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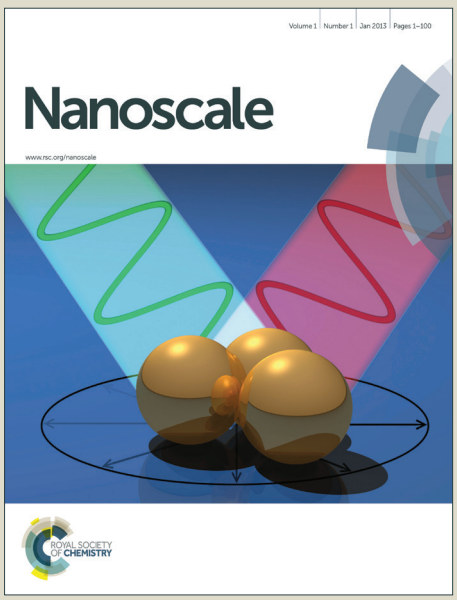

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Bifunctional redox tagging of carbon nanoparticles

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KEYWORDS

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ABSTRACT

Despite extensive work on the controlled surface modification of carbon with redox moieties, to date almost all available methodologies involve complex chemistry and are prone to the formation of polymerized multi-layer surface structures. Herein, the facile bifunctional redox tagging of carbon nanoparticles (diameter 27 nm) and its characterization is under taken using the industrial dye Reactive Blue 2. The modification route is demonstrated to be via exceptionally strong physisorption. The modified carbon is found to exhibit both well-defined oxidative and reductive voltammetric redox features which are quantitatively interpreted. The method provides a generic approach to monolayer modifications of carbon and carbon nanoparticle surfaces.

INTRODUCTION

Carbon materials have widespread applications in modern technologies. This is not only due to their high natural abundance, low cost, adjustable size, shape and porosity, but also due to the fact that a variety of different surface functionalities can be introduced. Due to the diverse structural morphologies and its inherent conductivity nanoparticulate carbon,[1] in particular, is used extensively within the field of electrochemistry, for both energy applications[2] and electrochemical sensors.[3-6] Recent work has also demonstrated how related graphene materials may be used directly as DNA labels.[7] Beyond electrochemistry one of the major uses of carbon nanomaterials is as a general adsorbent for the removal of organic species from waste streams.[8,9] Nano-graphite lends itself well for this application due to its large surface area and ability to form strong pi-pi bonds. Apart from the aromatic 'basal' plane character of the nano-graphite, the structure also possesses numerous 'edge' sites. These edge sites are heavily oxygen functionalized.[10-12] In the case of graphene oxide materials this chemical functionalization can lead to significant inherent electroactivity.[13] However, in this work the variety of surface environments will be employed to combine both of the mentioned main applications of carbon nanoparticles; it will be used as an adsorber for redox moieties and subsequently employed in electrochemical studies.

Within the literature, numerous reports focus on routes by which carbon materials are surface modified with redox active species to create selective sensors or designer electrode materials for energy transformation goals.[14-16] Of the available methods the overwhelmingly dominant strategy employed utilizes diazonium salts as reactive precursors for surface binding.[14] However, such a methodology is hindered by polymerization and subsequent multi-layer formation; controlled authentic monolayer formation is difficult.[17] Multi-layer formation, although allowing high surface loadings, commonly results in non-ideal and distorted voltammetric responses and thus limits the applicability of modified carbon materials in the above-mentioned applications. Hence, recent work has focused on relatively elaborate methods by which single monolayer or sub-monolayer coverages may be enabled via use of diazonium salt chemistry.[17-19] Alternatively, electrochemical radical formation from the cleavage of carbon-halogen bonds represents another more industrially applicable modification stratedgy.[20-22] Hitherto, exclusively *covalent* attachment strategies have been adopted to tag/functionalize carbon materials with redox-active

species; in this paper we report the use of very strong physisorption to ensure exclusive monolayer formation. Utilizing the well-known observation of strong physisorption on carbon surfaces, this approach opens up a simple *generic* route towards redox-actively modified carbon materials. In the following we present a simple molecular species which shows both reductive and oxidative electrochemistry

Of the redox active groups chosen for carbon surface attachment, quinones and their numerous derivatives have been the focus of extensive attention, finding much use in oxygen reduction catalysts,[23,24] DNA detection,[25] carbon surface characterization[26,27] and pH measurement,[28] among many other applications. Quinones also find use within the textile industry as a chromophore present in many dyes. A number of (reactive) dyes are available which have been designed for the purpose of being able to undergo covalent chemical binding. These dyes contain both a chromophore and at least one reactive substituent commonly able to undergo nucleophilic substitution to form a chemical bond with a carbon based substrate (for instance cellulose).[29]

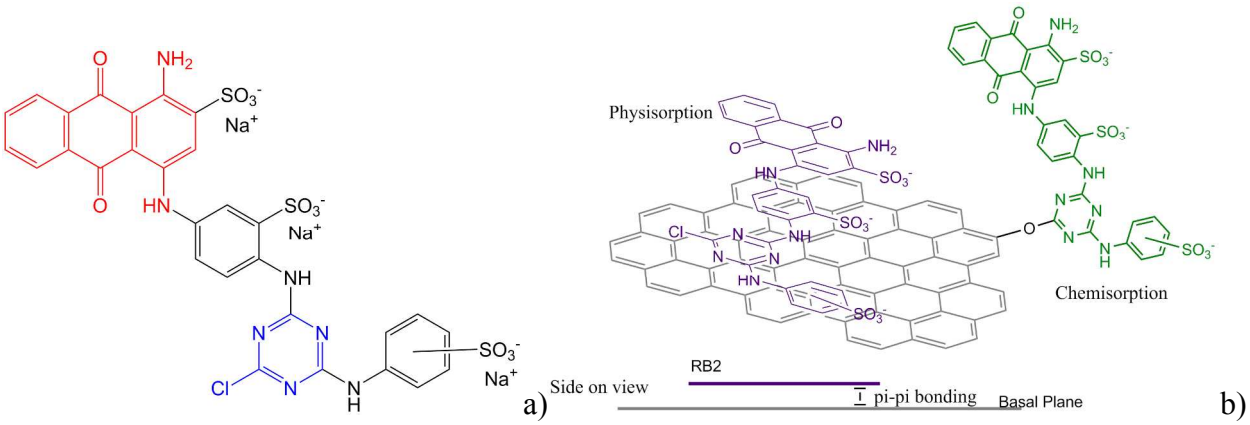


Figure 1: a) Chemical structure of the dye 'Reactive Blue 2'; the redox active substructure 1,4-diaminoanthraquinone is highlighted in red and the reactive mono-chlorotriazine moiety is highlighted in blue. B) schemeatic showing the plausible binding routes for the RB2, via chemi- (green) or physisorption (purple).

Below we report the use of the reactive dye, Reactive Blue 2 (RB2), shown in Figure 1, for carbon nanoparticle modification. The chromophore of RB2 is a 1,4-diaminoanthraquinone derivative linked to a mono-chlorotriazine. Hence, modification of carbon nanoparticles with RB2 might in principle be achieved via two distinct binding routes, namely physi- or chemi-sorption. The work herein demonstrates, perhaps surprisingly, the physisorption pathway to be the dominant modification pathway, even under conditions which relatively favour covalent fixation, so ensuring monolayer coverage, at maximum loading. Furthermore, the resulting well

defined voltammetric behavior of the surface bound RB2 is evidenced. Importantly, the 1,4-diaminoanthraquinone has bi-redox-functionality, such that it exhibits an additional and clearly defined oxidative feature related to the oxidation of the 1,4-diamino-benzene moiety in the molecule.[30] Due to the modification not involving covalent binding, the reaction route is beneficially limited to sub-monolayer coverage, ensuring a non-distorted voltammetric response of the immobilised redox species. The use of strong physisorption for the modification of carbon nanomaterials is evidenced as a powerful and general yet unexplored route for carbon nanoparticle redox tagging, avoiding many of the problems and pitfalls associated with other modification procedures.

EXPERIMENTAL

Chemicals and reagents

All voltammetric experiments were carried out in a 0.1 M phosphate buffer solution (containing 0.1 M potassium chloride) at pH = 6.8. All reagents are provided by Sigma-Aldrich in reagent grade unless otherwise stated. Reactive Blue 2 (RB2) (60% dye content), was used to modify the nanoparticle surface in order to observe any significant electrochemical response. Sodium sulphate (Na_2SO_4) was added in two modification experiments, as described below. Sodium carbonate (Na_2CO_3) was added as a base to minimize possible hydrolysis of RB2. A modification experiment using anthraquinone-2-sulphonic acid (AQMS) was done for comparison. All reagents were used without further purification. All solutions were prepared with deionised water of resistivity not less than 18.2MΩcm at 298K (Millipore, Billerica, MA). All electrolytes were degassed with pure nitrogen gas.

Electrochemical Procedures

Voltammetric experiments were done with a glassy carbon working electrode (GC, BAS Technicol, USA, diameter 3mm). The GC electrode was polished using successive grades of diamond lapping spray (Reishauser Diamond Spray SW300, 100, 50) from 3 μm to 0.5 μm particle size. The electrode was then rinsed with deionised water and dried by blowing the surface with a jet of pure nitrogen gas. Potential control was achieved using a computer

controlled μAUTOLAB-Type III potentiostat (Autolab, Metrohm Autolab, Utrecht, The Netherlands). Due to the use of staircase voltammetry the sample point (alpha value) was selected to be 0.3 so as to approximate true linear sweep voltammetry.[31] All experiments are done with a Standard Calomel Electrode (SCE) as the reference electrode and a platinum gauze as the counter electrode. Drop casts were done using micropipettes in two steps, one drop of 2 μL and one of 3 μL.

Modification of carbon nanoparticles

Batch 0 modification: 0.50 g of carbon nanoparticle was added into a round bottom flask with a magnetic stirrer. 50 mL of 0.01 M NaOH was added into the flask. With stirring (500rpm) slowly added 10mL of the 0.46mM RB2 dye solution. The suspension was heated with stirring up to 60^{o}C for 1 h. The suspension was then suction filtered using a sintered funnel. The filtered solids were then washed with 100 mL 60^{o}C deionized water or until filtrate is no longer coloured. With the vacuum still on, the powder is further washed with 200 mL of acetone. The solids were then dried in room temperature for 12 h, inside a dessicator in vacuum prior to use.

Batch I modification: 0.50 g of carbon nanoparticle (CB, diameter 27 nm, Cabot, Monarch® 480) was added into a round bottom flask, to which 50 mL of deionised water was added. 10 mL 3.02 mM RB2 aqueous solution we also added into the flask and the mixture was heated to 80^{o}C in a water bath with stirring (500 rpm). The mixture was heated for 35 min. Within the 35 min, 10.9 g sodium sulphate was slowly added into the mixture. After 35 min, 30 mg of sodium carbonate was added into the mixture and the mixture was heated, with stirring, to 80^{o}C for 1 h. After the one hour, the mixture was removed from heat and quickly transferred into four 15 mL centrifuge tubes. The solids were then worked up. The tubes were placed inside a centrifuge (Eppendorf Centrifuge 5702) and processed for 4 min in 4400 rpm. The liquids were poured out and the solids were rinsed 3 times using 15 mL deionised water for each tube, using the centrifuge for separation. Each time a small spatula was used to stir up the solids for through rinsing. Then the solids were rinsed using acetone (Sigma-Aldrich) for 2 times, 15 mL for each tube, or until solution no longer appears blue. Each rinsing required stirring of the solids before

reentering the centrifuge. After pouring out the liquid, the solids were dried for a period of 12 h inside the tubes using a desiccator in vacuum prior to use.

Batch II modification: same procedures as Batch I without the addition of sodium sulphate.

Batch III modification: same procedures as Batch I without the addition of both sodium carbonate and sodium sulphate.

AQMS modification: 0.50 g CB was placed inside a round bottom flask. 15 ml of 13.6 mM of aqueous AQMS solution was added into the flask at room temperature. The mixture was then stirred (550 rpm) for 30 min. The working up procedures of rinsing with water and acetone were completely analogous to those of Batches I, II and III.

Nanoparticle Characterzation

SEM analysis of carbon nanoparticles: The size of the purchased nominally 27 nm (in diameter) sized carbon nanoparticles was confirmed by field-emission scanning electron microscopy (SEM, LEO Gemini 1530, Zeiss). The carbon powder was immobilized on a SEM sample holder using adhesive carbon tape. To reduce electrical charging during the measurement, a thin layer of gold was sputtered (Cressington sputter coater 108 auto) on top of the sample. The SEM images shown in Figure 2a, were obtained using an in-lens detector and a beam voltage of 5 kV.

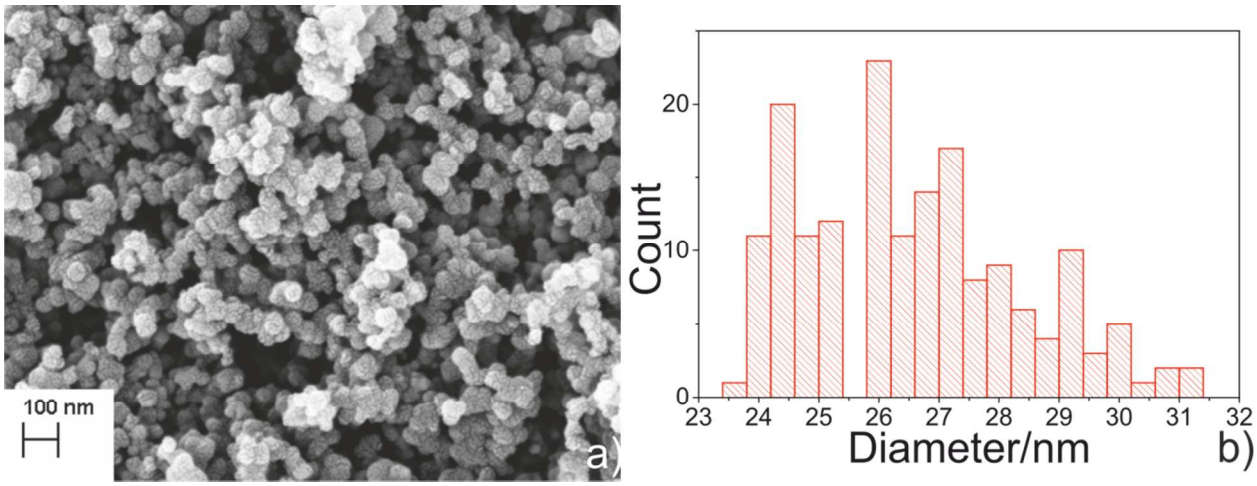


Figure 2: a) SEM image of the unmodified commercial 27 nm sized carbon material used in this study and b) depicts the measured size distribution (mean = 26.7, standard deviation = 2.3nm)

Using the software ImageJ, the SEM image is analysed to elucidate the size distribution of the carbon nanoparticles, shown in Figure 2 b). The carbon nanoparticles have a mean diameter of 26.7 nm and a standard distribution of 2.3 nm. The values of diameter range from 24 nm to 35 nm. This is in good agreement with the nominal diameter of 27 nm listed by Cabot and characterization done by Lowinsohn et al.[32]

XPS analysis of modified and unmodified carbon nanoparticles: To evidence the successful modification of the used carbon nanoparticles, an unmodified carbon nanoparticles sample, a sample of RB2 modified carbon nanoparticles ("Batch I" modification procedure) and a sample of the AQMS modified carbon nanoparticles were analysed using X-ray Photoelectron Spectroscopy (XPS). Spectra were measured on a Thermo Scientific K alpha utilizing monochromated Al k-α radiation. Spectra were charge corrected by shifting the C1s peak to 285.0 eV.

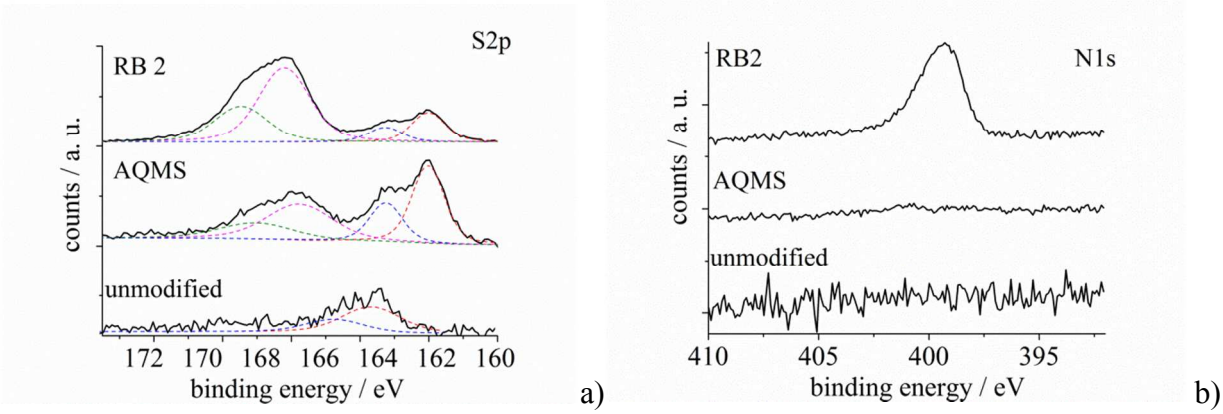


Figure 3: a) Shows S 2p XPS spectra for unmodified carbon nanoparticles and particles modified with RB2 and AQMS dyes. All samples, including the unmodified sample, show a small amount (0.3 atomic%) of elemental sulfur. Modified samples show an additional environment around 168 eV. B) depicts the corresponding N 1s peak where a distinct nitrogen signal is recorded in the presence of RB2.

As carbon nanoparticles typically contain a significant amount of oxygen, the sulphur-containing sulphonate group(s) of the RB2 and AQMS molecules were used to testify the successful tagging of the carbon nanoparticles. As shown in Fig. 3a, all three samples, including the unmodified sample, show a small sulphur signal with S $2p_{3/2}$ peak at a binding energy of 164.0 eV. This may correspond to elemental sulphur, or sulphur in a thiol environment. The amount of this sulphur environment in all three samples was constant at around 0.3 atomic%. The modified samples

both showed an additional sulphur signal not present in the starting material. The RB2 and AQMS modified samples showed a S $2p_{3/2}$ peak at 168.0 eV and 167.8 eV respectively. This matches with sulphonate groups in polyvinylsunfonate, reported at 168.0 eV[33] Note that sodium sulphate, used in the preparation of Batch I samples, is reported with S $2p_{3/2}$ binding energy of around 168.8 eV, considerably higher than observed here. Additionally, the RB2 modified carbon nanoparticles showed a N 1s peak that was absent in either of the other samples, assigned to the presence of N-functionalities in the RB2 (Fig 3 b). These results indicate the successful modification of the carbon nanoparticles with the redox dyes.

RESULTS AND DISCUSSION

Reactive Blue 2 is an industrial quinone based dye for cellulose materials, A mono-chlorotriazine group is utilized as a reactive moiety able, under basic and relatively high temperature conditions, to bind to deprotonated hydroxyl groups via nucleophilic substitution. In general for reactive dyes to increase their water solubility they commonly also contain charged substituents; consequently, the dying conditions often use high salt concentrations to ensure the dye molecule is not coulombically repelled from the substrate. Here it will first be demonstrated that Reactive Blue 2 can be used to tag carbon nanoparticles with a redox-active moiety. Second, different modification conditions will be applied to identify whether the modification is due to chemi- or physisorption of the dye molecules and which experimental conditions are required to avoid multi-layer formation/ensure (sub-)monolayer coverage, minimising distortion of the electrochemical response typically observed for multi-layer coverages. Third, a chemically inert redox-active molecule (AQMS) is used to demonstrate the successful modification/redox-tagging of carbon nanoparticles by physical adsorption only.

Redox-activity of Reactive Blue 2 tagged carbon nanoparticles

First, carbon nanoparticles were modified with RB2, via the procedure outlined as “Batch 0 modification” in the experimental section. The reaction suspension was basic and of high ionic strength to promote, so far as possible, the chemical bonding of the molecule to the carbonaceous

surface. After modification, the dried carbon material was subsequently suspended in chloroform and 25 µg of this suspension was drop cast onto the glassy carbon electrode surface. The voltammetric response of the modified carbon was recorded in a 0.1 M phosphate buffer solution (containing 0.1 M KCl) at a scan rate of 100 mV s^{-1}, as depicted in Figure 4. Two well-defined and reversible redox features are observed at ca. -0.7 V (System A: reductive peak, -0.71 V; oxidative peak, -0.68V) and +0.5 V (System B: reductive peak, 0.49V; oxidative peak, 0.55V) vs SCE. In the absence of RB2, i.e. using the un-modified carbon material no voltammetric features were observed. In the absence of RB2, i.e. using the un-modified carbon material no voltammetric features were observed, as depicted in the inlay of Figure 4.

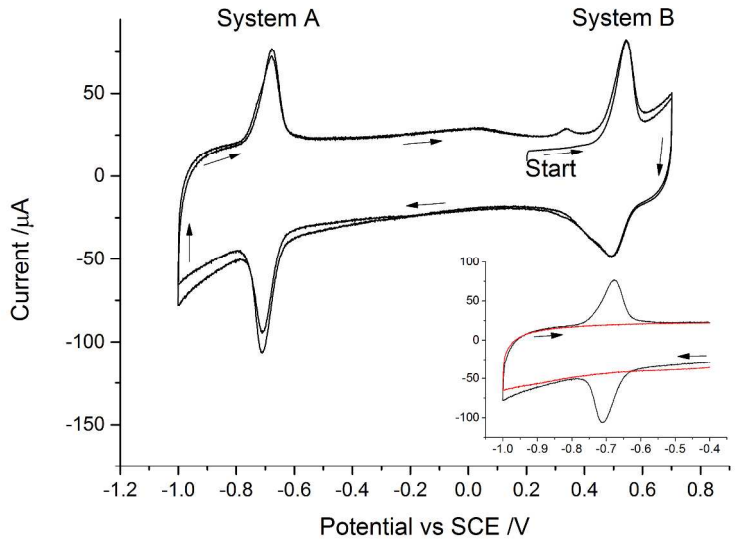


Figure 4: Voltammetric response, first and second scan (100 mV s^{-1}), of a GC electrode drop-cast with 25 ug of RB2-modified carbon nanoparticles showing two characteristic reversible features at +0.5 and -0.7V (vs. SCE). The inlay depicts the reductive voltammetric response of both modified and un-modified carbon nanoparticles.

At suitably cathodic electrode potentials and under buffered conditions quinone functionalities may be readily reduced to the corresponding hydroquinone.[34,35] The reduction is known to be a two-proton, two-electron process (at pHs below the respective pK_as). Consequently, the voltammetric wave at -0.7V vs SCE is taken to be the reduction of the quinone functionality. The recorded waveshape and small peak-to-peak separation (~33mV) indicates that the quinone is

surface bound. The surface bound nature of the quinone may be further evidenced by studying the variation of the peak height as a function of scan rate (see later discussion). From integration of the area under the peak at -0.7 V vs SCE and with use of Faraday's first law (number of electrons n = 2) the surface coverage of the redox active moieties may be assessed. Taking the carbon nanoparticles to have a surface area[36] of 84m^2 g^{-1} and using the known mass of material drop-cast onto the electrode the surface coverage of redox active species is 1.17 ± 0.34 x10^{-7} mol m^{-2}. Hence, for an average carbon particle diameter of 27 nm the average number of redox moieties per nanoparticle is found to be 150 ± 50 molecules per nanoparticle. Taking the geometric area of an RB2 molecule as 228.8 Å^2,[37] a monolayer coverage of the used carbon nanoparticles corresponds to the adsorption of about 1000 RB2 molecules per nanoparticle. Thus, a sub-monolayer coverage of redox active species is achieved, despite the excess of dye molecules during the nanoparticle modification. Among other reasons this sub-monolayer coverage may origin from, the molecular surface area, its attachment methodology/modification conditions or the heterogeneity of the carbon surface. Physical insight into the attachment route will be the focus of work reported later within this article.

Apart from the cathodic signal at -0.7V vs SCE, the anodic response at +0.5 V is of distinct interest. Equal charges are observed for both the peaks at +0.5 and -0.7 V vs SCE; consequently, the oxidative feature at +0.5 V is also ascribed as being related to the bifunctionality of the 1,4-diaminoanthraquinone species. Figure 5 gives the proposed electrochemical reaction mechanism.

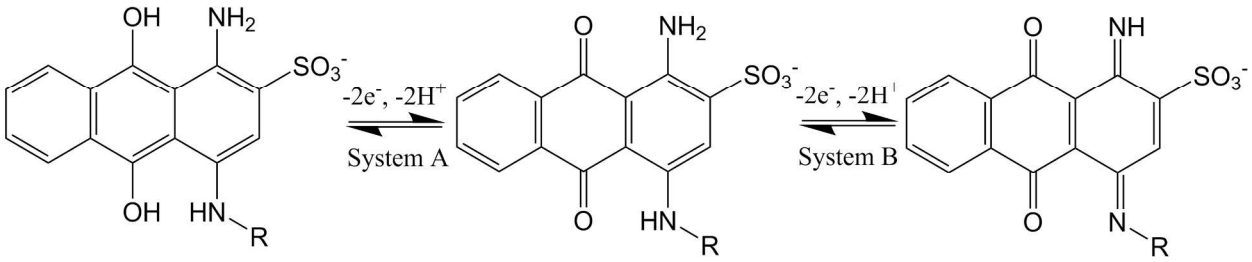


Figure 5: Proposed electrochemical mechanism for the reduction and oxidation of the 1,4-diaminoanthraquinone sub-structure contained within the RB2 dye.

Influence of the modification procedure on the redox-tagging of carbon nanoparticles

To further optimise the surface coverage of the quinone redox moieties and to further elucidate the modification methodology three differing carbon nanoparticle modification synthesis were undertaken. For Batch I the methodology was the similar as that used for Batch 0 but with a higher concentration of RB2 (3.02 mM). Batch II was synthesized in the absence of additional salt and Batch III was synthesised in non-basic conditions. Thus, in contrast to batch 0 and I, batch II and III were prepared under conditions that do not facilitate the covalent modification of carbon nanoparticles with RB2 dye molecules. Finally, a control experiment utilizing anthraquinone-mono-sulphonate (AQMS) as the modifying agent was undertaken (full modification procedures are provided in the experimental). Note AQMS does not contain any reactive moiety consequently it may only physically bind to the carbon surface; covalent modification is impossible under the applied experimental conditions. Figure 6 depicts the reductive voltammetric response, as a function of scan rate, of a glassy carbon electrode drop-cast with 7.55 μg of Batch I carbon nanoparticles. Again a clear reversible surface bound wave is observed at -0.7V vs SCE. The peak current is found to vary linearly as a function of scan rate (not plotted). In accordance with the work of Laviron[38] this result strongly corroborates the conclusion of the 1,4-diaminoanthraqunone being surface bound. For a surface bound voltammetric feature the peak current is known to vary linearly as a function of scan rate- as opposed to varying with the square root of scan rate for a diffusional redox species. This difference in scan rate dependency is commonly taken as a diagnostic of the surface bound or solution phase nature of the redox active species. The inlay of Figure 6 depicts the variation of the peak potential as a function of the decadic logarithm of the scan rate, demonstrating that the surface bound species shows near full reversibility, as evidenced by the small peak-to-peak separation (see inlay of Fig. 6).

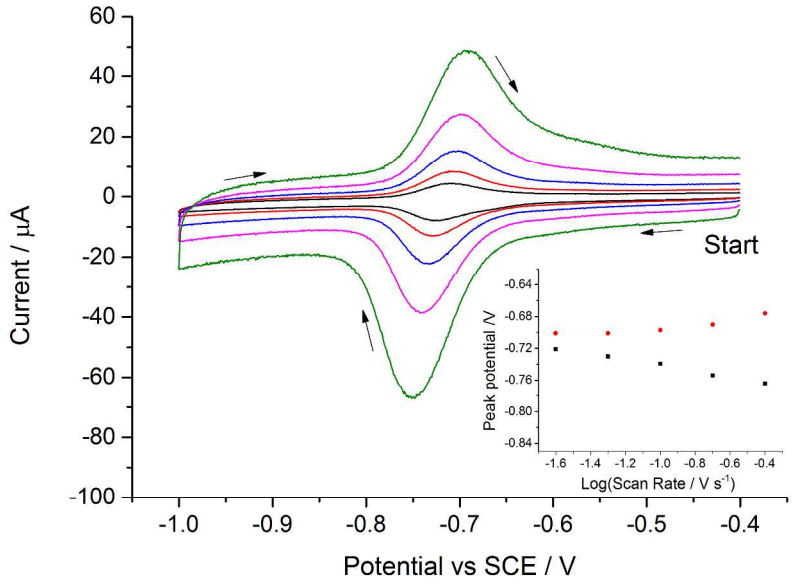
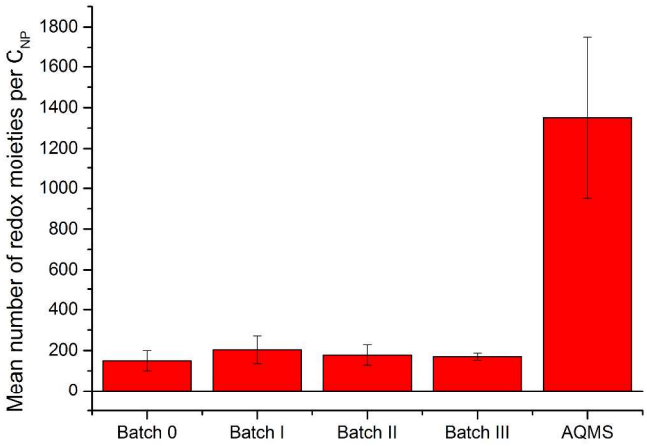


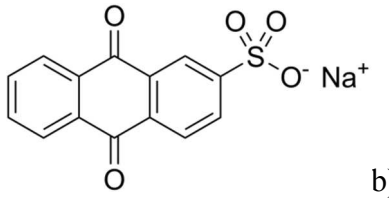
Figure 6: The voltammetric response of a glassy carbon electrode modified with Batch I carbon nanoparticles (7.55 µg) recorded as a function of scan rate (25 mV s^{-1}, black line; 50 mV s^{-1}, red line; 100 mV s^{-1}, blue line; 200 mV s^{-1}, pink line and 400 mV s^{-1}, green line). The inlay depicts the variation of the voltammetric peak potential as a function of the decadic logarithm of the scan rate.

Figure 7 depicts the mean number of redox molecules per carbon nanoparticle as assessed from the integration of the reductive quinone peak. First, from comparison of the surface coverages obtained for the modification used in Figure 4, it can be seen that the surface density of the redox moieties is relatively insensitive to the concentration of RB2 used within the synthesis. Second, the surface coverages are relatively insensitive to the modification procedure. Consequently, we propose that the functionalization of the carbon surface is not occurring through covalent bond formation but is more likely predominantly related to the physisorption of the RB2 to the carbon surface. The relative insensitivity of the modification procedure towards the presence of base and/or additional salt (Batches II and III) strongly implies that the binding does not involve covalent bond formation as the chlorotriazine requires deprotonation of the surface bound hydroxyl groups in order to undergo nucleophilic substitution.[29] This conclusion is further corroborated by the significantly higher surface coverages obtained when the carbon nanoparticles are modified with anthraquinone-mono-sulphonate. For this species chemical binding is not feasible but physisorption of a larger number of molecules (ca. 2000 per carbon nanoparticle) can be achieved. Considering the significantly smaller molecular size of AQMS as compared to RB2 (see Fig. 1 and 7 b), this way an increased number of redox-moieties per

nanoparticles can be obtained while maintaining a sub-monolayer coverage of the carbon nanoparticles and thus an un-distorted redox signal.



a)



b)

Figure 7: Mean number of redox moieties per carbon nanoparticle with error bars. Results from voltammetric responses of a glassy carbon electrode modified with Batches 0 (7.5 µg), I (7.55 µg), II (7.9 µg), III (7.5 µg), and AQMS (7.75 µg) modified carbon nanoparticles and molecular structures of AQMS (b).

Having evidenced the binding method for the RB2 to be predominantly via physisorption, the stability of this binding was investigated by exposing the modified carbon nanomaterial to both high and low pH conditions using two 15ml washes of either 0.1M NaOH or 0.1M HCl, respectively. After exposure to these extreme pH environments, the carbon material was filtered, washed and re-suspended in a chloroform solution. Modification of a glassy carbon electrode with this material and recording of the subsequent voltammetric response indicated that no significant loss of the redox active material occurred in either the high or low pH conditions.

CONCLUSIONS

The redox functionalization of carbon materials often involves complex reaction schemes which are liable to polymerization and multilayer formation. Conversely, physisorption onto carbon nanomaterials provides a rapid and simple methodology that, as evidenced, results in a material that exhibits clear, well-defined redox signals and monolayer modification. Even in the absence

of chemical binding, the redox moieties are found to be stable to extremes of pH and several washing steps. In the present work the successful modification of 27 nm diameter carbon nanoparticles has been demonstrated using two different examples, both of which were found to result in redox-active carbon nanoparticles. While modifications with the commercial dye Reactive Blue 2 yielded a bi-functionalized material, modification with anthraquinone-monosulphonate provided a mono—functionalized carbon material, exhibiting both oxidative and reductive charge transfer reactions.

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