Supporting Information

Surface Patterning of Polyacrylamide Gel Using Scanning Electrochemical Cell Microscopy (SECCM)

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S1 – Experimental

Solutions. Copper(II) chloride (Sigma-Aldrich), N-hydroxyethyl acrylamide (Sigma-Aldrich), potassium chloride (Sigma-Aldrich) and benzyltributylammonium chloride (98%, Alfa Aesar) were used as received. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesised according to literature procedures [1] and spectroscopically characterised to ensure purity. 2 mM $CuCl_2$, 2 mM Me_6TREN and 1 M N-Hydroxyethyl acrylamide (HEAA) in Milli-Q water (Millipore Corp) were used for SECCM polymer deposition experiments, with $CuCl_2$ and/or Me_6TREN not included where stated for control experiments. 20 mM potassium chloride in Milli-Q water was used for SECCM oxygen reduction experiments. Solutions were also deaerated for all experiments performed under argon or nitrogen. For cyclic voltammetry experiments, 2 mM $CuCl_2$, 2 mM Me_6TREN, 1 M HEAA and 100 mM benzyltributylammonium chloride (BTBACl) in Milli-Q water were used.

Preparation of Au and SAM/Au Electrodes for SECCM. Au substrates were prepared on silicon/silicon oxide wafers (n-type, 525 µm thickness with 300 nm of thermally grown SiO_2 on both sides, IDB Technologies Ltd., U.K.) using a Moorfield MiniLab deposition system (Moorfield Nanotechnology, U.K.) to thermally evaporate a 60.0 nm Au film on top of a 2.5 nm Cr adhesion layer. Two alkanethiols with different terminal groups were employed to form SAMs. 2-hydroxyethyl disulphide ($HO-C_2H_4-S_2-C_2H_4-OH$, Sigma- Aldrich) was used as received and bis[2-(2-bromoisobutyryloxy)ethyl] disulphide ($Br(CH_3)_2C-COO-C_2H_4-S_2-C_2H_4-OOC-C(CH_3)_2Br$) was synthesised according to literature procedures[2] and spectroscopically characterised to ensure purity. SAMs were formed by placing the Au substrates into a propan-2-ol (IPA) solution containing 20 mM of the required alkanethiol for at least 24 hours. Subsequently, they were rinsed with water to remove any excess alkanethiol followed by a further rinse with IPA before drying under nitrogen. The SAM/Au substrate was then placed on to a 3 x 3 cm glass slide and the edge connected to insulated copper wire using conductive silver epoxy (Circuitworks, ITW Chemtronics). It was then left to dry overnight before use the next day.

Probes. Dual barrel borosilicate glass theta pipettes (o.d. 1.5 mm, i.d. 0.23 mm, Harvard Apparatus) were pulled using a laser puller (Model P-2000, Sutter Instruments) to produce tapered pipets of either 1 μm diameter (for grid deposition), 200 nm diameter (for spiral deposition) or 1.5 μm diameter (for oxygen reduction experiments). Pipette dimensions were accurately measured using field emission-scanning electron microscopy (FE-SEM Zeiss SUPRA 55 VP).

SECCM Measurements. Deposition experiments were performed within a Faraday cage using the set-up shown in Figure 1. The procedure for SECCM has been described previously.[3, 4] The Au or Au/SAM working electrode was mounted on a high-precision *x,y*-piezoelectric stage (P-622.1CL or P-622.2CL PIHera, PhysikInstrumente, Germany) and connected to a custom built electrometer for surface current (i_{surface}) measurements. Probes were filled with the appropriate aqueous solution, and Ag/AgCl quasi reference counter electrodes (QCREs) were inserted into each barrel. The probe was then mounted on a high-dynamic z-piezoelectric positioner (P-753CD LISA, PhysikInstrumente, Germany). The QCREs were connected to a custom made bipotentiostat, which was used to control the bias voltage between the QCREs (V_2). The potential of the substrate (V_{surface}) was defined by applying a second voltage (V_1) to the bipotentiostat, so that upon contact of the probe meniscus and the surface the working electrode potential was defined by $V_{\mathrm{surface}} = -V_1 - V_2/2$. The probe was oscillated in the z direction to induce tip height modulation (~10 % of the tip diameter) by applying a frequency of 259.7 Hz via a lock-in amplifier (SR830, Stanford Research Systems, USA). This oscillation induced an alternating current component ($i_{barrel\,AC}$) in the barrel current (i_{barrel}) due to the changing geometry, and thus resistance, of the meniscus upon contact with the surface, which was used for positional feedback to maintain a constant distance between the probe and surface. For SECCM experiments under argon, the set-up was encased in a sealed environmental cell which had been deaerated for at least an hour. SECCM experiments were controlled through a LabVIEW interface (version 13.0, National Instruments, USA) using a 70 k samples/sec FPGA card (PCIe 7852R, National Instruments, USA).

Macroscopic Cyclic Voltammetry (CV). A CHI-730A potentiostat (CH Instruments, Inc., USA) was used to record macroscopic CVs in a standard three-electrode set-up. An AgCl-coated Ag wire and a Pt wire were used as a quasi-reference electrode and counter electrode, respectively. Prior to experiments, the Au working electrode (2 mm diameter) was immersed overnight in an IPA solution containing 20 mM Bis[2-(2-bromoisobutyryloxy)ethyl] disulphide to ensure full coverage of the self-assembled monolayer (SAM).

AFM Measurements. All AFM images were recorded using a Bruker Innova Atomic Force Microscope with Nanodrive version 8.02 software (Bruker, U.K.). AFM tips were purchased from Bruker (Model RFESP) with 3 μm long cantilevers made from antimony (n) doped silicon.

X-ray Photoelectron Spectroscopy. XPS analysis was conducted using a Kratos Axis Ultra DLD photoelectron spectrometer, with a monochromated Al kα X-ray source (1486.69 eV) operating at 150 W. All measurements were performed under ultra-high vacuum (UHV) conditions with a spectrometer base pressure of 2×10^{-10} mbar. Survey and core level spectra were collected with pass energies of 160 eV and 20 eV respectively with a 1 mm spot size, obtaining a resolution of ca. 0.4 eV for core level scans. All data collected were subject to Shirley background subtraction.

Optical Images. Optical images were taken using an Olympus BH2-UMA optical microscope.

S2 - XPS Data for poly(HEAA) Patterned Au/Br$_{SAM}$ Surface

X-ray Photoelectron Spectroscopy (XPS) was utilised to ensure successful patterning of the Au/Br$_{SAM}$ surface. This surface sensitive technique allowed the top few nanometres of the sample surface to be characterised.

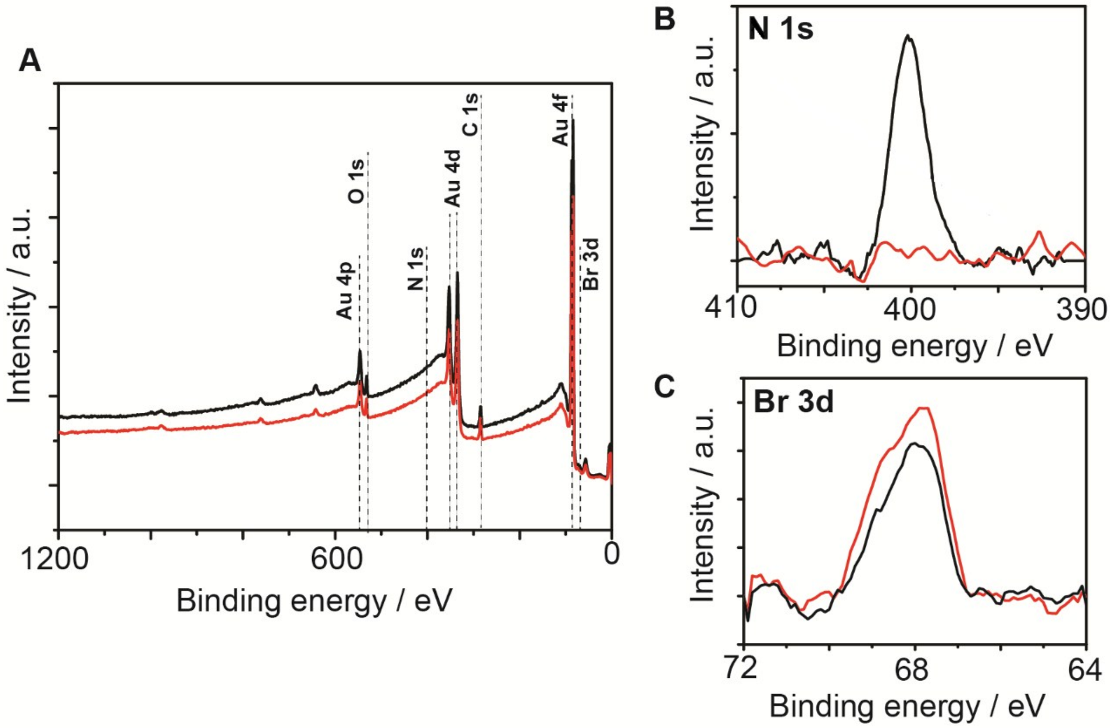

Figure S1. XPS spectra of the patterned (-) and unpatterned (-) surface including: (A) survey scan and core level scans for N 1s (B) and Br 3d (C).

XPS survey spectra (Figure S1A) were collected for both the patterned (black) and unpatterned (red) surfaces in order to identify peaks of interest and ensure there was no contamination of the Au surface during sample preparation and loading. The analysis was conducted using a Kratos Axis Ultra DLD instrument, with a monochromatic Al source (1486.69 eV) with a 1 mm spot size. In both spectra the expected Au (4p, 4d and 4f) peaks are present as well as O 1s, with no obvious contamination for other elements observed.

In order to resolve the N 1s (400.1 eV) and Br 3d peaks (67.7 eV), core level XPS spectra were collected, shown in Figures S1B and S1C respectively. No detectable nitrogen is present on the unpatterned surface (Figure S1B), whilst a clear N 1s peak is observed after patterning. This is attributed to the N-C bond in poly(HEAA).[5] Furthermore, a Br 3d is observed (Figure S1C) on both the patterned and unpatterned surfaces due the presence of the Br_{SAM} on both samples,[6] but a smaller Br 3d signal intensity is observed after patterning, which is consistent with a layer of poly(HEAA) deposited on the surface.

S3 - Optical Image of SECCM Tip after poly(HEAA) Deposition

Figure S2 shows optical images of a 1 μm diameter SECCM tip following poly(HEAA) deposition experiments on an Au/Br_{SAM} surface.

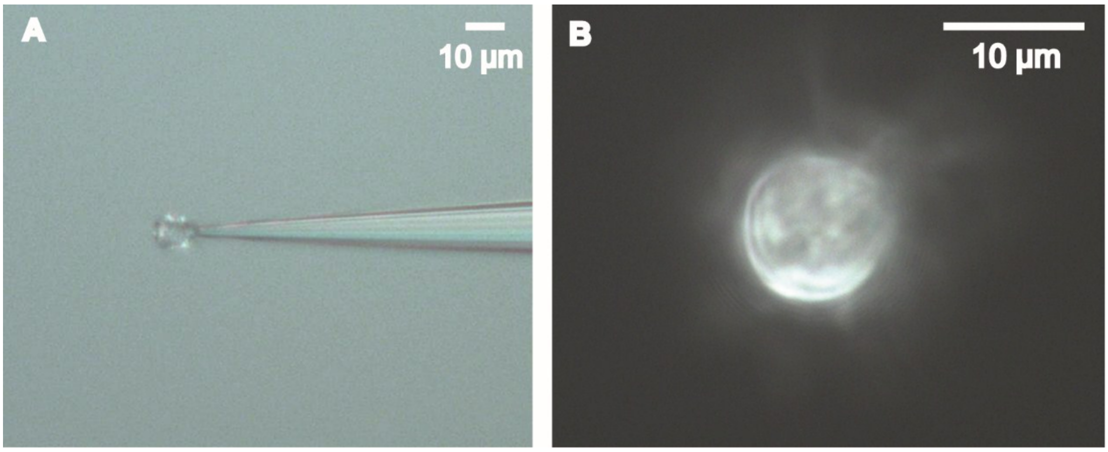

Figure S2. Side-view (A) and top-view (B) optical images of a 1 μm diameter SECCM tip following poly(HEAA) deposition on an Au/Br_{SAM} surface.

S4 - CVs for Deaerated and Aerated Solution of HEAA and Me_6TREN on an Au/Br_{SAM} Macro Electrode

Figure S3 shows macroscopic CVs recorded on a 2 mm diameter Au/Br_{SAM} working electrode immersed in a deaerated or aerated aqueous solution of 2 mM Me_6TREN, 1 M HEAA and 100 mM BTBACl. The CVs show no discernible peaks under deaerated conditions, confirming that neither Me_6TREN nor HEAA should reduce using the cathodic potentials applied during SECCM experiments.

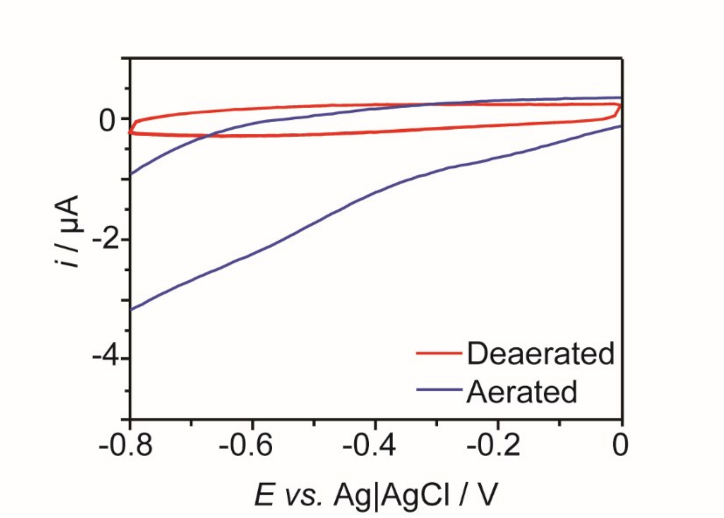

Figure S3. Macroscopic CVs recorded in a deaerated or aerated aqueous solution of 2 mM Me_6TREN, 1 M HEAA and 100 mM BTBACl. Scan speed was 100 mV s^{-1}.

S5 - AFM Images for poly(HEAA) Deposited Under Argon at Different Potentials

Figure S4 shows AFM images of poly(HEAA) deposited on an Au/Br$_{SAM}$ surface under argon for 80 seconds by SECCM using a deaerated 1 M aqueous solution of HEAA. A different $V_{surface}$ was applied in each case, and there is a rough correlation between increasing cathodic potential and amount of material deposited (denoted by the increasing deposition height with potential). Ring shapes are thought to be due to sluggish polymerisation rate without $CuCl_2$/Me_6TREN, causing less material to be left behind after deposition.

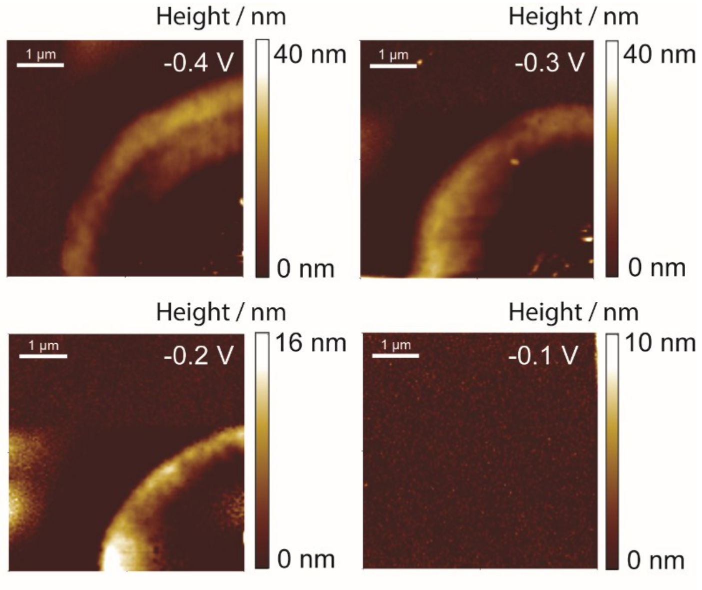

Figure S4. AFM images of poly(HEAA) deposited for 80 seconds during SECCM patterning using a probe containing a aqueous solution of 1 M HEAA. Each image corresponds to a different applied $V_{surface}$.

S6 - AFM Image Following SECCM under Aerated Conditions

Figure S5 shows an example of AFM image collected on an Au/SAM surface following an attempt to pattern poly(HEAA) using SECCM under aerated conditions. Features shown on the image are attributed to contact between the ~~tip~~ meniscus and surface during scanning and not poly(HEAA) deposition.

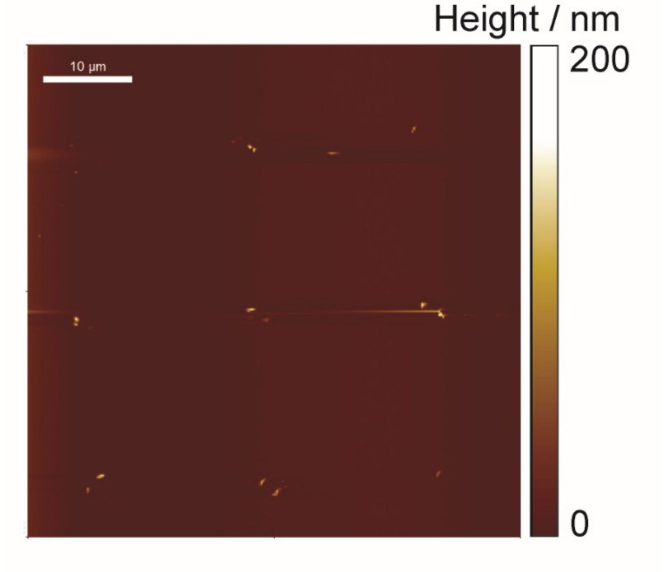

Figure S5. AFM image of the area on an Au/Br$_{SAM}$ surface where SECCM poly(HEAA) deposition was attempted under aerated conditions using a $V_{surface}$ of -0.55 V *vs.* Ag|AgCl. Experiments were carried out using an aerated aqueous solution of 1 M HEAA.

S7 - AFM Images of poly(HEAA) Deposition Under Argon in the Absence of CuCl$_2$/Me$_6$TREN

Figure S6 shows AFM images of an Au/ Br_{SAM} surface patterned with poly(HEAA) via SECCM using a probe containing a deaerated aqueous solution of 1 M HEAA (S3A) and 1 M HEAA/2 mM Me_6TREN (S3B).

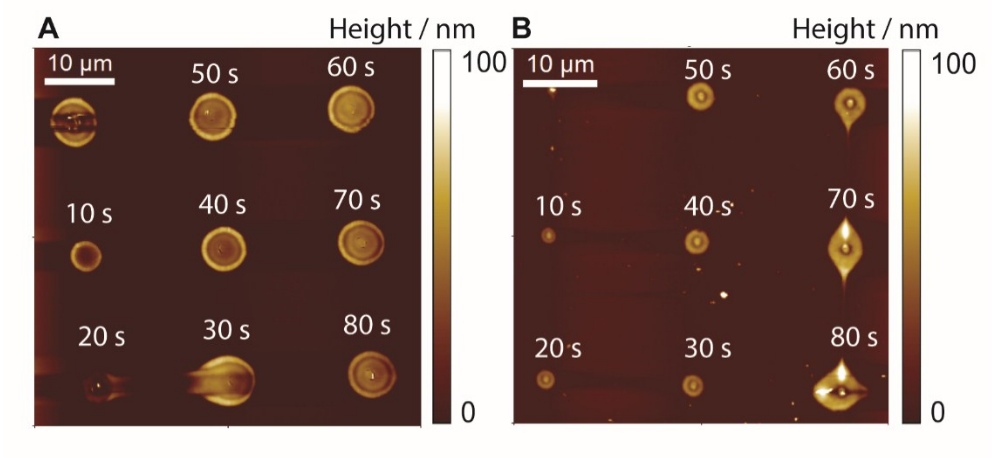

Figure S6. AFM images of poly(HEAA) deposited for different times using SECCM on an Au/Br_{SAM} surface at -0.55 V *vs.* Ag|AgCl. Experiments were carried out using a deaerated aqueous solution of 1 M HEAA (S3A) and 1 M HEAA/ 2 mM Me_6TREN (S3B).

References

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