Nat. Chem.*, 2012, **4**, 724.
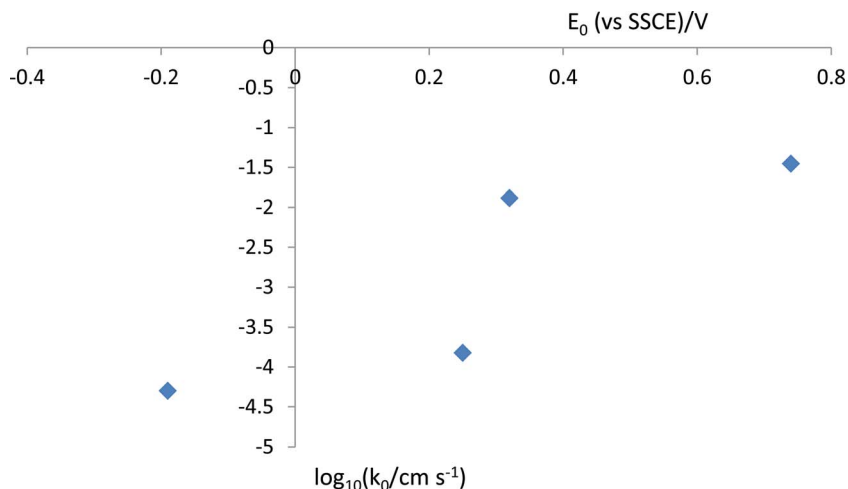2 N. Ritzert *et al.*, *Langmuir*, 2013, **29**, 1683.

Fig. 1 Decadic logarithm of the standard rate constant on monolayer graphene as a function of the standard reduction potential.

Matěj Velický addressed Richard McCreery and Robert Dryfe: Rob Dryfe mentioned that the low electrode kinetics observed for the hexaamminer-uthenium (HAR) redox mediator are possibly related to the fact that the standard redox potential of HAR could be close to the Dirac point in graphene – where the density of states (DOS) is low – which would result in slower kinetics. This is indeed one of the early explanations we adopted, however, our recent work on graphene *vs.* bulk graphite electrodes (unpublished) indicates that there might be another explanation for this behavior. Monolayer graphene does generally exhibit kinetics slower than bulk graphite, however, the absolute value of HAR kinetics is still relatively slow on bulk graphite (~10^{-5} to 10^{-4} cm s^{-1}), which does not support the Dirac point proximity explanation. Furthermore, unpublished results suggest that the variation in kinetics is most prominent for thin graphene samples (*i.e.* below 10–20 layers), which makes sense as the DOS in these flakes will be affected much easier than in bulk graphite. Also it is important to add that the work presented here has been carried out using natural graphite, in contrast with the vast majority of electrochemical studies on HOPG, so any comparison with other literature data is very limited.

Julie Macpherson asked Robert Dryfe: Is acetone and chloroform doping in graphene p-type or n-type and by how much does the Fermi level shift? Where would the E^o for ruthenium hexamine ($Ru(NH_3)_6{}^{3+}$) sit on the band diagram for doped graphene?

Robert Dryfe replied: Chloroform is reported to intercalate between graphene and the oxide-covered silicon wafer support[1] leading to significant (by *ca.* 0.5 eV) p-doping of the graphene: we see slightly slower kinetics for the chloroform-treated sample. The same reference reports that acetone leads to much lower doping than chloroform.

1 H. H. Kim *et al.*, *ACS Nano*, 2013, **7**, 1155.

Patrick Unwin enquired: Studies from our group (*e.g.* ref. 1 and 2) have shown that there are apparently significant changes in the HOPG surface and resulting electrochemical response over time, and that one needs to make measurements as soon as possible after cleavage to capture the behaviour of a freshly cleaved surface. How do you deal with the time issue for studies of exfoliated graphene and what happens to the electrochemical response over time?

1 S. C. S. Lai, A. N. Patel, K. McKelvey and P. R. Unwin, *Angew. Chem. Int. Ed.*, 2012, **51**(22), 5405–5408.
2 A. N. Patel *et al.*, *J. Am. Chem. Soc.*, 2012, **134**(49), 20117–20130.

Robert Dryfe responded: This is another good point and my answer relates to the one given to Julie Macpherson, in response to her question about adsorbates in graphene. The time issue is difficult to control in our mechanically exfoliated samples since we generally identify and transfer the flake first, and make electrical contact afterwards, meaning that there is a long atmospheric exposure time (typically 24 h). Dr Velický has, however, used our pipette approach to perform an 'in situ' cleavage of graphite, that is to use the pipette to exfoliate fresh material which is immediately exposed to the solution and not the atmosphere (currently unpublished data). We find much more reversible kinetics for the slowest of the redox couples, *i.e.* the ruthenium hexamine species, for the freshly exfoliated samples. This is not, admittedly, done for thin 'graphene-like' samples, as it would be difficult to perform such a cleave without breaking a thin sample, but – at least for graphite – our findings certainly agree with the work reported in the two papers you cite from your laboratory.

Julie Macpherson asked: Given the issues surrounding graphene contamination during transfer and solvent washes, with even the length of time the material is exposed to the atmosphere or solution of interest potentially playing a role, do you foresee an application role for graphene electrodes in the future?

Robert Dryfe answered: This is a good question; the short answer is yes, I do, but it is essential that we do further work to reveal the intrinsic electron transfer response of 'true' graphene, *i.e.* one free of accidental contamination. I think that, as well as contamination due to polymer residues and solvents, adsorption of organic material from the atmosphere is a significant factor behind much of the variability seen in graphene electrochemistry. We need to develop protocols to isolate and transfer graphene samples without exposure to such adventitious carbon. I don't think this has been achieved yet.

Aleix Güell remarked: It is quite well known, the influence of the substrate on graphene's electronic properties, and electron transfer in particular.[1] This is the reason for the search focusing on screening methods such as h-BN, silane monolayers, *etc.* My concern is that, working with such big graphene flakes, and considering its known impermeability,[2] the chances to trap air-humidity between graphene and the substrate are high. How would this affect macroscopic

experiments? Have you observed variation within a flake in electrochemical activity when using microscopic droplet experiments?

1 Q. H. Wang *et al.*, *Nature Chemistry*, 2012, **4**, 724.
2 J. S. Bunch *et al.*, *Nano Lett.*, 2008, **8**, 2458.

Robert Dryfe replied: We do see localised variation of electrochemical activity within single flakes. I accept the questioner's suggestion that trapped solvent (or other) residues underneath the flake could be responsible for this variation, however, similarly local adsorbates on top of the flake (as alluded to above) could equally be responsible, so for the moment we cannot readily distinguish between these two possibilities.

George Zheng Chen opened the discussion of the paper by Keith Stevenson: I was very impressed by your insightful talk on single layer graphenes. How large are these single layer graphenes in terms of area? Will the size of the graphene layer affect the double layer capacitance, or will the graphene layer itself be charged?

Keith Stevenson responded: Thanks for your comments. The original nature materials paper[1] that describes the growth of single layer graphene on SiC indicates that the SiC terraces are about 3×50 µm and that the graphene forms single domains over the individual terraces. Our Sandia researcher (Calvin Chan) says that the physical grains of graphene are actually much larger than that, on the order of 100s of microns to millimeters. They typically cut the SiC wafer to 1 cm^2 sizes and grown graphene on SiC of this size. At Sandia they have performed LEEM studies and don't see multiple graphene domains at once, as the microscope's field of view is smaller than 100 micrometers. The question is, what do you really refer to as a grain of single layer graphene, because even though a single graphene crystallite is millimeters large, whenever it goes over a terrace edge on SiC it will be interacting with another layer of graphene in that region. These samples are approximately 20% bilayer graphene. We haven't looked specifically at the double layer capacitance in aqueous electrolytes, only in ACN TBAPF6 electrolytes. To our knowledge the single layer graphene on hydrogen intercalated SiC has no residual surface charge. The single and double atom vacancies are possibly passivated by hydrogen or other heteroatoms, but we don't see anything in the STM images to suggest that the defects are trapping charge at these sites.

1 K. V. Emtsev *et al.*, *Nat. Mat.*, 2009, **8**, 203.

Robert Dryfe said: Fig. 11, in particular Fig. 11(e), of your paper shows the comparison of surface coverage between your graphene samples and glassy carbon. Given the debate about the relative reactivity of graphene *vs.* graphite, and about the activity of the graphene basal plane, could you comment on the relative reactivity of your graphene samples *vs.* HOPG?

Keith Stevenson replied: We did not perform any studies on HOPG. The problem with HOPG is that the quality of the substrate is strongly dependent on the provider, therefore it is hard to establish a clear correlation between the local properties (*e.g.* the density of step edges and basal plane defects) of the HOPG and

the reactivity. We plan to obtain some high quality HOPG from McCreery and perform complimentary experiments to compare the relative reactivity of single layer graphene *vs.* HOPG.

Patrick Unwin remarked: We have recently studied the diazonium function-alisation of HOPG surfaces at both the macroscale and microscale.[1] Our data suggest that step edge defects play little role in the electrochemical generation of diazonium radicals or the subsequent modification (resulting in passivation of the electrode surface). At the macroscale, we studied 2 different grades of HOPG whose step edge density differed by more than 2 orders of magnitude. The cyclic voltammetric response during repetitive sweeps, during which the HOPG surfaces became increasingly passivated, was independent of the HOPG grade, with both materials showing similar electrochemical responses (Fig. 2). At the microscale, we have used scanning electrochemical cell microscopy (SECCM)[1] to pattern high quality HOPG at a series of spots, through meniscus contact from the SECCM pipette, under chronoamperometric conditions for defined time periods (1–17 s). As shown in the AFM images in Fig. 3, local functionalization creates well-defined spots on the surface and there is no noticeable change in the spots in regions with step edges compared to those without. Modification of the sp^2 graphite surface was confirmed by Raman microscopy.[1]
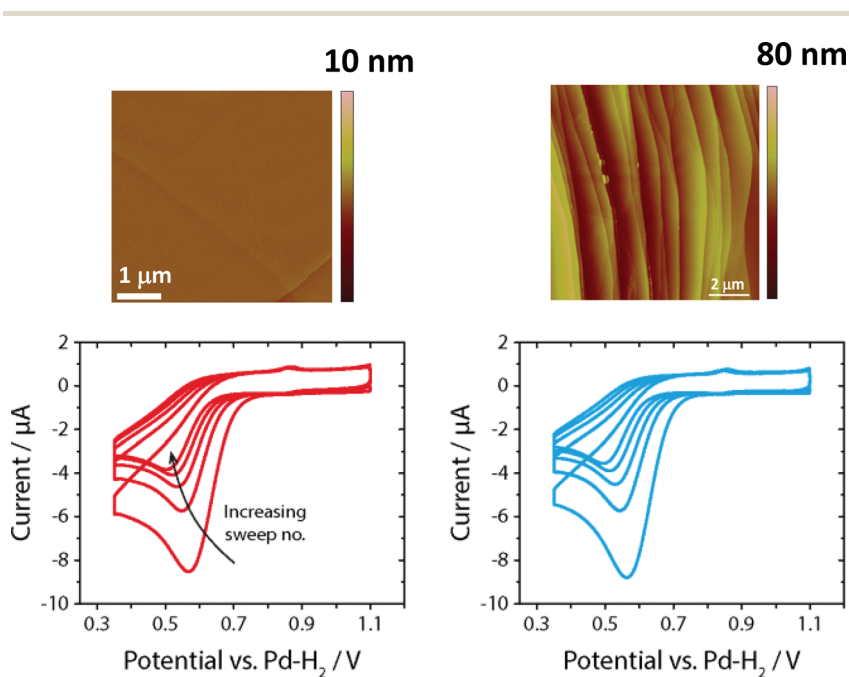

Fig. 2 CVs (0.2 V s^{-1}) for the reduction of 4-carboxybenzenediazonium (0.1 mM in 50 mM aqueous H$_2$SO$_4$) as a function of increasing sweep number for 2 grades of HOPG with widely different step edge densities. Left: ungraded, high quality HOPG, originating from Dr Arthur Moore and kindly provided by Prof. Rick McCreery (University of Alberta). Right: SPI-3 grade HOPG. Voltammetric data from ref. 1.
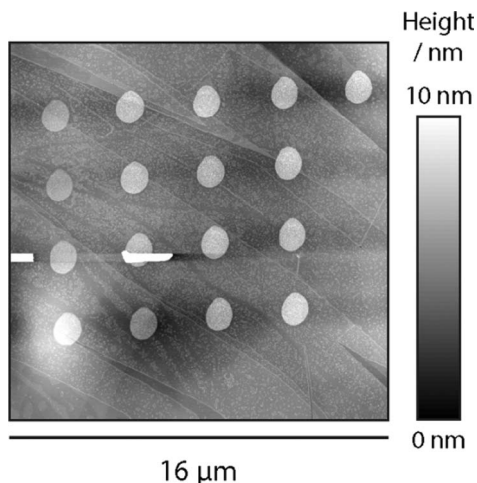
Fig. 3 Array of diazonium-functionalised spots on high quality HOPG, visualised by ex-situ AFM, following modification by SECCM for defined times from 0.5 s (top left) to 8.5 s (top right) at 0.5 s intervals, through the reduction of 4-carboxybenzenediazonium (0.1 mM in 25 mM aqueous H_2SO_4). The substrate potential was set at a value corresponding to the peak current of initial voltammetric scans on HOPG. Data taken from ref. 1.

1 P. M. Kirkman, A. G. Güell, A. S. Cuharuc and P. R. Unwin, *J. Am. Chem. Soc.*, 2014, **136**(1), 36–39.

Richard McCreery asked: Kariuki and McDermott reported images of 'mushrooms' formed by nucleation of diazonium-derived radicals attaching to edge plane sites on HOPG. Doesn't this indicate faster reactivity at edge sites?

Patrick Unwin answered: The CV responses (above and in ref. 1) at 2 grades of HOPG with a difference in step edge density of >2 orders of magnitude suggest that step edges are not important in controlling the functionalization of HOPG surfaces by diazonium-derived radicals and oligomers. Additionally, in the same study, the detailed AFM analysis we carried out on portions of the HOPG surface modified locally by SECCM showed fairly uniform deposits, with no detectable difference between the pristine basal surface and regions intersected by step edges. We did not see 'mushroom' features on the surface.

1 P. M. Kirkman, A. G. Güell, A. S. Cuharuc and P. R. Unwin, *J. Am. Chem. Soc.*, 2014, **136**(1), 36–39.

Richard McCreery commented: A general comment based on organic chemistry regarding the radical attack of HOPG: in order to attach to the basal plane the system would lose aromaticity in three rings, to form a sp^3 center. To attack an edge site and add to a double bond would affect aromaticity in only one ring. So basal attack would seem to be energetically more difficult.

Keith Stevenson responded: We agree that from a thermodynamic standpoint the energy required to break an sp^2 bond to form a sp^3 center at the basal plane of

HOPG should be higher than reacting at an edge site. We have performed preliminary theoretical investigations that support this model. However, since we do not find these single site modifications located close to single or double carbon vacancies as imaged by STM, this suggests that the reaction mechanism is kinetically controlled (*i.e.* the rate limiting step is not carbon–carbon bond breaking but rather a concerted reaction involving possibly the LUMO of graphene and the radical of the iodonium salt. Since we are performing electrochemical reactions we are far from thermodynamic equilibrium, so a thermodynamic argument does not seem to hold when trying to understand the reactivity at basal planes *vs.* defects and step edges. In the presented studies we find that the reactivity is rather controlled by kinetics as suggested by data presented in the paper (see Fig. 11f).

Richard McCreery remarked: Breton *et al.*[1] reported that diphenylpicrylhydrazil (DPPH), which is a radical scavenger, limited many diazonium modifications to real monolayers, by trapping additional phenyl radicals in solution formed after the initial monolayer. We haven't tried it, but others have said it works well.

1 Breton *et al.*, *Chem. Mater.*, 2013, **25**, 2905.

Keith Stevenson answered: This is an excellent suggestion. We are currently conducting more experiments to see if this changes the surface coverage.

Julie Macpherson asked: How do you control the reaction conditions in the functionalization of graphene so that you do not disturb the hexagonal symmetry?

Keith Stevenson replied: Wherever the covalent attachment occurs, it does break the hexagonal symmetry (A-B symmetry) which is accompanied by strong alteration of the grephene's local electronic properties. This is evidenced by the pronounced scattering observed in the STM images around the modifications (Fig. 10b of the paper).

Philip A. Ash opened the discussion of the paper by Daren Caruana:† Recently there have been several demonstrations of photodriven catalysis using immobilised light harvesting moieties. For example, light-triggered H_2 production by hydrogenases bound to CdTe quantum dots[1] or CdS nanorods,[2] or graphene quantum dots as photosensitizers for solar cell applications.[3] With regards to your graphene nanoflakes, is it possible that a systematic study of the effect of edge termination on the rate of electron transfer could provide insight into desirable linker characteristics for covalent attachment of quantum dots to electron acceptors such as semiconducting surfaces or electrocatalysts? Could you use the nanoflakes to inject electrons photochemically into directly attached redox-active species?

1 Greene *et al.*, *J. Am. Chem. Soc.* 2012, **134**, 11108–11111.
2 Wilker *et al.*, *J. Am. Chem. Soc.* 2014, **136**, 4316–4324.

† Daren Caruana's paper was presented by Katherine Holt, University College London, London, UK.

3 Roy-Mayhew *et al.*, *Chem. Rev.* 2014, **114**, 6323–6348.

Katherine Holt responded: This is a very exciting idea for an application! As the edge groups of our GNF are so well-defined, it make systematic study and controlled modification a real possibility. Also we should be able to control the numbers and distribution of the attached species on the flakes. However, the photochemical stability of the GNF needs to be studied to ensure they could be used in photo-driven catalysis.

Matteo Duca asked: Have you tried adding crown ethers to the electrolyte to sequester K^+ ions, thus highlighting their role in ion-pair formation with ferricyanide?

Katherine Holt answered: This is a good idea and definitely something to explore. I am not aware of any previous studies using ferricyanide where this has been attempted.

Matteo Duca said: Concerning the oxidation of hydroquinone at c-GNF (subsection 3.6 of your paper), experiments in unbuffered media should confirm or rule out the occurrence of a concerted proton-coupled electron transfer (CPET). If CPET is operative, the oxidation wave is expected to shift to a higher potential with respect to a buffered media having the same pH, while its peak potential should be independent of the pH for pH < pK_a of the phenolic OH. Additionally, the use of D_2O instead of H_2O can highlight a kinetic isotope effect, thus corroborating the CPET mechanism. Similar experiments played a pivotal role in the mechanistic study of CPET during the oxidation of phenol at a glassy carbon electrode in aqueous media.[1]

1 C. Costentin *et al.*, *PNAS*, 2009, **106**, 18143–18148.

Katherine Holt replied: We have some additional experimental data that can be used to answer this question. Experiments were carried out in unbuffered media in the pH range 5.5 to 8.2. The oxidation peak potentials are plotted in Fig. 4b together with data from experiments in buffered media. The data show that in unbuffered media the E_p is shifted to higher potentials compared to buffered solutions and, crucially, the E_p values are independent of pH over this pH range. The behaviour of hydroquinone in D_2O was also studied. Fig. 4a shows the oxidation wave at clean BDD and c-GNF modified BDD in H_2O and D_2O. The pD of the D_2O solution, based on the smaller dissociation constant of D_2O, is estimated to be 0.4 units higher than the pH of a corresponding H_2O solution and therefore about 6.6. When D_2O is used as the solvent, the main oxidation peak potential shifts to higher values compared to H_2O of similar pH.

A second set of peaks at more negative potentials appear in unbuffered solutions after the initial oxidation wave. Fig. 5a gives a comparison of the CVs at clean BDD and c-GNF modified BDD at pH 8.21. The ratio of peak I to peak II is plotted in Fig. 5b as a function of pH. The peak separation of *ca.* 60 mV is indicative of reversible kinetics, and the peak potentials are independent of pH over the pH range examined. The fact that the peak height of this reversible redox wave decreases with decreasing pH suggests it is due to a stepwise PET as
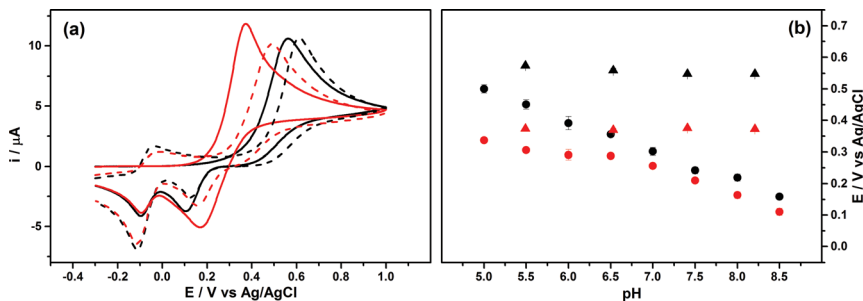
Fig. 4 (a) CV of 0.5 mM hydroquinone at clean BDD electrode (black line) and c-GNF modified electrode (red line) in H_2O (solid line) and D_2O (dashed line). Supporting electrolyte: 0.1 M KCl. The pH of the H_2O electrolyte solution was adjusted to 6.5 with KOH. Scan rate: 50 mV s^{-1}. First scans shown. (b) Peak potential of hydroquinone oxidation as a function of pH at a clean BDD electrode (black) and c-GNF modified electrode (red). Circles represent buffered media and triangles unbuffered media.
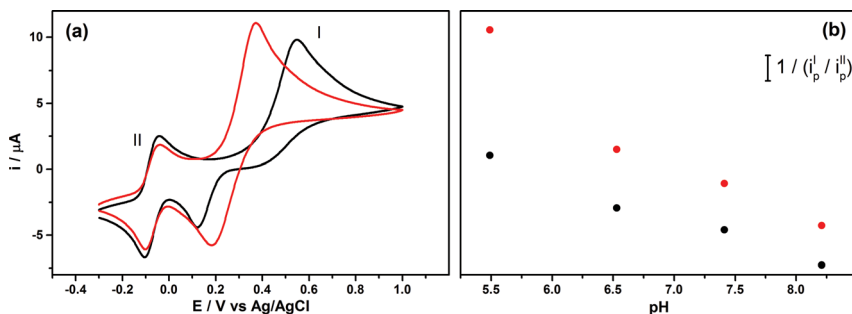

Fig. 5 (a) CV of 0.5 mM hydroquinone at clean BDD electrode (black line) and c-GNF modified electrode (red line) in unbuffered H_2O. The pH of the H_2O electrolyte solution was adjusted to 8.21 with KOH. Supporting electrolyte: 0.1 M KCl. Scan rate: 50 mV s^{-1}. Second scans shown. (b) Ratio of peak heights of hydroquinone oxidation as a function of pH at clean BDD electrode (black) and c-GNF modified electrode (red).

described by Costentin et al.[1] The reversible kinetics support the assignment of this mechanism. Upon modification of the electrode with c-GNF, there is no shift in E_p, but the peak height is smaller. These observations are in agreement with the conclusions made in Section 3.6 of our paper regarding the role played by COOH groups in the reaction mechanism. When c-GNF are present on the electrode surface they can act as a proton source and sink, allowing the reaction to proceed to a greater extent *via* the concerted pathway. The results presented here are in agreement with those reported by Costentin et al.[1] in the above-mentioned paper and strongly suggest that the oxidation of hydroquinone at both BDD and c-GNF modified BDD follows the CPET mechanism in buffered media. In unbuffered media, two competing pathways are operative: CPET, which dominates in acidic solutions, and PET in basic conditions.

1 C. Costentin et al., *J. Am. Chem. Soc.*, 2008, **130**, 15817–15819.

Keith Stevenson asked: The pH titration slide that you showed is very intriguing as the extrapolated pK_a for carboxylic functionalities is more basic than in solution. Is this similar to that seen for SAMs? What fraction of functionalised sheets contain these surface functionalities? How do you know that you don't have mixtures of sheets with varying functionalities and surface coverages?

Katherine Holt answered: We have been quite cautious about extrapolating a pK_a value from this titration curve, as while we can identify an equivalence point the curve is not the form we would expect for one single solution species. However, it does seem that being bound to the nanoflakes does influence the pK_a in a manner that might be observed for other surface bound acid groups, for example in a SAM. Although we are reasonably sure that carboxylic acid groups are the only acidic oxygen functionality present on the flakes, it is difficult to know their distribution. For example, we could have a population of flakes with most of the edge functionalised and another population that is less functionalised. So far we have assumed an average edge coverage for all of the flakes, but identifying different fractions in the sample would be useful. We think most flakes must be terminated as they are dispersible in water. Size may also be a factor – the flakes are a range of diameters, so of course the smaller flakes may experience more interactions between neigbouring groups than larger flakes.

Patrick Unwin enquired: In your paper you mentioned that you were carrying out studies to determine the film morphology and architecture, which will clearly be important in understanding the electrode responses. Have you made any progress with this?

Katherine Holt replied: This work is still ongoing as it is very difficult to characterise these small, optically transparent flakes and the BDD electrodes are likely too rough to allow AFM imaging of the flake distribution on the surface. TEM imaging of drop-cast films (on a TEM grid) shows some evidence of stacking parallel to the surface and we could assume that the flakes align in a similar manner on the electrode surface. In order to control the film morphology better we are exploring two approaches: (i) adding divalent cations to the GNF suspension to bring about their complexation and precipitation; the structures formed can then be characterised *ex situ* before being drop-coated onto the electrode; (ii) modifying a working electrode (*e.g.* SAM on gold) and then assembling the flakes on this layer in defined orientation to explore electron transfer across the flake from edge to edge.

George Zheng Chen remarked: In Fig. 3 of your paper, why is there almost no change in the double layer charging current?

Katherine Holt responded: It is true there is only a small increase in double layer charging for the modified electrode (*e.g.* over the potential range 0–0.4 V). We haven't investigated this aspect of the response in great detail, but perhaps this suggests only a very thin and relatively non-porous layer of GNF on the surface and hence no significant increase in surface area.

John Foord asked: How porous are the graphene films? Are you sampling only the outer layers or the entire film in the electrochemical experiments?

Katherine Holt answered: It is difficult to characterise the films on the electrode as they are so thin and optically transparent, but we suspect they are a few layers thick. If you add more graphene to the electrode surface it simply falls off as it is so hydrophilic and hence dispersible in solution. TEM imaging of flakes drop-coated onto the TEM prism show some evidence of stacking, so we are probably studying electron transfer through multiple layers (and therefore contact with the redox probe may only be at the outer layer) but there will be some porosity allowing some ingress of the redox probe to the inner layers. We need to have more control and understanding of how the GNF order onto the electrode to have better understanding of their behaviour.

Julie Macpherson remarked: In your diamond nanoparticle study[1] you report evidence of FcMeOH adsorption on the 'sp^2' or defected surface of the nano-diamond and you refer to work by Abrūna (reference 3 in your paper) who also reports FcMeOH adsorption on graphene surfaces. You don't see any evidence for FcMeOH adsorption on your graphene nanoflakes. Do you think we should be concerned about the possibility of FcMeOH adsorption on sp^2 surfaces? By tradition FcMeOH is considered outer sphere and therefore non-interacting with the surface.

1 T. S. Varley, M. Hirani, G. Harrison and K. B. Holt, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00041B.

Katherine Holt replied: In the diamond nanoparticle study[1] we see evidence from cyclic voltammetry and IR spectroscopy that FcMeOH and FcMeOH$^+$ adsorb onto the diamond surface. However the adsorption is quite weak, as removing the modified electrode from the solution and rinsing it seems to remove the adsorbed species. We also see no evidence of the FcMeOH species on the rinsed diamond powders in subsequent XPS analysis. In the case of the diamond surfaces it also seems that adsorption of FcMeOH$^+$ is stronger than adsorption of neutral FcMeOH, which seems to indicate an electrostatic interaction with the negatively charged, oxidised diamond, as well as some pi-pi interactions. In Abruña's work[2] he reports electrochemical evidence for adsorption of FcMeOH to a graphene surface. Much is weakly adsorbed and is removed with repeated cycling. However, about 1% of a monolayer appears to be very stable. He suggests this adsorption occurs "predominantly at local defect sites". He also states "This value is comparable to what we observe on bulk graphite surfaces (~2% monolayer coverage)". Additionally he cites a reference for adsorption of ferrocene on multiwalled carbon nanotubes[3] which makes interesting reading. In the latter publication they see ferrocene adsorption onto the walls of nanotubes in different orientations (though it should be noted that surfactant may be present and play a role). They suggest that certain orientations are preferred and adsorption is increased when oxygen functionalities are present on the nanotubes, and that interaction is perhaps preferably with the Fc$^+$ species in this case. So to answer your question, a variety of sources seem to suggest that FcMeOH (and Fc) can interact with sp^2 surfaces either *via* pi-pi interactions (weak) with the pristine

surface, or perhaps more importantly *via* some electrostatic interaction with oxygen groups or defect sites (stronger). However we do not see any obvious signs of adsorption in the case of our graphene nanoflakes. However your question raises an interesting point about the outer sphere nature of these probes. I think electron transfer can still be called as outer sphere because interaction with the surface is not necessary for fast electron transfer, but that is not to say that some interaction cannot take place.

1 T. S. Varley, M. Hirani, G. Harrison and K. B. Holt, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00041B.
2 W. Li *et al.*, *ACS Nano*, 2011, **3**, 2264.
3 D. Zheng *et al.*, *Thin Solid Films*, 2008, **516**, 2151.

Surbhi Sharma said: You prepare carboxylated graphene sheets by unzipping CNTs. How do you confirm or establish that the carboxylation process does not leave any other oxygen related defects (particularly –OH groups that are almost unavoidable) on the basal and edge planes? Do you perform any XPS analysis?

Katherine Holt responded: We have used two different types of c-GNF in our studies. One sample was identical to that reported in ref. 1, where the carbon 1s XPS peak could be fit with constituent peaks at 284.7 eV, 286.7 eV and 288.4 eV. The peak positions are consistent with C–C sp^2 bonding, C–O bonding (alcohol, epoxide, ketone *etc.*) and C(O)O bonding (carboxylic acid, anhydride, lactone) respectively. The second sample was used for all studies in this paper and the C 1s data could be fit very satisfactorily with 2 peaks – at 284.7 eV and 288.4 eV. In other words the C–O content was very small, if present at all. Although only data for the second sample is reported here, we see broadly similar behaviour for the first sample in the pH dependence of the responses for the different redox probes. The responses are however more enhanced for the flakes used in this study, we believe because the concentration of carboxylic acid groups is higher.

1 C. G. Salzmann, V. Nicolosi and M. L. H. Green, *J. Mater. Chem.*, 2010, **20**, 314.

Fulian Qiu asked: In Fig. 5 and 6 of the paper, the ferri/ferrocyanide redox reaction showed slower responses on the –COOH modified graphene. If the –COOH group on the modified graphene is reduced electrochemically, and the electrode becomes a graphene electrode, what do you expect from the ferri/ferrocyanide redox reaction?

Katherine Holt answered: When the –COOH GNF is modified to give an amide termination we find that the electrochemical response to ferri/ferrocyanide becomes reversible. This suggests that it is the acidic group which is causing the slower response. I would imagine if the –COOH groups were also reduced electrochemically (*e.g.* to –OH or even –H termination) the response towards the redox probe would also be reversible as the acid groups have been removed.

Philip A. Ash remarked: You have studied the effect of ionic strength and pH on the ferri/ferrocyanide redox reaction at graphene nanoflake electrodes. Have you also tried adding a small positively charged redox mediator such as methyl viologen? High concentrations of KCl are known to solubilise Prussian blue, and

oligomeric hexacyanoferrate moieties have been proposed as possible 'blocking' species at electrode surfaces. Such species will lead to a build-up of negative charge at the nanoflake edges that could lead to a greater electrostatic repulsion than the COOHCOO⁻ termination alone. Is it possible that a positively charged mediator would restore reversibility of the ferri/ferrocyanide redox reaction if this were the case?

Katherine Holt replied: This is something we have not tried but would be a simple experiment to test the inhibiting mechanism.

Philip A. Ash continued: Could you use infrared or Raman spectroscopy to identify the 'blocking' species responsible for the irreversibility of the ferri/ferrocyanide redox couple with the COOH-terminated nanoflakes? Spectroscopic techniques should give insight into protonation/deprotonation equilibria and reactions occurring at the nanoflake edges as a function of potential, pH *etc.* Do you think that direct spectroelectrochemical measurements of the electrode-immobilised nanoflakes would be helpful in this respect, as you should observe oxidation and reduction of an adsorbed species even in the case where it 'blocks' the solution response?

Katherine Holt responded: We are currently exploring using *in situ* IR spectroelectrochemistry to investigate the stability of ferri/ferrocyanide in the presence of the c-GNF. We have also looked at the protonation state of the flakes in solutions of different pH and these results are being prepared for publication. Direct spectroelectrochemistry would be useful because we can observe changes to the GNF termination, as well as changes to the redox species itself. We'd like to use Raman spectroscopy as well, however for some reason our flakes fluoresce so we have been unable to get good low enough backgrounds to see the Raman response.

Philip A. Ash said: If cyanide ligand loss occurs due to dynamic protonation equilibria at the COOH-terminated nanoflake edges below pH 8, you would expect to see evolution of HCN in a time-resolved infrared measurement, and subsequent appearance of peaks due to the 'blocking' species. Such a measurement would be complicated, however, by peaks due to mixed-valence species containing bridging cyanide (such as Prussian blue, Berlin green *etc.*) that all have peaks in the 2040–2100 cm^{-1} region, *i.e.* between those observed for ferri- and ferrocyanide. It is also unclear whether the extent of adsorption would be limited to monolayer formation or whether the edge of the nanoflakes could nucleate growth of a thicker hexacyanoferrate film.

Katherine Holt answered: Yes, our preliminary IR data has suggested formation of species which absorb strongly in this region when the c-GNF are present. It is very difficult to assign the bands to specific species as many reports in the literature are not too precise about their assignments! However it is clear that precursor molecules to film formation are formed over time in the presence of the c-GNF. We are presently studying the time dependence of this repsonse under different conditions, including in the presence of D_2O rather than water.

Julie Macpherson commented: In section 3.5, in regard to the bare BDD surface, the authors comment "The ferri/ferrocyanide electron transfer process has been shown to be inhibited at oxygen terminated surfaces, however we observe effectively reversible electron transfer kinetics at the (oxidised) BDD electrodes used in this study". We also see reversible electron transfer kinetics at our oxidised BDD electrodes (but for the reverse process *i.e.* ferro/ferricyanide) in 0.1 M KNO_3. The surface is alumina polished prior to use and we used XPS to characterise the surface functional groups on the oxygenated surface; the surface was found to contain C–O–C, C–OH and C=O groups. The electrode was poly-crystalline, doped above the metallic threshold and thick enough to be removed from the wafer so it was freestanding. It also was shown to contain negligible sp^2 carbon. It was only when we anodically pretreated the electrode in 0.1 M H_2SO_4 using applied potentials *e.g.* 3 V for 60 s, that the electron transfer kinetics for this couple slowed considerably. XPS now showed the surface to contain groups such as COOH on the surface. Hence we thought that in some way these groups were responsible for the change in electron transfer kinetics. The authors note in their paper that the response of ferricyanide is very inhibited by the presence of carboxylic acid terminated GNF at pH < 8. We describe our work in ref. 1.

1 Hutton *et al.*, *Anal. Chem.*, 2013, **85**, 7230–7240.

Katherine Holt responded: Very interesting that the same functionalities as diamond have been shown to inhibit the ferri/ferrocyanide redox couple! We find in general that all of our BDD electrodes, if carefully polished and cleaned by electrochemical cycling, show reversible responses towards this redox couple. Its clear that we are using good quality BDD (little sp^2 content) that is not over-oxidised.

Julie Macpherson opened the discussion of the paper by Stephen Hodge: If you were able to use metallic nanotubes of a defined chirality where all metal catalyst had been removed, do you think this material would show greater reductive capabilities than the KC_8 and KC_{24} materials you worked with, given the different band structures and DOS?

Stephen Hodge answered: At high charging stoichiometries, the differences between metallic and semi-conducting SWCNTs tend to disappear, as the Fermi level will shift beyond the band gap. At low doping levels (below 1 charge to 100 C atoms) there will be obvious differences in the electron affinity of metallic *vs.* semi-conducting species. The total amount of charge that might be successfully transferred to SWCNTs before the appearance of excess alkali metal in equilibrium, is unknown; the threshold may be slightly higher for SWCNTs than graphite (based on some of our own preliminary data). However, investigating the maximum levels of doping for SWCNTs is more challenging than graphite, due to the heterogeneity of the samples; ARPES which generates excellent data for doped graphites is not readily accessible for SWCNTs.

For the same M : C charging ratios, the tendency for charge dissociation is likely to differ between SWCNTs and graphene salts due partly to the density of states, but probably more significantly due to changes in geometry and solvation energies/entropies. The capacitance of SWCNTs is also likely to be different from

graphene, creating a different Coulombic shift. The dependence of effective dielectric constant or polarisability on nanotube type, as a function of doping level, also remains to be determined. Overall, since SWCNTs can probably be charged to a higher M:C ratio than graphite, one would assume that they have a lower reducing power at an equivalent M:C ratio.

Julie Macpherson continued: Do you think you will be able to reduce Al^{3+} using your graphene intercalated materials? If not, would it be possible using the nanotube system proposed in the previous question?

Stephen Hodge replied: The reactivity with manganese chloride was only slight (~3% yield). Since the standard reduction potential for Al^{3+} is a further 0.5 V, it is unlikely that Al^{3+} could be reduced with KC_8. Perhaps lithium intercalated graphite *e.g.* LiC_6, or more highly charged carbon nanotubides could provide the necessary higher reduction potentials for Al deposition.

Robert Dryfe enquired: Can you say something about the product that you form? Is monolayer graphene produced?

Stephen Hodge responded: We did not do any microscopy studies in this paper, but there are published papers showing the formation of monolayer graphene sheets following charging methods such as the route deployed here.[1] Simple discharging causes restacking, unless preventative measures are taken. The degree of exfoliation may be a factor in limiting the reduction potential of the graphenide.

1 Milner *et al.*, *J. Am Chem. Soc.*, 2012, **134**, 8302–8305.

Robert Dryfe continued: Your method is based on the exfoliation and stabilisation of graphene through charging of the graphene sheets. However, the data presented suggests that there is significant re-aggregation of the graphene: is it possible to use the metal deposition to prevent re-aggregation?

Stephen Hodge answered: The reduction of the metal salts to metal nanoparticles discharges the nanocarbons causing re-aggregation and a high level of restacking. Graphenide reactions that deposit less mobile, more localised species can help to prevent restacking or even enhance solubility.[1] It may be possible to produce a similar effect with metal or metal-containing species. Alternatively, to produce monolayer graphene decorated with metal nanoparticles, it may be simpler to deposit or assemble the monolayer graphene first and then submerse the film in a solution containing the metal salts.

1 Morishita *et al.*, *J. Mater. Chem. A*, 2014, **2**, 15022–15028.

Keith Stevenson remarked: What is the degree of reduction of the potassium? Is it metallic?

Stephen Hodge replied: In the paper we discussed the model proposed by Ebert[1] for the GIC KC_8, which proposes the presence of a mixture of metallic K^0

and K$^+$ ions between the graphite layers, relating to incomplete charge transfer to the graphite. For our solubilised graphenide species, and based on our experimental results, the potassium is likely to have transferred all of its charge to the carbon giving purely K$^+$ species. The central hypothesis of our paper is that the redox potential of the transferred electron depends on the level of doping, in a continuous fashion depending on the density of states and Coulombic effects. At the most charged level, the redox potential approaches that of metallic potassium.

1 L. B. Ebert, *Carbon*, 1985, **23**, 585–587.

Keith Stevenson continued: Have you measured the open circuit potential in solution? Can it be used to understand if you have a more reduced form of carbon?

Stephen Hodge responded: In fact, the original basis of this paper was to study the redox reactions on carbon nanotubide solutions using open circuit potential (OCP) measurements. In principle, this method would have allowed us to study the kinetics of the reactions and the OCP should have plateaued at the reduction potential of the metal salt. Unfortunately, there appeared to be a slow but significant self-discharge process occurring independently of any metal salt addition, and we could not obtain reliable results. The delay between experiment setup and stable OCP measurement was enough to have significantly lowered the carbon reduction potential. Therefore, we went down the route of performing the reactions as shown in this paper, but it is an experiment we should return to at a later date.

John Foord said: Can you vary the size of the metal nanoparticles by changing reaction conditions, and how adherent are the particles to the supports?

Stephen Hodge answered: In the case of ZnCl$_2$ reactions, we demonstrated that with increased metal salt to charge ratio the nanoparticle size was increased from 10s of nanometres to ~100 nm. There is most likely a balance between thermodynamics (nucleation) *vs.* kinetics (growth), depending on the redox potential of the metal, the degree of carbon charging, and the salt concentration. Further experiments might explore these effects more explicitly to generate smaller metal nanoparticles which might, for example, be more catalytically active.

Andrew Rodgers asked: Are the negatively charged carbon nanomaterials soluble in aqueous solutions?

Stephen Hodge replied: Unfortunately not, as the charge required to dissolve nanotubes/graphene is beyond the water and oxygen reduction potentials. All experiments must be performed in a glove box; subsequent exposure of these charged nanocarbons to the atmosphere results in their rapid discharge and possible covalent functionalisation *via* protonation and hydroxylation (see ref. 1).

1 Hof *et al.*, *J. Am. Chem. Soc.* 2013, **135**, 18385.

John Foord enquired: You mention in your paper that one of the motivations is to develop more practical processing conditions for carbon nanomaterials. But the work you describe seems to focus on rather air-sensitive chemistry. Is this practical?

Stephen Hodge responded: We use reductive charging methods as a route to non-destructive processing, avoiding the concentrated acid treatments, ultra-sonication and ultracentrifugation typically employed. We have a number of publications in this area and typically use the increased reactivity for a variety of practical processing steps, including producing solutions, purification, or covalent modification reactions.[1,2] The focus of this Faraday paper was to use mildly dispersed materials to explore some fundamental issues, rather than to develop the process chemistry further. Although air-sensitive chemistry is required, these methods are actually highly scalable, and can be applied to bulk volumes (unlike, for example, ultracentrifugation). As an example, the nanotubide chemistry has recently been commercialised.[3] In fact, air sensitive chemistry can become easier as volumes increase since adventitious moisture becomes less significant.

1 Fogden *et al.*, *ACS Nano*, 2012, **6**, 54.
2 Hodge *et al.*, *ACS Nano*, 2013, 7, 1769.
3 http://www.linde-gas.com/en/products_and_supply/electronic_gases_and_chemicals/carbon_nanotubes/index.html.

John Foord continued: It appears from the work that XPS gave you rather unreliable results. I was wondering why this was – it normally works quite well for nanocomposite materials provided they are homogeneously prepared?

Stephen Hodge answered: The resulting hybrid metal nanoparticle–nanocarbon materials are not particularly homogeneous, and metal nanoparticle sizes differ (10–100 nm) with varying metal salt stoichiometry. Since even the smallest metal nanoparticle sizes are around the critical range of the XPS depth sensitivity, significant changes in apparent composition can be anticipated due to sampling artefacts.

Katherine Holt opened the discussion of the paper by Fernanda Juarez: In your paper you describe that modelling shows the most thermodynamically stable arrangement for oxidised zig-zag edges of graphene are carboxylic acid groups. For armchair edges lactone rings are preferred. In the paper we presented earlier[1] we found that our graphene nanoflakes are almost exclusively carboxylic acid terminated. Does your data therefore suggest that our flakes must have zig-zag edges rather than armchairs?

1 M. M. Lounasvuori *et al.*, *Faraday Discuss.*, 2014, DOI: 10.1039/c4fd00034j.

Fernanda Juarez replied: It is rather difficult to say how a real (experimental) system looks like just using computational simulation results, but it is not impossible. In a previous work,[1] we studied in detail the thermodynamic stability of more than 80 possible endings for zigzag and armchair steps. We obtained 8 zigzag and 5 armchair structures that are thermodynamically stable in different H_2/O_2 environments, and 4 of these endings (2 zigzag and 2 armchair) have

carboxylic groups. Therefore, it is possible to have armchair steps with carboxylic groups. Nevertheless, more information is necessary to decide whether the endings are zigzag or armchair carboxylic groups. One way to do it is by calculating infrared frequencies of the stable systems, which are very sensitive to changes in the surrounding structure.

1 Soldano *et al.*, *Carbon*, 2014, **78**, 181.

Katherine Holt continued: How do the carboxylic acid groups stack around the edges?

Fernanda Juarez responded: In Fig. 5 of our manuscript there is a picture showing the distribution of the carboxylic groups on the zigzag edges. To describe this better we can say that the carboxylic groups are perpendicular to the graphene surface, face-to-face, but with the –OH groups on opposites sides. One important observation is that there are no hydrogen bonds in this arrangement.

Julie Macpherson asked: In the introduction to your paper you state "... if the applied potential is high enough, a complete oxidation of the defects takes place and spontaneous reduction of the metal cannot occur". Please can you clarify this statement, in particular what do you mean by complete oxidation and why is spontaneous reduction not possible?

Fernanda Juarez answered: Typical pre-treatment of the HOPG to avoid spontaneous deposition is anodic polarization. Several authors claim that this process completely eliminates all the reducing functionalities (ref. 3, 15 and 16 in our manuscript). However, both the nature of such species and the mechanism of this pre-oxidation treatment in order to avoid spontaneous deposition are unclear. It was suggested by Penner (ref. 3 in our manuscript) that the incompletely oxidized functionalities act as electron donors during the spontaneous reduction of the metals.

Julie Macpherson continued: For the work on the adsorption of Pt on oxidised steps, you say that the energy obtained on the oxidised step is smaller than on the bare or hydrogenated steps. However I thought that Penner always advocated that in order to obtain preferential electrodeposition along step edges and not the basal plane on HOPG, it was necessary to apply potential pulses in order to selectively oxidise the step. This seems to contradict your findings?

Fernanda Juarez replied: This contradiction is actually apparent and there are two aspects to be considered. First, as we have already explained in the previous question, the nature of the functionalities is unknown. We can only claim that the oxidized systems, which we have investigated, are less favorable for the deposition than bare steps. It is also expected that the process on the former should not be spontaneous and additional energy is required so the reaction can occur. Second, the procedure followed by Penner involves the application of an external potential pulse in order to form the nucleus (non-spontaneous deposition), not contradicting our findings.

Richard McCreery enquired: Your computer model considers mainly thermodynamic stability of metals on various graphene sites. Does it take into account the effect of hydration of the metal ions from which the metals are deposited?

Fernanda Juarez responded: Our model does not consider the hydration in any explicit or implicit manner. In DFT there are some models to add solvent implicitly, like using the polarizable continuum method (PCM). Unfortunately, the PCM can only be used in systems without periodic boundary conditions, like we did. Besides the fact that we did not use solvent, we believe that its role can be important in the kinetics of the reaction. However, in our manuscript we were focussed on disentangling the nature of the interactions between the carbon edges and the metal wires. A second stage of this work should be adding the solvent.

Manuel Alvarez-Guerra said: I was wondering about the computational time required for dealing with such complex structures in your *ab initio* approach. What size of sample or number of molecules can you include to obtain results in reasonable time?

Fernanda Juarez replied: In the calculation of those systems by DFT, there are a lot of steps that are not published but that require a considerable effort. These steps usually involve running several tests in order to find both the optimal computational conditions (functionals, pseudopotentials, basis sets) and the best software (in some complicated cases). However, if we do not consider that stage, then it usually takes a week to optimize the structure of a system with 40 atoms (where 20 of them are free to move), using at least 32 processors. Properties calculations can take one day per system, but the post-processing of the information takes much more time.

Deborah Lomax asked: The study aims to pair experimental with computational methods to investigate metal deposition at step edges on HOPG. With HOPG, the deposition environment involves step edges – several layers in height – on a terrace, whilst the modelling considers only the edge of a single graphene layer. Is it valid to compare results from these different approaches given the different substrate geometries, and how can the modelling be improved to reflect this?

Fernanda Juarez answered: As we already said in our manuscript: "In this contribution, we have set the starting points at the two extremes of a bridge between experiments and theory to understand the metal decoration of step-edges on HOPG". We truly believe that the real system is much more complex than our extremely simple simulation, and we know the limits of the simplifications we made. However, the study of real systems must be done in several steps, disentangling the nature of different interactions at each stage. We also think that this is a helpful first step in the right direction. A more realistic description that includes several layers of graphene, should describe correctly both metal/graphene and graphene/graphene interactions. This is not so easy from a computational point of view. The problem is that the interactions between

the graphene layers are only well described by the functionals (and pseudopo-tentials) including Van-der-Waals corrections. It has not been systematically tested yet, how accurate these functionals reproduce the metal/graphene and metal/metal interactions.

Deborah Lomax continued: Has the influence of relativistic effects on the metal-step edge interactions been investigated?

Fernanda Juarez responded: As is usual, we have included the relativistic effects in the pseudopotentials, for all our calculations. There is a very interesting review[1] showing that relativistic effects are well represented in the valence electrons by the pseudopotential approximation and are successfully transferred to molecules or to the solid state. In particular, and as far as we know, there are no studies about this effect in the metal/graphene step interaction. However, in a recent publication,[2] it has been shown that the relativistic effects can strengthen the Au–C bond and they must be included in order to observe the adsorption of CO in metal clusters. A similar effect has been observed for platinum.[3]

1 P. Schwerdtfeger, *ChemPhysChem*, 2011, **12**, 3143.
2 Kuang *et al.*, *Physica E*, 2012, **44**, 2132.
3 Heinemann *et al.*, *J. Chem. Phys.*, 1996, **104**, 4642.

John Foord remarked: The calculations you describe are based on thermo-dynamic predictions. But many growth processes are driven by kinetic effects. How computationally expensive would it be to introduce kinetic barriers into the theory?

Fernanda Juarez replied: This is an interesting question because there is more than one possible answer. In studying chemical reactions, it has been a major problem to develop an accurate theory to calculate reaction rates. One simply way to do this is by obtaining the kinetic barriers of the most relevant reactions, through the nudge elastic band (NEB) method. However, the main difficulty it is to find the 'relevant' reactions, and there is always the chance to 'forget' the reaction with the lowest barrier. In any case, and just talking about the compu-tational cost, this procedure can be applied to any of the studied systems in reasonable time.

On the other hand, there are some important points that are not going to be represented using the NEB method: the charge transfer and the role of the solvent. In theory, solvent molecules can be added explicitly during NEB calcu-lations, but it is not feasible to obtain results in a rational time. In our group, Schmickler and Santos have developed a theory that allows kinetic barriers to be obtained, considering the solvent effect and electron transfer.[1] Nevertheless, using this theory requires extended work to obtain the 'relevant' reactions. In this sense, our manuscript is setting up the foundations to find those reactions. Another way to obtain reaction rates is through molecular dynamics. Here again, a previous work has to be done to obtain a wide range of chemical potentials to represent the interactions between the graphene (edges and terraces) and the metal atoms. This is the step that is always done with the very accurate tool of DFT calculations. I want to remark that the objective of this work is to understand the

chemical nature of the metal–carbon bond in the graphene edges, and it is only a preliminary step to unravel the chemistry of the very complicated experimental system.

1 Santos *et al.*, *Phys. Rev. B*, 2009, **79**, 235436.

John Foord continued: I was interested to see that the silver particles deposited are (100) terminated cubes rather than (111). Is this a manifestation of the role of the solution in interacting with the surfaces involved?

Fernanda Juarez communicated in reply: During the meeting, I did not have an answer for that question, and we have not realized the importance of that result. Now, we have found in another publication[1] that silver nanocubes with (100) facets are difficult to prepare in solution, and a capping agent must be used. In that case, it was found that the coordination of the silver nanoparticles was made through the O and N atoms of the pyrollidone group. Our hypothesis is that in our experimental system, the sulphate/bisulphate anions could stabilize the (100) facets over the (111), which are usually more stable. However, a deeper experimental and theoretical study is required.

1 Sun *et al.*, *Science*, 2002, **298**, 2176.

Julie Macpherson opened the discussion of the paper by Thomas Varley: In the experimental section you say that all nanodiamond surfaces were treated in a furnace to remove any graphitic sp^2 carbon from the surface and to maximise the number of oxygen terminating groups. However, your explanation for what is going on assumes redox groups on the surfaces associated with sp^2 carbon. Can you describe for me what the surfaces of the two different nanodiamonds (detonation and HPHT) look like after the experimental treatment process?

Thomas Varley replied: The two different types of nanodiamond have very similar surface functionality (as shown by FTIR), which is due to the pre-treatment method employed. We heated the samples to 425 °C for 4 h as outlined in the referenced paper by Osswald *et al.*[1] This falls within the narrow temperature range that removes amorphous and sp^2 carbon material by oxidation, leaving the sp^3 crystalline core intact. Depending on the experimental conditions, Osswald and co-workers found that the surface functionalities could be controlled. By heating in air, carbonyl, acid and alcohol functionalities were created. Our attempts at using this method agree with the author's findings, although, the exact mechanism of how the oxygen containing groups form is still an on-going debate in the literature. It is likely that the outer shell (a few atomic layers) of the detonation nanodiamond particles is closer in structure to tetrahedral amorphous carbon than diamond and this is why oxygen functionalities that have sp^2 character are formed on the surface.

1 Osswald *et al.*, *J. Am. Chem. Soc.*, 2006, **128**, 11635–11642.

Julie Macpherson continued: How does the surface of the HPHT diamond change after mechanical grinding (this also relates to the previous question)?

What is the source of the HPHT? Is it in microcrystalline form, single crystal, and how pure is the material to start with?

Thomas Varley responded: We obtained the HPHT diamond used in this study from a collaborator and as such do not have information on the surface chemistry of diamond prior to the grinding. However, we have characterised our as-received material *via* FTIR and XPS and no evidence of metallic impurities was present. The heat treatment (oxidation) we employed was carried out in order to standardise our samples, in addition to providing the oxygen containing surface functionalities. As we don't have much information about the origin of the HPHT diamond samples used in this study, we have started instead to use similar diamonds from a different commercial source (Microdiamant), from whom we receive quite detailed technical information about their origin. The characterisation we have carried out so far suggests similar surface chemistry for the samples from different origins.

Julie Macpherson added: How does the density of sp^2 or 'defect' sites vary between detonation diamond and mechanically ground HPHT?

Thomas Varley answered: Detonation nanodiamond has a surface that contains large amounts of tetrahedral amorphous carbon,[1] meaning it is very defective compared to the surfaces formed through mechanical grinding. Therefore, the density of defect sites is much greater for the nanodiamonds fabricated by detonation synthesis as opposed to those made by mechanical grinding.[2]

1 V. N. Mochalin, O. Shenderova, D. Ho and Y. Gogotsi, *Nature Nanotechnology*, 2012, **7**, 11–23.
2 K. B. Holt, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2048–2058.

Robert Hamers asked: Could you explain the catalytic feedback process a bit more? I think most of us are familiar with the catalytic feedback process in an AFM where there are two electrodes and so the product at one electrode can diffuse and become a reactant at the other electrode. In your experiments, with only one electrode, it is less clear how a catalytic enhancement could occur. Could you please explain in more detail?

Thomas Varley replied: In the case presented in this paper, there are two mechanisms for catalytic enhancement: 1) *via* surface states on the nanodiamond, and 2) mediated by adsorbed FcMeOH/FcMeOH$^+$. The first mechanism has been described by us previously for the $[Fe(CN)_6]^{3-/4-}$ redox couple[1] and generally results in current enhancements of up to 2 times the diffusion-limited current compared to the non-modified electrode. The second mechanism seems more specific to FcMeOH and is a consequence of its ability to adsorb on the nanodiamond surface. This mechanism is largely responsible for the much larger enhancements observed for this redox species (*ca.* 10 times the diffusion-limited current). To describe the first mechanism in more detail: at sufficient potentials FcMeOH can undergo oxidation at the surface of the BDD electrode to produce FcMeOH$^+$. In the presence of nanodiamond, FcMeOH$^+$ can be reduced by redox

active surface functionalities on the nanodiamond, resulting in the regeneration of FcMeOH. The regeneration of FcMeOH in the electrode diffusion layer results in an enhanced catalytic current. On the reverse scan, the opposite process is proposed to take place; FcMeOH generated at the electrode is immediately oxidised back to FcMeOH$^+$ after donating an electron to the nanodiamond surface. For this mechanism to be feasible, the oxidation and reduction of nanodiamond surface functionalities must occur at similar potentials to the standard potential of the solution redox probe, *i.e.* FcMeOH. I guess the heart of your question is how this mechanism is sustained? It's different from feedback between two electrodes of course, because we need to explain how the nanodiamond can continuously regenerate the redox species, *i.e.* do the nanodiamond surface states not eventually run out of electrons (or holes) to allow the catalytic process to continue? The answer to this is that under some conditions the catalytic feedback cannot be sustained. It can be sustained as long as there are available surface nanodiamond functionalities within the diffusion layer. This is a function of redox probe concentration (low concentrations allow the mechanism to be sustained), scan rate (too slow and the nanodiamond states get depleted due to the thick diffusion layer; too fast and the large flux of the redox probe causes diffusion-controlled currents to dominate over the catalytic response – there is an optimum intermediate scan rate to observe the effect), surface chemistry of the nanodiamond (*i.e.* density of surface groups), electrode coverage of nanodiamond and potential of the redox probe relative to the available nanodiamond surface states. Under some conditions, for some probes, the enhancement we observe is decreased significantly after the first CV cycle; in other cases it can be maintained with continuous cycling. There are also a few routes to 'recharging' of the nanodiamond surface states, allowing them to continue contributing to the redox cycle. Within tunnelling distance of the electrode, those surface groups with reversible redox chemistry can be directly oxidised and reduced at the electrode;[1] as we cycle the potential during the experiments they are able to exchange electrons with the electrode and become 'recharged'. Further from the electrode, depending on their potential relative to the redox probe, the surface groups can exchange electrons with the redox probe and also become 'recharged'. Finally, due to the complex nature of the nanodiamond surface, electronic communication, *via* conjugation of pi systems, may result in electrons being able to conduct from one side of a nanodiamond particle to the other, again providing electrons to maintain the redox cycle. In addition to this mechanism, is the one mediated by adsorbed FcMeOH, as described in the paper. This results in much larger currents than those we have observed previously, and the currents are more easily sustained over repeated cycling. The positively charged FcMeOH$^+$ interacts very strongly with the negatively charged nanodiamond surface and becomes adsorbed (this strong interaction is illustrated in the IR studies presented in Fig. 7 of the paper). The contribution of the Gibbs energy of adsorption can shift the redox potentials of an adsorbed species relative to the solution species and results in the observation of pre-peaks in the voltammogram. The surface adsorbed FcMeOH$^+$ also participates in the catalytic feedback mechanism (as shown in Fig. 8 of the paper), by undergoing electron exchange with solution FcMeOH, to generate solution FcMeOH$^+$ and adsorbed FcMeOH. The adsorbed FcMeOH can be re-oxidised to adsorbed FcMeOH$^+$ by the underlying BDD electrode or by a redox process with nanodiamond surface groups. FcMeOH has a very fast rate constant

for electron self-exchange (classic Marcus theory) and also rapidly undergoes outer sphere electron transfer with the underlying BDD electrode. It is actually the accumulative influence of the nanodiamond surface and adsorbed $FcMeOH^+$ processes that explains why currents are so significantly enhanced for the $FcMeOH/FcMeOH^+$ redox couple compared to others previously studied.

1 *e.g.* K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.

Matteo Duca remarked: With respect to the observed 'off-set' reduction current and the spontaneous oxidation of FcMeOH at nanodiamond, has the open circuit potential been measured upon immersion of the working electrode in the FeMeOH-containing solution? This is a key parameter for comparable processes, such as 'electroless' deposition.

Thomas Varley responded: This is something we have planned to measure, but as yet have not. I completely agree that it is an important parameter and would provide useful information, especially when measured in different solutions (*i.e.* varying the electrolyte concentration, redox species concentration, nanodiamond coverage, pH, *etc.*).

Matteo Duca continued: With respect to the off-set current, can it be avoided by immersing the electrode into the electrolyte under potential control (in particular, by keeping the potential negative enough)?

Thomas Varley replied: The off-set current is a result of the nanodiamond oxidising the FcMeOH species in solution upon contact; this generates $FeMeOH^+$ at the electrode interface and it is the reduction of this species that gives rise to the off-set current. The only way you could prevent the off-set current is to ensure all the redox-active surface sites are fully reduced prior to introducing the nanodiamond to the FcMeOH. It is unlikely this can be achieved electrochemically as not all the surface sites that can carry out the oxidation will be within tunnelling distance of the electrode. Making the potential more negative will only increase the driving force for the reduction of the spontaneously formed $FcMeOH^+$ at the electrode. However, we have shown in other data that if you hold a potential of 0.0 V (*vs.* Ag/AgCl sat. KCl) for 300 s prior to starting the experiment, you no longer observe the off-set current, as this is sufficient time to reduce the $FcMeOH^+$ spontaneously generated by the nanodiamond at the electrode surface (the off-set current steadily decreases as the equilibration time approaches 300 s).

John Foord asked: Could the signal enhancements you describe be explained by adsorption/absorption/preconcentration effects, as commonly seen in porous layers, rather than the catalytic electron transfer cycle?

Thomas Varley answered: As shown in the paper we do suggest that the ferrocene methanol species is adsorbing, and this is contributing towards the overall current. However, on the time periods of our experiments it is unlikely, but cannot be ruled out completely, that pre-concentration is occurring. In addition, you would expect surface adsorbed species to exhibit a current which is proportional to scan rate. Thus at higher scan rates, the associated peak would dominate

the voltammetric response as the diffusional component will only scale with the square root of scan rate; this is not what we observe. Finally, other spectroscopic data presented within the paper and previous work[1,2] shows that interaction with surface redox groups on the nanodiamond is occurring; these interactions can explain the observed enhancements. For example, if the current increases were solely due to absorption of redox probe into the porous nanodiamond layer, we would expect oxidation and reduction peaks to be equally enhanced in all cases – this is not observed for many redox probes.[3] However, the contributions towards the current enhancements are quite complex and likely include adsorption, absorption, catalytic effects and perhaps some mass transport effect. Which process dominates will depend on the redox probe used and solution conditions.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.
2 J. Scholz, A. J. McQuillan and K. B. Holt, *Chem. Commun.*, 2011, **47**, 12140–12142.
3 K. B. Holt, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2048–2058.

Matteo Duca enquired: A possible way to establish the nature of the adsorbed species would involve generating the adsorbate at the electrode, which is then transferred to clean electrolyte for a voltammetric measurement. Has such an experiment been tried and, if so, has it yielded any significant results?

Thomas Varley replied: This experiment has been tried but the adsorbed FcMeOH or FcMeOH$^+$ species are not bound strongly enough to detect when transferred to clean electrolyte. Similar experiments were carried out with XPS analysis of the nanodiamond modified electrode surface and nanodiamond powders that had been previously exposed to FcMeOH. The lack of any signal at the binding energy for iron and the lack of electrochemical response suggests the adsorption is non-specific.

Robert Hamers said: Have you investigated the dependence of the cyclic voltammogram peak height as a function of scan rate? That is a common way of distinguishing between reactions in solution (which become diffusion-limited) *vs.* reactions that involve surface species (and are therefore limited by available surface sites).

Thomas Varley responded: We have. Log-log plots of peak height *vs.* scan rate gave slopes between 0.6–0.8. A slope of 0.5 is expected for diffusion controlled reactions, whereas a slope of 1.0 is expected for surface confined reactions. Our values suggest a mixed response, which is what our mechanism suggests.

Philip A. Ash remarked: The FTIR data you report is very seductive, as it clearly implies preferential adsorption of the oxidised FcMeOH$^+$ species, suggesting that electron transfer could indeed be mediated by redox-active groups at the nanodiamond surface as you suggest. I wonder if it would be possible to take this experiment further, by adding a cocktail of solution redox mediators to change the solution potential and initiate or inhibit this electron transfer step in a stopped-flow potentiometric experiment? In principle the high surface area nanodiamond film could enhance the sensitivity of your spectroscopic measurement sufficiently to allow you to observe intermediates in the course of

reaction, either through the use of isotope exchange or through the inclusion of a ferrocene derivative with a suitable redox-dependent infrared active marker. It is doubtful that this approach would be successful at a planar diamond electrode, however, as the overall absorbance of your adsorbed films is quite low.

Thomas Varley answered: This is an excellent idea and something we should consider. However, careful consideration of which are the redox species to be used in such a solution would be required. Regarding the preferential adsorption of FcMeOH$^+$, it is likely that both species are adsorbed through pi-pi stacking. However, the positively charged FcMeOH$^+$ will also be attracted to the negatively charged nanodiamond surface, although this interaction is pH dependant.

George Zheng Chen asked: Are the nanodiamond particles not insulators? If they are, how can electron transfer reactions proceed on them or be affected by them? Could it be the boundary region between the nanodiamond particle and the electrode substrate that is responsible for your observed catalytic effect?

Thomas Varley replied: Diamond is an insulator with an approximate band gap of 5.5 eV. However, it has previously been shown[1] that surface sites have redox activity and thus must have energies that are within diamond's band gap. It would not be correct for us to rule out effects due to the boundary region, however, spectroscopic evidence of changes in surface functionality after reactions with specific redox probes[2] coupled with the observation that the enhancement varies depending on the properties of the redox probe, provides strong evidence towards our proposed feedback mechanism.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.
2 J. Scholz, A. J. McQuillan and K. B. Holt, *Chem. Commun.*, 2011, **47**, 12140–12142.

George Zheng Chen continued: Fig. 3b of the paper shows CVs obtained from electrodes loaded with nanodiamond particles of very different sizes, and it is clear that very similar kinetics are governing the electrode reactions. If so, how can the catalytic activity be affected by the particle sizes? Or, was your observed catalytic effect simply due to the sum of lengths of the boundaries between the particles and the electrode substrate increasing with decreasing particle size?

Thomas Varley responded: The kinetics of the catalytic reaction are not affected by the size of the nanodiamonds. This is because it is the same functionalities (but perhaps not identical species) that are responsible for the enhancement. The size of the nanodiamonds affects the density of the surface sites, thus the magnitude of the enhanced current.

George Zheng Chen asked: How can the nanodiamond particles attach to the electrode surface? What is the nature of the interaction?

Thomas Varley answered: We have not explored in any great detail the mechanism that holds the drop-coated nanodiamond particles onto the electrodes surface, but they are physisorbed quite strongly. We have checked that the material isn't affected by immersion into a solution using before and after optical

images obtained *via* a microscope and the nanodiamond layer remains intact unless removed *via* rough physical treatment (*e.g.* polishing).

George Zheng Chen contined: Have you compared the current change with the number and size of the nanoparticles?

Thomas Varley replied: We have shown in this paper that the size of the nanodiamonds has a dramatic effect on the magnitude of the enhanced current. Smaller particles give larger enhancements due to the increased surface area. Previous work carried out in the laboratory has shown that the amount of nanodiamond present also affects the enhanced current.

George Zheng Chen added: Would it be possible that the electrochemistry proceeded at the boundary between the nanodiamond particles and the electrode substrate, instead of the insulating nanodiamond particles? Also, there must be a strong interaction to make the nanodiamond particles remain stable on the electrode surface, what could this interaction be?

Thomas Varley responded: The nanodiamond core is extremely resistive, and a good example of an electrical insulator as diamond is known to have a large band gap of *ca.* 5.5 eV. Previous work in our group[1] shows that nanodiamond has redox active surface sites that have orbital energies within diamond's band gap. Boundary region effects cannot be completely ignored, however spectroscopic evidence of changes in surface functionality after exposing nanodiamond with hexachloroiridate(IV), coupled with the observation that the enhancement varies depending on the properties of the redox probe,[2] reinforces our proposed feed-back mechanism. Indeed there must be a strong interaction holding the nano-diamond particles onto the electrode surface. We have checked that the nanodiamond layer(s) aren't affected by immersion and removal from a solution (*via* optical microscopy). The nanodiamond layer remains constant unless removed *via* rough physical treatment (*e.g.* polishing). Nanodiamond is known to aggregate into small (*ca.* 50 nm) clusters, due to electrostatic and even covalent linkage of the particles. These clusters can again aggregate forming secondary clusters, but these are known to be less stable. Since we are using a carbon electrode it is highly feasible that similar interactions are occurring. Also, all of the experiments presented in this paper were conducted at positive potentials, which would provide strong attraction forces for the negatively charged nanodiamonds.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.
2 J. Scholz, A. J. McQuillan and K. B. Holt, *Chem. Commun.*, 2011, **47**, 12140–12142.

Mark Newton said: Synthetic diamond is well know as an ideal material for ATR, particularly when studying very hard solids. It is well know that with hydrogen terminated intrinsic diamond, the surface conductivity[1] is sufficient to permit electrochemical investigations over a limited range of potentials and conditions. Is it possible to contemplate combining FTIR and electrochemistry on a diamond ATR prism?

1 F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, Origin of Surface Conductivity in Diamond, *Phys. Rev. Lett.*, 2000, **85**, 3472.

Thomas Varley answered: This is an excellent idea. The experimental requirements, however, would be quite tricky although collaboration with a researcher who has the facilities to deposit such diamond films would make this type of experiment more feasible. That said, the requirement for the diamond to be hydrogen terminated, to permit the surface conductivity, would mean losing the redox-active surface sites (this would be a good experiment to prove they are required). It might be possible to incorporate nanodiamond particles into the surface of the film, in which case the *in situ* FTIR spectroelectrochemical measurements could be performed.

Julie Macpherson enquired: Have you observed any redox couples which don't show a response with the nanodiamonds?

Thomas Varley replied: Currently, we have tested $[Fe(CN)_6]^{3-/4-}$, $[IrCl_6]^{3-/2-}$, $[Ru(NH_3)_6]^{3+}$, $[Ru(CN)_6]^{3-/4-}$, ferrocene methanol, ferrocene di-methanol, ferrocene carboxylic acid and ferrocene di-carboxylic acid. All of these species showed a catalytic enhancement but to varying extents. Testing species that have E^o values further from the nanodiamond values are likely to exhibit no enhancement, but as yet none have been tested. It is difficult to identify a potential where the nanodiamond surface does not have surface active sites from the current potential windows investigated.[1] If the nanodiamonds are hydrogen terminated, then the catalytic enhancement has been shown to disappear for some redox probes, *e.g.* $[Ru(NH_3)_6]^{3+}$ (ref. 2). This is suggested to be because it is the oxygen content of the surface which gives rise to the redox activity. Once the oxygen groups are removed then the enhancement can no longer take place.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.
2 K. B. Holt *et al.*, *Phys. Chem. Chem. Phys.*, 2008, **10**, 303–310.

Julie Macpherson continued: Do you know what the E^o is for the proposed redox active groups on the nanodiamond surface?

Thomas Varley responded: The redox active groups on the nanodiamond surface vary with pH and span a range of potentials between 0.1 V (pH 4) to 1.0 V (pH 9), *vs.* Ag/Ag/Cl. The potentials of these surface groups/states were obtained using differential pulse voltammetry of a layer of nanodiamond immobilised on an electrode[1]. Distinct peaks at discrete potentials were observed for the nanodiamond layer, some of which suggested reversibility in the redox response. The response is actually quite complex and varies with pH and with previous electrochemical cycling.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.

Keith Stevenson asked: The CVs remind me of those of Royce Murray's charging of soluble gold clusters, where they exhibit a potential dependent charging response similar to charging an ultrasmall capacitor with different

charge states. Is it possible that the nanodiamonds have an inverse charge storage structure? Have you done the experiment with soluble nanodiamonds?

Katherine Holt communicated in reply: Yes – an interesting observation! And something I noted when I carried out the original experiments. The evenly spaced peaks do seem to suggest the type of capacitive charging seen for gold nanoparticles terminated with an insulting SAM layer. In our case it would be an insulating core, coated with a conducting coating. It is certainly an interesting and exciting possibility that this could be taking place – however we have suggested that the peaks are due to redox chemistry of surface functionalities on the diamond surface, that can undergo oxidation and reduction at specific potentials. The reason for this is the pH dependence of the response and the fact that the peaks shift *ca.* 60 mV with each change in pH unit, suggesting a proton coupled electron transfer. A possible origin of this redox chemistry is quinone-type species on the surface of the nanodiamond.

Chi-Chang Hu queried: Due to the possible diffusion effect from the microelectrode, what is the coverage of the nanodiamond?

Thomas Varley replied: Experiments such as varying the surface coverage contributed towards us eliminating any microelectrode effects. Varying the coverage changes the enhancement factor, but not the voltammetric shape that would change if the nanodiamond were creating an array of microelectrodes on the BDD surface. An example of the effect that varying the amount of nanodiamond has on the voltammetry is shown in ref. 1, Fig. 1. Other evidence against a microelectrode effect includes the dependence shown of current on the identity of the redox species and solution pH. If the current enhancement were simply attributed to mass transport effects this should be independent of these factors. The coverage of the nanodiamond in the present work was measured by optical imaging, and estimated at *ca.* 40%. However, due to the size difference between the particles and the electrode, this technique is susceptible to errors. Therefore, coverage was controlled by the amount of material deposited, which was set at 4 µg per coating.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.

Chi-Chang Hu continued: Can the author try to change the mass loading of nano-diamonds (*e.g.* 2 sizes) to evaluate the microelectrode effect?

Thomas Varley responded: This is something we have explored and reported previously.[1] Such experiments are important as they allow us to observe the effect of nanodiamond loading on the voltammetric wave shape and the extent of the Faradaic current enhancement to be explored. Further analysis of our data should subsequently help contribute towards determining the number of active sites per nanodiamond.

1 K. B. Holt, D. J. Caruana and E. J. Millán-Barrios, *J. Am. Chem. Soc.*, 2009, **131**, 11272.

Fulian Qiu commented: Inert nanodiamond immobilised on a electrode surface showed two catalytic processes for the oxidation of FcMeOH. You could disperse nanodiamonds into an electrolyte solution rather than immobilisation. If the mechanism of the two catalytic processes is singular, cyclic voltammograms should show the same behaviors as those recorded for the immobilised nano-diamond electrodes regarding the pHs and sizes of nanodimonds. This will rule out possible surface diffusion processes.

Jingping Hu asked: Nanodiamonds are known to tend to aggregate together easily. Does the aggregation issue have any big influence on your results? Have you considered using boron doped nanodiamonds in future experiments?

Thomas Varley answered: This is a good point. We do not expect the aggregates to affect our observations, other than dictating the amount of accessible surface area. Using boron doped nanodiamonds is not something we have considered, but is an excellent and interesting idea, as the conductivity of these nanoparticles would no doubt lead to an interesting electrochemical response.

Robert Hamers said: In your experiments, do you correct for differences in the microscopic surface area of your samples?

Thomas Varley replied: No, the reason for this being we are interested in determining the effect of the surface area on the catalytic current. We have shown that the enhancement is inversely proportional to particle size, thus, for the same mass of diamond, smaller particles (and so more surface area) produce a higher enhancement. However, this isn't a standard relationship, and further experiments are required to fully understand this observation.

Robert Hamers continued: Is it possible that the differences you see could be accounted for through differences in microscopic surface area? It seems possible that perhaps the detonation nanodiamond may not be completely insulating, and so you could be seeing effects due to changes in accessible microscopic surface area. Is that possible ?

Thomas Varley responded: The measured relationship between the effect of particle size and current enhancement does not agree with this hypothesis. For example, peak current should be directly proportional to the increase in area, but this is not what we observe. Of course, it is difficult to know exactly what the accessible surface is, due to aggregation for the smaller particles and orientation for the larger particles. Also, the fact that the enhancement is different for different redox species means that the current is related to specific interactions between the redox probe and the nanodiamond, not changes in the apparent electrode area. We cannot completely rule out surface conduction, although it has previously been reported that conductivity is only achieved for nanodiamond that is hydrogen terminated, or through the presence of defects within the extended diamond structure (*e.g.* boron doping). Surface defects and impurities become more important as the size of the diamond decreases. This has a huge effect on the observed properties of the nanodiamond.[1]

1 K. B. Holt *et al.*, *J. Phys. Chem. C*, 2009, **113**, 2761–2770.

John Foord enquired: How do the electrochemical peak currents you see at the nanodiamond treated electrode compare with those calculated from planar diffusion – are they bigger?

Thomas Varley answered: The peak currents are significantly bigger than those calculated from planar diffusion. In the paper, the enhancement is *ca.* 10 times greater than the expected current.