

Exploring the origins of the apparent “electrocatalytic” oxidation of kojic acid at graphene modified electrodes

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Abstract

We explore the recent reports that the use of graphene modified electrodes gives rise to the electrocatalytic oxidation of kojic acid. It is demonstrated that large quantifiable voltammetric signatures are observed on bare/unmodified graphitic electrodes, which are shown to be analytically useful and superior to those observed at graphene modified alternatives. This work is of importance as it shows that control experiments are critical and must be undertaken before “electrocatalysis” is conferred when investigating graphene in electrochemistry.

In terms of the electroanalytical response of graphene modified electrodes, a bare edge plane pyrolytic graphite electrode is shown to give rise to an improved linear range and limit of detection, questioning the need to modify electrodes with graphene.

Keywords: Graphene; Kojic acid; Electrocatalysis; Graphene electrochemistry; Electroanalysis.

Introduction

The design, synthesis and fabrication of analytical sensors and sensing systems is a highly diverse field and a global pursuit.^{1,2} Many sensors have been continuously developed for a number of years, such as optical, thermal, mass-based and electrochemical devices, which have a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analysis.³⁻⁶ Electrochemical derived sensors attract attention due to their ability to convert chemical information into an electrical signal and through careful design can give rise to sensitive, selective, experimentally simple and low cost sensors.^{1,2,7} The output of an electrochemical sensor is a variable current, of which the peak height (maxima) is proportional to the concentration of the electroactive species of interest (analyte), which arises from applying electrode potentials at suitable values to give rise to electron transfer to or from the target analyte.² In this area of research, electrochemists are constantly searching for new electrode materials that can give rise to improvements in the analytical signal (peak height) through the application of more facile electrode potentials (*i.e.* lower over-potentials), with the former potentially giving rise to lower detection levels.² As such, electrochemists typically modify electrode surfaces with materials such as micro- and nano- particles, mediators and catalysts.⁸⁻¹² Other approaches involve the modification of electrode surfaces with carbon nanomaterials,¹³ such as carbon nanotubes, which have been reported to give rise to improvements in electrochemical processes when compared to the underlying electrode surface which is used to support the modifier and allow electrical connection.^{14, 15}

Following such approaches, graphene has been used for the modification of electrode surfaces with the aim of improving electrochemical processes.² Graphene is potentially the world's thinnest electrode material and has captured the attention of electrochemical researchers worldwide;² as such it is being applied into areas such as energy storage and generation and in the development of analytical sensors.¹⁶⁻²⁰ For example, it has been reported that graphene modified electrodes give rise to beneficial improvements for the sensing of acetaminophen, hydroquinone and dopamine.²¹⁻²³ In these cases, and in many more, the modification of electrode surfaces has been shown to provide improvements in the analytical signal when compared to the previously unmodified/bare electrode surfaces.¹⁸⁻²³ Inspired by such approaches, in this communication we explore the use of a graphene modified electrode for electroanalysis. Intrigued by the report that

graphene modified electrodes gives rise to an apparent ‘electrocatalytic’ response towards the electrochemical oxidation of kojic acid,²⁴ we explore the electrochemical detection of this analyte at graphitic electrodes and critically compare the responses to that of graphene modified electrodes.

Experimental section

All chemicals used were of analytical grade and were used as received from Sigma-Aldrich without any further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 M Ω cm and were vigorously degassed prior to electrochemical measurements with high purity, oxygen free nitrogen.

Voltammetric measurements were carried out using an ‘Autolab PGSTAT 101’ (Metrohm Autolab, The Netherlands) potentiostat. All measurements were conducted using a three electrode system. The edge plane pyrolytic graphite (EPPG) working electrode (Le Carbone, Ltd. Sussex, U.K) was machined into a 4.9 mm diameter, with the disc face parallel to the edge plane as required from a slab of highly ordered pyrolytic graphite (HOPG: highest grade available; SPI-1, equivalent to Union Carbide’s ZYA grade, with a lateral grain size, L_a of 1–10 μm and $0.4 \pm 0.1^\circ$ mosaic spread); alternatively, the basal plane pyrolytic graphite (BPPG) working electrode (4.9 mm diameter, Le Carbone, Ltd. Sussex, U.K) was machined as above however with the disc face parallel to the basal plane as required; a glassy carbon (GC) electrode (3 mm diameter, BAS, USA) and a boron-doped diamond (BDD) working electrode (3 mm diameter, BAS, USA) were also utilised. A platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. The working electrodes were diligently polished prior to commencing experiments.

The graphene was commercially obtained from ‘Graphene Supermarket’ (Reading, MA, USA) and are known as ‘Pristine Graphene Monolayer Flakes’ comprising entirely of pristine graphene platelets dispersed in ethanol (1 $\mu\text{g mL}^{-1}$) that have not been oxidised, reduced or chemically modified in anyway and are free from surfactants.²⁵ ESI Figure S1A depicts a typical Transmission Electron Microscope (TEM) image of the commercially purchased graphene and ESI Figure S1B shows a high resolution TEM image where a hexagonal arrangement of carbon atoms, which is characteristic of graphene, is clearly evident. The graphene flakes were synthesised *via* a substrate free gas-phase method, as previously reported,^{26, 27} and are sonicated in ethanol to form a homogeneous suspension before being dispatched by the manufacturer (further details regarding the fabrication process and the physicochemical characterisation of the pristine graphene flakes are provided in the ESI). The graphene has an average flake thickness of 0.35 nm (1 monolayer) with an average particle (lateral) size of 550 nm (150–3000 nm).²⁵ Independent X-

ray photoelectron spectroscopy (XPS) chemical analyses were performed with a VG-Microtech Multilab electron spectrometer and revealed the material to comprise of 95.04 % atomic carbon and 4.96 % atomic oxygen; the low O/C ratio suggests near true graphene.^{2, 28}

For comparison, experiments were performed where the electrodes were modified with graphite powder; synthetic graphite powder was commercially obtained from ‘Gwent Group’ (Pontypool, UK) (P2010808P2, batch number: 2080512.05)²⁹ and as above was not oxidised, reduced or chemically modified in anyway prior to use. The graphite was dispersed in ethanol:water (50:50) at a concentration of 1 mg mL⁻¹ to replicate the conditions of the graphene solution. XPS analysis revealed the graphite material to comprise of 97.9 % atomic carbon and 2.1 % atomic oxygen. Furthermore, for the purpose of stringent control measures, commercially available graphene oxide (GO) was purchased from ‘Graphene Supermarket’ (Reading, MA, USA)²⁵ and consists of ‘single layered graphene oxide’ dispersed in ethanol:water (50:50) at a concentration of 1 mg mL⁻¹. The GO was synthesised using a modified Hummers oxidation method that has been reported and characterised previously,^{30, 31} and has an average flake size of between 0.5 and 5.0 µm and a thickness of 1 atomic layer, with at least 80 % of the sample being single layer GO.²⁵ A typical SEM image of the GO, supplied by the manufacturer, is presented in ESI Figure S2. XPS analysis was performed on the sample: de-convolution of the XPS spectra reveals 59 % (284.6 eV) to correspond to graphitic groups, with 29 % (286.8 eV) characteristic of C–O bonds and 11.5 % (288.2 eV) corresponding to C=O bonds, which is in excellent agreement with previous literature reports regarding GO.^{32, 33}

Once received from the supplier, aliquots of the graphene, graphite or GO solutions were carefully pipetted onto the electrode surface using a micropipette and allowed to dry at room temperature under nitrogen flow in order to eliminate oxidation of the material by the presence of atmospheric oxygen, following which the electrode was ready to use. As such, this approach allows one to ‘electrically wire’ the graphene (and related) material and is a widely adopted approach within the literature.

Note that the graphene, graphite and GO solutions utilised in this study have been electrochemically characterised previously.^{28, 34, 35} Furthermore, control experiments in terms of ethanol modified electrodes for the purpose of ensuring that electrochemical responses observed are not a result of the solvents utilised have also been previously reported.^{28, 34, 35} Such control experiments revealed that ethanol has no effect on the responses observed.

Results and discussion

It has been reported that chemically reduced graphene oxide (producing reduced graphene sheets (RGSs)) immobilised upon a GC electrode can be beneficial for the sensing of kojic acid.²⁴ Cyclic voltammetric responses were reported to be optimal when using the RGS modified GC electrode over that of a bare (unmodified) GC electrode and a graphite electrode towards the electrochemical oxidation of kojic acid, where it was noted that the peak current was ‘faint’ and ‘not well identified’ in the latter two cases.²⁴ Given that the presence of RGSs on the GC electrode greatly increased the peak current compared with the inverse case (when the RGSs are absent), the authors attributed this to indicate that the RGSs have a high electrocatalytic activity towards the electrochemical oxidation of kojic acid.²⁴ Interested by this report, we first consider the electrochemical oxidation of kojic acid at various unmodified carbon based and graphitic electrodes. Figure 1 shows the electrochemical oxidation of kojic acid at BDD, GC, BPPG and EPPG electrodes. To our surprise, we find that large well-defined voltammetric signatures are observed at all of the electrodes studied. Of note is the voltammetric potential at which the electrochemical oxidation peak appears, where peak potentials of *ca.* 1.21, 1.13, 0.91 and 0.86 V (vs. SCE, 50 mVs⁻¹) are evident for the BDD, GC, BPPG and EPPG electrodes respectively. Clearly there is a dependence on the electronic structure of the graphite electrodes where the electrochemical oxidation is observed to occur at the lowest potential (most beneficial electrochemical response) using the EPPG electrode, which is due to its large coverage of edge plane like- sites/defects giving rise to fast electron transfer properties/kinetics in comparison to the alternative electrodes.^{2, 28, 36} Additionally, the EPPG electrode gives rise to the largest electrochemical signature (peak current), which is optimal when compared to the other graphitic/carbon electrodes studied. Insights can be derived from Tafel analysis which involves analysis of the voltammograms corresponding to the electrochemical oxidation of kojic acid, plotted as potential *versus* log₁₀(current). Such analysis was constructed for the EPPG electrode, resulting in a value of 95 mV per decade being obtained. Using the following equation: $b = 2.303RT / \alpha n' F$, where b (measured in V) is the slope of potential against log₁₀(current), α is the electron transfer coefficient and n' is the number of electrons transferred in the rate determining step; a value of 0.44 for $\alpha n'$ was deduced. This value suggests that it is the transfer of the first electron which is electrochemically irreversible, so that $n' = 1$ and $\alpha =$

0.44.

The voltammetric signature at the EPPG electrode was monitored as a function of pH in terms of both peak height and potential. A plot of peak potential (V) versus pH was found to be linear ($E/V = 0.0525 (V/pH) + 1.14 \text{ V}$; $R^2 = 0.98$; $N = 6$) over the pH range of 2 to 8, where beyond this pH range up to more alkaline values deviation from linearity was observed, which is due to the pK_a of kojic acid being 7.9. The gradient of 52.5 mV pH^{-1} suggests an equal number of protons and electrons are involved in the electrochemical oxidation of kojic acid. Indeed, recent work has suggested that this value is 1. ²⁴

An approximate diffusion coefficient value was calculated (using the EPPG electrode) based on experimental data for the diffusion controlled electrochemically irreversible reaction (*vide infra*), in which the first electron transfer is rate-determining, using the following Randles–Ševčík relationship:

$$I_p = -0.496n\sqrt{n'\alpha}FCA\sqrt{\frac{FvD}{RT}}$$

where I_p is the voltammetric peak current, n is the total number of electrons transferred and n' is the number of electrons involved in the charge-transfer step, F is the Faraday constant, R is the universal gas constant, T is absolute temperature, A is the electrode area, D is the diffusion coefficient of the analyte, v is the applied scan rate and C is the concentration of the electroactive species. Using a value of 0.44 deduced above for $\alpha n'$ and a value of 1 for n' , the diffusion coefficient was estimated from the above equation to correspond to $6.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is in agreement with the reported value of $D = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for RGS modified GC electrodes. ²⁴

We next turn to exploring whether the introduction of graphene onto the EPPG surface improves the electrochemical oxidation of kojic acid as suggested by Wang and co-workers. ²⁴ Figure 2A depicts the typical cyclic voltammetric response observed at an EPPG electrode, where upon the immobilisation of increasing masses of graphene onto the supporting surface the voltammetric potential corresponding to the oxidation of kojic acid is observed to shift to higher over-potentials resulting in the following peak potential values: *ca.* 0.84, 0.91, 0.94 and 1.00 V

(vs. SCE, 100 mVs⁻¹) for the EPPG electrode after modification with 0, 10, 20 and 30 ng of graphene respectively; note that there is no observable peak present in the case of the immobilisation of 40 ng of graphene. In addition to the observable shift in the peak potential, a reduction in the I_p is also evident when immobilising increasing masses of graphene (as depicted in Figure 3). It is clear from the above results that the introduction of graphene onto the EPPG electrode serves to simply block the electrochemical process at the underlying substrate rather than giving rise to any ‘electrocatalysis’. The above observation is as expected and in agreement with previous literature reports given that graphene’s geometry results in an electrode material with a low coverage of edge plane like- sites/defects,^{2, 28, 34} which are well known to be the origin of fast heterogeneous electron transfer kinetics at graphitic materials and thus a larger coverage of such sites gives rise to an electrode material with a beneficial electronic structure (density of states) and improved electrochemical properties/performance.^{37, 38} Note that undeniably the electrochemical oxidation of kojic acid can be readily observed at the bare/unmodified EPPG electrode prior to the addition of graphene (in addition to the unmodified GC and BPPG, see Figure 1), suggesting that in these cases the coverage of edge plane like- sites/defects is adequate for the electrochemical process to occur (and indeed for electrochemical sensing, *vide infra*) rather than attributing this to the ‘electrocatalytic’ nature of graphene.

Given the contrasting report by Wang (and indeed by many others with regard to other possible analytes)¹⁸⁻²³ one must question where this ‘electrocatalysis’ originates from in such cases. Thus we next turn to exploring the possible source of the commonly reported ‘electrocatalytic’ effect of graphene *via* the implementation of further control experiments. Note that prior work has established that the coverage and orientation of graphene immobilised on a supporting electrode substrate is highly important and influences the observed electrochemistry.²⁸ Based on this understanding, in the above experiments the mass of graphene utilised was selected such that it corresponded to *Zone I* coverages²⁸ since we want to create an electrode with near-true single layer graphene coverage (rather than multi-layer graphene which would be akin to graphite, *Zone II*). It is clear therefore that if a graphene experimentalist was to immobilise too large a quantity of graphene onto an electrode surface, the resultant coverage would correspond to that of *Zone II*²⁸ where the graphene is likely to stack and coalesce into multi-layered graphite, aided by the high cohesive van der Waals forces. Given the above insight we explore whether the introduction of graphite onto a BPPG surface improves the electrochemical

oxidation of kojic acid. Figure 2B depicts the typical cyclic voltammetric response observed at a BPPG electrode, where upon the immobilisation of increasing masses of graphite the voltammetric potential corresponding to the oxidation of kojic acid is observed to shift to lower (more beneficial) over-potentials, resulting in the following peak potential values: *ca.* 0.90, 0.88, 0.86, 0.84 and 0.83 V (*vs.* SCE, 100 mVs⁻¹) for the BPPG electrode after modification with 0, 4, 10, 15 and 20 µg of graphite respectively. Additionally, note that increments in the I_p are evident with the addition of graphite (as depicted in Figure 3). It is clear that the introduction of graphite onto the BPPG electrode (an underlying electrode material that possesses a low coverage of edge plane sites and hence slow electron transfer rates) serves to improve the electrochemical properties and the observed performance, which can be attributed to graphite's geometry in terms of its large global coverage of edge plane sites. Resultantly, introducing graphite onto a supporting substrate that possesses a low coverage of such sites gives rise to beneficial voltammetry *via* incurring fast heterogeneous electron transfer kinetics. Returning to the case of the 'electrocatalysis' reported at graphene, it is evident that if experimentalists use an electrode coverage of graphene that corresponds to *Zone II* as defined in Ref. [28] then the 'electrocatalytic' nature of the 'graphene' likely arises from the formation of multi-layered graphene structures and indeed deviation from the structural conformation of true single layer graphene. Furthermore, note that given the said improvements arise due to an increment in the available edge plane like- sites/defects (graphite>>graphene, in terms of edge plane sites contributing to their geometry) ³⁹ such improvements can also originate when using defect abundant graphene and it is therefore advisable to utilise as near pristine graphene as possible (and to stay within *Zone I* coverage) to avoid misinterpretation of experimental data. ²

In electrochemistry the vast majority of studies reporting the use of graphene fabricate their 'graphene' *via* the reduction of GO (as was the case for Wang *et al.* ²⁴). Thus it is appropriate to investigate the electrochemical response of GO towards the oxidation of kojic acid to determine the effect of any oxygenated species remaining on the graphene due to its incomplete reduction. It was found that the immobilisation of GO onto the surface of a BPPG electrode resulted in a shift in the electrochemical oxidation potential towards lower over-potentials, corresponding to *ca.* 0.92, 0.88, 0.87, 0.85, 0.83 and 0.81 V (*vs.* SCE, 100 mVs⁻¹) for the BPPG electrode after modification with 0, 2, 4, 10, 15 and 20 µg of GO respectively. The improved electrochemical response likely arises due to the level of edge plane like- sites/defects

on the structure of GO, where the defects give rise to improvements in electron transfer kinetics. As depicted in Figure 3, note that in addition to the improved electron transfer rates at GO, alterations occur in the observed I_p . It is evident that the addition of 2 μg of GO onto the BPPG surface results in an increased voltammetric peak height. However, notably, extending coverage of the GO beyond 2 μg impedes the electrochemical process and a decreased I_p is evident with further additions. It is likely that in the initial case the contribution of the oxygenated species is beneficial towards the electrochemical process (or that the quantity of said species is small such that it has little influence/contribution to the observed voltammetry) and in conjunction with the high degree of edge plane defect sites across the basal plane surface of the functionalise graphene sheet, gives rise to favourable electrochemistry. In the latter case however, it is apparent that larger coverages of GO lead to higher levels of oxygenated species across the electrode surface, that are likely detrimental to the electrochemical process in terms of disrupting favourable interaction and thus electron transfer across the electrode | solution interface: it is only when large quantities of oxygenated species are present that their combined effect are encountered and observable in the voltammetry. From the above observations, it is evident that in the case of a partially reduced graphene electrode, the reported ‘electrocatalytic’ effects most likely result from the presence of a large number of edge plane like- sites/defects present on the basal plane of the graphene surface, which would not be present if using pristine graphene. It is also clear that the presence of oxygenated species plays a part in contributing to the observed electrochemistry either beneficially or detrimentally.^{2, 35}

Note that Tafel and pH analysis was performed on all of the modified electrodes in addition to each of the unmodified electrode substrates, where as expected, no mechanistic changes were observed in the electrochemical oxidative process of kojic acid at the various graphitic/carbon materials explored. Furthermore, scan rate studies were performed on all of the (modified)electrodes utilised, which indicated there to be no contributions in the observed voltammetry arising from thin-layer effects,⁴⁰ in which case all electrodes were governed by diffusional processes: as expected and as previously reported for the graphitic materials utilised.^{28, 35}

Figure 3 provides a summary of the effect of different graphitic and graphene modifiers. It is clear that the electroanalytical detection of kojic acid using a bare/unmodified EPPG electrode provides a beneficial electrochemical signature. As such, this questions the need to modify

graphitic electrodes with graphene (see Figure 3). We now turn to exploring the analytical performance of the bare EPPG electrode where the responses arising from successive additions of kojic acid into a PBS are shown in Figure 4, in which a large linear range from 0.75 to 15 μM is clearly evident with a limit of detection (LOD, based on 3σ) found to correspond to 0.23 μM . The inter-reproducibility of the electroanalytical measurement is evident from inspection of Figure 4B where error bars are shown with the largest % Relative Standard Deviation (% RSD) found to be 6.6 %. Such a response is comparable, even superior, to that of the RGS modified GC electrode described in Ref. [24], where a linear range from 0.01 to 0.14 mM was reported (with a current sensitivity of 42.9 $\mu\text{A mM}^{-1}$) and an inter-reproducibility of 7.5 % (note that whilst the LOD was not strictly reported, the lowest concentration utilised corresponded to 10 μM).²⁴ Table 1 depicts the sensitivities and LODs of various electrode materials and modifications utilised throughout this study. Upon comparison of the EPPG response to that of the other electrode materials it is evident that the choice of EPPG gives rise to a beneficial electrochemical performance, which is clearly analytically useful.³⁶ Note that poor LODs and analytical sensitivities are observed in the case of the graphene modified electrodes questioning the need, in analytical terms and a practicability (and cost) point of view, to modify electrodes with graphene. Evidently, the immobilisation of graphene onto the EPPG results in an impeded/reduced electroanalytical performance, which is supported by the fact that the unmodified EPPG electrode out-performs the RGS modified GC electrode reported by Wang and colleagues.²⁴

In summary, throughout the literature graphene is reported to be a beneficial sensor substrate with electrocatalytic effects widely claimed.¹⁸⁻²³ It is evident that the vast majority of said work claims such ‘electrocatalysis’ when only comparing the response of the graphene modified electrode to that of the underlying electrode substrate, which is usually a poor electron transfer mediator in terms of exhibiting unfavourable electrochemical characteristics (GC or BPPG for example). Here we have demonstrated, utilising kojic acid as a representative example of the literature, that graphene is not so beneficial if compared and contrasted sufficiently to graphitic alternatives which possess favourable electrochemical properties; allowing one to confirm the origins (or lack thereof) of the ‘catalytic’ response at pristine graphene.

Conclusions

In this paper we have shown that adequate control experiments (in the form of a range of graphitic electrodes and additionally graphite and graphene coverage studies) need to be performed when “electrocatalysis” is conferred at graphene modified electrodes. We have demonstrated that the electrochemical sensing of kojic acid is not beneficial at graphene modified electrodes, which is in contrast to recent literature claims.²⁴ Graphene’s poor electrochemical performance is likely due to its low edge plane content^{2, 28, 34} and rather bare graphitic electrodes give rise to analytically superior and useful responses.

Table 1: Comparison of the analytical sensitivities and resultant LODs (based on three-sigma) obtained at various electrode materials and modifications as utilised throughout this study towards the (electro)analytical detection of kojic acid in PBS (pH 6, 0.1 M KCl) ($N = 3$).

Electrode Substrate/Modification	Sensitivity / A M⁻¹	LOD (3σ) / μM
GC	0.102	0.283 (± 0.019)
EPPG	0.730	0.230 (± 0.015)
EPPG / 10 ng Graphene	0.106	1.033 (± 0.068)
EPPG / 10 μg Graphite	0.718	0.308 (± 0.020)
EPPG / 10 μg GO	0.489	0.555 (± 0.037)

Figure 1

Cyclic voltammetric profiles recorded for 1 mM kojic acid in PBS (pH 6, with 0.1 M KCl) at EPPG (solid line), BPPG (dashed line), GC (dot-dot-dashed line) and BDD (dotted line) electrodes. Scan rate: 50 mVs⁻¹ (vs. SCE).

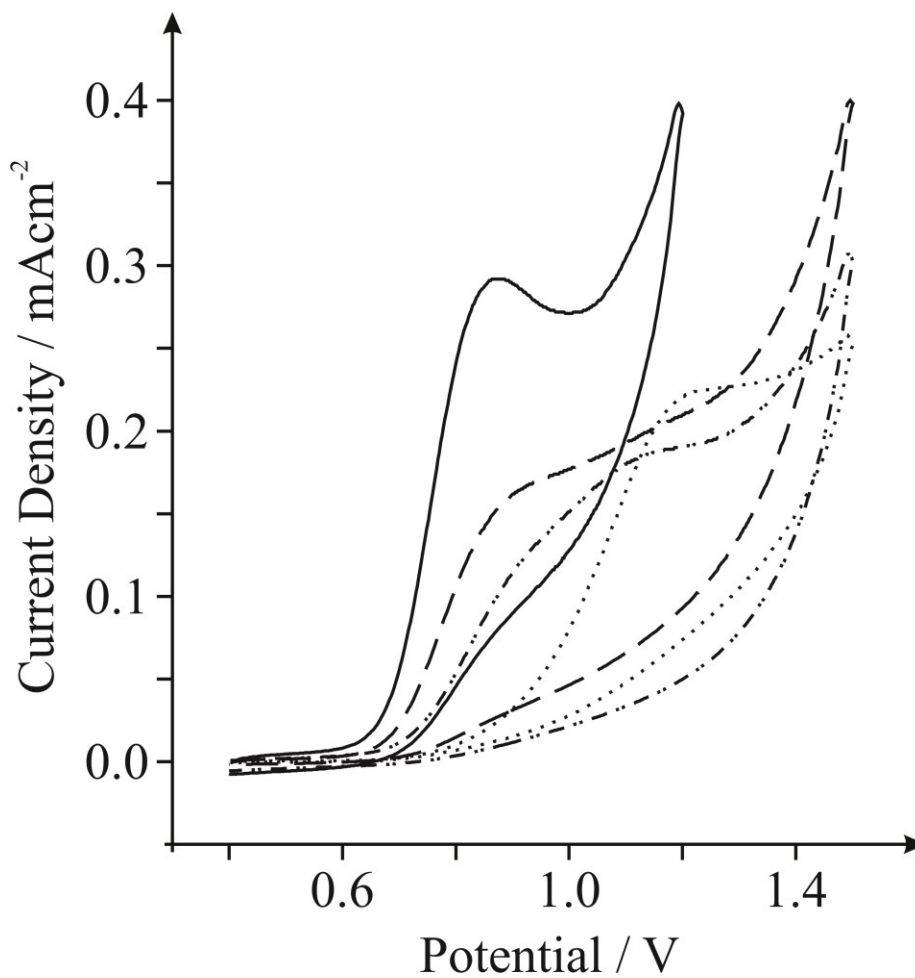


Figure 2

Cyclic voltammetric profiles recorded for 1 mM kojic acid in PBS (pH 6, with 0.1 M KCl) at a scan rate of 100 mVs^{-1} (vs. SCE). **A:** using an EPPG electrode (dotted line) with the addition/immobilisation of increasing masses/amounts of 10, 20, 30 and 40 ng graphene (solid lines). **B:** using a BPPG electrode (dotted line) with the addition/immobilisation of increasing masses/amounts of 4, 10, 15 and 20 μg graphite (solid lines).

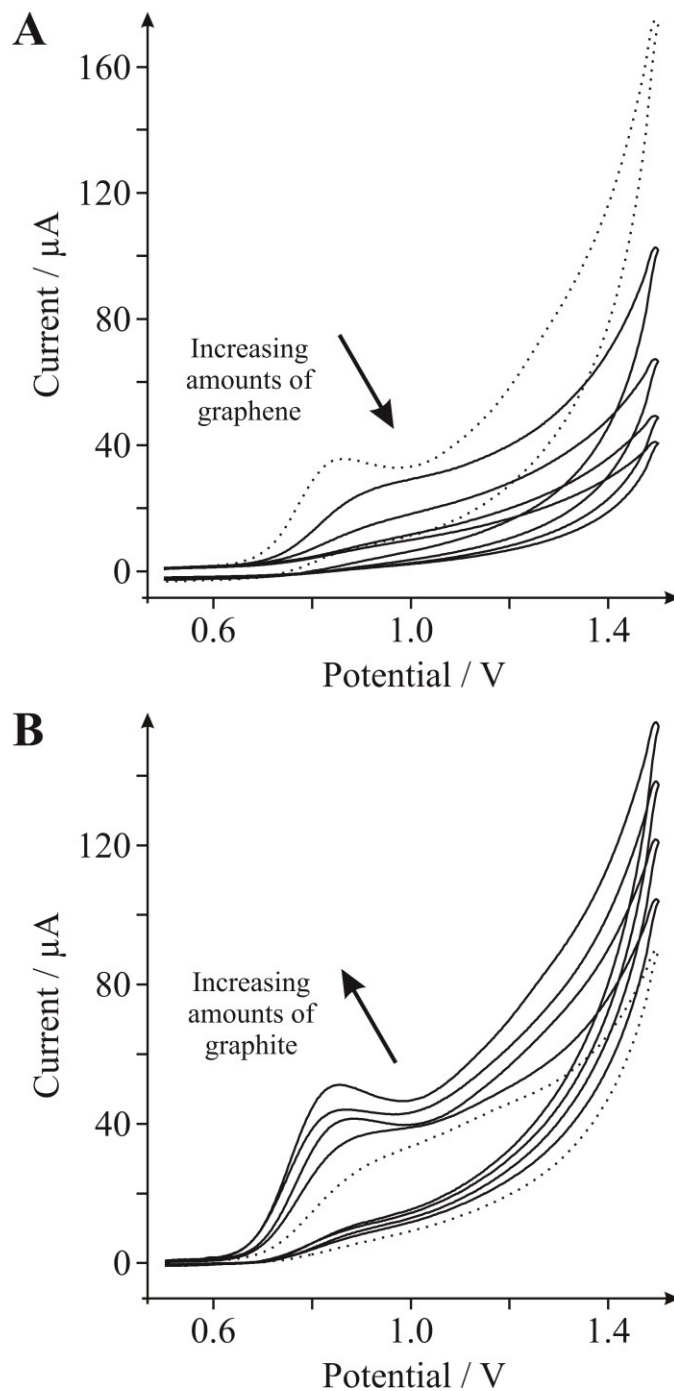


Figure 3

A plot depicting the relationship between ‘the mass of a given graphitic material deposited/immobilised upon a supporting electrode substrate’ and ‘the voltammetric peak current recorded due to the oxidation of 1 mM kojic acid in PBS’ (pH 6, with 0.1 M KCl). Cyclic voltammograms utilised a scan rate of 100 mVs^{-1} (vs. SCE). *Squares*: additions of 10, 20, 30 and 40 ng graphene onto an EPPG electrode, *Circles*: additions of 4, 10, 15 and 20 μg graphite onto a BPPG electrode, and *Triangles*: additions of 2, 4, 10 and 15 μg GO onto a BPPG electrode. Note that increasing additions relate to their respective ‘addition number’ on the x-axis, where ‘0’ (addition of material) represents the voltammetry observed at the bare/unmodified supporting electrode in each case.

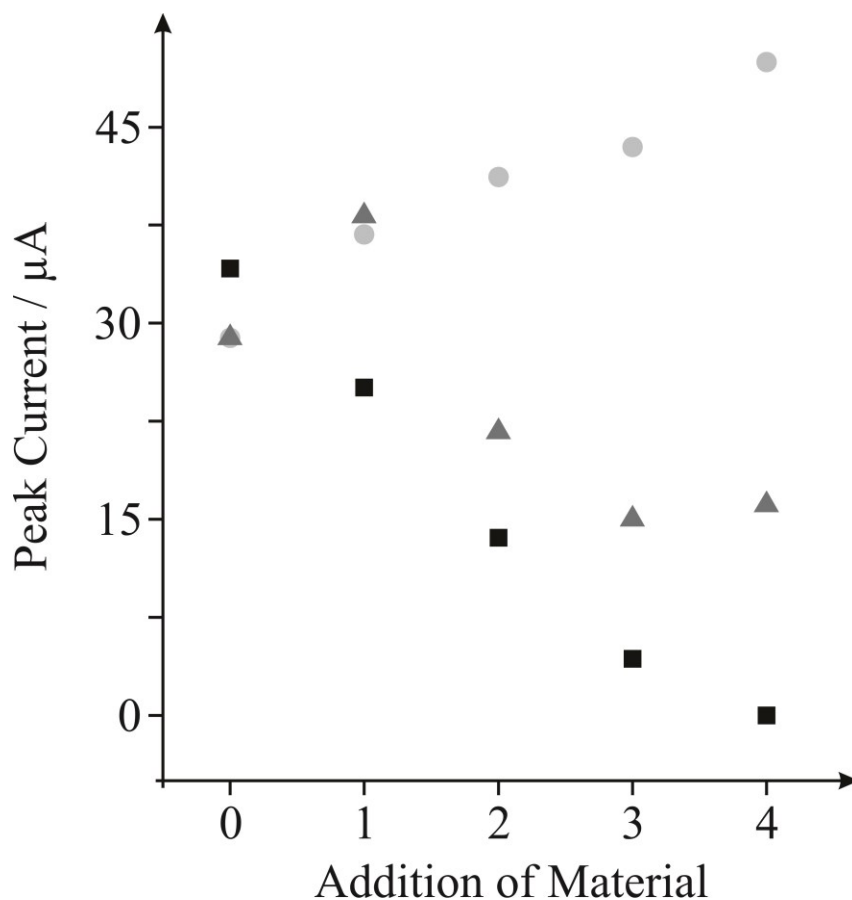
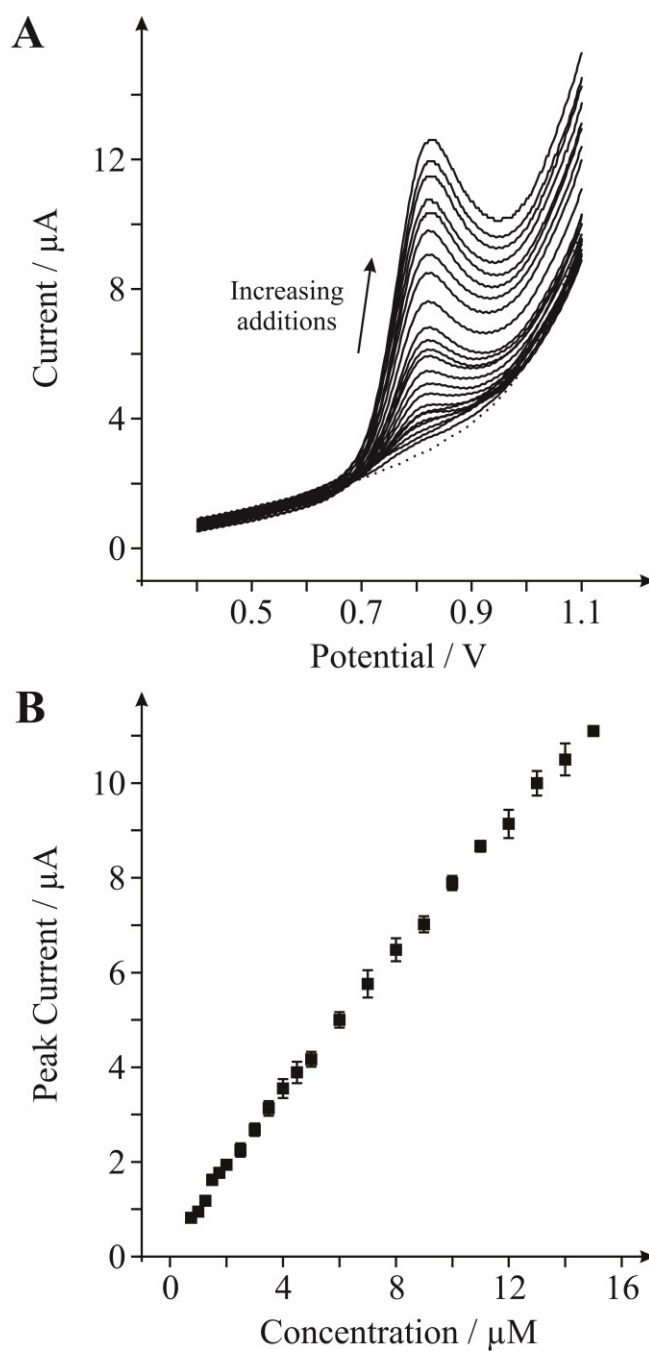


Figure 4

A: Linear sweep voltammograms recorded utilising an EPPG electrode in a PBS (pH 6, with 0.1 M KCl), 'blank' (dotted line) and following the successive addition of kojic acid into the buffer solution to give the following concentration range: 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.50, 3.00, 3.50, 4.00, 4.50, 5.00, 6.00, 7.00, 8.00, 9.00, 10.00, 11.00, 12.00, 13.00, 14.00 and 15.00 μM (solid lines). **B:** A calibration plot of kojic acid concentration *versus* the voltammetric peak current obtained at the EPPG electrode. All data obtained at a scan rate of 100 mVs^{-1} (vs. SCE).



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