Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Adsorption on graphene: flat to edge to end transitions of phenyl hydroquinone

Lifu Chen, Eden E. L. Tanner and Richard G. Compton*

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University,
South Parks Road, Oxford OX1 3QZ, UK

*To whom correspondence should be addressed

Email: richard.compton@chem.ox.ac.uk

Phone: +44 (0) 1865 275957 Fax: +44 (0) 1865 275410

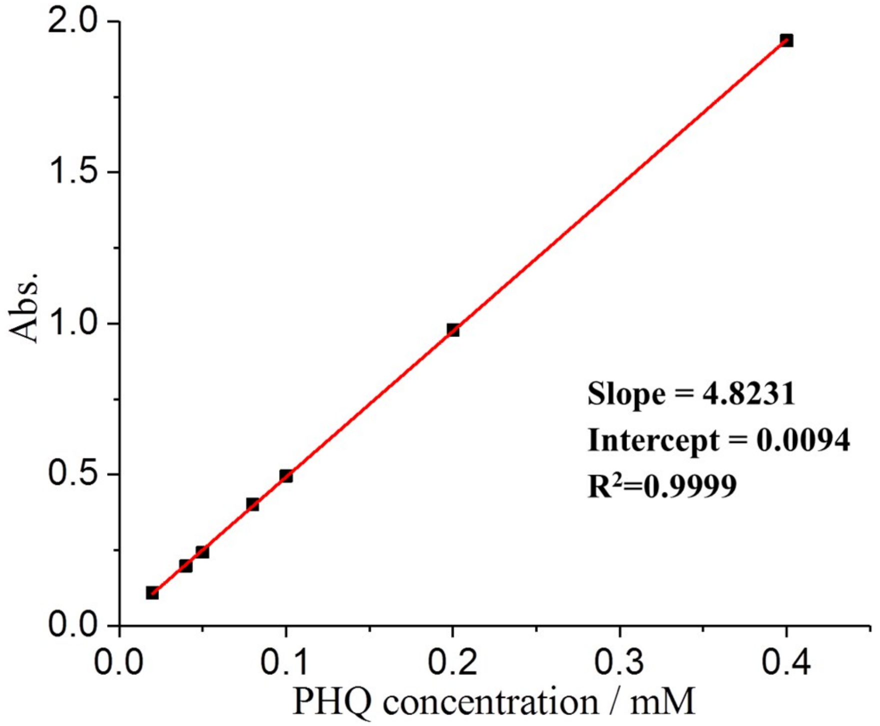

Figure S1. Calibration line of phenyl hydroquinone in buffered solution (19.75 M methanol and 0.2 M HCl)

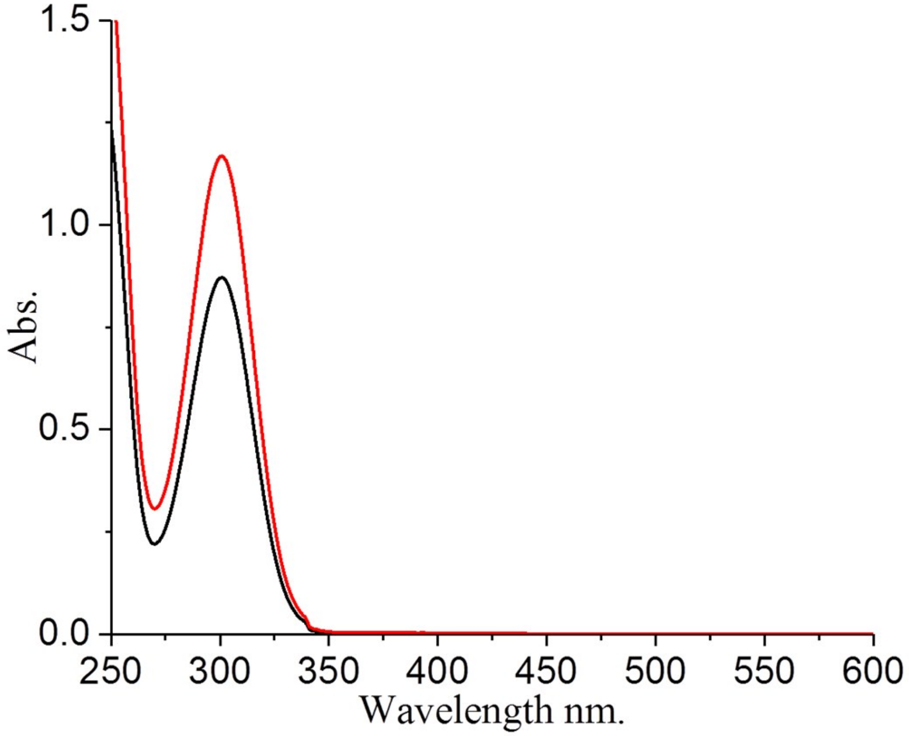

Figure S2. UV-Vis absorption of a buffered solution (19.75 M methanol and 0.2 M HCl) containing 5 mM phenyl hydroquinone before GNPs adsorption (red line) and after adsorption (black line); Dilution factor = 20.

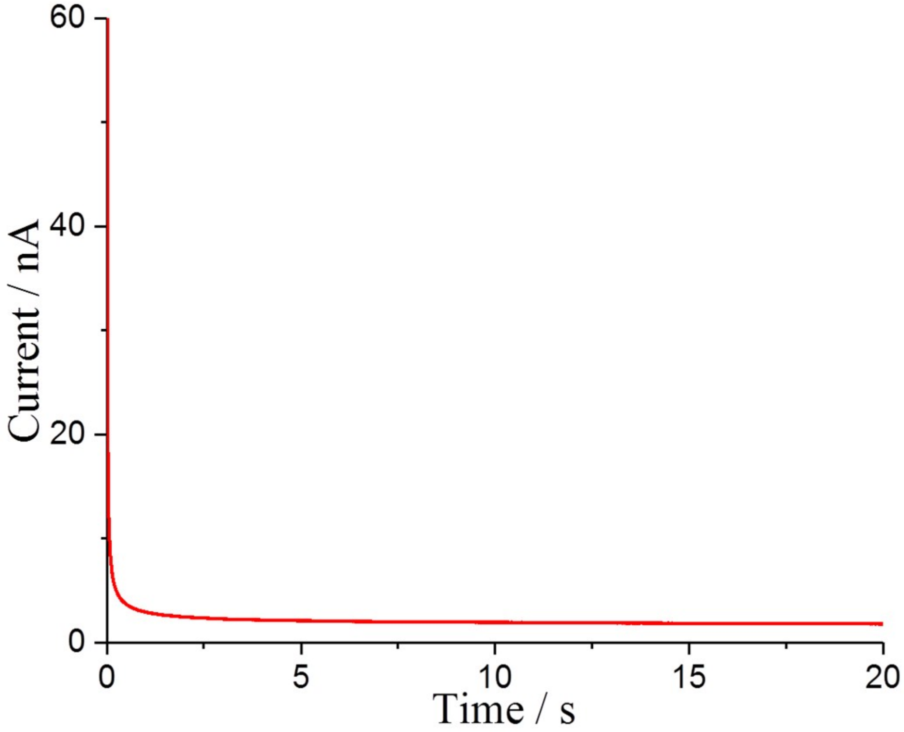

Figure S3. Representative chronoamperometric profiles of buffered solution containing 19.75 M methanol and 0.2 M HCl without addition of PHQ-GNPs suspension at +1.0 V *vs.* SCE.

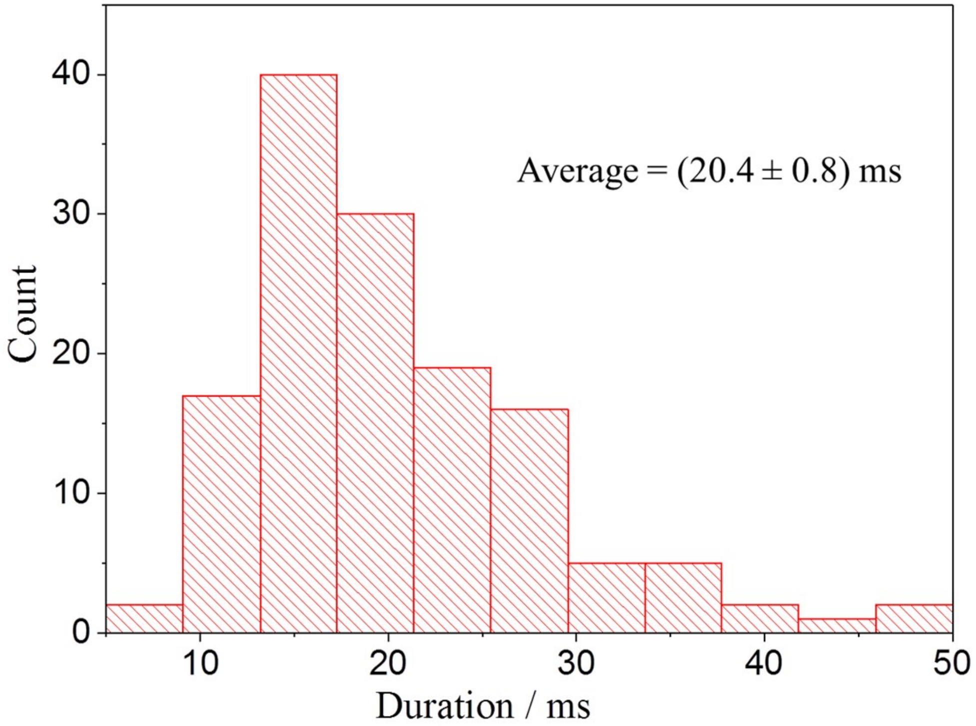

Figure S4. Distribution of spike duration from oxidation of single PHQ-GNPs by analysis of the 146 current spikes at + 1.0 V *vs*. SCE. Average duration = (20.4 ± 0.8) ms

Maximum surface coverage ($\Gamma_{\max}$) of PHQ on GNPs from UV-Vis studies:

For single GNP particle, average surface area of GNP is 297 ± 152 μm^2 and the thickness is 7.1 ± 2 nm (estimated from scanning electron microscopy[1]). Hence the volume (V) of a single GNP can be estimated as $(2.11 \pm 1.08) \times 10^{-18}$ m^3. The bulk density of the GNPs is 1×10^5 g m^{-3} reported by the supplier.[2] For loose powders, the density of a single GNP is assumed to be the same as graphite, 2.26×10^6 g m^{-3}. [3] Therefore, the mass for single GNP can be estimated as $(4.77 \pm 2.44) \times 10^{-9}$ mg.

The amount of PHQ adsorbed onto 1 mg of GNPs (n) reaches the first plateau at $n_{\max} = 1.2 \times 10^{-7}$ mol mg^{-1}. For 1 mg of GNP, the total surface area is:

$$\frac{1}{(4.77 \pm 2.44) \times 10^{-9}\, mg} \times (2.97 \pm 1.52) \times 10^{-6}\, cm^2 = (6.23 \pm 3.19) \times 10^2\, cm^2\, mg^{-1}$$

Therefore, the maximum surface coverage ($\Gamma_{\max}$) at the first plateau can be determined as:

$$\Gamma_{max} = \frac{1.2 \times 10^{-7}\, mol\, mg^{-1}}{(6.23 \pm 3.19) \times 10^2\, cm^2\, mg^{-1}} = (1.9 \pm 0.6) \times 10^{-10}\, mol\, cm^{-2}$$

A similar calculation is conducted to obtain $\Gamma_{\max}$ at the second plateau and the third plateau.

Surface coverage (Γ_{max}) of PHQ on GNPs from nanoimpact method:

For nanoimpact method, the charge passed (Q) can be related to the number of PHQ molecules adsorbed per GNP (N) *via* $Q = nNe$, where n is the number of electrons transferred during oxidation of PHQ ($n = 2$), and e is the charge per electron.

$$N = \frac{Q}{ne} = \frac{(94.4 \pm 7.4)\ pC}{2 \times 1.60 \times 10^{-7}\ pC} = (29.5 \pm 2.3) \times 10^{7}$$

The surface coverage (Γ) can be obtained *via* $\Gamma = N / (N_A\ S_{GNP})$, where N_A is the Avogadro constant and S_{GNP} is the surface area of the GNP (equivalent to 297 ± 152 μm^2).[2]

$$\Gamma = \frac{N}{N_A\, S_{GNP}} = \frac{(29.5 \pm 2.3) \times 10^{7}}{6.022 \times 10^{-23}\ mol^{-1} \times (2.97 \pm 1.52) \times 10^{-6}\ cm^2} = (1.6$$

The area occupied by each individual PHQ molecule ($S_{R\text{-}PHQ}$) on the GNP can be determined *via* $S_{R\text{-}PHQ} = S_{GNP} / N$.

$$S_{R-PHQ} = \frac{S_{GNP}}{N} = \frac{(2.97 \pm 1.52) \times 10^{-6}\ cm^2}{(29.5 \pm 2.3) \times 10^{7}} = (10.1 \pm 4.1) \times 10^{-15}\ cm^2$$

Experimental

Chemicals

Graphene nanoplatelets (GNPs, 15 μm in width, 6-8 nm in thickness) were purchased from Strem Chemicals (MA, USA). Unless specified otherwise, all other chemicals were provided from Sigma-Aldrich at reagent grade and used as received without further purification. All solutions were made up with deionised water of resistivity not less than 18.2 MΩ cm (Millipore) at 298 K and degassed thoroughly with pure nitrogen (BOC Gases plc, UK) prior to use. The buffered solution (19.75M methanol and 0.2 M HCl) was freshly prepared from pure methanol (99.8%) and 1 M HCl. This amount of methanol was determined experimentally for the minimal amount of methanol required to make a 300 mM PHQ aqueous solution, and thus all following experiments were conducted in this buffer.

UV-Vis Spectroscopy

A wide range of concentrations (from 0.1 mM to 300 mM) of PHQ in the buffered solution were made. A certain amount of GNPs were then mixed with 1 mL of different concentrations of PHQ solutions. The amount of GNPs used for each PHQ solution was determined by calculation such that the GNPs used must reduce at least 20% of PHQ concentration, assuming a full monolayer coverage of PHQ on GNPs. The mixture of GNPs and PHQ solution was then sonicated (FB15050, Fisher Scientific, 50/60 Hz, 80W, Germany) for 35 min to promote adsorption, followed by centrifugation (Eppendorf Centrifuge 5430 R) for 15 min at 14000 rpm. The original PHQ solution before adsorption and the supernatant after adsorption were both diluted into calibration region then measured by UV-Vis spectroscopy.

UV-Vis studies were performed in 10 mm width quartz cells by a Shimadzu UV-1800 UV spectrophotometer. In all cases, a baseline correction was conducted prior to measurement, and the absorbance was recorded from 600–220 nm.

Preparation of PHQ-GNP Stock Suspension

A suspension of 3.3×10^{-13} M of PHQ-GNPs was prepared by mixing 2.8 mg of GNPs with 10 mL of 3 mM PHQ in buffered solution and then sonicated (FB15050, Fisher Scientific, 50/60 Hz, 80W, Germany) for 35 min to allow the full adsorption of PHQ onto GNPs. The well dispersed mixture was then divided into ten portions by being transferred into ten microcentrifuge tubes (1.5mL, Fisherband) equally, followed by centrifugation (Eppendorf Centrifuge 5430 R) for 15 min in 14000 rpm. 1 mL of buffered solution was then added into settled modified GNPs powder. The mixture was shaken on a vortex (Whirlmixer, Loughbough, UK) for 30 s and sonicated for 20 s. This dispersion procedure was repeated 3 times to get an even suspension. The above stock suspension was freshly prepared every day.

Carbon fibre micro electrode fabrication

The method of carbon fibre micro electrode fabrication follows that developed by Ellison *et al.*[4] Briefly, a carbon fibre (diameter 7.0 μm, Goodfellow, Cambridge, UK) was adhered to a metal wire *via* silver epoxy (RS Components Ltd.) conductive adhesive, which was then placed in an oven at approximately 60 °C for 15 min to set the adhesive. Next, the wire was threaded through a plastic pipette tip. The interstice between wire and tip was sealed using cyanoacrylate adhesive and the wire slowly pulled down, leaving only the carbon fibre extended out of the end, and left overnight to set the cyanoacrylate adhesive. Finally, the carbon fibre was cut to approximate 1 mm length.

Electrochemical procedures

Electrochemical experiments were conducted at 25 °C inside a Faraday cage with a standard three-electrode system by using a μAutolab II potentiostat (Metrohm-Autolab BV, Netherlands) and NOVA 1.10 software. For the cyclic voltammetry measurements, a basal-plane pyrolytic graphite (BPPG) electrode was used as the working electrode, a saturated calomel electrode (SCE, ALS distributed by BASi, Tokyo, Japan) as the reference and a graphite rod as the counter electrode. The BPPG electrode was produced from pieces of the highly ordered pyrolytic graphite (HOPG) (Le Carbone, Sussex, UK). Prior to each modification, the BPPG electrode was polished using the electrode surface on sand paper P2500 and P4000 grade respectively, followed by repeatedly pressing with cellotape (Henkel AG, Dusseldorf, Germany) 10-15 times. The electrode was subsequently rinsed with water and dried with nitrogen. Cyclic voltammograms were then recorded at different scan rates in a degassed 3 mM PHQ solution containing 19.75 M methanol and 0.2 M HCl.

In nano-impact experiments, chronoamperometry was conducted at a carbon fibre wire electrode with the same reference electrode and counter electrode as above. Note that the potentiostat used in this work accurately conserves the charge transferred due to a particle-impact process despite possible alteration in the spike shape.[5, 6] 4 mL of buffered solution was bubbled with nitrogen for 5 min and then 1 mL of the PHQ-GNPs stock suspension was added while the nitrogen was kept bubbling for further 5 s to get an even suspension, followed by immediate chronoamperometric scans at + 1.0 V for 20s. The program "SignalCounter" developed by Dr. D Omanovic (Centre for Marine and Environmental Research Zagreb, Croatia) was used for impact spike identification and individual spike area determination.[7]

References

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