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Submicron Probes for Scanning Electrochemical Microscopy

Michelle S. M. Li, Fraser P. Filice, and Zhifeng Ding*

Abstract

To improve the spatial resolutions of scanning electrochemical microscopy (SECM) imaging, the laser-pulled submicron electrode fabrication method was explored in this work. Manual polishing of a laser-pulled Pt nanoelectrode exposed a Pt tip diameter of 250 nm with a ratio of the tip glass to exposed Pt disc (RG) 30. This fabricated submicron probe was then utilized to study the electrochemical functionality of an independently addressable microband electrode (IAME) sample using SECM. In the constant imaging mode of SECM, where the probe is scanned linearly across the sample at a fixed z position, SECM demonstrated higher resolution than that of the conventional micrometer electrodes when the feedback currents from the Pt and glass microbands were characterized. In addition, the depth scan imaging mode of SECM was also used to extract experimental horizontal line scans and probe approach curves for analysis. 3D simulations of the IAME-SECM probe experiments were explored for the first time to quantify the tip-to-sample distances, tilt angle of the sample (or electrode) and height of the Pt microbands. The experimentally characterized height was found to be similar to manufacturer specification (125 nm vs 110 nm). Furthermore, the more computationally-demanding 3D simulation of the true IAME sample geometry (110 nm height of the Pt microbands) revealed minimal difference in feedback behaviors in comparison to the idealized flat geometry. The removal of this simulation complexity was proved to be sufficient for SECM analysis of the IAME sample by a 250 nm Pt probe, which saves greatly the computation resources.

31 **Keywords:** Scanning electrochemical microscopy, SECM imaging, laser-pulled Pt probes,
32 independently addressable microband electrodes, finite element analysis

33

Draft

Introduction

Since its emergence in the late 1980s,¹⁻⁴ scanning electrochemical microscopy (SECM) has been used for a variety of applications, including but not limited, to microstructure fabrication,⁵⁻⁶ probing sample kinetics,⁷⁻⁸ and electrochemical imaging.^{9-11, 12, 13} This technique utilizes a biased electrode, less than 25 μm in diameter, that is scanned with extreme precision over a sample submerged in an electrolyte solution.^{1, 11, 14-17} Due to the potential bias and probe size, the redox mediator is fully converted to its oxidized or reduced form at the electrode tip in a diffusion-controlled process. When the biased probe is in close proximity to a sample (within distances of several tip radii away), the feedback current will deviate from the steady state current since the flux of the mediator from bulk solution to the tip is no longer a diffusion-controlled process. If the sample is conductive, the tip current will increase since cyclic regeneration of the mediator at the sample-electrolyte interface (positive feedback) increases as tip-to-sample distance is minimized. However, if the sample is insulating, the current will decrease due to the depletion of the mediator at the electrode tip (diffusion-limited, negative feedback).

This relationship between tip current and probe position can be represented as single line scans or in the form of multiaxis current maps (images). In the Ding lab, SECM depth scan imaging is often used since the tip current and probe coordinates (x, z) are embedded into a 2D image.¹⁸⁻²⁰ A significant advantage to this method is that each image provides hundreds of usable experimental horizontal line scans and probe approach curves. In addition, this method also provides the real-time generation of the SECM image which allows the experimentalist to

monitor the feedback current and electrode's position relative to the sample. This may prevent collision damage between the SECM tip and the sample.

Resolution of the SECM instrument is commonly limited by electrode size. Larger SECM probes provide stronger electrochemical feedback, however, that feedback is comprised of an averaged signal over the entire electrode surface area. By reducing the electrode size, smaller sample features or regions of increased electrochemical activity can be observed. Here, we use the laser-pulled nanoelectrode fabrication method²¹⁻²³ to greatly reduce the commercially obtainable Pt wire from 25 μm diameter to the submicron (nanometer) scale. This reduction in Pt diameter would greatly improve the resolution of SECM images relative to micrometer electrodes. To demonstrate the improvement in SECM resolution, an independently addressable microband electrodes (IAME) sample was characterized by the use of a manually polished laser-pulled 250 nm Pt electrode.

3D finite elemental analysis simulations of the depth scan experiment were carried out for the first time to fit to horizontal and vertical line scans extracted from the experimental SECM depth scan image, which allows quantitative analysis of sample characteristics, such as the physical properties and reaction kinetics.²⁴ These simulations provide insight into the effects of tilt angle, microband height and feedback current in SECM when a probe significantly smaller in stature, relative to the microbands of the IAME (5 μm band width), is used. Furthermore, a comparison between an idealized IAME sample geometry (where Pt microband heights are ignored) and a computationally-demanding 3D simulation of the true IAME sample geometry was explored. These results indicate the extended complexity of the simulation geometry (and

therefore higher utilization of computational resources) may not be required for SECM analysis of the IAME sample by a 250 nm Pt probe.

Experimental

Materials

Hexaamineruthenium(III) chloride ($\text{Ru}(\text{NH}_3)_6\cdot\text{Cl}_3$, 98%) and potassium chloride (KCl, 99%) were acquired from Sigma-Aldrich (Mississauga, ON) and Alfa Aesar (Ward Hill, MA), respectively. 10 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ with 0.1 M KCl as the supporting electrolyte was prepared in deionized water (18 M Ω .cm, MilliQ water, Etobicoke, ON). The Pt IAME sample was purchased from ABTECH Scientific, Inc. (IAME 0504-Pt, Richmond, VA). This IAME has 4 alternating (independently addressable) Pt and glass microbands, each 5 μm in width. The Pt microbands are 110 nm in height according to manufacturer specifications (100 Å Ti/W and 1000 Å Pt).

Electrode Fabrication

The nanoelectrodes were fabricated in-house using a P-2000 laser-based micropipette puller (Sutter Instrument, Novato, CA) adapted from the established procedure reported by the Mauzeroll Group.^{21, 25-26} Briefly, a 25 μm Pt wire (Goodfellow Metals, Cambridge, UK) was inserted into a quartz glass capillary tubes (o.d.: 1.00 mm, i.d.: 0.50 mm, length: 10.00 cm, Sutter Instrument). In place of a single line setting used by the Mauzeroll Group, two single line settings on the P-2000 puller were required in our experimental configuration. A custom-designed vacuum line was applied to the two ends of the micropipette and Pt wire set to be heat-

sealed and pulled. The first of the two is a partial quartz seal program using the line setting of Heat: 580, Filament: 003, Velocity: 140, Delay: 060, Pull: 000. This was followed by the complete quartz seal at Heat: 580, Filament: 002, Velocity: 140, Delay: 060, Pull: 000. These two quartz seal programs were performed with the linear carriages locked in place, securing the capillary in a fixed position. These two line settings were found to improve the integrity of the Pt wire for our experimental configuration. Once the Pt was completely sealed within the quartz capillary, the locking of the linear carriages were removed, followed by the final pull step at a single line setting of Heat: 780, Filament: 002, Velocity: 060, Delay: 140, Pull: 200 was employed. This fabrication procedure produced two Pt nanoelectrodes (NEs).

Freshly pulled Pt NEs were first checked optically under a microscope for obvious breakages in Pt wire, followed by extension of the internal electrical connections. Scanning electron microscopy (SEM) was used to confirm the reduction in Pt tip size and RG values (**Fig. 1**). Typically, SEM revealed that the Pt wires were recessed within the pulled quartz capillary (**Fig. 1a**). Focused ion beam (FIB)-milling and SEM imaging were performed using a LEO Zeiss 1540 XB (Zeiss, Oberkochen, Germany). Up to a thousand times reduction in Pt diameter size, from 25 μm to 25 nm, as well as RG values greater than 25 were observed (**Fig. 1b**). In addition to FIB-milling, the Pt tips were exposed using a homemade polishing wheel attached with abrasive alumina-coated polishing pads (0.05 μm , Buehler, Whitby, ON). NEs were tested for electrical conductivity and Pt size by means of cyclic voltammetry (CV).

Figure 1

Electrochemical Measurements

Electrochemical experiments were performed using an electrochemical analyzer (CHI 800B, CH Instruments, Austin, TX) with a CHI 200 Picoamp Booster (CH Instruments). The current signals were recorded by the Alpha-SNOM instrument (WITec, Ulm, Germany).^{18, 27} The Pt NEs were used as the SECM probe (working electrode) and a Ag/AgCl electrode was used as a combined auxiliary/reference electrode. The nanoelectrodes were biased at -0.350 V (vs. Ag/AgCl) to reduce $\text{Ru}(\text{NH}_3)_6^{3+}$ to $\text{Ru}(\text{NH}_3)_6^{2+}$ in a diffusion-controlled manner.

SECM Experiments

The SECM instrumentation and operation procedure has been described elsewhere in great detail.^{18-19, 28-29} Briefly, SECM measurements were performed on the IAME sample adhered with 3M double-sided tape (conductive side exposed) onto a glass bottom petri dish (P35G-0-20C, MatTek Corporation, Ashland, MA). The petri dish was mounted onto the scanning stage (P-517K064, Polytec PI, Germany) of the Alpha-SNOM instrument. Utilizing the Alpha-SNOM positioning system along with an inverted Nikon objective lens (50x lens, N.A.: 0.55, Japan), the SECM images were collected using the confocal mode setting within the WITec software. This resulted in the real-time collection of 2D SECM images (current vs. probe coordinates). The depth scan image comprised of 512 x 200 pixels, a scan width of 20 μm and depth of 10 μm and an integration time of 0.01 s per pixel. The constant height images include 512 x 512 pixels, a scan width and height of 20 μm each and an integration time of 0.01 s per pixel. These experiments were carried out at ambient lab conditions (23 ± 1 °C).

Simulation Geometry and Methodology

The SECM imaging of the IAME sample was simulated using the finite elemental analysis software, COMSOL Multiphysics v.5.3 (COMSOL, Boston, MA). The simulation model was designed in full 3D geometry with a central symmetry plane. The model geometry was constructed to closely represent the experimental system under study (**Fig. 2a and b**). The SECM probe was configured to have a Pt tip size of 250 nm (diameter) and an RG of 10. In fact, the RG of the 250 nm Pt NE was simplified from 30 to 10 due to minimal effects on feedback current for RG values greater than 10.¹⁴

Figure 2

The IAME substrate consisted of 4 sets of alternating Pt and glass microbands, each 5 μm in width (**Fig. 2b**). The microbands were designed with two differing geometries; such that the simulation could be computed with flat (flush) Pt and glass microbands or raised Pt microbands (110 nm as per manufacturer specifications) and flat glass microbands. The simplified, idealized flat Pt microband structures provided a significant reduction in the complexity of the simulation model. This greatly reduces the demand on system resources and computation time (nearly 10x computation time with 110 nm step geometry). The 110 nm height of the Pt microbands represents the true experimental geometry; however only affects the simulated curves under certain conditions.

The simulation model was designed with a symmetry plane that passes through the center of the electrode, perpendicular to the Pt microbands of the IAME sample (**Fig. 2a**). This allows a further reduction in the complexity of the model since half of the geometry can be eliminated. As a result, the number of meshing elements is halved without affecting the functionality of the

model. The symmetric boundary allows the model to be mirrored across this plane and for the flux of solution across the symmetry boundary into the symmetrical region opposite the boundary.

The glass of the IAME sample was configured as a thin insulating boundary (**Fig. 2a and b**).²³ The conductive Pt microbands were set to regenerate the initial bulk solution concentration of $\text{Ru}(\text{NH}_3)_6^{3+}$, behaving as an ideal conductive boundary. The lower region of the model geometry was created to facilitate the impermeable tilting substrate and has no interaction with the upper region under study (**Fig. 2b**).

The initial solution concentration of $\text{Ru}(\text{NH}_3)_6^{3+}$ was set at 10.0 mM to match the stock solution concentration used in the experiments. The diffusion coefficient for $\text{Ru}(\text{NH}_3)_6^{3+}$ was taken as $6.7 \times 10^{-10} \text{ m}^2/\text{s}$.^{24, 30-31} When the 250 nm Pt NE is biased at -0.350 V, the one-electron reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ to $\text{Ru}(\text{NH}_3)_6^{2+}$ is a diffusion-controlled process that follows Fick's second law of diffusion (eqn 1):

$$\frac{\partial C_B}{\partial t} = D_B \left(\frac{\partial^2 C_B}{\partial x^2} + \frac{\partial^2 C_B}{\partial y^2} + \frac{\partial^2 C_B}{\partial z^2} \right) \quad [1]$$

The boundaries interfacing with the bulk solution were set to match the initial concentration of $\text{Ru}(\text{NH}_3)_6^{3+}$. This has the effect of regenerating the mediator in the region under study and simulating the relatively infinite solution of the mediator in the petri dish given the reaction scale which occurs at the probe tip. The probe's sheathing (quartz) boundaries were set as no flux boundaries to simulate the insulating characteristics of these substrates. The Pt disk of the SECM tip was configured to remove $\text{Ru}(\text{NH}_3)_6^{3+}$ from solution, generating a concentration of 0 M at the disk surface.

A tetrahedral mesh was utilized to mesh the entire 3D simulation model (**Fig. 2c**). The meshing element size was further refined at the regions where the greatest concentration changes could be expected (electrode tip and microbands). An element scale size of 0.2x was set at the Pt tip, while the microbands were set to 0.4x. The minimum element size was defined as 0.01 μm , with a maximum element growth rate of 1.25x. This growth rate was defined to ensure a fine mesh in proximity to these boundaries of interest, up to a maximum element size of 10 μm .

The electrode's x and z positions were set as parameterized variables in the creation of the model geometry. This allows the automated movement of the probe over the IAME, which are simulated sequentially over numerous simulations. The sequential computation of all combinations of specified parameters generates large sets of data rapidly. Concentration maps of $\text{Ru}(\text{NH}_3)_6^{3+}$ in solution were generated and the tip flux was integrated over the Pt surface (**Fig. 2d**).

Due to the symmetry plane, the integration of the semicircular electrode tip boundary has to be doubled to obtain the total electrode tip current, i . The surface integration follows eqn 2:

$$i = 2n\pi FD \int_0^a r \left[\frac{\partial c(r,z)}{\partial z} \right] dr \quad [2]$$

where a is the radius of the Pt disk, n is the number of electrons transferred in the reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ (1 e^-), F is the Faraday constant (96,485 C/mol), and D is the diffusion coefficient of $\text{Ru}(\text{NH}_3)_6^{3+}$. The resulting tip current for all electrode tip locations were normalized with respect to the bulk solution current at the disk electrode (simulated at a distance far away from the substrate, i_∞), yielding:

$$I(x, z) = \frac{i(x, z)}{i_\infty} \quad [3]$$

I in this case represents the normalized current. PACs were obtained by plotting the normalized tip current (eqn 3) versus the normalized distance, L (eqn 4):

$$L = \frac{\text{tip-to-sample distance}, d}{\text{electrode radius}, a} \quad [4]$$

Results and Discussion

SECM Imaging of an IAME by a 250 nm Diameter Pt NE (RG30)

Constant height mode

This laser-pulled Pt NE fabrication method provides significant reduction in the diameters of the Pt wire, where decreases from 25 μm to 25 nm (1000x reduction, **Fig. 1**) are possible. Manual polishing of these laser-pulled electrodes exposed larger Pt tip diameters than those exposed by FIB. However, this exposure method is more cost-effective and the tips are still significantly smaller than the commercially obtained Pt wires used in the fabrications of ultramicroelectrodes (UMEs).

Figure 3

A manually polished 250 nm diameter Pt NE (RG 30) was used as the SECM probe to electrochemically image 2 pairs of alternating 5 μm glass and Pt microbands of the IAME sample (**Fig. 3**). This electrode illustrates the effectiveness of the manually polishing laser-pulled electrodes and Pt exposure method. **Fig. 3a** shows the 2D (x,y) current map image of the

microbands when the Pt NE is scanned at a constant z position above the sample, where the Pt microbands are represented in the bright white-yellow to orange-red colours and the glass microbands by the dark blue-black colours. The image resolution collected by this 250 nm Pt NE is higher than that with a micrometer diameter electrode.^{23, 29, 32} A 3D representation of the 2D image is shown in **Fig. 3b** for better visualization of the alternating nature of the microband array (insulating and conductive).

From **Fig. 3a**, one can see that the current feedback response of the first Pt microband is slightly wider than its surrounding glass microbands despite having the same physical widths (as specified by the manufacturer). This increase in feedback is a result of the cumulative effects of the increased signal strength of conductive substrates over insulators, the electrochemical cycling between the probe and adjacent Pt microbands and the height difference between the Pt microbands and interdigit glass space (110 nm). Therefore, a broader band of electrochemical feedback will be detected as the 250 nm NE scans over the Pt microbands (smaller tip-to-sample distance achieved). The simulation of the Pt microbands accounts for relative signal intensities of the two substrates and the diffusion limited cycling of the mediator species to the defined geometry. Higher feedback current was also observed as the 250 nm Pt NE scanned over the first (left) Pt microband as opposed to the second Pt microband. This signifies that the second Pt microband had a larger tip-to-sample distance as the scan progressed, indicating the IAME sample or electrode are likely tilted relative to each other (**Fig. 3a and b**). It is also likely (due to the tilt), the large RG (and therefore, diameter of the quartz sheathing) prevents the Pt tip from minimizing the tip-to-sample distance further (right half of the horizontal line scans 1-3 in Fig. 3c-e).

Idealized 3D IAME simulations with flat Pt microbands

Horizontal line scans were extracted in three locations (start, middle and end of the image in **Fig. 3a**) were overlaid onto simulated horizontal sweep curves to quantify the tip-to-sample distances. Initially, the 3D IAME simulation model was simplified to have idealized flat Pt and glass microbands in order to reduce the complexity of the simulation model. This height differences between the Pt and glass microbands require a tip-to-glass distance to be offset by an additional 0.110 μm .

For these experimental curves, the tip current was normalized against the steady state current in the bulk. At the start of the image (line 1 (green), **Fig. 3a**), the 250 nm Pt NE scans over the first glass microband which shows its insulating properties through a decrease in normalized tip current ($I = 0.90$ (negative feedback), green circles, **Fig. 3c**). Following this glass microband, the NE scans over the first of the two Pt microbands where the normalized tip current increased to 1.08 (positive feedback). As the NE continues its horizontal scan, the adjacent insulating glass microband causes another decrease in electrochemical feedback ($I = 0.94$), followed by increased electrochemical feedback at the second Pt microband ($I = 1.04$). However, the feedback current from the second Pt microband is less than that of the first Pt microband (1.04 vs 1.08), which reinforces the conclusion that either the sample or electrode is tilted.

This tilt can be confirmed through the successful overlay of the experimental horizontal curve onto simulated curves (**Fig. 3c**). A tip-to-sample distance of approximately 0.6 μm was reached over the first Pt and glass microbands, while the scan over the second Pt microband revealed a tip-to-sample distance of 1.0 micron. This indicates a 1.53° tilt across sample without considering the tilting of the other plane, which is significant relative to the size of this NE. Horizontal line scans taken midway (line 2, blue) and at the end of the SECM constant height

image (line 3, black) also confirms that sample or electrode tilt occurs (**Fig. 3d and e**). Therefore, for the collection of this constant height image, the 250 nm Pt NE was scanned approximately 0.6 μm above the IAME sample.

Depth scan imaging

Following the constant height image collection, the NE was raised by the z piezoelectric actuator of the Alpha SNOM instrument to perform SECM depth scan imaging of the microbands such that the final horizontal scan of the depth scan image mirrored the z position of the tip in the constant height scan (**Fig. 4**). From the SECM depth scan, the electrochemical feedback from the Pt and glass microbands can be seen as the NE approaches the IAME from above. Specifically, the strong feedback current from the conductive Pt microbands onto the NE is observed (minimal insulating or negative feedback from the glass microbands). As previously mentioned, this is partially due to the height difference between the Pt and glass microbands (110 nm, equivalent to $L = 0.88$).

Figure 4

A horizontal line scan extracted near the bottom of the SECM depth scan (red line, **Fig. 4a**) revealed a tip-to-sample distance of 0.75 μm when overlaid onto the simulated horizontal curves (**Fig. 4b**). This tip-to-sample distance is comparable to the fixed z position of the probe in the collection of the constant height image. The immediate horizontal line scan extracted below this red line indicates that the NE tip collided with the microbands (**Fig. 4a**). Since the RG of

this NE is quite large (30), the tilt of the sample and diameter of the glass sheath prevents the Pt disk from approaching the bands closer.

While achieving tip-to-sample distances of approximately 0.75 μm may be ideal for larger UMEs, for an electrode with an effective Pt diameter of 250 nm, this would equal to normalized distances greater than 6 for the Pt bands and 7 for the glass microbands (accounting the height differences between the microbands). At these normalized distances, the fitting of experimental PACs onto simulated curves would not hold much accuracy. However, the normalized feedback currents from the SECM depth scan image can be used to determine their corresponding tip-to-sample distances using the simulated PACs to the center of the glass and Pt microbands (**Fig. 5**).^{1, 31} For example, from the SECM depth scan (**Fig. 4**) the highest normalized current towards a Pt microband was identified as 1.07. Using the simulated PACs to the center of a Pt microband (red, **Fig. 5**), the corresponding normalized distance can be identified as 5.10.

Figure 5

Similarly, the lowest normalized current towards a glass microband was identified as 0.95 and its corresponding normalized distance was identified as 6.10 (black, Fig. 5). The difference between these normalized distances is therefore 1.00 or 125 nm (eqn 4). This height discrepancy is in close agreement with manufacturer specification of 110 nm. This also gives a tilt angle of 1.43° across the x plane of the SECM depth scan which was similar to the tilt angle of the constant height scan (1.53°).

Considering the height of the Pt microbands in the 3D simulations greatly increases the complexity of the simulation model, requiring heavy utilization of computational resources. Using experimental horizontal curves from the constant height (line 1, **Fig. 3**) and depth scan (**Fig. 4**) images; these curves were overlaid onto the simulated curves with the 110 nm Pt microband height accounted for (**Fig. 6**). The first half of the experimental constant height curve overlaid well onto the simulated curve 0.575 μm above the IAME (green circles onto the solid purple curve, **Fig. 6a**). This value agrees closely with the tip-to-sample distance determined using the idealized model, estimated to be 0.6 μm (**Fig. 3c**). When the height of the Pt microbands is considered, the tip-to-sample distance reached in the depth scan image corresponds to 0.725 μm (red circles on solid olive curve, **Fig. 6b**). This value also shows close agreement with the tip-to-sample distance determined from the idealized curves (0.750 μm).

Figure 6

Using the maximum and minimum normalized currents from the SECM depth scan image (Pt and glass microbands, respectively, **Fig. 4**), the corresponding normalized distances were determined (**Fig. 7**). Simulated PACs were generated to the center of the Pt or glass microbands, where the height difference of the microbands is accounted for in the simulation model. For both normalized currents, ($I_{\text{Pt}} = 1.07$ and $I_{\text{glass}} = 0.95$), the corresponding normalized distances was identified as 5.10, relative to the top of the Pt bands. This result was expected since the height of the Pt microbands is considered in this simulation model.

Figure 7

Comparison between 3D Simulation Models

The comparison of the results from the two different simulation models indicates that the height of the Pt microbands have minimal effects on the feedback current. The height is 110 nm, which, to a 250 nm Pt electrode, is almost a normalized distance of 1 away ($L = 0.88$). It was expected with a much larger SECM probe (micron-sized), the additional surface area of the Pt microband plays minimal effect, while smaller probes, such as the electrode used in these experiments, would have influence on the detected feedback current. We suspect the 110 nm height difference to play a more significant role upon closer approach of the 250 nm Pt electrode or with further reduction in the electrode size.

Conclusions

The laser-pulled quartz sealed Pt NEs were used as an SECM probe to image the Pt and glass microbands of the IAME sample. SEM of these laser-pulled Pt NEs confirmed a significant reduction in the diameter of the Pt wire: from 25 μm to 25 nm (1000 times reduction). However, it also revealed that the Pt wires of these NEs are commonly recessed within the pulled quartz capillary. After FIB milling was used to expose the Pt tips, the resulting RG of these laser-pulled NEs were found to be greater than 25. An alternative exposure method is through manual (abrasive) polishing, which is simpler and more cost-effective, however the resulting NE probes often have larger exposed Pt disks. Needless to say, the tip diameters of the manually polished

electrodes are frequently found to be significantly smaller than the commercially obtained Pt wires (currently, the smallest commercially available is 10 μm diameter (non-Wollaston)).

Here, a manually polished 250 nm Pt NE (RG30) was used to characterize the Pt and glass microbands of an IAME sample. The submicron probe was very effective for SECM imaging regardless of its high RG value. The constant height images indicated weak redox cycling between 5 μm Pt microbands which were separated by a 5 μm glass interdigit space (microband). In conjunction with theoretical simulations completed in COMSOL Multiphysics, the tip-to-sample distances could only be determined through fitting of the experimental horizontal line scans. Utilizing an idealized IAME geometry (flat microbands), it was determined that the 250 nm Pt NE was scanned approximately 0.6 μm above the IAME sample. In addition, the presence of either sample or electrode tilt of 1.53° was identified in the electrodes imaging of the IAME.

The SECM depth scan image obtained over the IAME demonstrated strong electrochemical feedback upon approach to the conductive bands. This was due to the smaller normalized distances achieved to the Pt microbands since there is a height discrepancy (110 nm) between the Pt and glass microbands. The final horizontal line scan of the SECM probe in the experimental depth scan was set to mirror the fixed z position of the probe during the collection of the constant height image. Utilizing a horizontal line scan at the bottom of the depth scan image revealed a tip-to-sample distance in close agreement to that from the constant height image (0.75 μm). Since this tip-to-sample distance corresponds to a normalized distance greater than 6, the fitting of experimental PACs to simulated curves becomes difficult. Therefore, the maximum and minimum normalized currents were matched to the simulated PACs to the respective Pt and glass microbands. This allowed the determination of the corresponding

normalized tip-to-substrate distances to the Pt and glass microbands. Using the idealized flat geometry of the bands the normalized distances revealed a 125 nm height variation which is similar to manufacturer's specifications (110 nm). At these tip-to-sample distances, the height of the Pt microbands was found to play a minimal effect on the feedback current. 3D simulation modelling was utilized for the first time, allowing characterization of these horizontal curves above and across the microbands of the IAME to quantify the probe's tip-to-sample distance and sample characteristics, such as tilt and height of the microbands.

Due to the size of the SECM probe, it was expected that the height of the Pt microbands would play a significant role on the feedback current detected at the IAME. However, finite elemental analysis simulations of this SECM study accounting for the height of the Pt microbands revealed minimal effect on current feedback. These results indicate that the idealized geometry of the IAME (flat microbands) can be used in the simulations, greatly reducing the computational times and resources required. The combinations of these 3D finite elemental analysis simulations and nanoelectrodes will be advantageous in nanoscale SECM studies.

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467 Figure Captions

468 **Fig. 1.** Labelled SEM images of a laser-pulled Pt nanoelectrode (a) before and (b) after FIB-
469 milling to expose the Pt tip. The Pt wire was reduced by a factor of one thousand (25 μm to 25
470 nm) and an RG greater than 25 can be observed.

471 **Fig. 2. (a)** The labelled stimulated model geometry of the SECM analysis of an IAME sample
472 with the symmetry plane shown in blue. **(b)** A zoomed in and labelled model of the Pt and glass
473 microbands, where the heights of the Pt microbands are taken into account (110 nm). **(c)** The
474 tetrahedrally-meshed simulation model with further refinement of the mesh at the electrode tip
475 and the microbands of the IAME to improve the accuracy of the simulation. **(d)** An example of
476 a simulated concentration map of the experiment, where the SECM probe is positioned in bulk
477 solution (several tip radii distances above the sample).

478 **Fig. 3. (a)** and **(b)** are the constant height SECM images of two alternating pairs of Pt and glass
479 microbands collected in 10 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ solution with 0.1 M KCl as the supporting
480 electrolyte. **(a)** is the 2D current map view and **(b)** is a 3D view to provide stronger visualization
481 of the electrochemical behaviour of the Pt and glass microbands. The scale bars in the images

represent 4 μm and the current scale bar in **(a)** is been normalized against the steady state current. **(c)-(e)** are the experimental horizontal line scans taken at the locations specified in **(a)** and have been overlaid over simulated curves generated at 0.50, 0.75, 1.00, 2.00 and 3.00 μm above the sample. From successful overlays, the 250 nm Pt NE was scanned approximately 0.6 μm above the sample. The simulation geometry of the working electrode was simplified to a 250 nm Pt NE with an RG of 10.

Fig. 4. (a) SECM depth scan image towards the glass and Pt microbands of the IAME sample. A horizontal line scan (red pentagons) is extracted near the end of the scan. **(b)** The experimental horizontal scan is overlaid onto theoretical curves to quantify tip-to-sample distance.

Fig. 5. The simulated PACs towards the center of (flat) Pt and glass microbands (red and black, respectively). The normalized currents from the SECM depth scan were used to identify their corresponding normalized distance.

Fig. 6. Horizontal line scans extracted from the **(a)** constant height image (line scan 1) and **(b)** depth scan image overlaid onto theoretical curves generated over an IAME with the height of the Pt microbands (110 nm) taken into account.

Fig. 7. Theoretical PACs of a 250 nm Pt NE's approach to 110 nm Pt and glass microbands (red and black) of the IAME.

Fig. 1. Labelled SEM images of a laser-pulled Pt nanoelectrode (a) before and (b) after FIB-milling to expose the Pt tip. The Pt wire was reduced by a factor of one thousand (25 μm to 25 nm) and an RG greater than 25 can be observed.!! †

82x121mm (299 x 299 DPI)

Fig. 2. (a) The labelled stimulated model geometry of the SECM analysis of an IAME sample with the symmetry plane shown in blue. (b) A zoomed in and labelled model of the Pt and glass microbands, where the heights of the Pt microbands are taken into account (110 nm). (c) The tetrahedrally-meshed simulation model with further refinement of the mesh at the electrode tip and the microbands of the IAME to improve the accuracy of the simulation. (d) An example of a simulated concentration map of the experiment, where the SECM probe is positioned in bulk solution (several tip radii distances above the sample).

186x102mm (299 x 299 DPI)

Fig. 3. (a) and (b) are the constant height SECM images of two alternating pairs of Pt and glass microbands collected in 10 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ solution with 0.1 M KCl as the supporting electrolyte. (a) is the 2D current map view and (b) is a 3D view to provide stronger visualization of the electrochemical behaviour of the Pt and glass microbands. The scale bars in the images represent 4 μm and the current scale bar in (a) is been normalized against the steady state current. (c)-(e) are the experimental horizontal line scans taken at the locations specified in (a) and have been overlaid over simulated curves generated at 0.50, 0.75, 1.00, 2.00 and 3.00 μm above the sample. From successful overlays, the 250 nm Pt NE was scanned approximately 0.6 μm above the sample. The simulation geometry of the working electrode was simplified to a 250 nm Pt NE with an RG of 10.!! †

194x94mm (299 x 299 DPI)

Fig. 4. (a) SECM depth scan image towards the glass and Pt microbands of the IAME sample. A horizontal line scan (red pentagons) is extracted near the end of the scan. (b) The experimental horizontal scan is overlaid onto theoretical curves to quantify tip-to-sample distance.!! +

98x94mm (299 x 299 DPI)

Fig. 5. The simulated PACs towards the center of (flat) Pt and glass microbands (red and black, respectively). The normalized currents from the SECM depth scan were used to identify their corresponding normalized distance.

56x25mm (300 x 300 DPI)

Fig. 6. Horizontal line scans extracted from the (a) constant height image (line scan 1) and (b) depth scan image overlaid onto theoretical curves generated over an IAME with the height of the Pt microbands (110 nm) taken into account.

104x96mm (300 x 300 DPI)

Fig. 7. Theoretical PACs of a 250 nm Pt NE's approach to 110 nm Pt and glass microbands (red and black) of the IAME.

56x25mm (300 x 300 DPI)