Identifying quinone-like species on the surface of graphitic carbon and multi-walled carbon nanotubes using reactions with 2,4-dinitrophenylhydrazine to provide a voltammetric fingerprint

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Quinone groups on the surface of edge-plane and basal-plane pyrolytic graphite electrodes, and, for the first time, "bamboo-like" multi-walled carbon nanotubes (b-MWCNTs), are labelled with a voltammetric "tag", namely 2,4-dinitrophenylhydrazine (2,4-DNPH). The voltammetric response of these materials is studied in both aqueous and non-aqueous electrolyte solutions, and mechanisms are proposed for each media involving the voltammetrically controlled cleavage of the 2,4-DNPH adduct. Thus, these materials can be used for potentiometrically controlled chemical release, and as such may find application in, for example, drug delivery systems. In aqueous media, this cleavage results in the conversion of the surface quinonyl groups into surface arylnitroso species. This conversion is confirmed by studying the voltammetric response of the arylnitroso/arylhydroxylamine redox couple, formed after cleavage of the 2,4-DNPH adduct in the presence of L-glutathione, which has been shown in our previous work to react with arylnitroso species on the surface of graphitic carbon materials.

1. Introduction

Carbon electrodes are widely employed in electrochemical applications due to their relatively low cost compared to precious metal electrodes, their relative chemical inertness and their wide potential window in most electrolyte solutions (typically −1 V to +1 V in aqueous electrolytes). Usually, carbon electrodes are formed from graphitic carbon (such as glassy carbon), highly ordered pyrolytic graphite (exposing either the edge-plane or basal-plane crystallographic faces), graphite powder, carbon paste electrodes or, more recently, carbon nanotube-modified electrodes, in addition to the use of conducting boron-doped diamond electrodes.[1–4]

Graphitic materials such as pyrolytic graphite typically consist of stacked sheets of fused hexagonal rings of carbon, while glassy carbon consists of interwoven graphitic ribbons, as shown in Fig. 1. The structure of carbon nanotubes (CNTs), discovered in 1978 by Wiles and Abrahamson,[5] and rediscovered in 1991 by Iijima,[6] can be thought of conceptually as "rolled-up" sheets of graphite; a single rolled up graphite sheet forms a single-walled carbon nanotube (SWCNT), whilst several sheets of graphite rolled into concentric tubes form multi-walled carbon nanotubes (MWCNTs). MWCNTs can be formed in a variety of morphologies, depending on the reaction conditions and method of formation, such as "bamboo-like" and "hollow-tube" multi-walled carbon nanotubes (b-MWCNTs and h-MWCNTs, respectively), the internal structure of which is also shown schematically in Fig. 1.

Two faces of a graphite crystal can be defined, the basal-plane, containing all the carbon atoms of a single sheet of graphite, and the edge-plane, which is perpendicular to the basal-plane. By analogy to graphite, the walls of a CNT can also be described as basal-plane-like, while the tube ends are considered to be edge-plane-like. The edge-plane sites on graphitic carbon electrodes, mainly glassy carbon, have been found to be decorated with oxygen-containing surface groups, notably carboxyl, hydroxyl and quinonyl groups (Fig. 1) using a variety of techniques, notably X-ray photoelectron spectroscopy (XPS),[7–12] thermal desorption methods,[13] vibrational spectroscopy,[14,15] NEXAFS[16] and electrochemistry.[1,2,17–27]

These oxygen-containing surface groups have often been considered to play a rôle in enhancing the electrode kinetic responses of graphite electrodes[28–30] and SWCNTs[23] towards a variety of redox-active species. However, for certain redox species studied on MWCNTs and also at an edge-plane graphite electrode, workers within our research group have found that the converse is true, and that the presence of oxygenated species on graphitic electrode surfaces may, in certain situations, inhibit the rate of electron transfer.[31,32]

Classically, the reagent used to test for the presence of aliphatic or aromatic carbonyl groups is 2,4-dinitrophenylhydrazine (2,4-DNPH) as the adduct, 2,4-dinitrohydrazone, derivative is distinctively coloured and can be used to crystallize out the product.[33–35] In their seminal work from 1976, in which the term "chemically-modified electrode" was first coined, Elliot and Murray applied the reaction of 2,4-DNPH to identify quinone groups on the surface of a graphite rod and a glassy carbon electrode.[19] However, only the resulting

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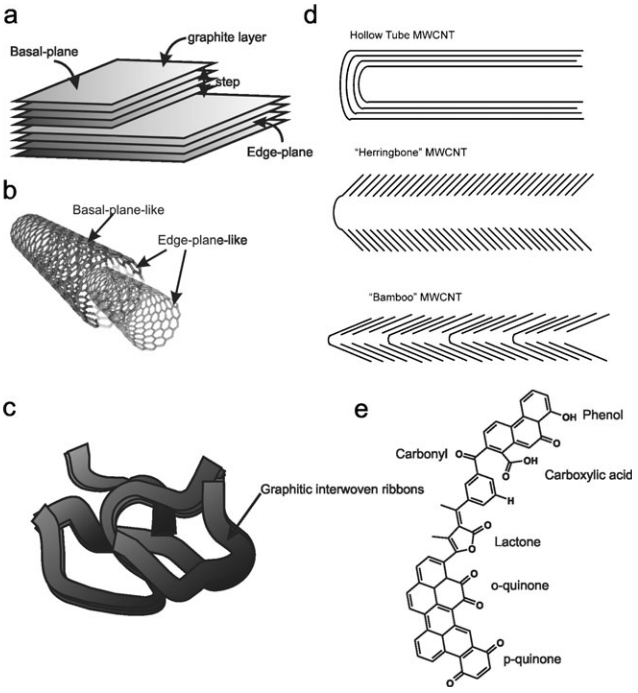
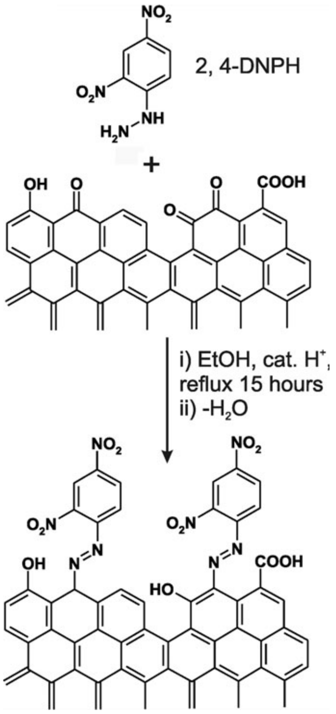


Fig. 1 Schematic representations of the structures of (a) a graphite crystal, (b) a MWCNT, (c) glassy carbon together with (d) a schematic cross-section through three different morphologies of MWCNT showing their different internal structures, and finally (e) a representation of the various oxygen-containing functionalities present on graphitic carbon surfaces adapted from ref. 1.



Scheme 1 The modification of surface quinonyl groups decorating an edge-plane-like defect site on a graphitic surface with 2,4-DNPH.

non-aqueous voltammetry of the 2,4-DNPH-modified carbon rod was presented, which was described as being ''poorly resolved''. They did, however, note that after the first initial voltammetric cycle, no further voltammetry corresponding to 2,4-DNPH could be observed. Using XPS techniques, they determined that this was attributed to the reduction of the nitro groups ''at least in part''. A residual peak could be seen in the N_{1s} spectrum after reduction of the 2,4-DNPH adduct, but this was attributed to the residual quaternary ammonium electrolyte salts used. The solution phase voltammetry of 2,4-DNPH and its adducts with quinone species was also discussed briefly, but the data was neither presented nor interpreted.[19] Later, as part of their substantial work investigating the surface sites on highly ordered pyrolytic graphite (HOPG) electrodes, McCreery *et al.* used 2,4-DNPH to label surface quinone groups, and the adduct was then investigated using Raman resonance spectroscopy. However, once again, no voltammetric data was presented.[14] McCreery's work shows the likely structure of the adduct of 2,4-DNPH with surface quinone groups, indicating that the π-electronic structure is delocalised over the entire molecule and that the adduct forms predominantly its azo-linked tautomer.

In this report, we label the surface quinone groups on edge-plane and basal-plane graphite with 2,4-DNPH, and also extend this technique to label surface quinone groups on b-MWCNTs with 2,4-DNPH for the first time. Scheme 1 shows the structure of the modified adduct of 2,4-DNPH with quinonyl groups on an idealised graphite or CNT edge-plane structure in the ''zig-zag'' arrangement. Note that, in reality, both ''arm chair'' and ''zig-zag'' motifs may be present, such that any surface quinone groups can be formed in *ortho* and *para* arrangements, and that as well as some disordered cross-linked cyclohexane-like structures, other oxygen-containing functional groups, such as ketones, lactones hydroxyl and carboxyl groups, are also likely to be present (Fig. 1).[1,26] The voltammetric responses of these labelled materials are explored in both aqueous and non-aqueous media, and we propose a mechanism to explain the resulting voltammetry, which in both aqueous and non-aqueous media involves the cleavage of the 2,4-DNPH adduct, effecting chemical release from the graphitic surface. Cleavage of the adduct of 2,4-DNPH and the surface quinone groups converts the quinonyl group into an arylnitroso group. The presence of such arylnitroso groups was confirmed by the studying the effect of added thiol, namely L-glutathione, on the voltammetric response of the arylnitroso/arylhydroxylamine redox couple in a manner based on the recent work of Abiman *et al.*[36] This process of chemical release may have possible applications in nanoscale analytical techniques and/or therapeutic applications in drug delivery systems.

2. Experimental

2.1 Reagents and equipment

All reagents were purchased from Aldrich (Gillingham, UK) with the exception of acetonitrile (synthesis grade 99.9%, Fisher Scientific, Loughborough, UK) and potassium chloride (Reidel de Haën, Seelze, Germany), were of the highest grade available and were used without further purification. Bamboo-like MWCNTs (b-MWCNTs, 30 ± 15 nm diameter, 5–20 μm length, <95% purity) were purchased from Nanolab (Brighton, MA, USA). Aqueous solutions with pH values in the range 1.0–6.8 were prepared in de-ionised water (minimum resistivity 18.2 MΩcm at 25 °C) as follows: pH 1.0, 0.10 M HCl; pH 4.6, 0.10 M acetic acid + 0.10 M sodium acetate; pH 6.8, 0.025 M Na_2HPO_4 + 0.025 M KH_2PO_4. These solutions contained, in addition, 0.1 M KCl as a supporting electrolyte. pH measurements were performed using a Jenway 3030 pH meter. Non-aqueous solutions were prepared using acetonitrile dried over molecular sieves and alumina powder to remove any trace water. 0.1 M tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte.

Electrochemical measurements were carried out using a μAutolab computer-controlled potentiostat (Ecochemie, Utrecht, Netherlands) in a cell of volume 10 cm^3 using a three-electrode configuration. Either a basal-plane or an edge-plane pyrolytic graphite electrode (bppg and eppg, respectively, area = 0.025 cm^2, Le Carbone, Sussex, UK) acted as the working electrode (see below). A bright platinum wire coil acted as the counter electrode, unless otherwise stated. A saturated calomel reference electrode (SCE, Radiometer, Copenhagen, Denmark) completed the cell assembly. All solutions were thoroughly de-gassed with pure N_2 for 15 min prior to performing any voltammetric measurements. Unless stated otherwise, all cyclic voltammetry was performed at a scan rate of 100 mV s^{-1}, step potential 2 mV. All square wave voltammetry (SWV) was performed at an optimised frequency of 17.5 Hz, step potential 2 mV, amplitude 2.5 mV.

2.2 Modification of graphite and b-MWCNT surface groups with 2,4-dinitrophenylhydrazine

Modification of the b-MWCNTs or the graphite electrodes with 2,4-DNPH was performed using a procedure adapted from Elliott and Murray[19] as follows: 50 mg of the native b-MWCNTs were suspended in 25 cm^3 of a 5 mM solution of 2,4-DNPH in ethanol, to which 0.25 cm^3 of concentrated hydrochloric acid was added. The solution was then heated under reflux with stirring for a period of 15 h. Subsequently, the mixture was filtered by water suction, in order to remove any unreacted species from the CNT surface, and washed with hot ethanol (60 °C), water and acetonitrile to remove any unreacted physisorbed 2,4-DNPH from the mixture. The newly functionalised b-MWCNTs were then dried under suction for a further 30 min, resulting in the final product, 2,4-DNPH-modified b-MWCNTs (DNPH-MWCNTs), as shown in Scheme 1.

The equivalent derivatisation of basal-plane and edge-plane pyrolytic graphite with 2,4-DNPH was achieved using clean bppg and eppg electrodes, respectively. Prior to modification, the electrode surfaces were polished in order to obtain a smooth, clean surface. The bppg electrode was polished on silicon carbide paper (P1000C) and washed with acetone. The eppg electrode was successively polished using a 1 μm and then a 0.3 μm alumina suspension, with rinsing and sonication in pure water and ethanol between polishings to remove any adhered alumina particles. The graphitic electrode surfaces were then reacted using the same reagents and conditions as for producing the DNPH-MWCNTs, as described above using a 1 mM solution of 2,4-DNPH, with the electrodes themselves held in the reaction mixture in place of the b-MWCNT powder. The electrode surface was similarly washed with hot ethanol, water and acetonitrile, and allowed to dry.

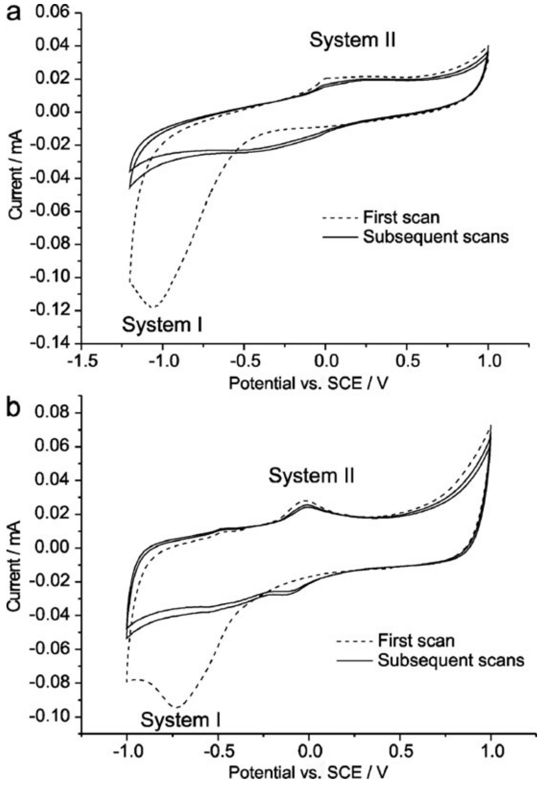


Fig. 2 The first five cyclic voltammetric scans of (a) an eppg electrode and (b) b-MWCNTs modified with 2,4-DNPH in aqueous solution (pH 6.8). Scan rate 100 mV s^{-1}, scanning initially from +1.0 V to −1.0 V *vs.* SCE.

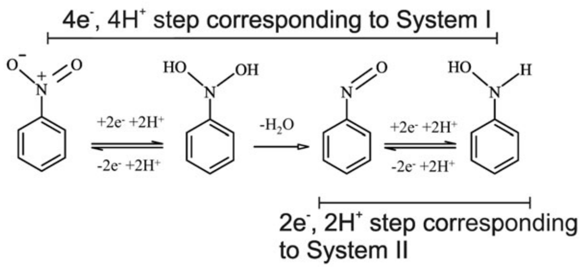
2.3 Immobilisation of MWCNTs onto the surface of basal-plane pyrolytic graphite electrode

Initially, the bppg electrode was polished as described above. The derivatised 2,4-DNPH-MWCNTs were then mechanically-immobilized onto the electrode by gently rubbing the electrode surface on a fine filter paper (Whatman) containing the functionalised MWCNTs.

3. Results and discussion

3.1 Voltammetric characterisation of 2,4-DNPH-modified graphite and MWCNT surfaces

The modified eppg, bppg and MWCNTs (abrasively-immobilised onto a bppg electrode) were characterised using cyclic voltammetry. Fig. 2a and 2b show the resulting voltammetric response of a 2,4-DNPH-modified eppg electrode and the 2,4-DNPH-MWCNTs in aqueous solution (note that the voltammetry at the modified bppg electrode was similar to that of the modified eppg). Upon first scanning in a reductive direction, a large voltammetric wave was observed at *ca.* −0.75 V and −1.0 V *vs.* SCE for the modified MWCNTs and the eppg



Scheme 2 Mechanism for the reduction of an aryl nitro group in aqueous media, exemplified by the model compound nitrobenzene.

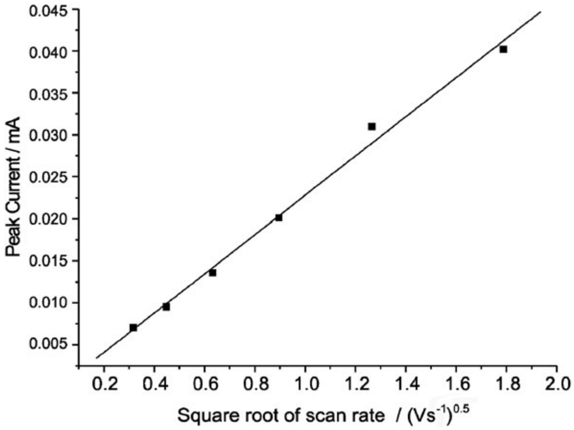


Fig. 3 A plot of peak current against the square root of scan rate for the 2,4-DNPH-MWCNTs abrasively-immobilised onto a bppg electrode.

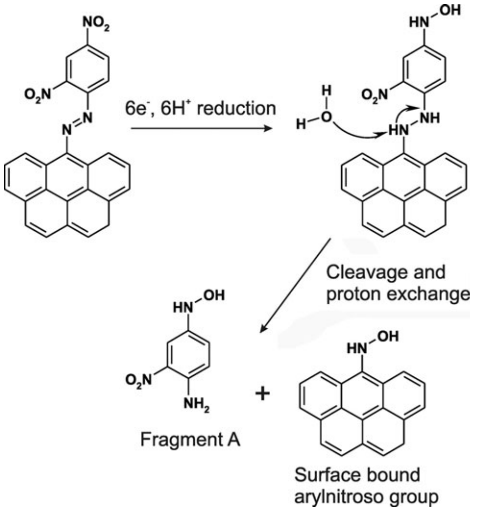
electrode, respectively, labelled as system **I**. Upon reversing the scan direction, no corresponding oxidation peak was observed, indicating that the reduction was electrochemically irreversible. Instead, a new oxidative wave was observed at less negative potentials than system **I**, and the corresponding reduction wave was then observed on subsequent scans, labelled system **II**, indicating that this system is electrochemically quasi-reversible. The exact peak potentials of systems **I** and **II** depend on the pH of the electrolyte solution used, and were found to shift to more negative potentials in a linear, Nernstian fashion by 60 mV per unit increase in pH.

This behaviour is characteristic of the voltammetric reduction of an aryl nitro group,[37–44] shown in Scheme 2 for the model compound nitrobenzene, where system **I** corresponds to the four-electron, four-proton reduction of each of the two aryl nitro groups in a chemically and electrochemically irreversible step to form the corresponding aryl hydroxylamine groups. System **II** then corresponds to the two-electron, two-proton quasi-reversible arylhydroxylamine/arylnitroso redox couple. However, a detailed discussion of the mechanism of the reduction of 2,4-DNPH modified graphitic surfaces will be reserved until Section 3.2.

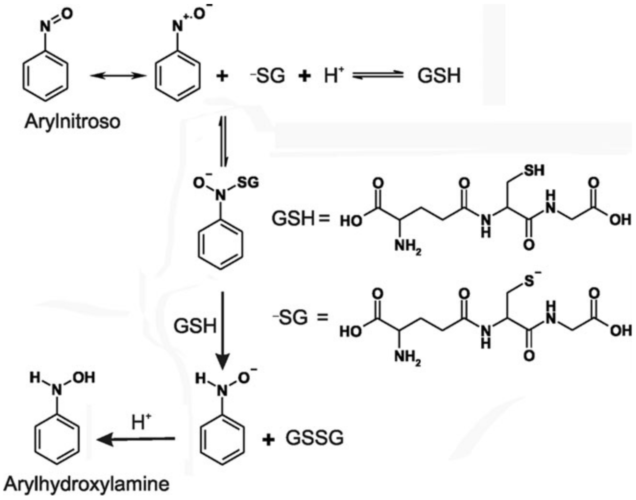
In order to voltammetrically characterise the graphitic materials as indeed being covalently modified with 2,4-DNPH, the quasi-reversible system **II** was used after an initial scan was performed to form this system, in conjunction with a well-established characterisation protocol. This protocol is detailed elsewhere[42–47] but briefly consists of: (i) Performing multiple (25–100) scans over system **II**; a stable voltammetric response indicates that the redox-active species is not desorbing from the electrode surface into solution. (ii) The electrode is removed from the buffer solution and placed into fresh buffer and a scan recorded; in all cases, this was found to overlay the last scan recorded, indicating that the redox-active species is only present on the electrode surface and is never found in solution. (iii) Finally, the scan rate is varied and the peak current recorded as a function of scan rate. Often, for a surface-bound species exhibiting fast electrode kinetics, a linear relationship between the peak current and the scan rate is observed.[48] However, for the 2,4-DNPH-MWCNTs, the peak current was found to vary linearly with the square root of the scan rate, indicating that the voltammetry is under diffusion control (Fig. 3). However, as long as the previous two tests indicate that the species is surface-bound, this voltammetric behaviour is not due to a species diffusing in solution. Instead, this phenomenon is attributed to the diffusion of charge over the surface of the modified particles on the electrode surface.[49] This behaviour has been seen for a wide variety of chemically-modified CNTs immobilised onto electrode surfaces,[42,44,46] and has been treated theoretically for the case of species exhibiting fast, slow and intermediate electrode kinetics elsewhere.[49,50] The characterisation protocol was applied to all the 2,4-DNPH-modified graphitic materials studied herein over the entire pH range 1–7, and in every case confirmed that the graphitic surface was covalently-modified with 2,4-DNPH. In the next two sections, we elucidate for the first time the mechanism for the reduction of 2,4-DNPH-modified graphitic materials in both aqueous and non-aqueous media.

3.2 Elucidating the mechanism for the reduction of 2,4-DNPH-modified graphite and MWCNTs in aqueous media

At first glance, the observed voltammetry of 2,4-DNPH-modified eppg, bppg or b-MWCNTs appears to be simply that of the reduction of an aryl nitro group, excepting that there are two reducible nitro groups in the 2,4-DNPH molecule. A comparison with the voltammetry of an aqueous solution of 1,3-dinitrobenzene reveals in this case that the nitro groups are reduced separately in two voltammetric peaks separated from each other by 130 mV (the exact peak potentials again depend on the solution pH). However, in the voltammetry of 2,4-DNPH, only a single voltammetric reduction peak is observed in system **I**, which provides a clue as to the underlying mechanism (see below). If only a single nitro group were being reduced then one would expect the ratio of peak areas of system **I** and system **II** to be approximately 2 : 1. In fact, the measured ratio of peak areas is found from repeated experiments to be 3 : 1 for all the modified substrates used herein. One possibility is that the nitro groups can be irreversibly reduced to the corresponding arylamine groups in a six-electron, six-proton process, but this is rarely observed under the conditions and scan ranges used here, except for the case of 4-nitrophenol, where the hydroxyl group plays an important role in facilitating the further reduction.[37–44] Furthermore, if this were the case, then system **II**, the arylhydroxylamine/arylnitroso couple, would not be observed.



Scheme 3 Proposed mechanism for the reduction of 2,4-DNPH-modified graphitic surfaces in aqueous media showing the cleavage of fragment **A** and the formation of a new surface-bound arylnitroso species.



Scheme 4 The reaction of glutathione with an arylnitroso species to form an arylhydroxylamine species.

An alternative explanation is that the adduct of 2,4-DNPH, with a surface quinone group, has, in addition to the reducible nitro groups, an azo linkage. We have previously demonstrated that aryl groups containing both nitro and azo linkages, exemplified by the azo dye Fast Black K (FBK, 2,5-dimethoxy-4-[4-(nitrophenyl)azo]benzenediazonium chloride), covalently attach to graphitic surfaces, undergo reduction of the aryl nitro group in the 4-position and the azo linkage at similar potentials, and result in the cleavage of the molecule, so effecting chemical release from the surface.[51,52] Based on this work, we propose that reduction of the azo linkage in the 2,4-DNPH adduct in the presence of water occurs at similar potentials to the reduction of the first nitro group in the 4-position in 2,4-DNPH, and therefore cleavage occurs before any further reduction of the nitro group in the 2-position can take place, as shown in Scheme 3. This results in cleavage of the 2,4-DNPH group, releasing a 1-amino-2-nitro-4-nitrosophenyl fragment (fragment **A** in Scheme 3) into solution and forming a new arylnitroso group on the graphite surface. If both the nitro groups are reduced before the azo linkage is cleaved, this results in a ten-electron, ten-proton reduction step, resulting in a ratio of peak areas of 5 : 1, which is not observed. Upon scanning in an oxidative direction, it is the newly formed arylnitroso/arylhydroxylamine couple on the graphitic surface that gives rise to the observed two-electron, two-proton voltammetric redox process, not the arylnitroso groups, which arise from the reduction of the nitro groups in 2,4-DNPH. This then gives the observed maximum ratio of peak area of 3 : 1. Note that there is sufficient time at the scan rates used for fragment **A** to diffuse out of the diffusion layer surrounding the electrode surface, and hence this fragment does not contribute to the voltammetry observed for system **II** (see below).

To further investigate this proposed mechanism, we took advantage of the recent work by Abiman *et al.*, who showed that arylnitroso groups on the surface of graphite can be used to analytically detect thiol species in solution.[36] This process is observed as a decrease in the reductive SWV response of the arylnitroso/arylhydroxylamine couple due to the reaction mechanism shown in Scheme 4, where the reaction between the thiol and the nitroso group reduces the surface concentration of arylnitroso species.[36] For our purposes, we used this process in reverse, in that the decrease in analytical signal of a known concentration of a model thiol, L-glutathione, was used to detect the presence of arylnitroso groups on the surface of modified graphite or b-MWCNTs.

To this end, a single cyclic voltammetric scan over system **I** was performed on either the 2,4-DNPH-modified eppg or bppg electrodes and the 2,4-DNPH-MWCNTs immobilised onto an unmodified bppg electrode in order to form the surface-bound arylnitroso groups. Next, SWV was performed over the potential window for the arylnitroso redox couple in two pH 6.8 buffer solutions, one containing 10 μM glutathione and one without glutathione, at 5 min intervals and the peak height recorded in each case. Fig. 4a shows the resulting square wave voltammograms and the corresponding plot of peak height (normalised to the value of the peak height in the absence of glutathione) *vs.* time of exposure to glutathione. For both the modified graphite electrodes and the modified MWCNTs immobilised onto a bppg electrode surface a steady decrease in peak height was observed. In the absence of glutathione, the peak height remained constant. This confirms that in the case of the modified MWCNTs, this effect is not simply due to the nanotubes "falling off" the electrode surface. The effect of increasing glutathione concentration on the SWV peak height of the modified graphite electrodes and the modified MWCNTs, taken after 5 min exposure to the solution of glutathione, was also recorded (Fig. 4b), and good agreement was found between the observed response and the previous work of Abiman *et al.*[36] These experiments confirmed that the decrease in the SWV signal was not due to desorption of the arylnitroso species, confirming that a new surface-bound arylnitroso group is formed and that the corresponding voltammetry is not simply due to physisorbed cleavage products such as fragment **A**.

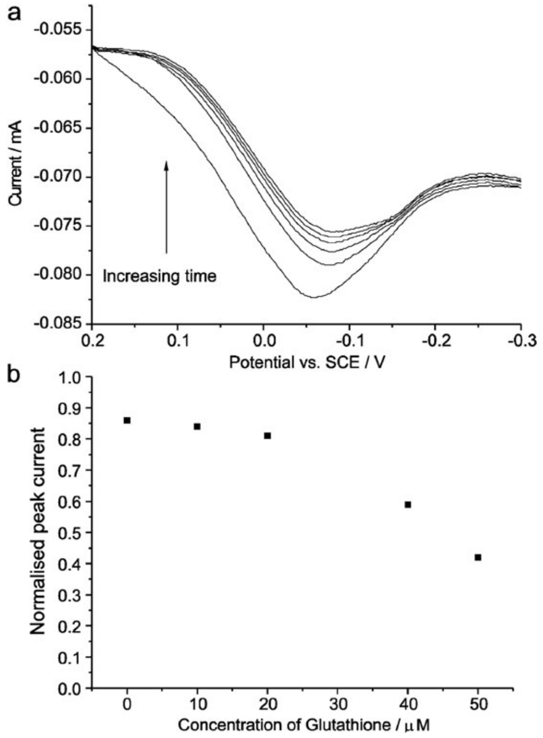


Fig. 4 (a) The reductive SWV response of the arylnitroso/arylhydroxylamine couple formed after the reduction and cleavage of 2,4-DNPH in pH 6.8 aqueous buffer recorded at 5 min intervals in a solution containing 10 μM glutathione. (b) A plot of the square wave reductive peak current, recorded after 5 min exposure to solutions of increasing glutathione concentration, normalised to the value of the reductive peak current recorded after exposure for similar times in the absence of glutathione.

3.3 Elucidating the mechanism of the reduction of 2,4-DNPH-modified graphite and MWCNTs in non-aqueous media

As mentioned in the Introduction, the seminal work of Murray *et al.*, in which the term "chemically-modified electrode" was introduced, first utilised 2,4-DNPH to modify the surface of a glassy carbon electrode.[19] In that article, the voltammetry of a 2,4-DNPH-modified glassy carbon electrode was presented, but no further discussion of the possible mechanism and species involved was given, except that a series of ill-defined waves were observed on the first scan, after which the subsequent voltammetry was "indistinguishable from that observed on unmodified glassy carbon".[19] In this section, we investigate the voltammetric behaviour of graphite electrodes and MWCNTs modified with 2,4-DNPH, as well as 2,4-DNPH in non-aqueous acetonitrile solution. Fig. 5 shows the voltammetry of an eppg electrode modified with 2,4-DNPH in acetonitrile. Three reductive peaks are clearly observed at –1.47, −1.13 and −0.91 V *vs.* a silver quasi-reference electrode on the first scan, in agreement with the voltammetry reported by Murray for a graphite rod and a glassy carbon electrode modified in a similar fashion.[19] Again, in agreement with Murray, upon reversing the scan direction, no voltammetric features are observed in subsequent scans, which differ from that of a blank graphite electrode. Identical behaviour was observed on a bppg electrode. The 2,4-DNPH-MWCNTs did exhibit ill-defined reduction waves at similar potentials, as observed on graphite, but the voltammetry was poorly resolved, largely due to the high capacitive charge obscuring any non-aqueous Faradaic processes. Therefore, the modified MWCNTs were not studied further in non-aqueous solution.

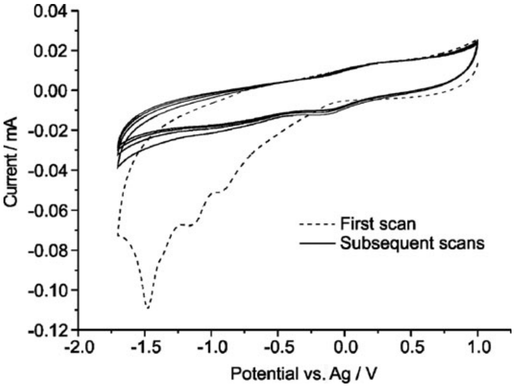


Fig. 5 The first five overlaid cyclic voltammetric scans (scan rate 100 mV s^{-1}, initial potential +1.0 V) of a 2,4-DNPH-modified eppg electrode in acetonitrile containing 0.1 M TBAP as a supporting electrolyte.

Cyclic voltammetry was then performed using a bppg working electrode in a solution containing 100 μM 2,4-DNPH in acetonitrile. As shown in Fig. 6, three reductive waves (labelled as **a**, **b** and **c**) could clearly be resolved at −1.29, −1.13 and −0.90 V *vs.* a silver quasi-reference electrode. A small reductive feature could also be distinguished at −0.71 V (see below). Upon reversing the scan direction, several new oxidative waves could be observed at −1.21, −1.06 and −0.25 V (labelled as **d**, **e** and **f**), which were not seen in the modified graphite electrode voltammetry. Cyclic voltammetry was then performed over each of the three main reductive features, reversing the scan direction before the onset of any further reduction to determine the reversibility of each system and to ascertain which, if any, of the oxidative features corresponded to the reduction waves shown in the overlaid scans in Fig. 6.

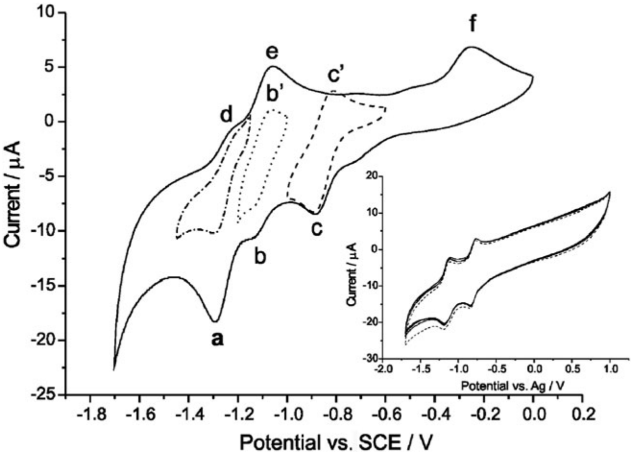


Fig. 6 The cyclic voltammetric response of a 100 μM solution of 2,4-DNPH in MeCN (0.1 M TBAP) on a bppg electrode. Inset: Five overlaid cyclic voltammograms of a 100 μM solution of 1,3-dinitrobenzene in MeCN (0.1 M TBAP) on a bppg electrode.

Systems **c** and **b** are clearly reversible with corresponding oxidative waves labelled **c'** and **b'**, a peak-to-peak separation of *ca*. 60 mV and a 1 : 1 ratio of peak currents.

A comparison of systems **c**/**c'** and **b**/**b'** with the voltammetry of a 100 μM solution of 1,3-dinitrobenzene in acetonitrile (inset Fig. 6) confirms that these systems are attributed to the sequential one-electron reversible reduction of the nitro groups in 2,4-DNPH to the corresponding radical anions. However, in the voltammetry of 2,4-DNPH, after scanning reductively over all three systems and then reversing the scan direction, there is no oxidative peak corresponding to **c'**. Furthermore, **b'** does not correspond to the oxidative process labelled **e**, despite the two waves having similar oxidation potentials, as the ratio of peak heights, peak widths and shapes do not match.

Finally, comparison of the voltammetry of 100 μM phenylhydrazine at a bppg electrode in acetonitrile confirms that system **a** and the small feature at −0.71 V in the voltammetry of 2,4-DNPH correspond to irreversible reduction of the phenylhydrazine group. We therefore propose that the non-aqueous voltammetry of 2,4-DNPH-modified graphite surfaces also involves the successive reduction of both the hydrazo and nitro groups. The products formed by the initial reduction of the 2,4-DNPH may then either react with themselves or with the parent molecule, or else disproportionate to form a new product that undergoes a series of reoxidations in peaks **d**, **e** and **f**. A detailed mechanistic study of solution phase 2,4-DNPH is beyond the scope of this report.

In the non-aqueous voltammetry of 2,4-DNPH-modified graphite electrodes, the reduction waves at −1.47, −1.13 and −0.91 V can be attributed to the successive one-electron reduction of the two nitro groups, and finally reduction of the azo linkage, by analogy to the solution phase voltammetry of 2,4-DNPH described above. A comparison of the peak heights of each of the three peaks indicates that the peak at −1.47 is twice that of the other two. If this is indeed the reduction of the azo linkage, then it must occur as a two-electron process for cleavage to take place. Thus, the non-aqueous voltammetry of 2,4-DNPH-modified graphitic surfaces also involves cleavage of the azo linkage and effects chemical release, in agreement with the behaviour observed in aqueous media.

4. Conclusions

The presence of quinone groups on the surface of graphite and b-MWCNTs have been voltammetrically labelled by a reaction with 2,4-DNPH. The voltammetric responses of the 2,4-DNPH-modified eppg or bppg electrodes and 2,4-DNPH-MWCNTs have been characterised voltammetrically in both aqueous and non-aqueous media. In aqueous media, a mechanism is proposed to explain the observed voltammetric response, whereby the azo linkage formed by the reaction of 2,4-DNPH with surface quinone groups is reduced and cleaved, inducing the chemical release of a fragment from the graphitic surface. One possible application of this is related to our previous work,[51,52] where we have demonstrated that similar systems involving chemical release from graphite and CNT surfaces may be used as a platform from which to develop potentiometrically controlled pulsative drug delivery systems, utilising implant devices such as that developed by Strano *et al.*[53] Derivatives of 2,4-dinitrobenzene have been found to have therapeutic value as anti-cancer agents,[54] and as such the chemical release of 2,4-DNPH derivatives from graphitic surfaces may prove to be a useful development for this novel targeted drug delivery strategy.

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