Supporting Information

Achieving nm Scale Tip-to-Substrate Gaps with µm-Size Ultramicroelectrodes in Scanning Electrochemical Microscopy

Mei Shen, Netzahualcóyotl Arroyo-Currás, and Allen J. Bard*

Center for Electrochemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, 1 University Station, A5300, Austin, Texas 78712-0165

Corresponding Author: ajbard@mail.utexas.edu

Abstract

The following document contains experimental details concerning the tip fabrication procedure mentioned in the original text. It also includes figures describing the method of aligning the SECM tip with the substrate electrode, some cyclic voltammograms presenting the oxidation of $Ru(bpy)_3^{2+}$ in acetonitrile and ferrocene methanol in water, and a complete description of the FEM model employed to compute the theoretical feedback at different electrode geometries.

1) Tip fabrication procedure.

A 7 cm long, 1.5 mm OD × 0.75 mm ID capillary tube was sonicated first in acetone and then in ethanol, dried, and sealed at one end by using a mixed oxygen/natural gas flame. A 10 μm diameter Pt wire was straightened and placed inside the sealed glass tube. The open end of the tube is connected to a vacuum line and heated with a nichrome wire helix to desorb any impurities or moisture on the wire. At the close end of the tube, one end of the wire is sealed in the glass by gradual sealing. Electrical connection was made between the unsealed end of the Pt wire and a conducing wire using Silver Epoxy resin (part A + part B, Epoxy Technology, Billerica, MA). Then Torr Seal Epoxy (Varian, Inc. Vacuum Technologies, Lexington, MA) is packed into the open end of the glass tube to fix the conducting wire. Silicon carbide paper (P180) was used to polish the sealed end of the capillary tube until the cross section of the wire was exposed. From there, the exposed surface of the wire was polished carefully using silicon carbide papers of progressively smaller grit size (P280, P400, P800, P4000), and then by suspensions of alumina of different sizes (1 μm, 0.3 μm, and 0.05 μm) on a microcloth pad (Buehler, Lake Bluff, IL). The glass wall surrounding the recently polished Pt disk was sharpened conically with silicon carbide paper (P400) on a polishing wheel, until RG <10, frequently checking the progress with an optical microscope. Subsequently, the tip was polished by hand on a silicon carbide paper (P800) until RG < 4. Finally, the tip was polished with silicon carbide paper (P4000) to reduce the RG to a minimum value, while holding it at such an angle that protected the metal disk from being affected. The resulting tip had a rounded insulation sheath, as shown in Figure 3 in the text.

2) Cyclic voltammetry of Rubpy oxidation.

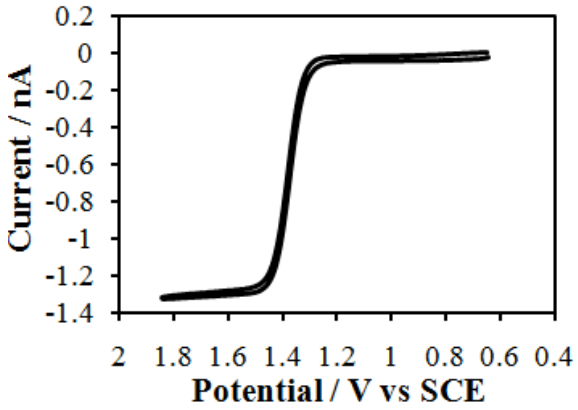

Figure S1. Cyclic voltammogram for oxidation of 0.38 mM Ru(bpy) in MeCN with 0.1 M $TBAPF_6$ as supporting electrolyte. A recently polished tip was used with a Pt disk (a = 5 μm) electrode.

3) Alignment of the tip and substrate electrodes for 0.38 mM Ru(bpy) in MeCN.

Two examples of SECM feedback response when the tip is scanning the x and y directions.

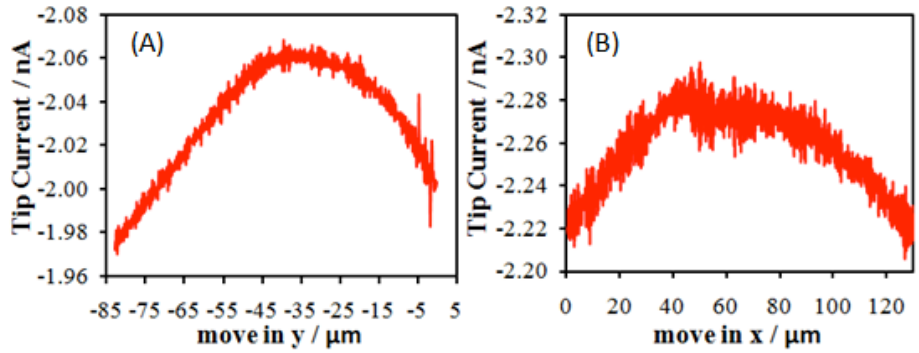

Figure S2. (A) Scan in the y direction while holding the SECM tip at 1.64 V vs SCE. Negative sign of y-axis means that the tip is moving backwards. (B) Same as (A) but scan along the x-axis.

4) Cyclic voltammetry of ferrocene methanol oxidation.

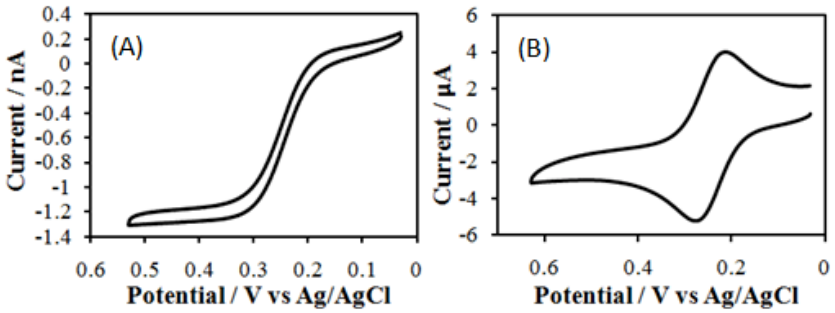

Figure S3. Cyclic voltammogram of 1 mM ferrocene methanol in water with 0.1 M KNO3 as supporting electrolyte. (A) at the tip, Pt disk (a = 5 µm); (B) at the substrate (a = 1 mm).

5) Alignment of the tip and substrate electrodes for 1 mM ferrocene methanol in water.

The figures below present the alignment procedure followed for the case of a solution containing 1 mM ferrocene methanol in water. The tip has a rounded insulation sheath surrounding the platinum disk (a = 5 µm). Figure S4(A) shows the tip was stopped at close distance to the substrate, and figures S4(B-D) are examples when scanning over the x- and y-axis.

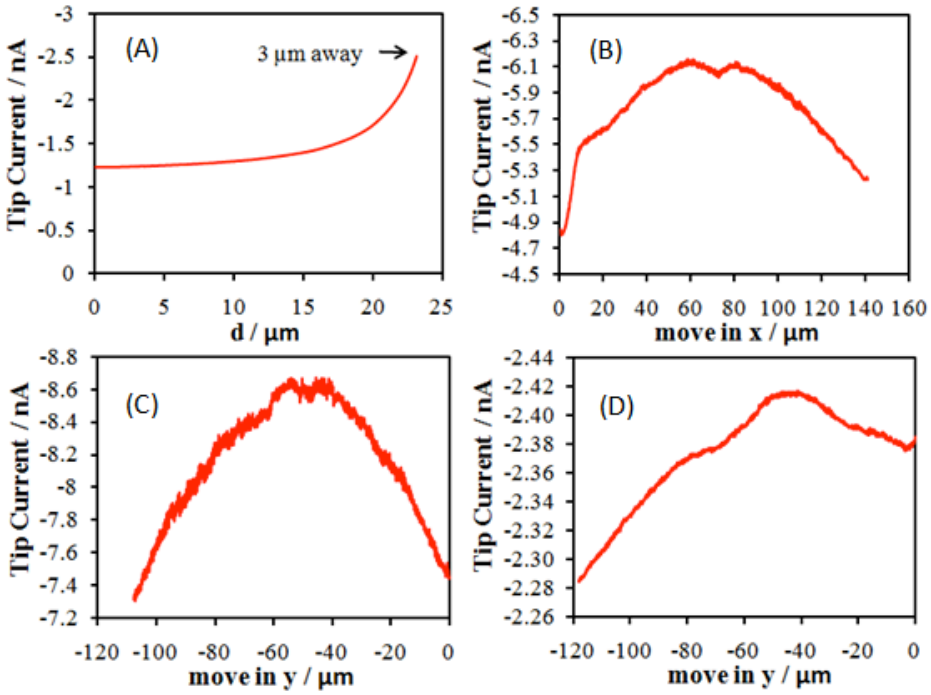

Figure S4. (A) First approach curve stopped at 3 µm away from the substrate electrode. Scanning of the tip over the substrate along x-axis (B), y-axis (C), y-axis (D). Solution containing 1 mM ferrocene methanol in water, with 0.1 M KNO3 as supporting electrolyte. Pt tip (a = 5 µm) and Pt substrate (a = 1 mm). After performing (B) and (C) scans, the tip was retracted and approached again to around 3 um away from the substrate (similar to (A), result not shown here). The scan shown in figure (D) was conducted after that last approach curve.

6) Description of the simulation model.

Digital simulations of the diffusion problem involved in the SECM feedback experiment were modeled with COMSOL Multiphysics software v.3.5 for a 2D-axial symmetry. The geometry of the simulation space was adjusted to fit the experimental conditions of the present study, where a = 5 µm and a_2 = 1 mm. For the tip electrode, RG < 1.1 and the shape of the

insulation sheath was imitated from SEM images of the apex of a typical electrode, as shown in Figure 3 of the original text. A depiction of the complete simulation space that includes the mesh employed and all relevant boundary labels is presented in Figure S5.

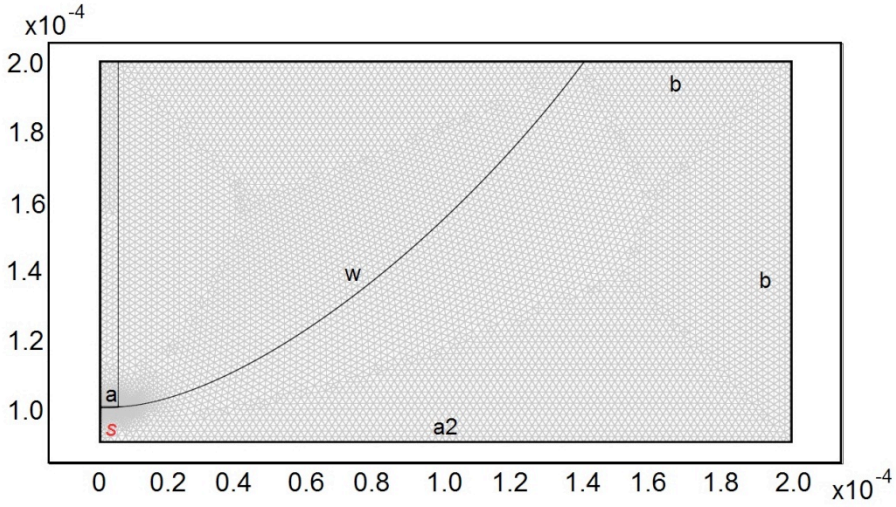

Figure S5. Schematics of the 2D axisymmetric environment chosen to conduct simulations of feedback response at SECM tip. *a*, tip electrode; a_2, substrate electrode; *w*, rounded insulation; *s*, symmetry axis; and *b*, limit boundaries of the cell.

In the model considered, the concentration of redox mediator is denoted as $C_o(r,z,t)$ and described by the diffusion equation in cylindrical coordinates as:

$$\frac{\partial C_o}{\partial t} = D_o\left(\frac{\partial^2 C_o}{\partial z^2} + \frac{\partial^2 C_o}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial C_o}{\partial r}\right) \qquad \text{(Equation S1)}$$

where C_o is the concentration of the mediator, D_o the diffusion coefficient, z and r the normal and radial directions from the tip surface, respectively, and t is time. The boundary conditions under steady state were defined as follows for all experiments:

$0 < t,\ 0 \leq r \leq a,\ z = 0$ (*tip electrode surface, a*)

$$C_o = 0$$

$0 < t,\ a \leq r,\ z = 0$ (*rounded glass insulation, w*)

$$\frac{\partial C_o}{\partial z} = 0$$

$0 < t,\ 0 \leq r,\ z = L$ (*substrate surface, a_2*)

$$C_o = 1$$

$0 \leq r,\ 0 \leq z$ (*all other boundaries, b*)

$C_o = 1$Finally, the current of the feedback response was integrated according to Equation S2:

$$i_T = -2\pi nFD_o \int_{r=0}^{r=a} r \cdot \frac{\partial C_{o(r,z)}}{\partial z} dr \qquad \text{(Equation S2)}$$