Electronic Supplementary Information (ESI)

Experimental Information

All chemicals (analytical grade or higher) 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 MΩ cm. Voltammetric and galvanostatic charge/discharge measurements were carried out using a μ-Autolab III (ECO-Chemie, The Netherlands) potentiostat. All measurements were conducted using a three electrode system; working electrodes were used as highlighted below, with a platinum (Pt) wire counter and a saturated calomel reference electrode (SCE) (Radiometer, Copenhagen, Denmark) completing the circuit.

Screen printed carbon electrodes (SPEs) were fabricated in-house with appropriate stencil designs using a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK). A carbon-graphite ink formulation was first screen printed onto a polyester flexible film (Autostat, 250 μm thickness) defining the carbon contacts, counter, and working electrodes. This layer was cured in a fan oven at 60 degrees for 30 minutes. Next a silver/silver chloride (Ag/AgCl) reference electrode was included by screen printing Ag/AgCl paste (Gwent Electronic Materials Ltd, UK) on to the plastic substrate, and curing again at 60 degrees for 30 minutes. Note that in the work presented in this communication, we chose to use a Saturated Calomel Electrode (SCE) as the reference electrode to allow a direct comparison with literature reports. Last a dielectric paste ink (Gwent Electronic Materials Ltd, UK) was printed to cover the connections and define the 3mm diameter graphite working electrode, note however that in this work a Pt wire counter electrode was utilised. After curing at 60 degrees for 30 minutes the screen printed electrode is ready to use. These electrodes have been characterised electrochemically in a prior paper using the ferro/ferricyanide redox probe and have heterogeneous rate constants of ~ 1.7×10^{-3} cm s^{-1}. [1]

The edge plane pyrolytic graphite working electrode (EPPG, 4.9 mm diameter, Le Carbone, Ltd. Sussex, U.K) was machined into a 4.9 mm diameter, with the disc face parallel with 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, La of 1 – 10 μm and 0.4 ± 0.10 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 with the basal plane as required.

Graphene Characterisation

The graphene (containing surfactant) was commercially obtained from NanoIntegris, (Illinois, USA) and are known as 'PureSheetsTM' (research grade) and comprise entirely pristine graphene platelets that have not been oxidised, reduced, or chemically modified in anyway. The graphene is produced *via* density gradient ultracentrifugation and the methodology has been reported and characterised previously. [2, 3] The process involves the bile salt sodium cholate which promotes graphite exfoliation resulting in graphene-surfactant complexes having buoyant densities that vary with graphene thickness. This results in a 'sorting' of the graphene and hence different fractions are observed meaning that graphite and multi-layer graphene is not inadvertently incorporated into the graphene samples. The graphene is in an aqueous solution (0.5 μg per 10 μL) with an ionic surfactant (2% w/v) and consists of a mean flake area of 10,000 nm^2. The graphene consists of: 27% single layer, 48% double layer, 20% triple layer and 5% 4+ layer and due to the fabrication approach does not have any graphite impurities.

Fig. 1A depicts a typical AFM image of several pristine graphene flakes on a SiO_2 substrate provided by the manufacturer. [2]

XPS chemical analysis of the graphene solution was performed with a VG-Microtech Multilab electron spectrometer. This reveals the presence of 74.66 % atomic carbon, 16.43 % atomic oxygen, 4.12 % atomic nitrogen, 2.63 % atomic sodium and 2.13% atomic sulphur. Interpretation of the XPS spectra for the case of the oxygenated species reveals the presence of hydroxyl, carbonyl, epoxy, and ether functional groups. Identification of nitrogen *via* XPS likely indicates pyridone type functionalisation which is likely due to an acid treatment performed prior to the density gradient ultracentrifugation process. We however note that this information is not easily de-convoluted from the contribution of the sodium cholate surfactant which is present. Additionally, XPS indicates the presence of sulfur, sodium, and nitrogen which might suggest that both anionic (in addition to sodium cholate) and cationic surfactants are present with the latter likely part of post-processing by the company supplying the graphene; however the company supplying the graphene are unable to comment on this.

The graphene (with no surfactant) 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 mg per 1 L) that have not been oxidised, reduced, or chemically modified in anyway and are free from surfactants and oxygenated functional groups. [4] The graphene is produced *via* a substrate-free gas-phase synthesis method, as previously reported. [5-7] The 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 graphene. [5, 6] The fabricated graphene sheets are sonicated in ethanol to form a homogeneous suspension before being distributed. [4, 7] 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). [4]

Fig. 2A depicts a typical TEM image of the commercially purchased graphene, Fig. 2B shows a high-resolution TEM image where a hexagonal arrangement of carbon atoms that is characteristic of graphene is evident, and Fig. 2C 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), [6] capable of clearly resolving individual carbon atoms, adsorbates, and defects on graphene at an accelerating voltage of 80 kV. [6]

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. [6] X-ray photoelectron spectroscopy (XPS) analysis measuring C, H, and N content revealed the mass composition of the graphene to be 98.9% C, 1.0% H, and 0.0% N respectively. [6] Direct measurement of oxygen showed a mass composition of 0.1%. [6] These results show that oxygen from the ethanol does not bond to the graphene during the synthesis process, and that the clean and highly ordered free-standing graphene sheets are free from functional groups. [6]

The graphene oxide was commercially obtained from 'Graphene Supermarket' (Reading, MA, USA), and are known as 'Single Layer Graphene Oxide Dispersion in Water', comprising of graphene oxide dispersed in aqueous solution (275 mg per L) that have a composition of 79 %

carbon and 20% oxygen. [4] The graphene oxide was synthesised using a modified Hummers oxidation method that has been reported and characterised previously; [8, 9] and has an average flake thickness of 1 atomic layer (at least 80%) and an average flake size of 0.5 - 5 microns. [4] Fig. 3 depicts a typical SEM image of the graphene oxide. [4]

Electrode Preparation

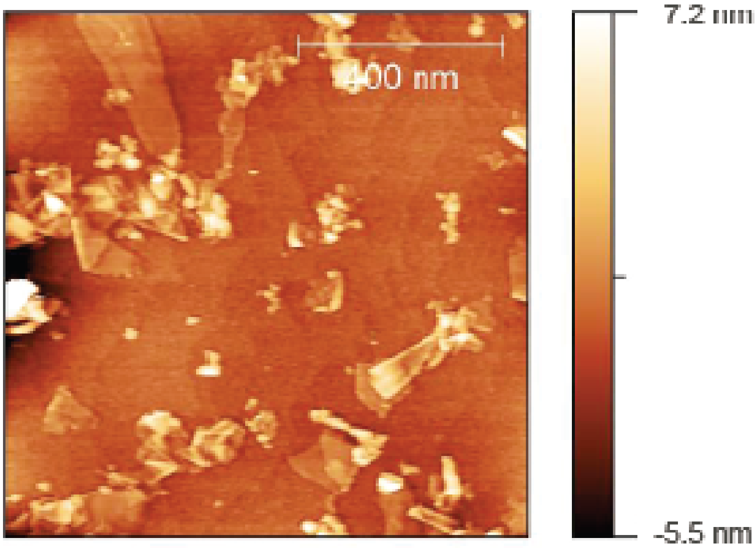
Aliquots of the graphene were carefully pipetted onto the electrode surface using a micro-pipette and allowed to dry at room temperature under nitrogen flow in order to eliminate oxidation of the graphene by the presence of atmospheric oxygen, following which the electrode can either be further modified or is ready to use. All comparison and control measurements, for example using the ionic surfactant sodium cholate (2% w/v) in the absence of graphene (note that surfactant deposited on the electrode was from a separate synthetic source), graphite (1 μg per 2 μL), and graphene oxide (as above) were conducted within the exact manner as with graphene. Where Nafion was employed in the presence of graphene the underlying graphene layer was first deposited using the above procedure, and when dry 40 μL of 0.05% Nafion (in ethanol) was added and dried using the same procedure. Where modified electrodes were utilised the capacitance of the unmodified electrode was subtracted from that of the modified electrode so that the true capacitance of the modified material could be determined.

Note that varying quantities of modified material in the experiments are utilised in-order to limit errors and is imperative for reproducibility; the amount of material supplied in suspension form is limited by the suppliers. However, note that we use specific capacitances, F/g and thus a direct comparison is achievable.

Please note also, within the main article where EPPG is shown to exhibit a larger capacitance than that of a BPPG electrode, it is inferred that edge plane sites (due to the lack of saturated carbons – not fully hexagonal forms) are highly reactive towards oxidation which incurs oxygenated species to be formed therefore increasing the capacitance of each individual graphene sheet comprising the EPPG electrode.

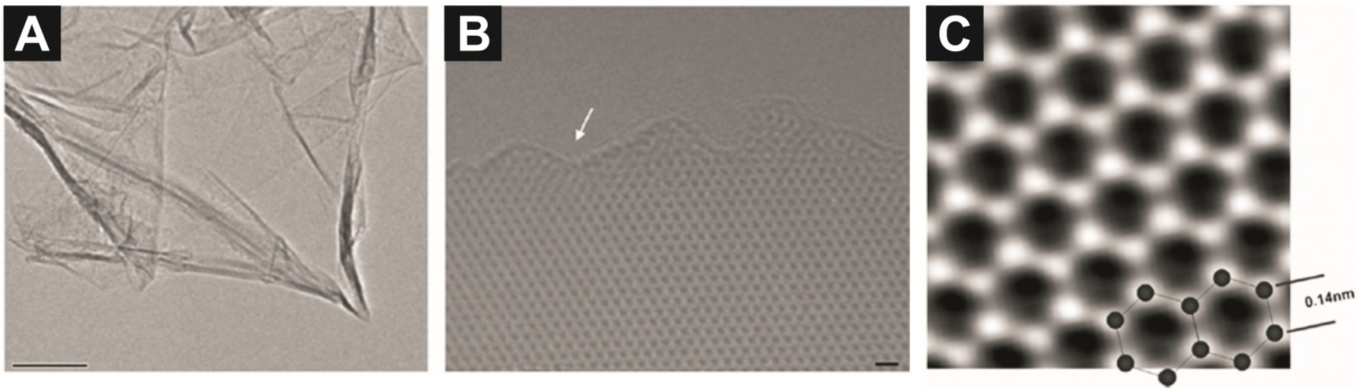
SI Figure 1

A typical AFM image of several pristine graphene flakes on a SiO_2 substrate provided by the manufacturer. [2]



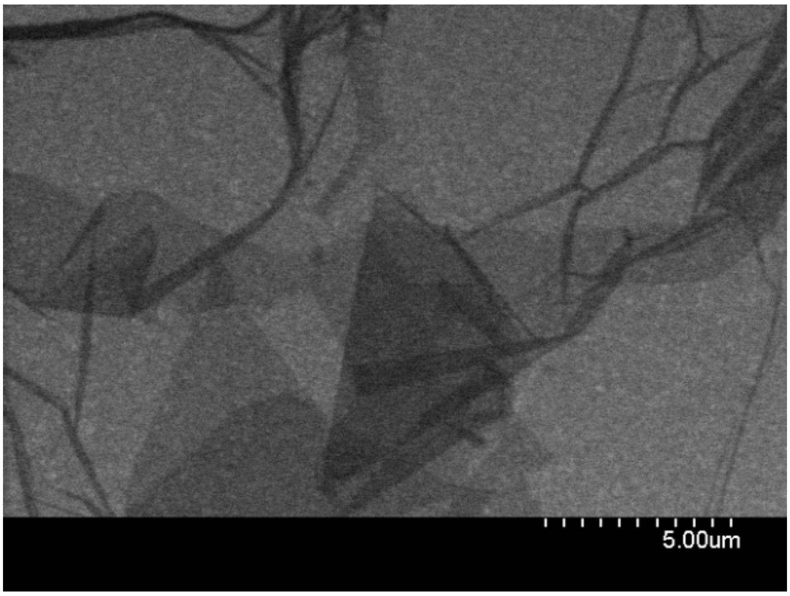
SI Figure 2

(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: [6]



SI Figure 3

A typical SEM image of the graphene oxide as provided by the manufacturer. [4]



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