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Achieving Nanometer Scale Tip-to-Substrate Gaps with Micrometer-Size Ultramicroelectrodes in Scanning Electrochemical Microscopy

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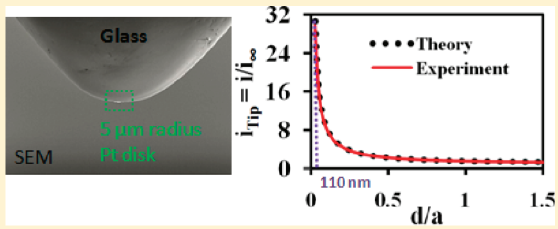
S Supporting Information

ABSTRACT: Scanning electrochemical microscopy (SECM) tips with rounded glass insulation around the metal wire (radius a = 5 μm) were fabricated (apparent RG < 1.1, where RG is the ratio of the radius of the insulation sheath divided by the electrode radius), and their SECM feedback approach curves were studied in solutions of tris(2,2′-bipyridine)-ruthenium(2+) (Rubpy) in acetonitrile and ferrocenemethanol in water with a platinum disk as the substrate electrode (radius a_s = 1 mm). Considerable enhancement of the normalized feedback current, $I_T(L) = i_T/i_{T,\infty}$, where $L = d/a$ and d is the distance traveled by the SECM tip, was observed in both systems (e.g., $I_T(L)$ = 15 in organic solutions and $I_T(L)$ = 30 in aqueous solutions) with good electrode alignment. This shows that tip-to-substrate gaps of ca. d = 110 nm can be achieved. To account for any deviations from the usual disk UME behavior and currents caused by possible changes in the tip electrode geometry, simulations of the feedback response were performed for a 2D axisymmetric environment. All simulated results match in a point-to-point comparison with experimental values (average relative standard deviation (RSD) = 0.01 ± 0.005).



There are important advantages in scanning electrochemical microscopy (SECM) to be able to position the SECM tip at a very small distance from a substrate electrode, for example, in measuring fast heterogeneous kinetics and in detecting short-lived tip-generated intermediates. SECM has a wide range of applications, covering fields of interest such as electrochemical imaging,[1] chemical kinetics,[2] biological redox processes,[3] and electrocatalytic reactions among others.[4,5] Factors like the size of the insulating sheath and difficulty in the exact alignment of the tip with the substrate limit the tip from approaching the substrate closer than that which yields, with positive feedback, a value of $I_T(L) = i_T/i_{T,\infty}$ of about 4 to 5, equivalent to a value of $L = d/a$ of about 0.2. Efforts have been focused on the fabrication of smaller tips, with radii in the order of a few nanometers, with the aim of achieving a close approach, even at L = 0.2, but we have found working with nanometer tips difficult. Although good results have been reported in the literature,[6] nanometer tips are difficult to fabricate, extremely fragile, and often stop working, probably because of contamination. They are also difficult to clean and regenerate the surface after use. Thus, applications of nanometer tips in SECM studies are few.

In the present work, we discuss ways of the use of larger tips (a = 5 μm) to attain nanometer-sized gaps by reducing the radius of the insulating sheath, RG, compared to the radius of the disk electrode tip. We also show how this limiting factor can be overcome without the need of smaller tips, by the use of a rounded insulation sheath that minimizes the magnitude of RG to values RG < 1.1. With this approach, we have attained $I_T(L)$ values up to 30. Finally, we compare the simulated feedback results and experimental approach curves to validate the measurements and demonstrate that small deviations in the disk preparation have only a very small effect.

■ EXPERIMENTAL SECTION

Anhydrous acetonitrile (MeCN) was obtained from Aldrich (St. Louis, MO) and transferred directly into an argon atmosphere drybox (MBraun Inc., Stratham, NH) without further purification. Electrochemical grade tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) was obtained from Fluka and used as received. Tris(2,2′-bipyridine)ruthenium(II) perchlorate (Rubpy) was obtained from GFS Chemicals, Inc. (Powell, OH). Ferrocenemethanol was obtained from Aldrich (St. Louis, MO). Details about SECM setup, SECM cell, and substrate electrode, as well as electrode cleaning have been described previously.[7] All SECM and other electrochemical measurements were carried out with a CHI 920C SECM station and bipotentiostat (CH Instruments, Austin, TX). Platinum (99.99%) 10 μm diameter wire from Goodfellow (Devon, PA) was used to fabricate the SECM electrodes by procedures similar to the ones described elsewhere.[5,8] A detailed tip fabrication procedure is included in the Supporting Information. The substrate electrode was a Pt disk (2 mm in diameter, CH Instruments, Austin, TX) sealed in Teflon. The tip and substrate electrodes were polished prior to use with alumina paste (0.3 and 0.05 μm) on microcloth pads

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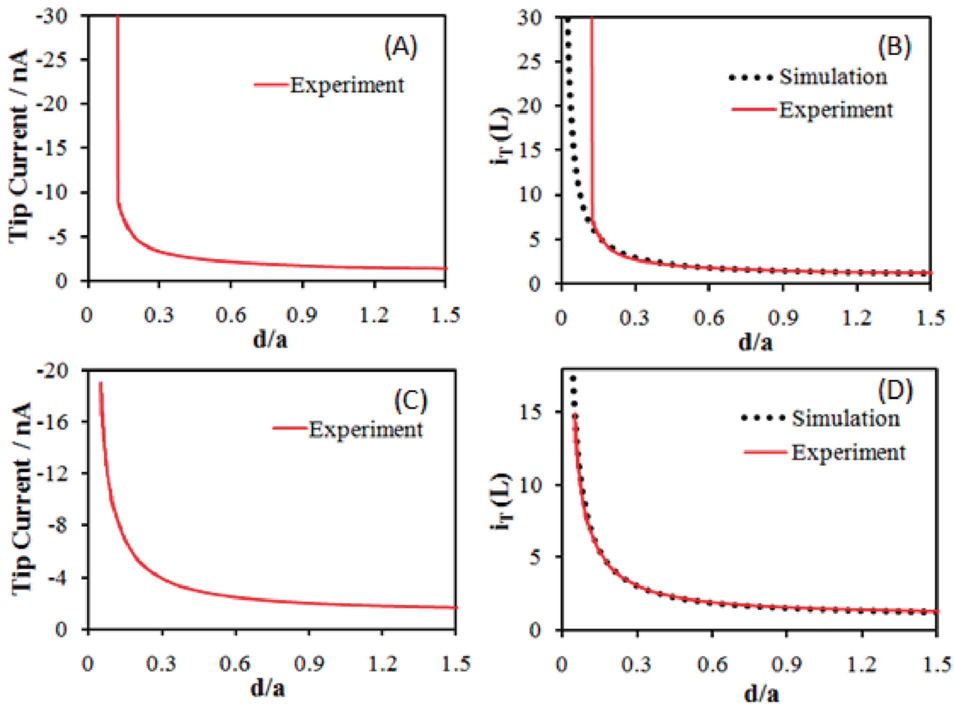

Figure 1. SECM approach curves for a Pt tip ($a = 5\ \mu$m) in 0.38 mM $Ru(bpy)_3^{2+}$ in MeCN with 0.1 M $TBAPF_6$ as supporting electrolyte. $i_{T,\infty}$= 1.3 nA. Experimental measurement was conducted with a SECM located inside a glovebox. (A, B) Approach curves obtained before alignment between the tip and substrate electrodes; (C, D) Approach curves obtained after electrodes were carefully aligned to find the highest point. E_{tip}= 1.64 V vs SCE; E_{sub}= 0.64 V vs SCE. See Figure S1 (Supporting Information) for cyclic voltammetry of Rubpy.

(Buehler, Lake Bluff, IL) and sonicated in Milli-Q deionized water and then in ethanol. A Zeiss Supra 40 VP scanning electron microscope (SEM) was used to check the tip geometry, where the tip was initially placed flat (horizontal) and then tilted to different angles to best characterize the tip end. A SEM picture of the tip is shown below.

RESULTS AND DISCUSSION

Experimental Feedback at Tips with Rounded Insulation. To investigate the effects that a rounded insulation sheath can have on the electrochemical feedback of a SECM tip, experiments were conducted in solutions of Rubpy in acetonitrile and ferrocenemethanol in water.

During the process of aligning the substrate electrode and doing $x-y$ scans, the substrate electrode, a 2 mm Pt disk, even when polished to a mirror finish, was found to have regions that were significantly higher than the surrounding regions. The SECM imaging of the substrate was accomplished by stopping the tip at a short distance from the substrate (Figure S4A, Supporting Information) and then alternately scanning over the x- and y-axis multiple times until the highest plateau showing the maximum current was found. The tip was then aligned at this $x-y$ position to carry out the approach to the substrate. This was always the position where the SECM kinetic studies were carried out.[7] Examples of scanning the tip in y and x directions over the substrate are shown in Figure S1 (Supporting Information) for Rubpy and Figure S4 (Supporting Information) for ferrocenemethanol.

Figures 1A,B show the approach curves before the electrode alignment while Figures 1C,D show after the alignment. The black dotted lines in Figures 1B,C correspond to the theoretical fit to positive feedback SECM obtained through eq 1:[5]

$$i_T(L) = 0.68 + 0.78377/L + 0.3315\exp(-1.0672/L) \quad (1)$$

From Figures 1A,B, before alignment, the tip current increases gradually until around 6 times the steady state current at the tip, $i_{T,\infty}$, and then increases sharply, indicating that the tip is touching the substrate electrode. The fact that one sees this rise to the tunneling regime is evidence that, even without alignment, the metal tip material touches before the insulation surrounding the tip does, because the metal is protruding somewhat. Figures 1C,D show the results obtained after careful alignment between the electrodes. Under these conditions, the tip does not touch the electrode and an enhanced SECM current of $i_T(L) \approx 15$ is obtained.

Similar experiments were conducted with an aqueous solution of ferrocene methanol, as seen in Figure 2. The experiments conducted without alignment of the electrodes (Figures 2A,B) show the same features as previously described; i.e., a progressive increase from $i_{T,\infty}$ to $i_T(L) \approx 12$, with a subsequent crash that sharply increases the current. Instead, the approach curves conducted after careful alignment of the electrodes do not show crashes, and the SECM current follows the theoretical curve to as high as $i_T(L) \approx 30$. The tip-to-substrate gap was extracted from the theoretical fit at $L = 0.022$, with mean values of $d = 110$ nm.

Simulation of SECM Feedback Response. The fact that the tip crashes involved contact of the tip metal to the substrate, rather than contact of the surrounding glass sheath, implies that the glass sheath is polished back away from the metal and that there may be some rounding of the metal disk in the tip. Electrochemical simulations of the SECM feedback signal were performed using COMSOL Multiphysics v.3.5 software to study the effect of a rounded insulation sheath and tip metal on the experimental

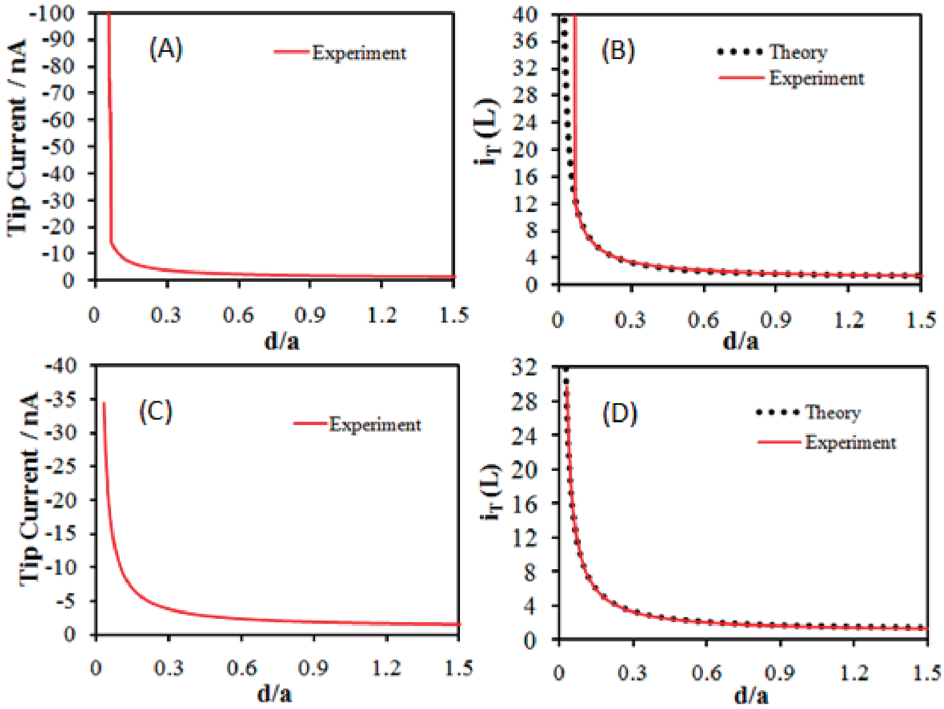

Figure 2. SECM approach curves for a Pt tip (a = 5 μm) in 1 mM ferrocene methanol in water with 0.1 M KNO_3 as supporting electrolyte. $i_{T,\infty}$= 1.23 nA. (A, B) Approach curves obtained before alignment between the tip and substrate electrodes; (C, D) Approach curves obtained after electrodes were carefully aligned to the highest substrate point. E_{tip} = 0.4 V vs Ag/AgCl; E_{sub} = 0.1 V vs Ag/AgCl. See Figure S3 (Supporting Information) for cyclic voltammetry of ferrocene methanol.

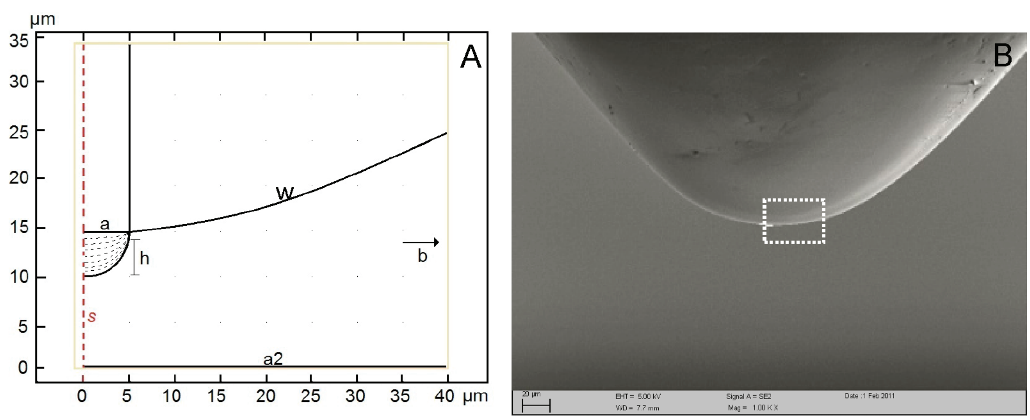

Figure 3. (A) Schematics of the 2D axisymmetric environment chosen to conduct simulations of feedback response at SECM tip. a, tip electrode; a_2, substrate electrode; w, rounded insulation; s, symmetry axis; and b, arrow indicating that boundaries of cell are not shown in caption. The dashed lines in the tip represent the different values of h evaluated in this study, ranging from $h = a$ to $h = 0$, in intervals of $\Delta h = a/10$; (B) SEM picture of the fabricated SECM tip tilted at 5°. The size marker in the lower left corner is 20 μm. A SEM picture of the tip tilted at 15° is given in reference 7.

feedback observed while approaching the SECM tip to the substrate. Moreover, it was important to detect any polishing effects on the geometry of the tip electrode, since deviations from a flat disk can potentially change the approach curve.

In Multiphysics, a 2D axisymmetric environment was created to model diffusion to the tip and substrate electrodes. Figure 3A shows this environment, where a represents the tip electrode of radius a = 5.00 μm and variable height h, s is the symmetry axis, a_2 represents the substrate electrode of radius $a_2 \gg a$, and w is the rounded insulation. To account for any effects on $i_T(L)$ associated with changes in the geometry of the tip electrode, the parameter h was given values ranging from $h = a$ (for a perfect hemisphere) to $h = 0$ (for a flat disk) in intervals of $\Delta h = a/10$. Furthermore, the shape and dimensions of the tip geometry used for the model were taken from real dimensions measured by SEM imaging, as shown by the dashed square in Figure 3B. A complete description of the simulated model can be found in the Supporting Information.

Figure 4 shows computed results of the described model. Each colored dotted line shows the computed approach curve for a specific value of h, ranging from $h = 2a/10$ to $h = a$. The two simulations corresponding to values of h below that range, i.e.,

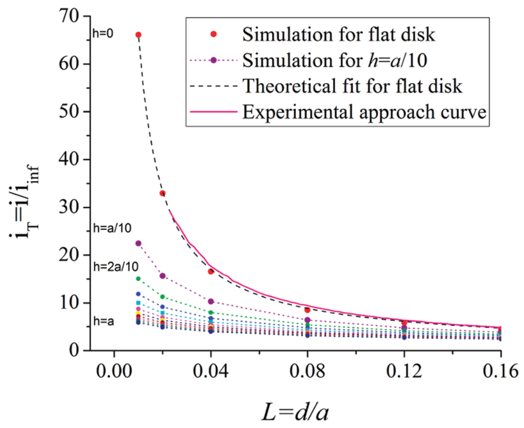

Figure 4. Simulated results of the finite element method (FEM) model for geometries ranging from $h = 0$ to $h = a$ in intervals of $\Delta h = a/10$. The pink line presents a typical experimental approach curve obtained with electrodes having a rounded insulation sheath. The dashed black line is a theoretical fit of the feedback curve using parameters (A, B, C, D) and the equation described above. The colored dots connected by colored dashed lines are computed results from the FEM model.

$h = 0$ and $h = a/10$, appear above the others and correspond to the maximum enhancements of the current attainable up to $L = 0.022$. As expected, the highest enhancement is seen for a flat disk, whose response is represented by the red circles in Figure 4. A theoretical fit of these points was accomplished using parameters $A = 0.2285$, $B = 0.600701$, $C = 0.387274$, and $D = -0.00982$ in the equation: $i_T(L) = A + B/L + C \exp(D/L)$. This equation simulates a diffusion-controlled SECM process under steady state conditions and takes into account the conditions of back diffusion to the electrode surface related to SECM tips with RG < 10.[5,9,10] A point-by-point comparison between the simulated values and the theoretical fit presents an average standard deviation of the normalized current of 0.01 ± 0.005.

On the other hand, a typical experimental approach curve observed with a tip having rounded insulation, like that shown in Figure 3B, is also shown in Figure 4 by the pink line. The experimental approach curve overlaps with the theoretical feedback represented by the dashed line, suggesting that the polishing procedure followed to make the rounded insulation did not appreciably affect the shape of the disk electrode. On the basis of a simulation, this implies that $h < 0.001$a.

CONCLUSIONS

The present work shows that 5 μm radius SECM tip electrodes with a rounded insulation sheath can achieve nanometer-size tip-to-substrate gaps after careful alignment of the tip and substrate electrodes. Alignment of electrodes was performed through SECM imaging to find the highest point (top plateau) on the substrate where optimal values for $i_T(L)$ are detected. This procedure offers feedback currents as high as 30 times the magnitude of $i_{T,\infty}$ and can attain tip-to-substrate gaps of about $d = 110$ nm with a tip of $a = 5$ μm. All experimental results were compared to theoretical fits and then evaluated against simulated results obtained through a FEM model. No significant deviations from the behavior of a flat disk electrode were found, suggesting that the polishing procedure employed to fabricate the rounded insulation did not cause significant changes (i.e., rounding) of the tip electrode geometry. The ability to attain such a close approach facilitates the use of the feedback mode of SECM for studies involving fast electron transfer kinetics without complications associated with the fabrication of tips with nanometer radii. As with all SECM tips and procedures, more detailed simulations may be appropriate when one has to deal with current density differences and kinetic effects.

ASSOCIATED CONTENT

S Supporting Information. The experimental tip fabrication, the method of aligning the SECM tip with the substrate electrode, cyclic voltammograms of $Ru(bpy)_3^{2+}$ in acetonitrile and ferrocene methanol in water, and a complete description of the Multiphysics model. This material is available free of charge via the Internet at http://pubs.acs.org.

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