Supplementary information for:

Electrochemical imaging of hydrogen peroxide generation at individual gold particles

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Preparation of AuNP ensemble electrodes. AuNPs were electrodeposited onto glassy carbon (GC) electrodes using a standard three electrode electrochemical cell with a mercury/mercurous sulphate (Hg/HgSO₄) reference electrode (BASi, Japan) and a platinum mesh counter electrode controlled by a Autolab PGSTAT 302N potentiostat (Metrohm, UK), operated using GPES software. Before use the electrochemical cells were washed using hot concentrated sulphuric acid and rinsed repeatedly with MilliQ water (resistivity 18.2 M Ω cm). The GC electrodes were polished using alumina slurry followed by sonication for one minute in MilliQ water, then electrochemically cleaned in 0.1 M HClO₄ by cycling the potential repeatedly between -1.1 V and 1.0 V vs Hg/HgSO₄, followed by a final preconditioning sweep between 1.0 V and 0.0 V vs Hg/HgSO₄. The electrode was stepped from open circuit potential to the deposition potential (0.3 V vs Hg/HgSO₄ for the low density ensemble electrodes, 0 V vs Hg/HgSO₄ for the high density electrodes) for 10 min in a solution of 2 mM H₂AuCl₄ in 0.1 M HClO₄.

AuNP characterisation. Lead underpotential deposition (PbUPD) was performed in a N_2 purged solution of 1mM Pb(NO₃)₂ in 0.1 M NaOH. CVs were measured for ten scans

between -1.0 V and 0.0 V vs Hg/HgSO₄ at 50 mV/s. Scanning electron microscopy (SEM) analysis was performed using a Supra (Zeiss, Germany) microscope at a typical accelerating voltage of 1 kV and a working distance of 5 mm.

RRDE voltammetry. Experiments were undertaken using a Pt/GC ring–disk electrode system (Pine Instruments, USA) controlled using a CHI 760C bipotentiostat (CH Instruments, USA). For ORR analysis, AuNP-decorated RRDE electrodes were rinsed thoroughly and transferred to an O_2 saturated solution of 0.5 M H₂SO₄. RRDE CVs were measured at a scan rate of 50 mV/s, with the Pt ring electrode held at 1.2 V vs Ag/AgCl to perform hydrogen peroxide oxidation. Values of *n* were calculated using the following equation;

$$n = 4 - \frac{2}{CE} \cdot \left(\frac{\dot{i}_{ring}}{\dot{i}_{disk}}\right)$$

where *n* is the average number of electrons transferred, *CE* is the collection efficiency (0.4) and i_{ring} and i_{disk} are the currents measured at the respective electrodes.

SECM–SICM Imaging and Probe Fabrication. Experiments were performed using a modified SICM instrument (Ionscope, UK) and in-house fabricated capillary probes as described in detail previously.¹ Briefly, quartz theta capillaries were pulled to a sharp point using a laser puller and one barrel was filled with carbon via pyrolysis of butane gas to form the SECM barrel. In order to increase sensitivity to hydrogen peroxide oxidation, Pt was deposited from 3 mM K₂PtCl₆ solution in 0.1 M HClO₄ by stepping to -0.3 V vs saturated calomel electrode for 5 s. This provided sufficient Pt for electrochemical signal enhancement without any significant overgrowth or change in electrode geometry (as previously documented).¹ Platinum deposition was confirmed by recording oxygen reduction CVs in

aerated 0.1 M NaOH an example of which is shown in Fig S1. Probes were typically aged for ~30 minutes in imaging solution to allow for limiting current response to stabilise.



Fig S1. Oxygen reduction CV of freshly platinised probe in aerated 0.1 M NaOH recorded at a scan rate of 20 mV/s

Scanning was performed in 0.1 M NaOH solution using a chloridised Ag wire as a quasireference electrode and an SICM barrel bias of 200 mV in 'hopping' mode with a current drop setpoint of 1.5-2.5 % and a hop height of typically 1-2 µm. Images were plotted using SPIP software (Image Metrology, Denmark). The system was operated in SG-TC mode with samples biased at a range of potentials to perform oxygen reduction and the SECM barrel biased to oxidise any generated hydrogen peroxide (typically 0.1 V vs Ag/AgCl). This approach was initially tested by positioning a larger SECM-SICM probe (~1 µm electrode radius) above a sputtered (polycrystalline) gold substrate in 0.1 M NaOH and sweeping the substrate to perform oxygen reduction (Fig S2), during which the expected hydrogen peroxide oxidation current is observed.



Fig. S2. Hydrogen peroxide collection CV in aerated 0.1 M NaOH. The tip here was positioned approximately 10 μ m above the gold surface and held at 0.1 V vs Ag/AgCl whilst the substrate potential was swept between 0 and -0.6 V at a scan rate of 20 mV/s.

Tip geometry, sizing and image resolution. The geometry of the theta capillary-based probe is approximately elliptical with both the open SICM and solid SECM barrel an approximate half ellipse shape, although tips are often somewhat irregular. Care must therefore be taken in describing the tip size and in our work we refer to the longest elliptical or semi-elliptical axis, unless stated otherwise.

SEM was used to characterise probe apex dimensions and geometry, see for example in Fig S3. We note that accurate SEM imaging of smaller probes (particularly below ~200 nm total diameter) is difficult due to charging and is generally impossible once the probe has been immersed in solution due to drying of salt. Characterising the 'mirror image' of the probe (i.e. the counterpart made in the pulling process) can provide a reasonable estimate of the probe apex dimensions although this can be misleading.



Fig S3. SEM image of pulled capillary probe apex (unmodified). Note the probe is at an angle to the axis of the electron beam.

For our work the total (maximum) probe total diameter, based on SEM imaging of the pulling program over a batch of probes, was determined to be in the range 400-500 nm. The electrode radius for these probes was approximately 100 nm which can also be estimated using voltammetry.¹ For simplicity the SECM barrel is assumed to be a disk with an RG (ratio of electrode plus glass to electrode alone) of 1.1.

The effect of the probe geometry on SECM-SICM imaging has not been studied in detail, with SICM users typically employing symmetrical, circular pore type probes. Recent experimental studies have indicated lateral resolution is close to 0.5 r_i (where r_i is the inner radius of the pipette) with circular tips using the Rayleigh criterion (≥ 26 % base line return) to define resolution.² However, some theoretical studies suggests the higher value of 2-3 r_i, although the definition of resolution often varies. In addition to probe size there are several other factors which affect the lateral resolution.² The tip-dependent parameters of particular importance are tip size, geometric features of the tip apex such as shape, symmetry, glass thickness and the semi-angle (or cone angle) of the capillary. Other factors include the separation from the surface, the shape of the features imaged and the surface charge. There has been no robust study of the resolution of the theta probes we have employed but given the

additional complexity of the geometry we assume the lateral topographical resolution to be somewhat less than that of circular pore probes.

Image cross sections. Fig S4 shows cross sections from the SICM topography channels of Fig. 3 and 5 with the corresponding SECM signals overlaid. The particle heights represent the particle sizes as measured by SICM, which were averaged at 434 ± 32 nm (Fig. 3) and 254 ± 87 nm (Fig. 5). The lateral size is exaggerated by the factors discussed above.



Fig S4. Topography channels from Fig 3 (a) and Fig 5 (b) with cross sections showing SICM topography (black) and SECM peroxide detection current (blue). The position of the cross section is indicated by the dashed lines. The SECM current line corresponds to the highest overpotential channels (0.4 V vs RHE for Fig 3 and 0.3 V vs RHE for Fig 5) and are displayed with the raw current range.

References

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- 2. A. E. Weber and L. A. Baker, J. Electrochem. Soc., 2014, 161, H924-H929.