Electronic Supplementary Information

Experimental details – graphene synthesis

Graphene is commercially obtained from 'Graphene Supermarket' (Reading, MA, USA) [1] and is produced *via* a substrate-free gas-phase synthesis method. [2-4] This single-step technique involves sending an aerosol consisting of liquid ethanol droplets and argon gas directly into a microwave-generated argon plasma (at atmospheric-pressure), where over a time scale in the order of 10^{-1} s, ethanol droplets evaporate and dissociate in the plasma forming solid matter that through characterisation by Transmission Electron Microscopy (TEM) and Raman spectroscopy is confirmed to be true graphene. [2, 3] The fabricated graphene sheets are sonicated in ethanol to form a homogeneous suspension before being distributed. [1, 4] Once received from the supplier, aliquots of the graphene were carefully pipetted onto the electrode surface using a micro-pipette and allowed to dry at room temperature under nitrogen flow in order to eliminate oxidation of the graphene by the presence of atmospheric oxygen, following which the electrode could either be further modified, or is ready to use.

Figure S1A depicts a typical TEM image of the commercially purchased graphene and Figure S1B shows a high-resolution TEM image where a hexagonal arrangement of carbon atoms, which is characteristic of graphene, is clearly evident. Additionally, this material has been characterised and reported previously by Dato and co-workers, [3] and Figure S1C from their work shows an atomic-resolution image that reveals a highly ordered synthesized single-layer graphene sheet – captured with an aberration-corrected transmission electron microscope (TEAM 0.5), [3] capable of clearly resolving individual carbon atoms, adsorbates, and defects on graphene at an accelerating voltage of 80 kV. [3] Fourier Transform Infrared spectroscopy (FT-IR) analysis was used to determine the presence of functional groups on the graphene, where it is evident that such groups were either absent or minimal. [3] X-ray photoelectron spectroscopy (XPS) analysis was performed (using a PHI 5400 ESCA/XPS utilising an Al Ka radiation source – the spot size used was 1.1 mm in diameter) and reported to reveal that oxygen from the ethanol utilised during the synthesis process does not bond to the graphene sheets, and it was additionally reported that the clean and highly ordered free-standing graphene sheets are free from functional groups. [3]

XPS – graphene characterisation

We independently acquired XPS chemical analysis of the ‘as received’ graphene (performed with a VG-Microtech Multilab electron spectrometer) which reveals the material to comprise of 95.04 % atomic carbon and 4.96 % atomic oxygen. Analysis of the XPS spectra reveals a large peak at 284.6 eV associated to C-H bonding and analysis of the oxygen peak at 531.64 eV is associated to C=O moieties. This is a very low O/C ratio, as expected for near true graphene.

Table S1:

A table detailing the respective linear regressions of best fit observed with regards to the sensing of various analytes of interest, regressions were obtained through analysis of voltammetric peak height (I_P) as a function of concentration at edge- and basal- plane pyrolytic graphite (EPPG and BPPG respectively) electrodes both prior-to and post modification with graphene (G), $N = 3$.

Dopamine hydrochloride (I_P^{ox})		
EPPG:	$I_P/\text{A} = 1.49 \times 10^{-1}\ \text{A M}^{-1} + 4.57 \times 10^{-7}\ \text{A}$	$R^2 = 0.997$
EPPG + 20 ng G:	$I_P/\text{A} = 1.00 \times 10^{-1}\ \text{A M}^{-1} + 9.69 \times 10^{-9}\ \text{A}$	$R^2 = 0.987$
BPPG:	$I_P/\text{A} = 8.17 \times 10^{-2}\ \text{A M}^{-1} + 7.20 \times 10^{-8}\ \text{A}$	$R^2 = 0.995$
BPPG + 20 ng G:	$I_P/\text{A} = 7.11 \times 10^{-2}\ \text{A M}^{-1} - 1.43 \times 10^{-7}\ \text{A}$	$R^2 = 0.984$
Uric acid (I_P^{ox})		
EPPG:	$I_P/\text{A} = 1.30 \times 10^{-1}\ \text{A M}^{-1} + 1.75 \times 10^{-7}\ \text{A}$	$R^2 = 0.988$
EPPG + 20 ng G:	$I_P/\text{A} = 8.89 \times 10^{-2}\ \text{A M}^{-1} - 6.21 \times 10^{-8}\ \text{A}$	$R^2 = 0.985$
BPPG:	$I_P/\text{A} = 8.41 \times 10^{-2}\ \text{A M}^{-1} - 8.53 \times 10^{-7}\ \text{A}$	$R^2 = 0.984$
BPPG + 20 ng G:	$I_P/\text{A} = 4.03 \times 10^{-2}\ \text{A M}^{-1} - 1.84 \times 10^{-7}\ \text{A}$	$R^2 = 0.987$
Acetaminophen (I_P^{ox})		
EPPG:	$I_P/\text{A} = 2.05 \times 10^{-1}\ \text{A M}^{-1} - 4.35 \times 10^{-8}\ \text{A}$	$R^2 = 0.995$
EPPG + 20 ng G:	$I_P/\text{A} = 1.39 \times 10^{-1}\ \text{A M}^{-1} + 4.15 \times 10^{-7}\ \text{A}$	$R^2 = 0.993$
BPPG:	$I_P/\text{A} = 1.21 \times 10^{-1}\ \text{A M}^{-1} + 1.98 \times 10^{-8}\ \text{A}$	$R^2 = 0.990$
BPPG + 20 ng G:	$I_P/\text{A} = 1.01 \times 10^{-1}\ \text{A M}^{-1} - 9.54 \times 10^{-8}\ \text{A}$	$R^2 = 0.985$
p-Benzoquinone (I_P^{red})		
EPPG:	$I_P/\text{A} = -1.39 \times 10^{-1}\ \text{A M}^{-1} + 6.98 \times 10^{-7}\ \text{A}$	$R^2 = 0.992$
EPPG + 40 ng G:	$I_P/\text{A} = -9.82 \times 10^{-2}\ \text{A M}^{-1} + 4.46 \times 10^{-7}\ \text{A}$	$R^2 = 0.981$
BPPG:	$I_P/\text{A} = -8.12 \times 10^{-2}\ \text{A M}^{-1} + 1.66 \times 10^{-7}\ \text{A}$	$R^2 = 0.987$
BPPG + 40 ng G:	$I_P/\text{A} = -8.04 \times 10^{-2}\ \text{A M}^{-1} - 1.36 \times 10^{-7}\ \text{A}$	$R^2 = 0.995$

Figure S1:

(A) A typical low-magnification TEM image of the graphene sheets; the scale bar is 100 nm. **(B)** A high-resolution TEM image, where the white arrow indicates the edge of the graphene sheet; the scale bar is 4 Å. **(C)** An atomic-resolution image (TEAM 0.5) of a clean and structurally perfect synthesised graphene sheet. Individual carbon atoms appear white in the image. The image was obtained through the reconstruction of the electron exit wave function from 15 lattice images using MacTempas software. Reproduced with permission from Ref: [3].

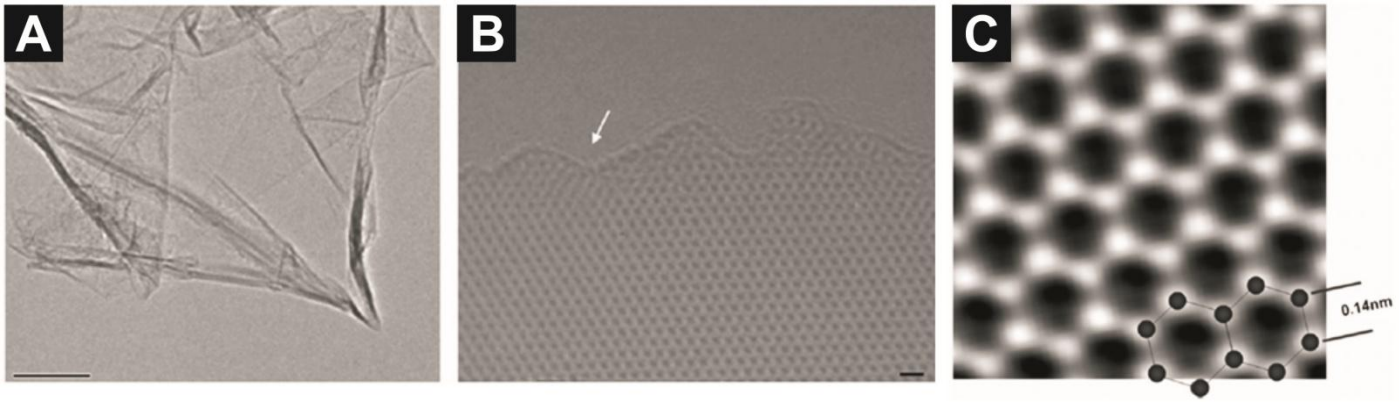
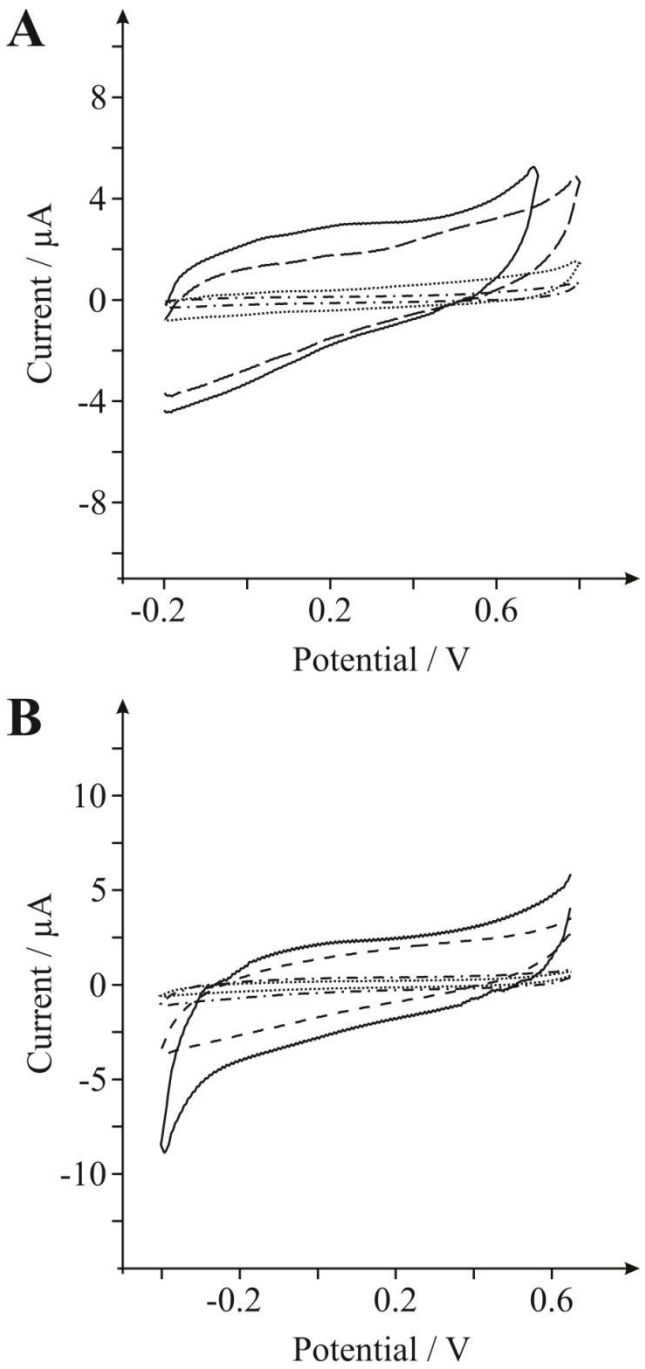


Figure S2:

Cyclic voltammetric profiles recorded in a pH 7 phosphate buffer solution using unmodified EPPG (solid line) and BPPG (dot-dashed line) electrodes, and graphene modified EPPG (dashed line) and BPPG (dotted line) electrodes, where within both the anodic (**A**) (20 ng graphene modifications) and cathodic (**B**) (40 ng graphene modifications) potential regions there are no evident voltammetric peaks prior to the addition of our analytes. Scan rate: 100 mVs^{-1} (*vs.* SCE).



References:

1. www.graphene-supermarket.com.
2. A. Dato, V. Radmilovic, Z. Lee, J. Phillips and M. Frenklach, *Nano Lett.*, 2008, **8**, 2012.
3. A. Dato, Z. Lee, K.-J. Jeon, R. Erni, V. Radmilovic, T. J. Richardson and M. Frenklach, *Chem. Commun.*, 2009, 6095.
4. Z. Lee, K.-J. Jeon, A. Dato, R. Erni, T. J. Richardson, M. Frenklach and V. Radmilovic, *Nano Lett.*, 2009, **9**, 3365.