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Experimental information:

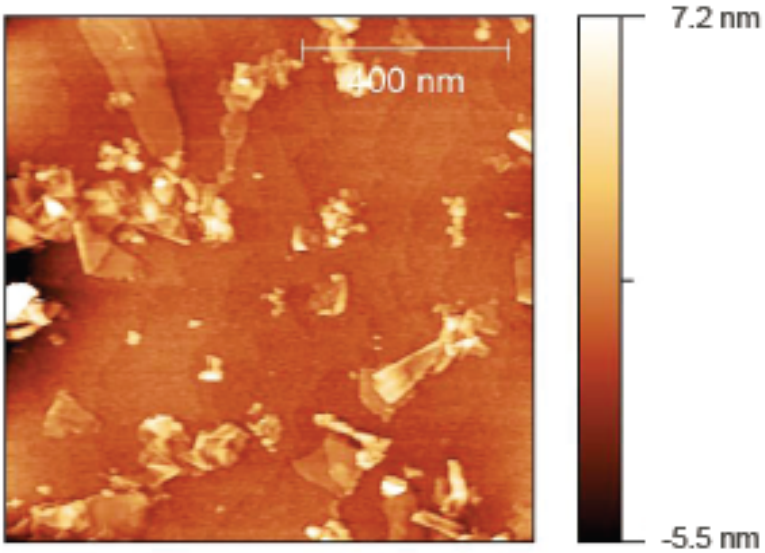
All chemicals used were of analytical grade and were used as received without any further purification and were obtained from Sigma-Aldrich. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm^{-1}.

Voltammetric measurements were carried out using a μ-Autolab III (ECO-Chemie, The Netherlands) potentiostat. All measurements were conducted using a three electrode arrangement. The working electrodes used were a basal plane pyrolytic graphite electrode (bppg, 4.9 mm diameter, Le Carbone, Ltd. Sussex, U.K) and an edge plane pyrolytic graphite electrode (eppg, 4.9 mm diameter, Le Carbone, Ltd. Sussex, U.K), and a highly ordered pyrolytic graphite slab (HOPG, 4.9 mm diameter, SPI supplies). The HOPG was purchased in the form of a 10 mm x 10 mmx 2 mm block from SPI supplies (PA, USA) and was of the 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 ± 0.1^0 mosaic spread. For bppg and eppg electrodes, discs of pyrolytic graphite were machined into a 4.9 mm diameter, with the disc face parallel with the edge plane, or basal plane as required. The counter electrode was a platinum wire, with a saturated calomel reference electrode (Radiometer, Copenhagen, Denmark) completing the circuit. The eppg electrode was polished on alumina compounds (3 μm) on soft lapping pads and then on diamond particles lapping compounds of decreasing sizes (1–0.25 μm). The bppg electrode surface was renewed using cellotape. This procedure involves polishing the bppg electrode surface on carborundum paper (2000 grade) and then pressing cellotape on the cleaned bppg surface before removing along with general attached graphite layers.

The graphene was commercially obtained from NanoIntegris, (Illinois, USA) and are known as 'PureSheets^{TM}' (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. [17] 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 with an ionic surfactant (2% w/v) and consists of a mean flake area of 10,000 nm^2. An AFM image of several pristine graphene flakes on an SiO_2 substrate provided by the manufacturer is shown below:



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. Aliquots of the graphene are carefully pipetted onto the bppg electrode surface 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 modified with more graphene is ready to use.

XPS chemical analyses were performed with a VG-Microtech Multilab electron spectrometer.