Electronic Supplementary Information

Epinephrine Electro-oxidation Highlights Fast Electrochemistry at the Graphite Basal Surface

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S. 1 Step edge analysis on basal plane HOPG by AFM

AFM analysis of SPI-3 grade HOPG was carried out on 10 images for 4 cleaved surfaces varying in scan size in order to estimate the step edge density for comparison against ZYA grade HOPG (for which analysis was carried out in a previous study).[1] A 5 × 5 µm topography image representative of the surface quality is shown in Figure S1(a) and analysis of the data obtained is summarised in Table S1. The percentage of step edge coverage (defined as step area compared to the geometric area of the surface) found on the SPI-3 grade surface was large (31 ± 24%) in comparison to ZYA grade (0.3 ± 0.25%).[1] The step height, in terms of the number of graphite layers, was also calculated, producing the histogram shown in Figure S1(b). The histogram shows that the SPI-3 grade exhibits predominantly multilayer steps, with less than 10% of the observed steps being monolayer, again contrasting markedly with ZYA grade HOPG where monolayer steps dominate.[1] The mean step density of the surface was found to be 8.0 ± 5.8 µm µm^{-2}, which contrasts with that of ZYA grade HOPG by at least an order of magnitude; 0.5 ± 0.1 µm µm^{-2}.[1, 2] The AFM analysis confirms the two grades of HOPG examined vary greatly in terms of the step edge density, making these two grades ideal for exploring the effect of step edges on the electro-oxidation of EP.

Table S1. Characterization of HOPG grade SPI-3 topography (*N*=10)

Mosaic spread[†]	Step density range (µm µm^{-2}) from AFM	Mean step density (µm µm^{-2}) from AFM	Step edge coverage on basal plane	Size (mm)
3.5° ± 1.5°	8.0 ± 5.8 (range 2.5 – 21.9)	8.0 ± 5.8 (*N* = 10)	31 ± 24% (range 10.1 – 78.0%)	10 × 10 × 1

[†] From www.spi2.com. The mosaic spread describes how ordered a sample is by providing the average angle of deviation of grains from the perpendicular axis.
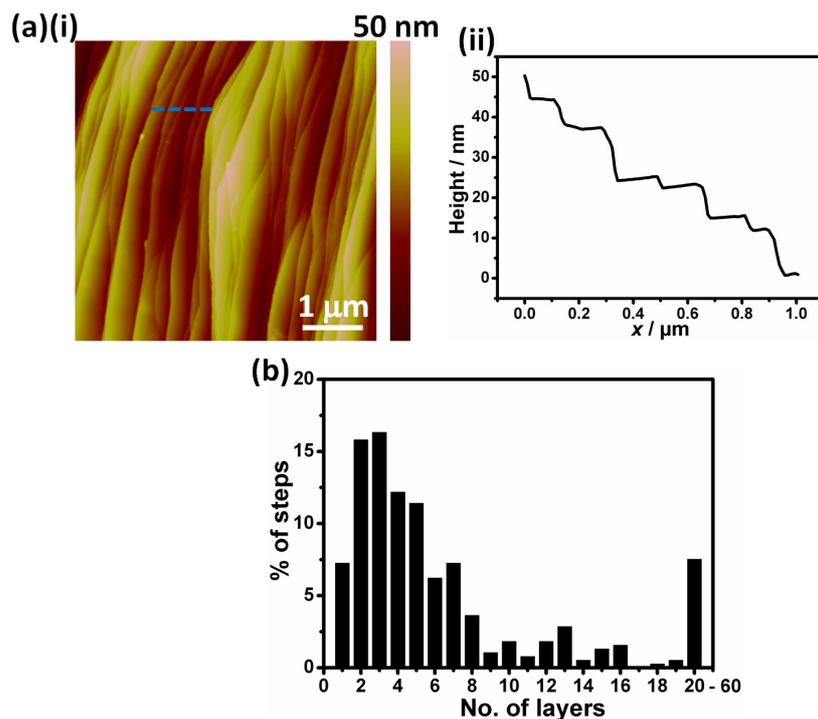
Figure S1. (a)(i) AFM topography image of SPI-3 grade HOPG and (ii) a cross section of the topography for the area marked in blue. (b) Histogram of step edge heights on SPI-3 grade freshly cleaved HOPG.

S. 2 Experimental

Materials and reagents: All chemicals were used as received and all solutions were prepared with high purity Milli-Q reagent water (Millipore Corp.) with resistivity 18.2 MΩ cm at 25 °C. (±)-Epinephrine and phosphate buffered saline (PBS) solution, pH 7.2, were purchased from Sigma-Aldrich. All solutions were prepared freshly on the day of the experiments and kept in the dark at all times when not in use. Two commercial grades of basal plane HOPG (ZYA and SPI-3) were employed, both from SPI Supplies (Aztech Trading, UK). An ungraded but high quality sample of HOPG (AM), originating from Dr. A. Moore, Union Carbide (now GE Advanced Ceramics), was used for SECCM imaging kindly provided by Prof. R. L. McCreery (University of Alberta, Canada).

Electrode fabrication and preparation: HOPG samples were contacted to a silicon wafer, coated with titanium and gold, using Acheson Electrodag (Agar Scientific, 1415M). An

external electrical contact was created by lowering a metal pin onto the gold surface using a micro-positioner. The basal plane HOPG surfaces were freshly prepared by gently pressing down single-sided scotch tape and gently removing the top layers.

Electrochemistry: Cyclic voltammetry (CV) was carried out in a three-electrode configuration using a potentiostat (CH Instruments Model 600, Austin, TX). A silver/silver chloride electrode (Ag/AgCl in 0.15 M NaCl) served as the reference and was used in conjunction with a Pt counter electrode to complete the cell. On freshly cleaved HOPG, unless stated otherwise, a Teflon cell designed in-house (and described elsewhere)[1] was used to provide a well defined 3 mm working area.

In-situ electrochemical AFM: *In-situ* AFM experiments were carried out using tapping-mode (TM-AFM) with an Environmental AFM (Enviroscope, Bruker) with Nanoscope IV controller and standard silicon nitride tips (NP-type). Electrochemical control of the working electrode surface was accomplished using a CH Instruments potentiostat model 800B (Austin, Texas), with the same counter and reference electrodes stated above.

SECCM: Full experimental details for SECCM have been given elsewhere.[2,3] For completeness, we provide key details here. The tip employed was a dual-channel borosilicate pipet (o.d. 1.5 mm, i.d. 0.17 mm, TGC150-10, Harvard Apparatus) pulled to a sharp taper using a CO_2-laser puller (P-2000, Sutter Instruments). This produced 2 closely identical pipets: one was used for SECCM and the dimensions of the tapered opening of the other were measured accurately with field emission-scanning electron microscopy (FE-SEM) for each experiment. The pipet was silanized to ensure a hydrophobic outer wall. Each channel was filled with the solution of interest and a chloridized silver wire (99.9%, Mateck) was inserted

into each channel; these wires served as quasi-reference counter electrodes (QRCEs). The pipet was mounted on a high-dynamic z-piezoelectric positioner (P-753.3CD LISA, Physik Instrumente), while the substrate of interest (HOPG) was mounted on an xy-piezoelectric stage (P-622.2CL PIHera, Physik Instrumente).

With reference to Figure 2 of the main text, a potential of -0.1 V was applied to QRCE 1 with respect to ground, V_s, with a potential bias, V_{bias}, of -0.1 V applied between the two QRCEs. This resulted in a conductance current across the meniscus and an effective bias of the surface of 0.15 V with respect to QRCEs. A sinusoidal oscillation (20 nm peak amplitude, 233.3 Hz) was imposed on the z-position of the tip, generated by a lock-in amplifier (SR830, Stanford Research Instruments). This produced an alternating current (AC) component of the conductance current at the same frequency, due to the periodic deformation of the liquid meniscus when in contact with the surface.[3, 4] The lock-in amplifier was used to pick out the AC component of the conductance current that, in turn, was used as a set-point during scanning to maintain a constant tip to surface separation. During each SECCM experiment, the conductance current between the QRCEs (both DC and AC components) and the current at the substrate, i_{act}, were recorded simultaneously, along with the xy and z position of the pipet probe. Data acquisition was achieved using an FPGA card (PCIe-7852R) with a LabVIEW2011 program written by Dr. K. McKelvey. Patterning was typically carried out to create a square spiral, which produced a distinctive continuous line shape, usually covering a length of 560 µm of the HOPG surface. The tip scan speed was 1 µm s^{-1} with 78 points recorded per second (each an average of 512 samples) resulting in > 40,000 individual spatially-resolved measurements for subsequent analysis.

   Scanning Electron Microscopy. A Zeiss Supra 55-VP, at acceleration voltage of 5 kV, was used for visualisation of the SECCM electrochemical patterning.

S. 3 Additional data from SECCM reactive patterning

An AFM image focusing on the starting point of the EP electro-oxidative patterning is shown in Figure S2, from which it can be seen that the deposition was initiated on the basal plane, without the influence from step edges.
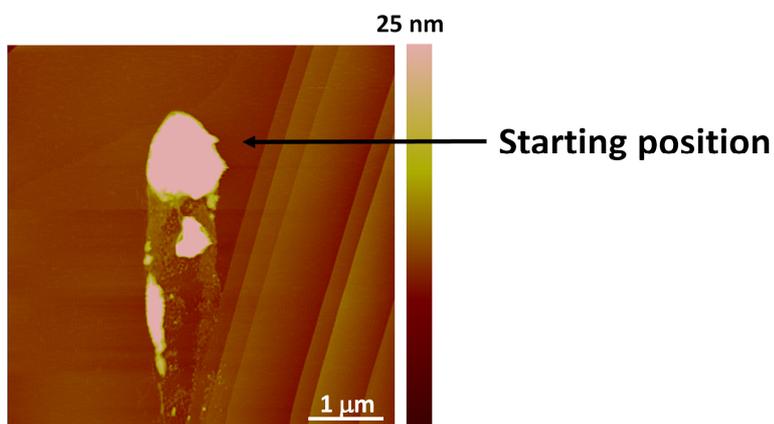

Figure S2. AFM image showing the starting point for EP electro-oxidation patterning.

References

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