Electronic Supplementary Information (ESI)

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

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Experimental details – graphene synthesis

Pristine graphene is commercially obtained from 'Graphene Supermarket' (Reading, MA, USA) [1] and is reported to be produced *via* a substrate-free gas-phase synthesis method. [1-4] 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]

Figure S1A depicts a typical TEM image of a graphene sheet that has been fabricated using the same method as that noted above *via* a non-commercial source and Figure S1B shows a high-resolution TEM image (from the same source) where a hexagonal arrangement of carbon atoms, which is characteristic of graphene, is clearly evident. [3] Additionally, this material has been characterised and reported 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]

Independent TEM and Raman analysis of the commercially sourced graphene (as received from the supplier and consequently as used throughout this work) is presented in Figures S3 and S4 respectively. Figure S3 depicts typical TEM images of the commercially sourced graphene. It is evident that the graphene domains comprise of predominantly of single-layer graphene sheets, which appear to exhibit an intraplanar microcrystalline size, L_a of between 500 and 5000 nm and an average interplanar microcrystalline size, L_c of *ca*. 0.34 nm (one monolayer), which compares well to pristine graphene as reported theoretically in the literature. [5] Figure S4 depicts the Raman spectrum of the commercially sourced graphene. The Raman spectrum reveals two characteristic peaks at *ca*. 1580 and 2680 cm^{-1}, which are due to the G and 2D (G') bands respectively. The highly symmetrical 2D (G') peak indicates that the surface is comprised of single-layer graphene (consistent with TEM images). [6] Additionally, the intensity ratio of the G and 2D bands (G/2D = 0.61) indicates that the graphene sheets are indeed comprised of single-layer graphene domains, where the low intensity of the G band in relation to the 2D peak is characteristic of monolayer graphene. [6] The presence of a small D band (1330 cm^{-1}) indicates a small number of structural defects on the graphene surface (limited basal plane crystal defects), however the relatively low intensity of the D band, which is not easily distinguishable from the 'base line', suggests that an ordered graphene structure is present which is of high quality and thus represents that of pristine graphene in nature. [6]

Through detailed inspection of the above presented independent analysis (TEM and Raman spectroscopy), one can clearly confirm the presence of single layered 'pristine' graphene sheets that possess low oxygen content and a low coverage of edge plane like-site/defects. This graphene has been used in our prior work. [7-10]

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. Note that all images (A, B and C) have been reproduced with permission from Ref: [3], which is a non-commercial source that produces graphene utilising the same method as reported herein. Resultantly, note that said images are not characterisation of the commercially sourced graphene used in this study and have been utilised only to demonstrate the high quality of graphene attainable through this approach. For detailed independent analysis of the commercially available graphene utilised in this work please see Figures S3 and S4, which are interpreted in detail in this ESI.

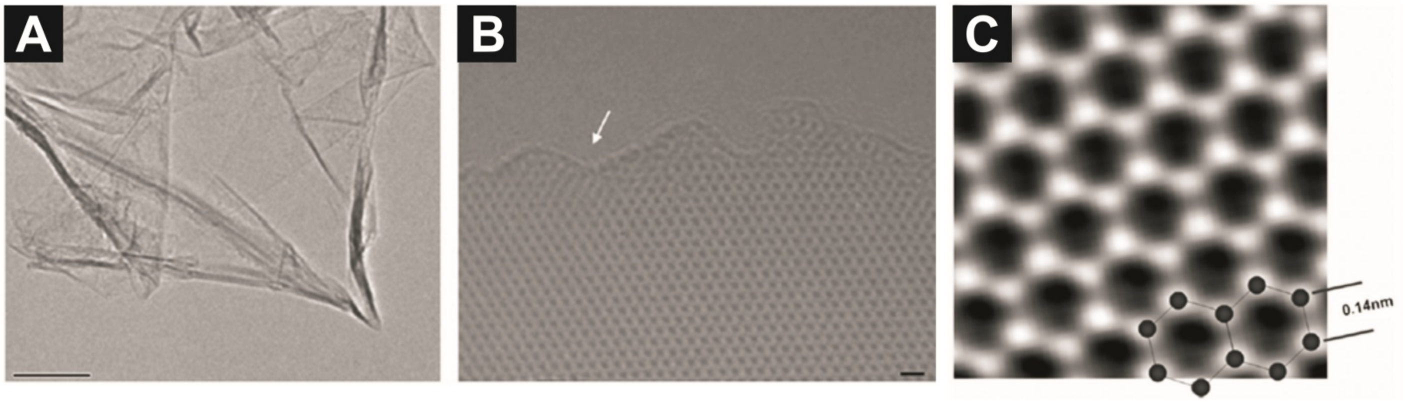


Figure S2

A typical SEM image of the commercially available graphene oxide, as provided by the manufacturer, Ref: [1].

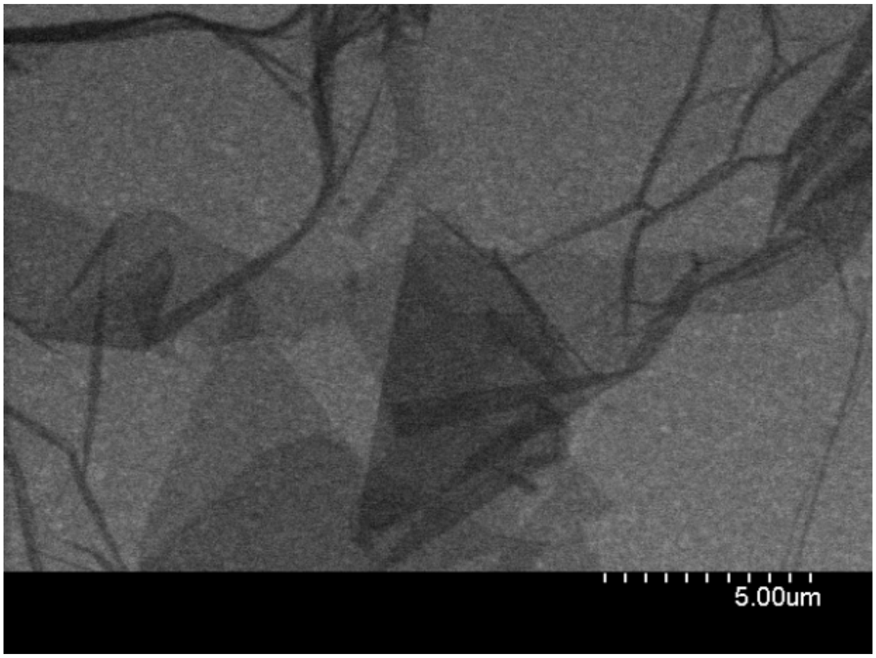


Figure S3

Typical TEM images of the commercially obtained graphene sheets utilised in this work, images taken at increasing magnification. TEM images were obtained using a JEOL JEM-2010 (Oxford, Inca Energy TEM 100).

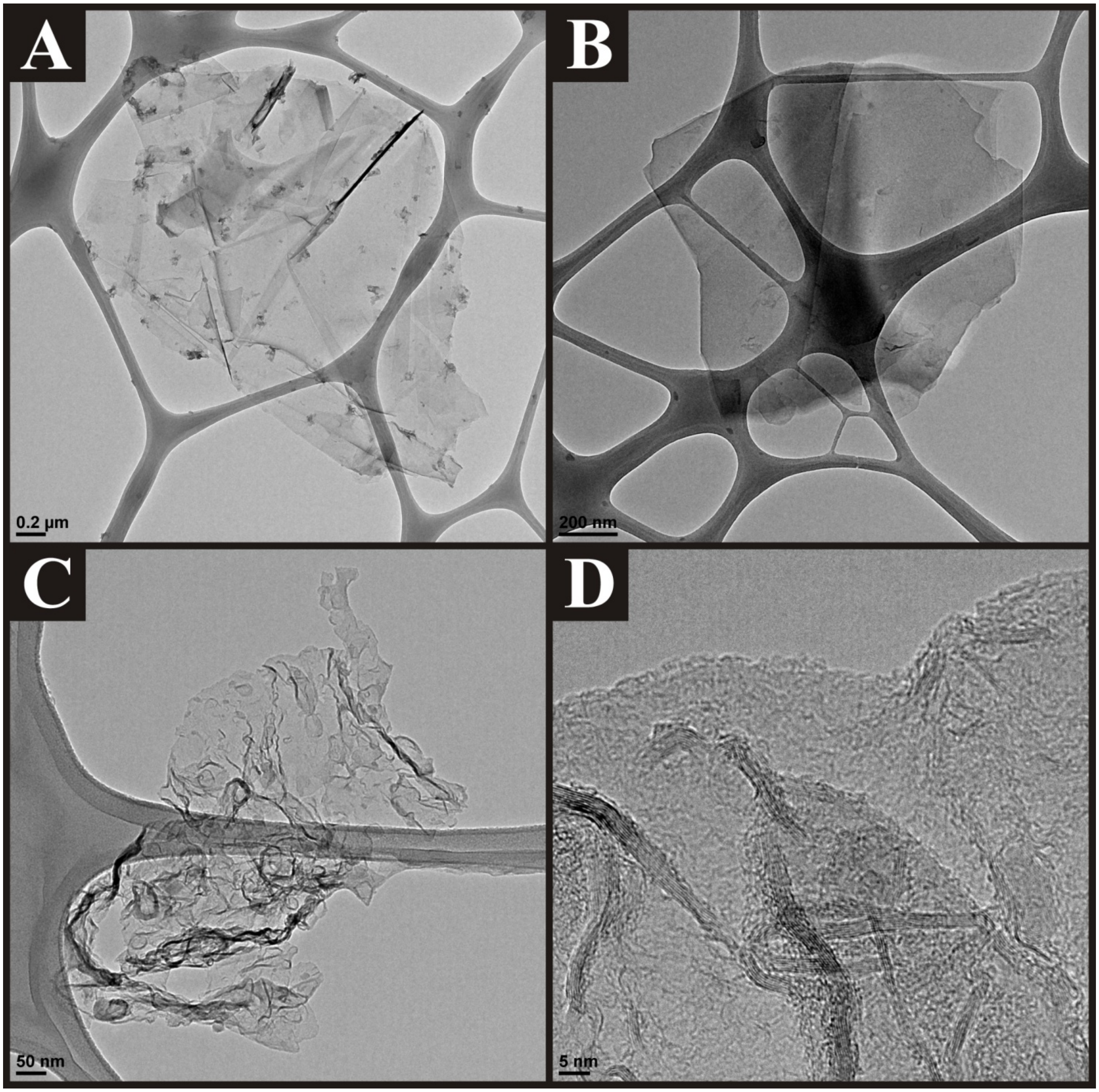
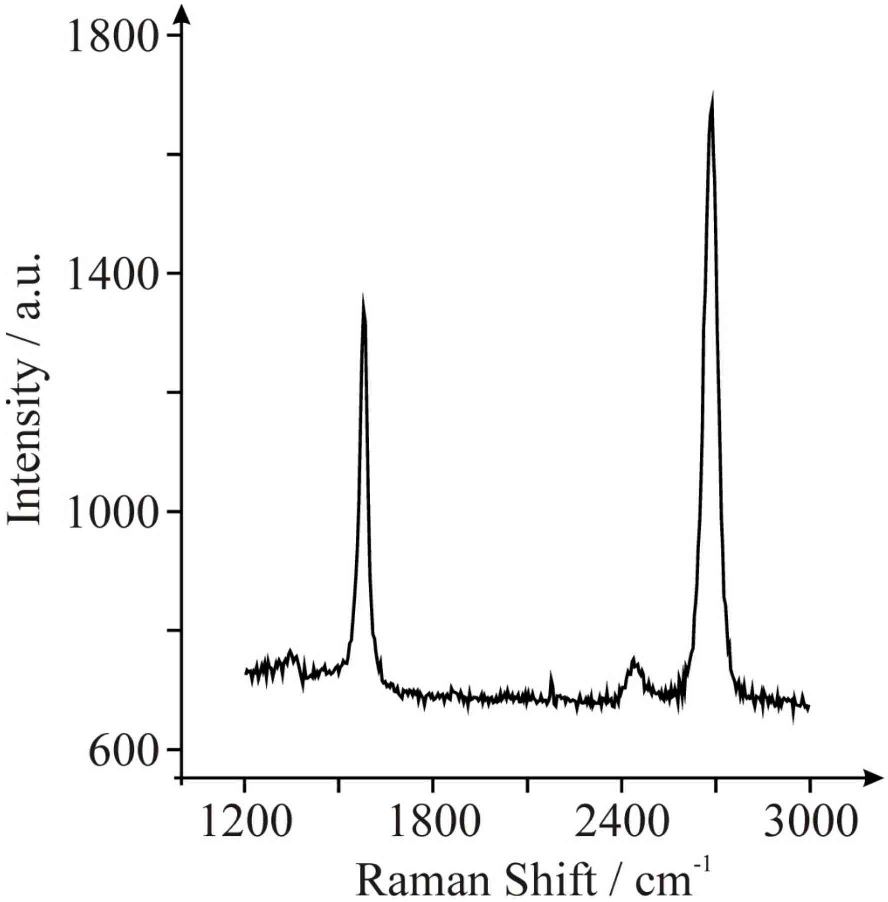


Figure S4

A typical Raman spectrum of a commercially obtained graphene sheet as utilised in this study. Raman spectroscopy was performed after the graphene solution was deposited (and solvent allowed to evaporate) onto a quartz slide Si/SiO_2 substrate (with a thickness of 300 nm SiO_2 on Si). Raman spectra were recorded using LabRam (Jobin-Ivon) with a confocal microscope (100× objective) spectrometer with a He–Ne laser at 632 nm excitation at a very low laser power level (0.9 mW) to avoid any heating effect.



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