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A mechanistic investigation into the covalent chemical derivatisation of graphite and glassy carbon surfaces using aryldiazonium salts

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Modification of carbon materials such as graphite and glassy carbon in bulk quantities using diazonium salts is developed. We used both 4-nitrobenzenediazonium tetrafluoroborate and 1-antharaquinonediazonium chloride to modify graphite and glassy carbon surfaces. Experiments were carried out in the presence and absence of hypophosphorous acid and the mechanism involved in both cases were studied using cyclic voltammetry. The observed peak potentials for both the 4-nitrophenyl and 1-anthraquinonyl modified materials were found to differ depending on whether or not the hypophosphorous acid reducing agent was used. In the absence of hypophosphorous acid the derivatisation reaction was inferred to go through a cationic intermediate, whilst in the presence of the hypophosphorous acid the mechanism likely involves either a purely radical intermediate or a mixture of radical and cationic species. Derivatisation experiments from 5 to 70°C allowed us to determine the optimum derivatisation temperature for both cases, in the presence and absence of hypophosphorous acid. Optimum temperature was 20°C for the former and 35°C for the later. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: graphite; glassy carbon; chemical modification; aryldiazonium salts; mechanism; radical; cationic

INTRODUCTION

Carbon electrodes are widely employed in electrochemical applications due to their relatively low cost compared to precious metal electrodes, relative chemical inertness and wide potential windows in most electrolyte solutions (typically −1 V to +1 V in aqueous electrolytes).[1,2] The chemical modification of carbon surfaces allows electrochemists to tailor-make electrodes providing distinct advantages for catalysis, analysis and biological applications and this area of electrochemistry has attracted considerable attention in recent years.[3–6]

One strategy of covalently attaching a modifying species to a carbon surface involves the use of aryldiazonium salts. A variety of methods have been used to generate reactive intermediates from the aryldiazonium salts such as electrochemical reduction,[3,4] thermolysis,[7–9] photolysis[10] and chemical reduction.[11–13]The resulting reactive intermediates formed, such as aryl radical or cationic species can then react with the carbon surface resulting in covalent bond formation. For example, the electrochemical reduction of various aryldiazonium salts, usually dissolved in a non-aqueous electrolyte solution such as acetonitrile containing 0.1 M tetraalkylammonium salts, yields dinitrogen gas and an aryl radical intermediate. The electrogenerated aryl radical can then covalently bond to the surface of the carbon electrode substrate.[14–27] Successful modifications have been performed at electrodes made of carbon fibre or powder,[3,19] edge plane and basal plane highly ordered pyrolytic graphite (eppg and bppg respectively),[3,14,20,21,24] screen-printed graphite electrodes,[28] and glassy carbon.[29]

However the principal drawback of using the electrochemical derivatisation method is that each electrode surface has to be individually modified, especially if the electrode surface is renewed by polishing between successive experiments. Therefore, alternative methods producing modified carbon materials in bulk quantities have been sought. Carbon surfaces, specially, carbon nanotubes can be modified in bulk quantities with aryldiazonium salts through thermolysis or photolysis. Bahr and Tour investigated the degree of functionalisation of carbon nanotubes via thermolysis of diazonium salts of five different para-substituted phenyl species and compared this to the degree of functionalisation obtained using direct electrochemical reduction. They found that heating at 60°C for 12 h produces a similar degree of functionalisation.[7] Li *et al*. developed another method for derivatising self-assembled films of carbon nanotubes using arydiazonium salts.[10] The ends of the carbon nanotubes were first opened oxidatively which is known to functionalise the ends of the tubes with carboxylic acid groups. These groups could then interact with the aryldiazonium modifying species through Coulombic interactions. These modified carbon nanotube films were found to be photosensitive such that photolysis and subsequent decomposition of the aryldiazonium group lead to covalent bond formation.[8] Belmont has also developed a method for the attachment of organic groups with carbon powders by dispersing them in water and mixing with 4-chlorobenzenediazonium hexafluorophosphate.[30]

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Recently a method of covalently derivatising graphite, carbon nanotubes and glassy carbon materials in bulk (gram) quantities has been developed in this laboratory, involving the chemical, as opposed to electrochemical, reduction of aryldiazonium salts with aqueous hypophosphorous acid as the reducing agent.[5,6,11–13,31]

Despite this method proving very successful in forming a variety of novel chemically modified materials for possible use in applications ranging from drug delivery,[32] water purification[33–35] and the development of improved pH sensors in particular,[13,31,36] the method has not been optimised. Furthermore the mechanism of covalent modification, that is whether radical or cationic intermediates are involved and to what type of sites on the carbon surface these intermediates react with, remains unclear.

In this report we have derivatised graphite powder and glassy carbon powder with two aryldiazonium salts, namely 4-nitrobenzenediazonium tetrafluoroborate and 1-anthraquinonediazonium chloride both in the presence of the hypophosphorous acid reducing agent and simply in pure water (i.e. with no hypophosphorous acid reducing agent). The derivatisation was also studied in each case over a range of different temperatures from 5 to 70°C. Each modified carbon material is then abrasively immobilised onto a bppg electrode and characterized using cyclic voltammetry.[5,6,11–13,31]

The observed peak potentials for both the 4-nitrophenyl and 1-anthraquinonyl modified materials were found to differ depending on whether or not the hypophosphorous acid reducing agent was used in the modification or not. Guided by chemical intuition, we speculate that in the absence of any reducing agent the derivatisation mechanism likely proceeds via a cationic intermediate, whilst in the presence of the hypophosphorous acid the mechanism proceeds through either a purely radical intermediate or a mixture of radical and cationic species. Depending on which intermediate the derivatisation proceeds through, the likely points of attachment and chemical structures formed are likely to be different giving rise to slight changes in the observed peak potentials. Therefore these differences in the observed peak potentials were used to explore the effects of varying the hypophosphorous acid concentration and the reaction temperature on the derivatisation mechanism. Furthermore a comparison between derivatised graphite and glassy carbon powders was made to try to further elucidate the likely attachment points of the aryl radicals and cations on each surface. Finally the optimum reaction conditions were determined to ensure maximum derivatisation of both types of carbon surface.

EXPERIMENTAL SECTION

Reagents and equipment

All reagents were obtained from Aldrich (Gillingham, UK) with the exception of glassy carbon powder (10–20 micrometres, spherical particles, type 1, Alfa Aesar, Heysham, UK) and were of the highest grade available and used without further purification. All solutions and subsequent dilutions were prepared using deionised water from a Millipore (Vivendi, UK) UHQ-grade water system with a resistivity of not less than 18.2 MΩ cm at 25°C. Electrochemical experiments were carried out at room temperature in pH 7 buffer solution (0.05 M Na_2HPO_4 and 0.05 M NaH_2PO_4). The synthetic graphite powder (Aldrich) consisted of irregularly shaped particles that were 2–20 μm in diameter.

Electrochemical measurements were carried out using a computer-controlled potentiostat, μAutolab computer (Eco-Chemie, Utrecht, Netherlands) with a standard three electrode configuration. A basal plane pyrolytic graphite electrode (bppg, 4.9 mm, diameter, Le Carbone Ltd. Sussex, UK) was used as working electrode. The counter electrode was a bright platinum wire, with a saturated calomel reference electrode (Radiometer, Copenhagen, Denmark) completing the circuit. Low temperature experiments were carried out in an ice bath and room temperature or elevated temperature experiments were performed in a double-walled glass cell, of 20 cm^3 volume, which was connected to a heated water bath at the appropriate temperature.

Chemical modification of graphite and glassy carbon powders with aryldiazonium salts

Initially 0.5 g of graphite or glassy carbon powder was mixed with 10 cm^3 of a solution containing either 5 mM 4-nitrobenzenediazonium tetrafluoroborate or anthraquinone-1-diazonium chloride, to which 10 cm^3 of hypophosphorous acid (H_3PO_2, 50% w/w in water) was then added slowly. The derivatisation procedure was repeated on separate samples of carbon powder at different temperatures over the range of 5–70°C with the reaction mixture stirred for 30 min at each temperature studied. After which time the solution was filtered by water suction and washed with deionised water to remove any excess acid and finally with acetonitrile to remove any unreacted diazonium salt. The carbon powders derivatised with 4-nitrophenyl (NP-carbon and NP-GC for the derivatised graphite and glassy carbon powders respectivley) and 1-anthraquinonyl groups (AQ-carbon and AQ-GC) were then air-dried by placing inside a fume hood for a period of 12 h prior to use. Finally the same procedures were carried out as described above but with the addition of 10 cm^3 of pure water rather than hypophosphorous acid added to the reaction mixture.

Abrasive immobilisation of the modified carbon onto a bppg electrode

A basal plane pyrolytic graphite electrode was modified by renewing the electrode surface with cellotape.[12] This procedure involves polishing the bppg electrode surface on carborundum paper, pressing cellotape onto bppg electrode surface and then gently removing the cellotape, along with several surface layers of graphite.[12] This was repeated several times to achieve the final surface. Finally the electrode is rinsed in acetone to remove any adhesive from the cellotape. Graphite or glassy carbon powder was abrasively immobilised onto the bppg electrode by gently rubbing the electrode surface onto a fine quality filter paper containing the 4-nitrophenyl or 1-anthraquinonyl derivatised carbon powder.

RESULTS

Voltammetric characterisation

Cyclic voltammetry of the carbon particles was carried out by immobilising the particles on a bppg electrode and recording the cyclic voltammetric response at pH 7 (phosphate buffer). For the

NP-carbon derivatised using hypophosphorous acid at 20°C, upon first scanning in a reductive direction, a large reduction wave is observed at *ca* −0.72 V *versus* SCE labelled as 'system 1' in Figure 1a. If the scan direction is then reversed at −1.0 V *versus* SCE no corresponding oxidation wave for system 1 is observed indicating that it is chemically irreversible. However, a new oxidation wave is observed at −0.05 V *versus* SCE. On subsequent scans, the corresponding reduction wave is observed at −0.13 V *versus* SCE corresponding to an electrochemically quasireversible process, labelled 'system 2'. 'Scheme 1' illustrates this behaviour for the generic example of nitrobenzene itself.[5,37] In this mechanism 'system 1' corresponds to the chemically and electrochemically irreversible reduction of the nitro group in a four-electron, four-proton process to form the corresponding arylhydroxylamine. This then undergoes an electrochemically almost-reversible two-electron, two-proton oxidation (system 2) to form the arylnitroso species. If the potential is only cycled around the region of the 'Scheme 2' then a stable voltammetric response is observed. Therefore after the initial scan beyond the 'Scheme 1' is performed to generate the arylnitroso/aryhydroxylamine couple all further scans are only performed over 'Scheme 2' between 0.4 and −0.5 V *versus* SCE.

Cyclic voltammetry on 'system 2' was carried out with many repeat scans on the abrasively immobilised NP-carbon, a stable response was observed indicating that the species is not desorbing into solution. This was then followed by replacing the buffer with fresh solution and recording a scan, which was found to overlay the last scan indicating that the redox material remains on the electrode surface and is not present in the background electrolyte. Also the scan rate was varied and a plot of peak current against scan rate confirmed that the nitrophenyl species were confined to the surface of the graphite particles.

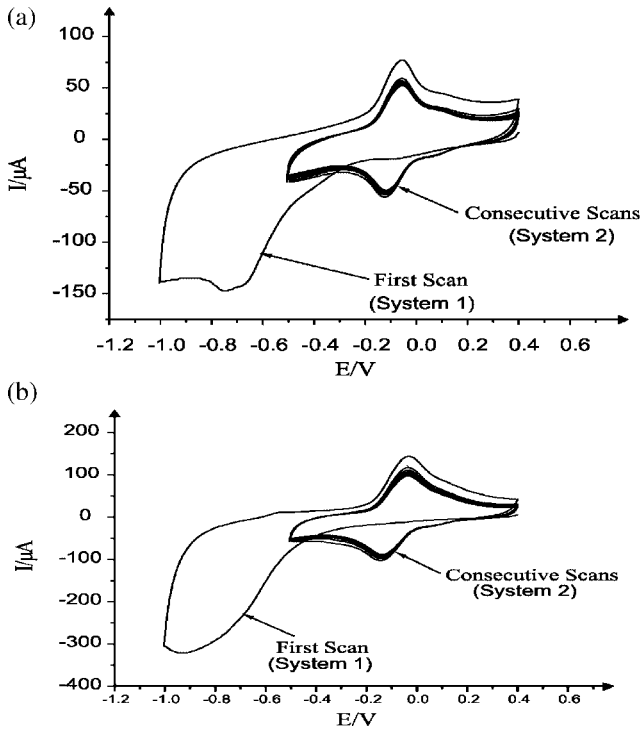
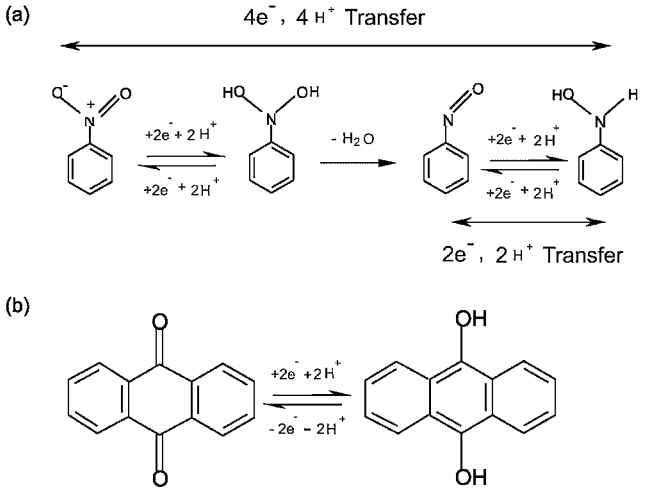


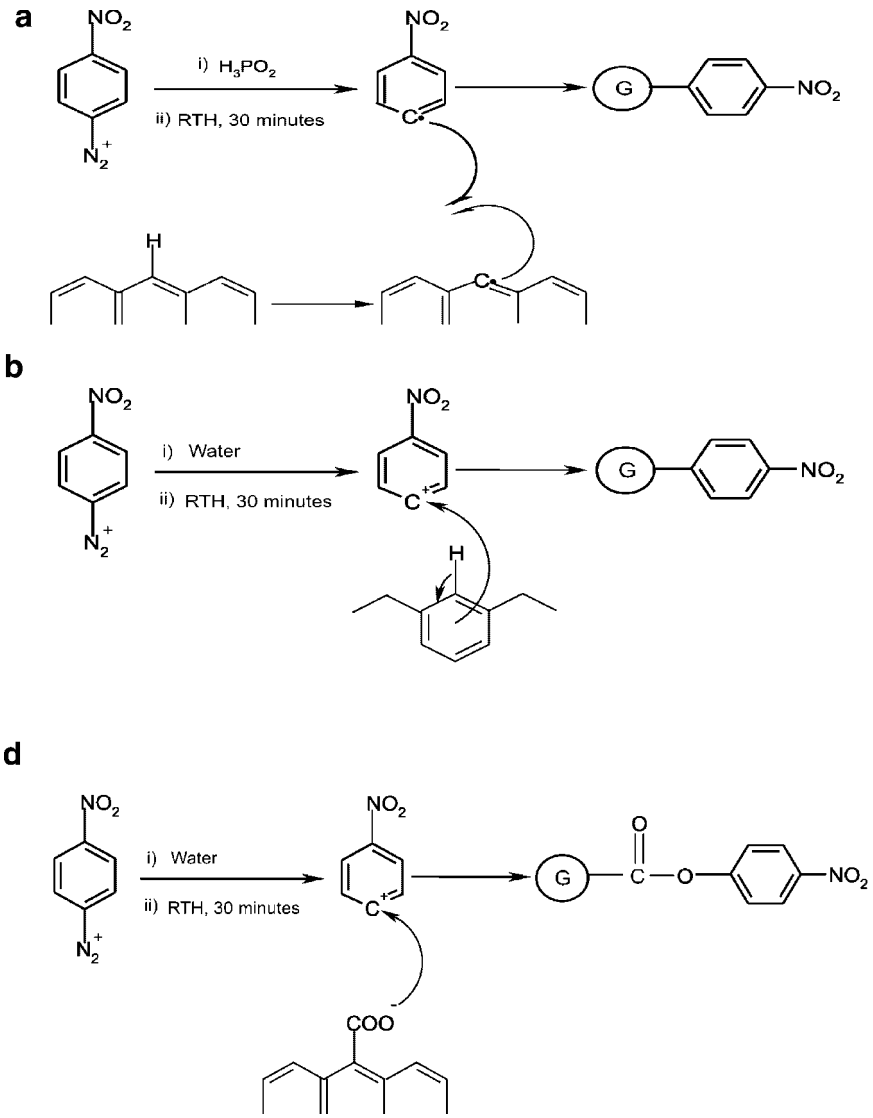
Figure 1. Ten consecutive voltammograms of NP-carbon derivatised (a) in the presence of hypophosphorous acid and (b) in the absence of hypophosphorous acid at 20°C



Scheme 1. The general mechanism for the electrochemical reduction of (a) an aryl-nitro group illustrated by nitrobenzene and (b) anthraquinonne in aqueous solution

Cyclic voltammetry was carried out for the NP-carbon, derivatised in the absence of hypophosphorous acid at 20°C as described above (Figure 1b). In this case the reduction peak of 'system 1' was found to shift to more negative potentials by 0.22 V from −0.72 to −0.94 V *versus* SCE. The peak potentials of system 2 were found to be almost identical in either case. A simple calculation using the peak area of 'system 2' of the NP-carbon derivatised with and without hypophosphorous acid indicates that the surface coverage of NP-carbon in the absence of hypophosphorous acid is more than three times that when hypophosphorous acid is used. The voltammetric characterisations of NP-GC powder derivatised with and without hypophosphorous were also performed. The voltammetry is almost identical in terms of both the observed peak potentials and the shift in peak potential depending on how the material was derivatised. However the peak areas of both systems 1 and 2, and hence the surface coverage of nitrophenyl groups are very much smaller in the case of the derivatised GC powders than the graphite powders.

The characterisation of AQ-carbon particles was carried out by immobilizing the particles on a bppg electrode and recording the cyclic voltammetric response in pH 7 buffer solutions. In the case of AQ-carbon particles derivatised using hypophosphorous acid at 20°C a reduction peak and the corresponding oxidation peak were observed at −0.58 V and −0.51 V respectively (Figure 2a) in a two electron, two-proton almost-reversible redox process (Scheme 1b). The cyclic voltammograms recorded using AQ-graphite particles derivatised without hypophosphorous acid are shown in Figure 2b. Again the reduction and oxidation peaks were observed at −0.58 V and −0.51 V, respectively. However an additional reduction and oxidation peak could be observed at −0.66 V and −0.62 V, respectively. Due to the small difference in peak potential the two waves could not be fully deconvoluted and appear as shoulders on the main voltammetric signal. The cyclic voltammograms recorded for AQ-GC powders made with and without hypophosphorous acid. The voltammetry is again



Scheme 2. Mechanistic illustration for the derivatisation of NP-carbon through (a) radical; (b) and (c) cationic intermediates. Note that in addition to radical–radical coupling, radical–aromatic coupling also may occur directly

almost identical to that observed at the derivatised graphite powders except that the surface coverage on the GC powder is lower than on the graphite powder.

The possible origins of the shifts in peak potentials of the NP-derivatised carbon powders and the appearance of additional peaks in the anthraquinone derivatised carbon powders is discussed in section 'Discussion' below.

The effect of varying hypophosphorous acid concentration

To investigate the effect of varying the concentration of hypophosphorous acid used in the modification of carbon surfaces using diazonium salts, a series of NP-carbon derivatisations were carried out at 20°C with the concentration of hypophosphorous acid added varying from 5 to 0.0001 M. The overlaid first scans of NP-carbon derivatised using different concentrations of hypophosphorous acid are shown in Figure 3. As the concentration of hypophosphorous acid decreases, the peak potential of system 1 gradually shifts from −0.7 V (5 M H_3PO_2) to −0.92 V (0.0001 M H_3PO_2) whilst the peak current gradually increases.

The effect of varying the temperature of the derivatisation reaction

Figure 4a and b show the first scan of NP-carbon, derivatised with and without hypophosphorous acid respectively, where the derivatisation was performed at a range of temperatures from 5 to 70°C, whilst Figure 4c and d show the similar behaviour of the NP-GC powders. Note that the voltammetry was always performed at room temperature.

In the case of NP-carbon derivatised using hypophosphorous acid as the reducing agent, a single broad reduction peak is observed when the derivatisation is carried out at low temperatures. As the reaction temperature increases up to 20°C, the peak becomes larger and a shoulder appears at slightly

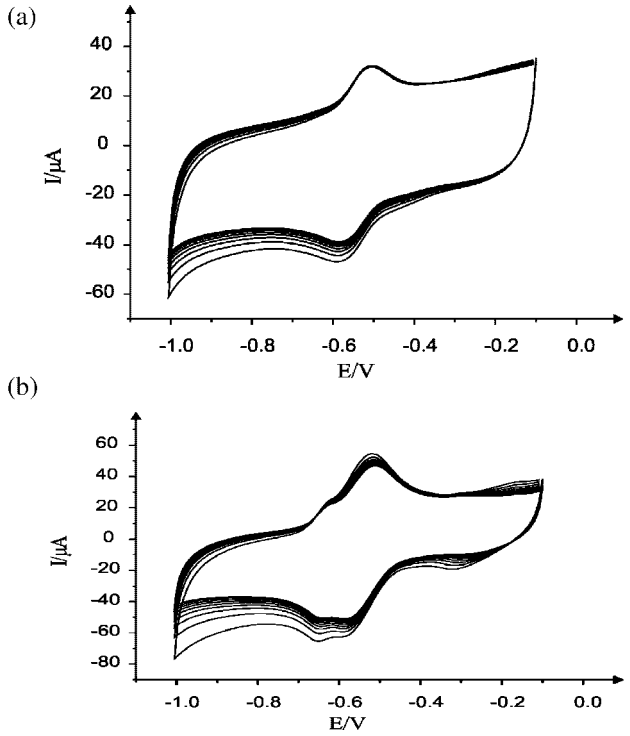


Figure 2. Ten consecutive voltammograms of AQ-carbon derivatised (a) in the presence of hypophosphorous acid and (b) in the absence of hypophosphorous acid at 20°C

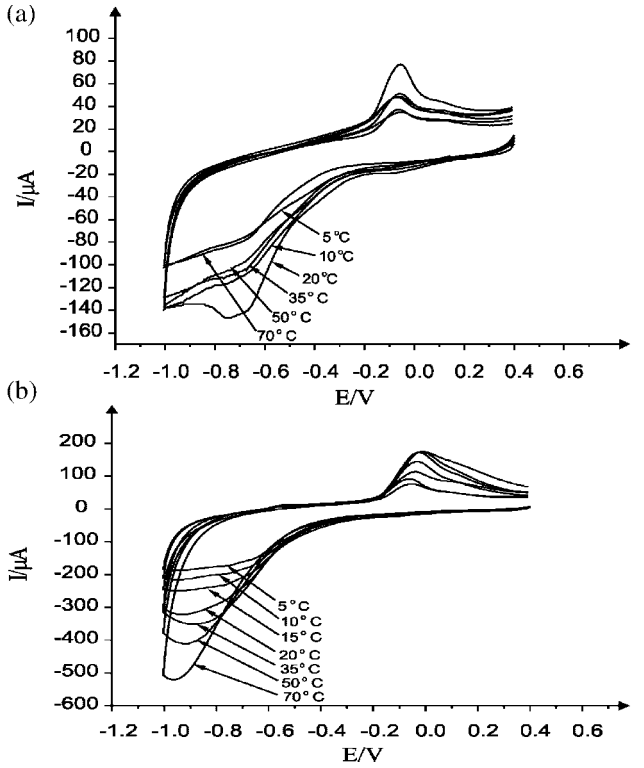


Figure 4. Overlaid first scan voltammograms of NP-carbon derivatised (a) in the presence of hypophosphorous acid and (b) in the absence of hypophosphorous acid at different temperatures

more negative potentials than the main reduction peak. Above 20°C the peak current again decreases, the peak broadens but the potential shifts to more slightly more negative potentials. In contrast, when NP-carbon is made in the absence of hypophosphorous acid the peak current increases with increasing temperature and the peak becomes narrower and more defined (at low temperatures the peak is rather broad and ill-defined) such that at higher temperatures the peak area (and hence the surface coverage of nitrophenyl groups) remains almost constant. The peak potential is more negative than when the NP-carbon is made using hypophosphorous acid. The broad peaks at low temperatures likely reflect the fact that the reduction process involves a complex series of heterogeneous electron transfer coupled with homogeneous chemistry (concomitant protonation). Similar behaviour is observed at the NP-GC powders as the NP-carbon powders but again with a reduced surface coverage.

The surface coverage of nitrophenyl groups on the graphite surface was calculated using the peak area for the NP-carbon made with and without the hypophosphorous acid and is plotted as a function of the reaction temperature in Figure 5. In the absence of any hypophosphorous acid the surface coverage

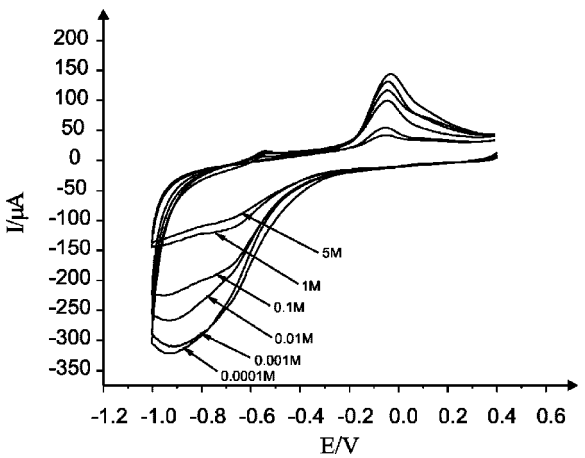


Figure 3. Overlaid voltammograms of NP-carbon, derivatised using different concentrations of hypophosphorous acid

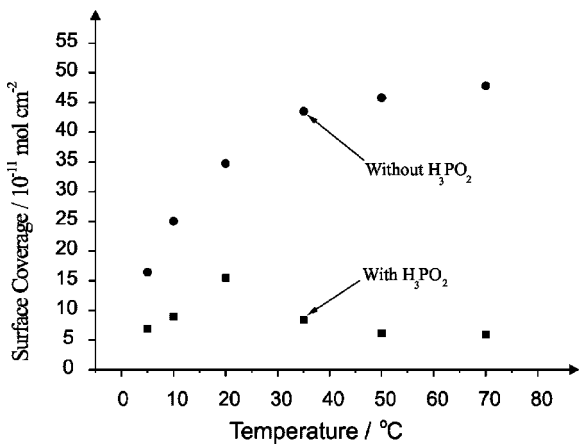


Figure 5. Surface coverages of NP-carbon derivatised in the presence and absence of hypophosphorous acid at different temperatures

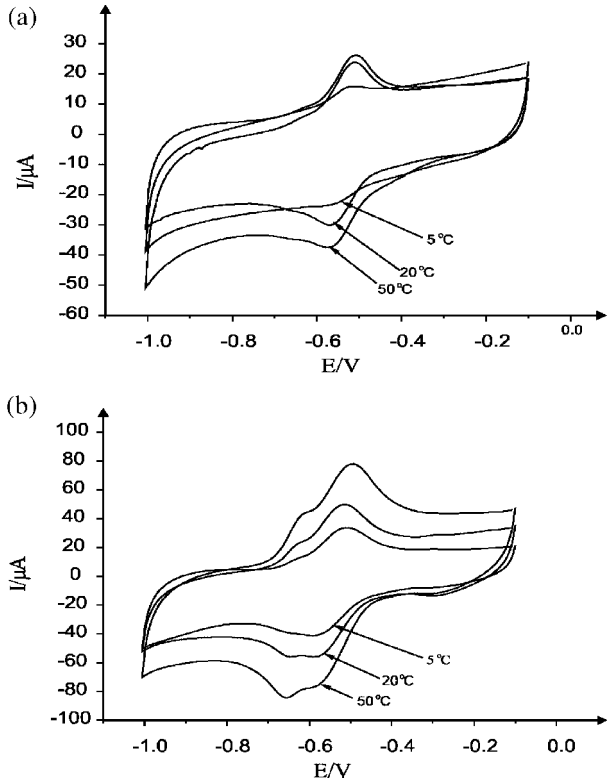


Figure 6. Overlaid first scan voltammograms of AQ-carbon derivatised (a) in the presence of hypophosphorous acid and (b) in the absence of hypophosphorous acid at different temperatures

gradually increases as the reaction temperature increases up to *ca* 35°C, after which the surface coverage remains almost constant. However in the presence of hypophosphorous acid the surface coverage passes through a maximum at *ca* 20°C likely reflecting competing mechanistic processes (see section 'Discussion'). We note from the work of Downard *et al.*[38] that the accurate electrochemical determination of the surface groups can be misleading and that not all nitro groups within a polymer layer may be electroactive. However what we do see clearly from Figure 5 is a significant difference in the electroactive surface coverage of the aromatic nitro groups.

Finally the derivatisation reaction was studied for AQ-graphite and AQ-GC over a range of different temperatures from 5–50°C again with and without the reducing agent. Figure 6 shows the corresponding overlaid cyclic voltammograms. When hypophosphorous acid is used as the reducing agent only a single voltammetric peak is observed for both the AQ-carbon and AQ-GC and the surface coverage found to limit above *ca* 20°C whereas in the absence of any reducing a new oxidation and reduction peak is observed at slightly more negative potentials that becomes more pronounced as the temperature increases. Again, for both the AQ-carbon and AQ-GC the surface coverage of anthraquinonyl groups is always greater when no hypophosphorous acid is used and when the reaction is carried out at higher temperatures.

Discussion

In the absence of any reducing agent the most likely decomposition pathway for an aryldiazonium salt is the entropically favoured loss of dinitrogen resulting in an aryl cation intermediate being formed. In the presence of a mild reducing agent such as hypophosphorous acid there are two possible decomposition pathways, one via the cation intermediate and the other involving the one electron reduction of the aryldiazonium species, again liberating dinitrogen gas, and forming an aryl radical intermediate.

Any aryl radicals formed by the action of the hypophosphorous acid reducing agent can form a carbon–carbon bond with the H-terminated graphitic carbon surface via a hydrogen abstraction mechanism as shown in Scheme 2a.[34] Whereas the same product can also be formed via the electrophilic addition (and subsequent loss of H^+) of an aryl cation to the graphitic surface as shown in Scheme 2b.[39,40] As the same product is formed with either intermediate then the product can be reduced at the same potential and it is this structure that is likely responsible for the voltammetric features observed at slightly more positive potentials in system 1 in the case of NP-carbon or NP-GC and in the voltammetry of AQ-carbon or AQ-GC.

There is an alternative reaction that the aryl cation intermediate can undergo which the aryl radical intermediate is unlikely to undergo. This is the reaction with surface carboxyl groups, which are known to decorate the edge-plane defects at the ends of the graphite sheets in graphite powder and the edges of the graphitic ribbon structure of GC powder, [41,42] to form arylester products as shown in Scheme 2c.[43] In a previous report we have demonstrated that the reduction potential of 4-nitrophenyl groups attached to a carbon surface via the formation of an ester linkage is shifted slightly to more negative potentials than if the 4-nitrophenyl groups are directly attached through a carbon–carbon bond.[34,44] Therefore we speculate that as the peaks at more negative potentials for both NP- and AQ-modified carbon powders are only observed when the hypophosphorous acid reducing agent is not used, then the modification mechanism must go through an aryl cationic intermediate and these peaks are attributed to the modification of the carbon surface through the formation of an aryl ester.

Such a mechanistic rationale as that proposed above explains the observed voltammetric response when the concentration of hypophosphorous acid is varied as shown in Figure 3. At high concentrations of hypophosphorous acid and at modest temperatures the modification mechanism proceeds predominantly through a radical intermediate. As the concentration of hypophosphorous acid decreases the mechanism increasingly proceeds through two competing pathways, one via the aryl radical intermediate, the other via the cationic intermediate. Both radical and cation can form the same C—C bonded product observed as the peak at more positive potentials, but in addition the cationic mechanism also allows the formation of 4-nitrophenylester groups via attack at surface carboxyl group sites. The surface coverage of nitrophenyl groups thus increases, the peak gets larger and broadens due to the convoluted contribution of the 4-nitrophenylester groups to the reduction peak at a slightly more negative potential.

If the mechanism proceeds via the cationic intermediate (i.e. without H_3PO_2) the surface coverage increase with increasing temperature up to *ca* 35°C after which the surface coverage remains almost constant. We speculate that this likely reflects either an increase in the rate of decomposition of the nitrobenzenediazonium salt forming the cation intermediate or the rate of electrophilic attack of the carbon surface by the cation intermediate. In the former case the overall yield (as measured by the surface coverage) of the derivatisation is limited by the rate of

competing reactions such as solvolysis such that the number of reactive intermediates in the vicinity of the carbon surface that can undergo reaction reaches steady state. In the latter case the surface coverage may be limited by the number of available sites of attack on the carbon surface.

In the presence of hypophosphorous acid the surface coverage passes through a maximum at *ca* 20°C probably due to the increasing rate of competing side reactions such as hydrogen abstraction by the aryl radical intermediate from the solvent.

CONCLUSION

The mechanism of covalent modification of graphitic carbon surfaces has been studied using 4-nitrobenzenediazonium and 1-anthraquinonediazonium salts in aqueous media. Depending on whether hypophosphorous acid is used as a reducing agent or not the mechanism is thought to proceed through either a radical intermediate or a cationic intermediate. Both mechanistic pathways can result in the formation of a C—C bond to the graphite surface, but in the case of the cationic intermediate a further product can be formed by reaction of the aryl cation intermediate with surface carboxyl groups to form an ester linkage to the modifying molecule. The covalent attachment of the modifier to the carbon surface via an ester linkage alters the peak potentials observed in the cyclic voltammetry of these materials, shifting them to more negative potentials.

The derivatisation procedure has been optimised by studying the effect of temperature and concentration of H_3PO_2. It is found that using hypophosphorous the optimum temperature to achieve the maximum surface coverage is 20°C. Higher surface coverage are always obtained in the absence of any added hypophosphorous acid with the optimum derivatisation temperature being in excess of 35°C. However this results in the modifying species attaching to various different reactive sites on the carbon surface leading to multiple closely separated peaks and shoulders being observed in the cyclic voltammetric response of such materials. In the presence of hypophosphorous acid only one single set of peaks is observed which is advantageous for electroanalytical applications of the modified carbon electrodes, for example the voltammetric measurements of pH using AQ-carbon which rely on accurately measuring changes in the observed voltammetric peak potential.[13,36]

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