**Enhancement of electrode performance by a simple casting method using sonochemically exfoliated graphene.**

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**Abstract**

We demonstrate within this paper a method for modifying commercial screen-printed electrodes with aqueous graphene suspensions to enhance their electrochemical activity. The graphene suspensions are synthesised by a simple ultrasonic exfoliation method from graphite, where re-aggregation is prevented by the addition of common cationic or anionic surfactants, thereby avoiding the use of organic solvents or harsh chemical procedures. These suspensions can then be simply cast onto the screen-printed electrodes. Cyclic voltammetry with a number of redox active species such as phenols, as well as impedance measurements, were made to characterise these systems. The modified electrodes are shown to demonstrate enhanced electrochemical activity and greatly lowered electron transfer resistances compared to the unmodified electrodes. Initial proof of concept applications of these electrodes, including the detection of heavy metals by absorptive stripping voltammetry, are also shown.

**Keywords**:

Graphene; screen-printed electrodes; heavy metals; dopamine; phenols

**1. Introduction**

Over the last few decades, there has been a dramatic increase in the utilisation of novel forms of carbon within the field of chemical and biochemical sensing. A host of new materials such as fullerenes, carbon nanotubes, carbon dots and graphene have made their appearance in sensors. Currently there is intensive study focussed towards the properties and uses of graphene, i.e. carbon in the form of two-dimensional carbon sheets - just one or a few atoms in thickness. Graphene displays a range of interesting properties such as high stiffness and optical transparency as well as high surface area and good electrical conductivity. It is the high surface area and its electrical properties that make graphene a candidate material for enhancing the performance of chemical and biosensors [1].

Graphene was initially produced in small quantities by mechanical exfoliation using adhesive tape [2], however this method only produces small amounts of graphene. Thin layers of graphene can be deposited using such techniques as chemical vapour deposition onto copper [3], allowing the construction of high quality films as large as 30 inches using a roll to roll production system. However these types of techniques are unsuitable for producing gram or kilogram quantities of graphene.

Many methods of producing graphene involve the exfoliation of graphite. Graphite can be oxidised using strong oxidising mixtures such as solutions of nitrate and permanganate in sulphuric acid [4] and the resultant dispersed graphite oxide can then be assembled onto thin films and reduced to graphene by chemical reagents such as hydrazine [5,6], by thermal methods or electrochemical approaches [7,8]. However the electrical properties of reduced graphene oxide can be very different to those of pristine graphene [1].

Ultrasonication has been utilised as a method for exfoliating graphite to give graphene flakes, with for example the ultrasonication of graphite in N-methyl pyrrolidinone giving dilute graphene suspensions [9]. This technique may also be applied to other layered materials such as molybdenum disulphide or boron nitride, however the strong Van der Waals interactions between graphene sheets generally mean only dilute solutions can be obtained. Aqueous dispersions can also be made providing a stabilising agent can be used and these may include common surfactants such as sodium dodecyl sulphate and cetyl trimethyl ammonium bromide, as well as polymeric materials such as the Pluronic series of surfactants [10], polyethyleneimine [11] and polyvinyl pyrrolidinone [12]. Using these methods it has proved possible to make dispersions containing up to 10 mg ml-1 of graphene, which they have shown to be mainly single layer graphene [10]. Recently mechanical exfoliation of graphite has been reported to produce high yields of graphene in aqueous or organic solvent systems [13].

To take advantage of the many distinct properties of graphene, various biosensors based on this material have been recently fabricated [1,14]. It has been demonstrated that modification of glassy carbon electrodes with graphene leads to an increase in oxidation peaks currents and the lowering of oxidation overpotentials [15]. The dominance of glucose detection in the biosensors market means that much work has been undertaken on utilising graphene in glucose biosensors. For the detection of glucose, graphene based sensors are usually modified with glucose oxidase (GOD) and this review compares a number of these systems [14]. Comparisons between similar sensors fabricated with graphene oxide and reduced graphene oxide demonstrated much higher sensitivities for the reduced graphene. Electrochemical impedance measurements showed a much higher charge transfer resistance for graphene oxide than its reduced form [16]. Other enzymes that have been immobilised onto graphene electrodes to give electrochemical biosensors include catalase [17], urease [18], horseradish peroxidase [19] and alcohol dehydrogenase [20]. Much of the work on the fundamental electrochemistry of graphene and its possibilities for sensing have been recently reviewed [21, 22].

Another important area under investigation is the development of sensors for the direct detection of small biomolecules without the use of enzymes. Graphene makes an ideal candidate for these electrochemical sensors because of its enhanced electro-catalytic effects and fast electron transfer kinetics, over that of traditional sensor materials. Dopamine is most widely investigated, because its concentration can be directly linked to a number of clinical conditions. Of particular interest is the development of a dopamine electrochemical sensor that can selectively distinguish dopamine even in the presence of uric acid and ascorbic acid, which have overlapping voltammetric responses [22]. Use of a 3D graphene foam combined with cobalt oxide nanowires gave a sensor which could determine glucose at level <25 nM [23]. A number of transition or noble metals combined with graphene have been utilised in similar schemes as reviewed here [1]. Seratonin can also be determined in the presence of dopamine and ascorbate by using reduced graphene oxide modified glassy carbon electrodes and differential pulse voltammetry [24]. Graphene/gold nanoparticle composites could be used to detect the neurotransmitter epinephrine with a limit of detection of 7 nM in the presence of ascorbate [25]. Direct oxidation of the four bases in DNA can also be detected with separate peaks being obtained for each base in both single and double-stranded DNA [15]. More recently, a series of commercial graphene inks suitable for screen-printing have been released and their structure and electrochemical behaviour when deposited as electrodes has been extensively examined, along with their suitability in detecting species such as dopamine, ascorbate and uric acid [26].

Sonochemically exfoliated graphene has been utilised previously for the modification of electrodes with mixed results. Commercial graphene is often mechanically or sonochemically exfoliated and stabilised using surfactants. Some studies have shown that the presence of surfactants can actually be detrimental to electrode performance, for example when using graphene stabilised with sodium cholate, the surfactant has been shown to be detrimental to the oxidation of species such as acetophen and NADH [27]. Similar effects have been noted in the construction of graphene based supercapacitors [28], where the presence of sodium cholate can increase the capacitance of these systems compared to unmodified electrodes and mask any changes due to the graphene itself. Other work has shown that graphene can in some cases hinder electron transfer at pyrolytic graphite electrodes, depending on the level of surface coverage [29].

Graphene modified electrodes have also be used in the field of impedimetric immunosensors, and genosensors as reviewed here [30].Immunosensors made by coupling antibodies to graphene-modified electrodes have been constructed for immunoglobins and while a detailed review is beyond the scope of this article, many of these have been previously described [1]. Antibodies have been coupled to a graphene sheet/methylene blue composite for the detection of prostate specific antigen. Methylene blue has an efficient absorption profile for antigens and shows improved electrical activity in the presence of graphene; sensors built using this methods show a detection limit of 13 pg ml-1 [31]. Sensors fabricated using graphene/silver nanoparticles/carbon nanotubes composites could be used for the detection of chorilonic gonadotrophin [32]. Graphite could be sonochemically exfoliated in the organic solvent N-methyl pyrrolidinone to give suspensions which when deposited onto glassy carbon electrodes demonstrated enhanced detection of a variety of analytes [33]. Other workers exfoliated graphite in water-ethanol mixtures to give graphenes of various thicknesses which could be applied to screen-printed carbon electrodes and used to measure the concentration of hydrogen peroxide [34].

The rationale behind this research was the challenge that biosensors can be very difficult to regenerate and also if used for analysis of physiological samples, can be subject to biofouling. One solution is of course the use of inexpensive, single-shot biosensors such as used in glucose monitoring. We therefore have attempted to combine the use of a simple ultrasonic method for generating graphene coatings with uncharged, anionic or cationic surfactants without the need for harsh chemicals or organic solvents [10], with the use of inexpensive screen-printed electrodes and simple casting methods.

**2. Materials and methods**

*2.1. Chemicals, equipment and electrodes*

Sodium dodecyl sulphate (SDS) and graphite powder (general purpose grade) were supplied by Fisher (UK). Cetyl trimethylammonium bromide (CTAB) dopamine, catechol, hydroquinone, potassium ferrocyanide, potassium ferricyanide, ferrocene carboxylic acid (FCA), cupric chloride, lead acetate and mercury chloride were obtained from Sigma-Aldrich Chemical Company (Gillingham, UK). The phosphate buffer solution (PBS) consisted of 18.9 g of Na2HPO4.12H2O, 1.79 g H2NaPO4, and 0.29 g NaCl, supplied by Fisher (UK) and dissolved in 1 L of deionised water. The water used was from a Milli-Q water purifier (Millipore).

All screen printed electrodes were supplied by Microarray Ltd. The electrodes consisted of 2 identical carbon working electrodes (which meant it was possible to have a modified and control electrode on the same platform), a carbon counter electrode, and a silver/silver chloride reference electrode. Figure S1 (supplementary information) shows the layout of the electrodes and their formulation. A Thermoscientific Megafuge 160 was used for centrifugation of samples. UV/Vis spectra were obtained using a Shimadzhu UV-2101PC spectrometer, particle sizing was undertaken with a Zetasizer 3000 (Malvern Instruments, UK) which measures particle sizes from below a nanometer to several µm using dynamic light scattering. Atomic force microscopy was carried out with a Bruker Dimension 3100 AFM and scanning electron microscopy (SEM) with a FEI XL30 ESEM and FEI XL30 SFEG. Freeze-drying was carried out using a Scanvac Coolsafe system (LaboGene ApS Industrivej, Lynge, Denmark). Raman studies were carried out using a Renishaw-InVia Raman microscope (laser wavelength: 532 nm). on freeze-dried graphene samples.

*2.2. Sonochemical production of graphene and characterisation.*

Sonochemical formation of graphene has been previously reported [9, 10, 33, 34]. Our procedure was based on a batch production method using surfactants previously described [10]. For graphene production, an ultrasonic horn operating at 20 kHz with a power output of 100 watts (Branson Digital Cell Disruptor, 250 series) was used. In a typical synthesis 200 ml of water, 2 g of graphite powder, and 43.5 mg of CTAB were combined. The concentration of CTAB (0.6 mM) is such to reduce the surface tension of the water to 41 mJ m-2, which is the surface free energy of graphene. The concentration of SDS, (to produce negatively charged graphene), needed to achieve this tension is 7 mM. The mixture of graphite and surfactant in water was then placed under a sonicating horn with the probe depth being 1.5-2 times the diameter of the probe tip for optimal sonication efficiency. The mixture was then left under sonication (100 W) for 5 minutes. During sonication, the surface area of the graphite/graphene will greatly increase, due to the ablation of graphene sheets from the graphite. This causes the surfactant to be absorbed from the solution onto the surface of the graphene, raising the surface tension. After 5 minutes, the majority of the surfactant has been absorbed onto the ablated sheets, and the sonication probe is turned off. Another batch of surfactant, equal to the first is then added to the mixture to lower the surface tension to the desired value again, and the sonication repeated. This process is repeated a total of 30 times.

After sonication, the resulting solution is then centrifuged at 1500 g for 15 minutes, to remove any large or aggregated particles, and the supernatant containing the graphene is syphoned off. The resultant suspensions were stable for at least several months at room temperature. It also proved possible to increase the concentration of the graphene by freeze drying the suspensions with the resultant solid material being able to be easily redispersed in water by sonication for a few minutes.

*2.3. Modification and characterisation of electrodes*

The graphene coated electrodes were prepared by pipetting 10 µl of graphene solution onto one of the two working electrodes (the untreated working electrode was used as a control). The solution was then left to air dry for several hours. After the drying period, the electrodes were immersed in deionised water to wash away any remaining surfactant. A similar casting method onto a silicon wafer was used to formulate samples for AFM and SEM.

Cyclic voltammetry was carried out using a Sycopel AEW-2 Potentiostat (Sycopel Ltd, Newcastle-Upon-Tyne) for all electrochemical studies: current/charge transients were recorded using a PC with dedicated software. CV measurements were performed between -800 and +800 mV at a scan rate of 50 mVs-1 unless otherwise stated. Adsorptive stripping voltammetry (ASV) was performed by firstly removing any oxidisable material from the electrode by polarising at +1 V for one minute, then depositing trace metal species by polarising the electrode at -1 V for five minutes and finally sweeping at 50 mV s-1 back to +1 V (vs. Ag/AgCl) to strip the metal. AC impedance measurements were performed using a Gill ACM Auto AC DSP frequency response analyser and potentiostat (Cark, UK) linked to a PC. For AC measurements a mixed solution of 5 mM each of K3Fe(CN)6 and K4Fe(CN)6 in PBS was used. The AC signal amplitude was 10 mV, the frequency range 1 Hz-10 kHz and a DC offset of 120 mV vs. Ag/AgCl was applied.

**3. Results and discussion**

*3.1. Characterisation of graphene*

UV-visible spectra of graphene solutions exhibited the expected peak at approximately 265 nm, indicating that for both CTAB and SDS treated graphite, exfoliation produced graphene. Measurement of the optical adsorption at 660 nm [9] indicated that solutions as concentrated as 0.2 mg ml-1 were obtained using our modified protocol [10]. Analysis of Zetasizer results indicated an average particle size of 117 nm for the SDS dispersed samples (G-) and 278 nm for the CTAB samples (G+). Raman studies (figure S2, supplementary information) clearly demonstrated the formation of graphene as was also shown by the original developers of our experimental protocol [10]. The Raman spectra indicates the formation of single or few layer graphene with the presence of some defects [35].

The Zetasizer models assumes that the particles are spherical, however a more accurate measurement of particle size was obtained using AFM and SEM. Figure 1 shows SEM and AFM images of G- cast onto a silicon wafer. As can be seen, the particle sizes are approximately as predicted by the Zetasizer measurements. Using the AFM it is possible to measure the thickness of the graphene flakes (figure 1c). Most of the flakes are under 5 nm in thickness and some under 1 nm indicating that we have single or few layer graphene; unfortunately it is not possible calculate how much of the thickness is due to the adsorbed surfactants.

*3.2. Impedance of graphene modified electrodes*

AC impedance measurements were made of both graphene-modified and unmodified working electrodes and the Nyquist plots are displayed in figure 2. There is a large and obvious difference between the electrodes when studied under AC impedance, showing that the graphene enhanced electrodes demonstrate a much higher conductance than the unmodified electrodes. The electron transfer resistance can be calculated from the semi-circle width of the Nyquist plots and demonstrates that the transfer resistance of the graphene-modified electrodes is over 50 times less than that of the unmodified carbon.

*3.3. Cyclic voltammetry of graphene modified electrodes in different redox couples*

Figure 3 shows cyclic voltammagrams of both electrode systems in 1 mM solutions of FCA and three phenolic redox couples. As shown, in all cases the graphene modified electrodes display an enhanced sensitivity as exhibited by the increased peak current values compared to those obtained for the same solution using the unmodified screen-printed electrodes. There are also noticeable shifts in the position of the peak, with the oxidation peaks showing lower over-potentials on the graphene modified electrodes. Also ΔEp is lowered for the modified electrodes and the peaks are noticeably sharper. This is consistent with results obtained by other workers [15] and indicates that graphene modified electrodes are more electroactive than their unmodified counterparts. Obvious explanations for this include the enhanced conductivity of the graphene and also larger surface areas. Table 1 shows the enhanced currents and narrower peak separations obtained by modifying screen-printed carbon electrodes with graphene.

Attempts were made to optimise the amounts of graphene used for electrode modification. Freeze dried graphene was re-dispersed in water and diluted to give a range of concentrations and 10 µL of each solution cast onto screen-printed carbon electrodes as previously described. CVs were then run for all the electrodes in 1 mM dopamine solution. A slower scan rate (10 mV s-1) was employed to permit enhanced signal differentiation. Figure 4 shows the obtained CVs and also the changes of oxidation peak current and ΔEp for differing graphene concentrations. As can be seen there appears to be a steady increase of peak current and decrease in peak separation up to a concentration of 0.2 mg mL-1, with the effect of higher concentrations tending towards a plateau after that and 0.2 mg mL-1 was therefore used as the optimum graphene concentration. At this concentration and using just 10 µL of solution, this corresponds to 2 µg per electrode. Taking the weight of single layer graphene to be 0.77 mg m-3 as commonly reported, if we assume that our graphene is of this type, this would correspond to an area of 2600 mm2, much greater than the surface area of the electrode (21.78 mm2). Previous workers [29] have described graphene coverage and effects on electrochemical activity as being either zone 1 (incomplete coverage of the substrate) or zone 2 (complete coverage with build-up of multilayers), our system is clearly in zone 2.

Since previous workers have reported surfactants to have a major effect, in some cases being the source for perceived enhancements in graphene-treated electrodes, controls were run by treating the electrodes with 5 µL concentrated CTAB solution (50 mg mL-1). As can be seen in figure 4 this led to some increase in peak current but much smaller than observed for graphene/CTAB composites and no shift in peak potential. A lower concentration (6.5 mg mL-1) showed minimal differences between a treated and an untreated electrode. This demonstrates that in our systems, the surfactant only has a small effect.

Cyclic voltammagrams obtained for graphene modified electrodes in 1 mM dopamine taken immediately after and one hour after continuous immersion in the solution showed only minimal differences, indicating that the graphene modification was stable over this time period, well in excess of that required for any measurements to be made.

A series of voltammagrams for FCA at different scans rates were also made (figure 5 shows the results for graphene modified electrodes) and clearly demonstrate good electro-chemical behaviour with the peak current being proportional to the square root of the scan rate, with a similar trend also being found for unmodified electrodes. The inset (figure 5) shows good linear correlation of peak current with the square root of scan rate for both electrodes (R2>0.995). This suggests that a possible limiting factor of the electro-chemical response of the graphene modified systems is the underlying carbon system itself and not the graphene layers per se.

*3.3. Absorptive stripping voltammetry of graphene modified electrodes*

Heavy metals are a major environmental threat, especially when waterborne and are commonly produced by mining areas as well as being naturally present in some parts of the world, such as mercury contamination of the environment in small gold mining communities [36]. The use of graphene modified electrodes for the detection of a range of heavy metals has been recently reviewed [37]. For example graphene-Nafion composites could be used for the anodic stripping voltammetric detection of lead and cadmium [38] and in further work was extended to the detection of copper and zinc [39]. However other workers have again reported that the use of surfactant (sodium cholate) stabilised graphene inhibited the stripping transition of cadmium metal to the ion and greatly reduced any peaks corresponding to this step [40]. We therefore report preliminary studies on the use of graphene-modified electrodes for the detection of three potential contaminants, namely copper, lead and mercury. It was suggested that graphene stabilised with an anionic surfactant would be more effective at binding metal ions and therefore graphene stabilised with SDS was produced. However SDS proved to be less effective as an exfoliating agent using our methodology and a solution containing 0.05 mg ml-1 graphene was obtained.

A range of individual metal ion solutions were produced and analysed by ASV. It is worth noting that as of yet we have not performed a conclusive study of the concentration/electrochemical or optimised the metal deposition and stripping procedure, and we intend this work to follow on in subsequent publications. However by comparing measurements obtained by the differing systems described herein, with the same concentrations of metal ions, it was once again obvious that the presence of graphene greatly enhanced the electrochemical detection of these species. An example of this is demonstrated in Figure 6 which shows the ASV of a solution containing 1 ppm each of the three metal ion species. As can be seen, both the anionic and cationic graphene modified electrodes display enhanced stripping currents for each of the metallic ions when compared to the unmodified electrodes. This demonstrates the potential for this simple treatment protocol to enhance the sensitivity of electrochemical detection of heavy metal pollutants.

**4. Conclusions**

We have developed a relatively simple protocol for sonochemical fabrication of graphene and its application by casting onto screen-printed electrodes. The resultant electrodes displayed lower electron transfer resistance and higher electrochemical activity when compared to the unmodified base screen printed electrodes. When used with ferrocene or phenolic redox active species, enhanced currents, reduced peak separation and lower oxidation potentials were apparent and no depreciation in electro-chemical behaviour was noted even after 1 hour continuous immersion. The graphene modified electrodes also displayed enhanced performance assessed for simultaneous detection of three toxic heavy metal species. The simplicity of the procedure, use of inexpensive screen-printed electrodes and modification techniques, as well as no requirement for harsh chemicals or organic solvents, suggest these systems have scope for use in single-shot ‘point of care’ or environmental monitoring applications.

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Figure 1. (a) SEM and (b) AFM measurements of sonicated graphene on silicon (c) height measurements across the silicon wafer.

Figure 2. Nyquist plots of screen-printed carbon electrodes, with and without graphene, in ferri/ferrocyanide solution (PBS). Insets show the Nyquist plot of the graphene electrode and the format of the screen-printed electrodes.

Figure 3. Cyclic voltammagrams of 1 mM solutions in PBS of FCA, catechol, dopamine and hydroquinone.

Figure 4. Cyclic voltammagrams of 1 mM dopamine solutions in PBS utilising electrodes constructed using different graphene concentrations. Inset: effect of graphene concentration on oxidative peak current and peak potential.

Figure 5. Cyclic voltammagrams of 1 mM solutions of FCA in PBS at differing scan rates.

Figure 6. Absorptive stripping voltammagrams on control, G- and G+ modified screen printed carbon in 1 ppm solutions of Cu2+, Hg2+and Pb2+ in 0.1 M HCl.

Table 1: Peak positions and separation of carbon and graphene CV peaks in 1 mM phenolic or FCA solutions. The RSD’s on both peaks positions and currents were <6% for all the redox couples studied.

Table 1.

|  |  |  |  |
| --- | --- | --- | --- |
| **Analyte & Electrode** | **Oxidative Peak Position** | **Reductive Peak Position** | **Peak Separation** |
| **Screen Printed Carbon** |
| FCA | 417 mV, 0.0145 mA | -47 mV, -0.00594 mA | 464 mV |
| Dopamine | 537 mV, 0.0229 mA | -910mV, -0.00890 mA | 1447 mV |
| Hydroquinone | 547 mV, 0.0414 mA | -412 mV, -0.0162 mA | 959 mV |
| Catechol | 653 mV, 0.0239 mA | -335 mV, -0.00919 mA | 988 mV |
| **Graphene Coated Carbon** |
| FCA | 241 mV, 0.0237 mA | 91 mV, -0.0129 mA | 150 mV |
| Dopamine | 281 mV, 0.0294 mA | -645 mV, -0.0159 mA | 926 mV |
| Hydroquinone | 312 mV, 0.0485 mA | -282 mV, -0.0329 mA | 594 mV |
| Catechol | 333 mV, 0.0502 mA | -178 mV, -0.0261 mA | 511 mV |

Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6.

