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Technical Note

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Examining Ultramicroelectrodes for Scanning Electrochemical Microscopy by White Light Vertical Scanning Interferometry and Filling Recessed Tips by Electrodeposition of Gold

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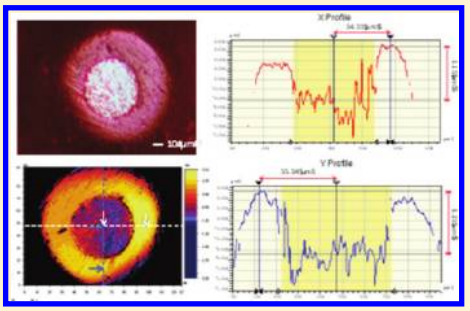
Supporting Information

ABSTRACT: In this paper, we present a technique to rapidly and directly examine ultramicroelectrodes (UMEs) by white light vertical scanning interferometry (VSI). This technique is especially useful in obtaining topographic information with nanometer resolution without destruction or modification of the UME and in recognizing tips where the metal is recessed below the insulating sheath. Two gold UMEs, one with a metal radius a = 25 μm and relative insulating sheath radius RG = 2 and the other with a = 5 μm and RG = ~1.5, were examined, and the average depth of the gold recessions was determined to be 1.15 μm and 910 nm, respectively. Electrodeposition of gold was performed to fill the recessed hole, and the depth was reduced to ~200 nm. With the electrodeposited gold electrode and a conventional microelectrode (a = 25 μm) as a tip and substrate, respectively, a tip/substrate distance, d, of 600 nm was achieved allowing scanning electrochemical microscopy (SECM) in positive feedback mode at a close distance, which is useful for measuring fast kinetics.



Ultramicroelectrodes (UMEs), with typical dimensions in the micrometer regime have found widespread applications in electrochemistry, for example, as scanning tips in scanning electrochemical microscopy (SECM). While such tips, usually disks embedded in a glass matrix, are often characterized by voltammetric measurements, relating the diffusion-controlled current to an apparent radius of the disk, this approach cannot be used to obtain the true tip geometry. For example, the metal disk is often recessed somewhat into the insulating sheath because of differential rates of polishing of metal and glass or other reasons. A recessed electrode limits the gap size because of the depth of the recessed metal, so that it is difficult to reach a normalized positive feedback current higher than 3 or 4 using such a tip.[1]

Optical microscopy and scanning electron microscopy (SEM) have been utilized to observe the geometric shape of a microelectrode surface.[2] These can obtain an image of the disk electrode but are less useful in providing quantitative topographic information in the needed submicrometer regime. Thus, there have been few reports that show the surface topography of an UME, e.g., to determine how deeply the metal is recessed below the insulator surface or how high it is above it, because of the difficulty of taking cross-sectional images of a UME. In SEM, the thickness of a deposited film or a step height between two films is measured by taking cross-sectional images from vertically cut films. In a microelectrode however, vertically cutting the middle of the electrode without collapsing the recessed hole is challenging.

White light vertical scanning interferometry (VSI), one of the modes in white light interferometry (WLI), is a noncontact optical technique that can accurately measure surface heights on a sample.[3] A VSI surface profiler obtains surface height information by passing a white-light beam through a beam splitter where half the beam is passed to the test surface and the other half of the beam is passed to a flat reference surface inside the instrument. The beams reflected from the test surface and the reference surface are recombined to form interference fringes, where the highest contrasts of the fringes occur at optimal focus. To determine surface heights, the instrument measures the degree of modulation contrast of the fringes as a function of path difference.[4] In practice, the surface profiling system performs a series of scans starting from above the focus and moving in the vertical direction to below the focus. As the lens moves in the vertical direction, the system captures and records the interference data at a number of evenly spaced intervals. This series of interference patterns allows the surface height to be determined for each point on the surface.

Here, we report an application of VSI to measure depths of metal recessions in microelectrodes and monitor the change in the depth of the recession after electrodeposition of gold inside the recessed hole. With an electrode that has undergone the electrodeposition process to reduce the metal recession depth as a tip in SECM, one can achieve a tip/substrate distance of only a few hundred nanometers.

EXPERIMENTAL SECTION

Chemicals. All solutions were prepared with deionized Milli-Q water, and the chemicals were purchased and used as

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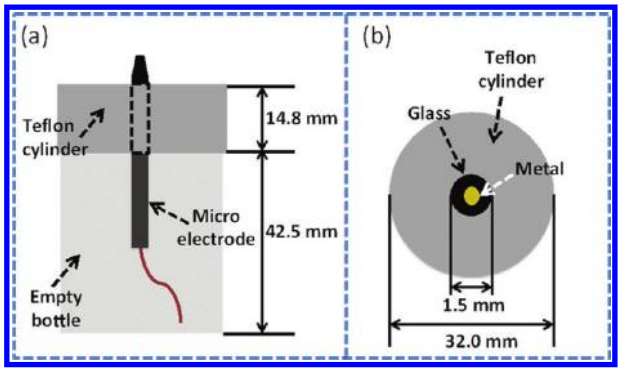

Figure 1. Depiction of (a) side and (b) top views of a homemade device for the observation of an electrode surface through a VSI microscope.

follows: ferrocenemethanol (FcMeOH, 97%) from Sigma-Aldrich; sodium nitrate ($NaNO_3$, ≥ 99%) from Fisher Scientific; and gold precursor solution (PURE GOLD SG-10) from Transene, Inc.[5]

Instruments and Measurement. Electrodeposition was performed with a CH 660, and SECM was done with CH 900 SECM station bipotentiostat (CH Instruments, Austin, TX).

Three electrodes were used in SECM: a gold UME with a = 5 μm as a working electrode, a carbon rod as a counter electrode, and a Ag/AgCl (in saturated KCl) reference electrode. The metal recession depths on the UMEs were measured using a Wyko NT9100 optical surface profiler (Veeco, New York).

Gold Microdisk Electrodes. Gold (99.99%) wires with a = 25 and 5 μm from Goodfellow (Devon, Pennsylvania) and a

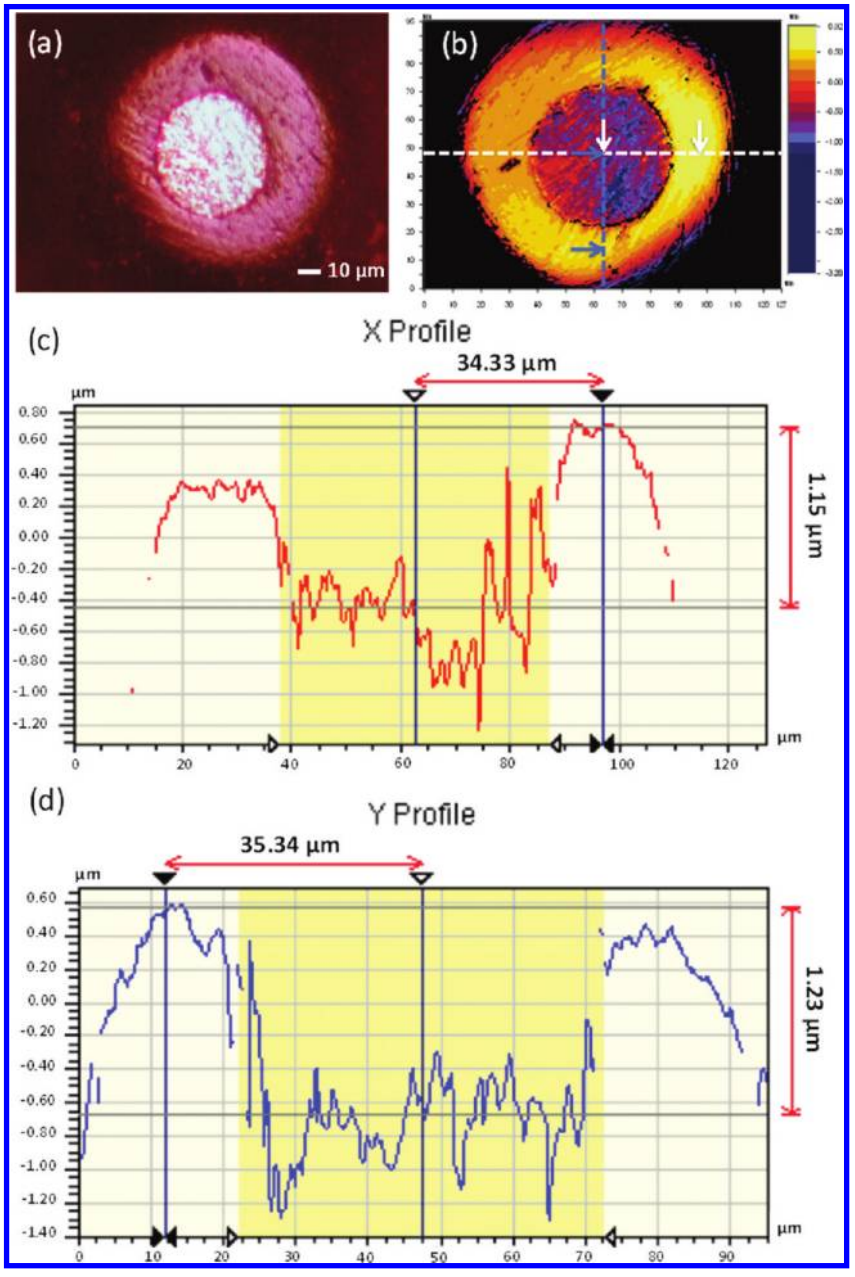

Figure 2. Two-dimensional surface images of a gold microelectrode (a = 25 μm) taken from (a) an optical microscope, (b) VSI microscope, and (c) its relative height profiles along x (white line shown in part b) and (d) y (blue line) axis. The depth of the recessed hole was measured by a difference of height between two sites on which arrows are designated in the image in part b.

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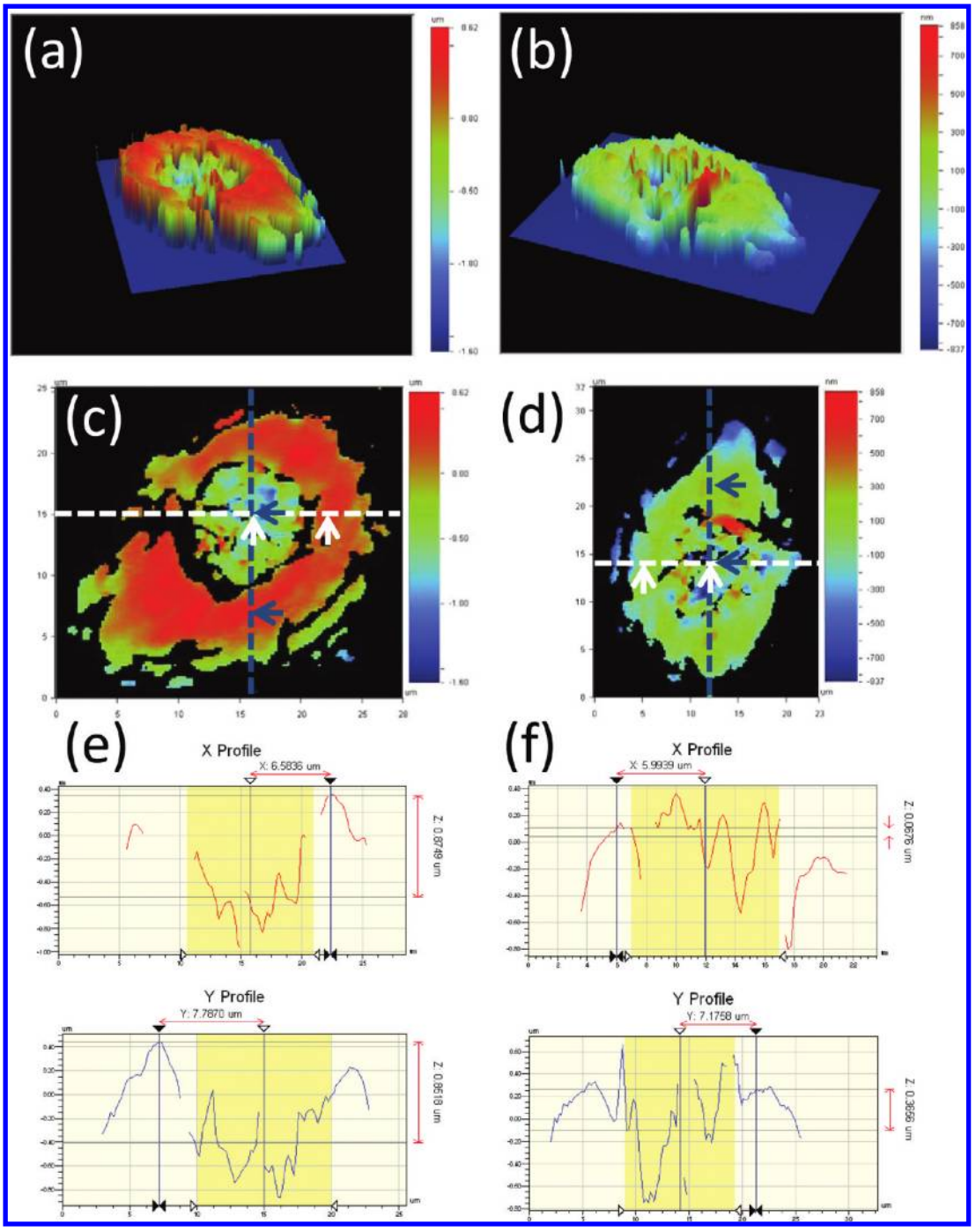

Figure 3. Three-dimensional and two-dimensional images and relative height profiles along the *x* (white line) and *y* (blue line) axis of a recessed gold electrode surface (a, c, e) and the same electrode surface after electrodeposition of gold inside the recessed hole (b, d, f).

borosilicate capillary with an outer diameter of 1.5 mm and an inner diameter of 0.75 mm from FHC (Bowdoin, Maine) were used to fabricate the UMEs. All were prepared by procedures described elsewhere.[6]

RESULTS AND DISCUSSION

Calibration. To confirm the accuracy of the surface profile images, surface height information was obtained for a calibrated step height standard (VLSI Standards Inc.).[7] This standard has a 8.407 ± 0.068 μm step etched in silicon. Figure S1 in the Supporting Information shows an optical image of the calibrated step height standard with the surface profiler. The surface profiler was focused on the upper portion of the step (left), so that the maximum contrast interference fringes are only visible on that section of the sample. Figure S2 in the Supporting Information shows both a two-dimensional and three-dimensional VSI image of the silicon step standard with the software term mask applied to alleviate any sample tilt. It is possible to calculate both the height profile across the step (Figure S3a in the Supporting Information) as well as a histogram of the height data for each point in the image (Figure S3b in the Supporting Information). Figure S3a in the Supporting Information shows that the measured height of the step, 8.4073 μm, corresponds very well to the quoted standard height (8.407 ± 0.068 μm). The height

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variation was also obtained by examining the histogram shown in Figure S3b in the Supporting Information. Two large peaks were observed; a peak around 0 μm corresponding to the points on the lower section of the step and a second peak of about 8.4 μm corresponding to the points which make up the upper section of the step. The agreement between the reported value for the step height and the measured value from the surface profiler demonstrates the accuracy and precision of VSI for obtaining surface height maps.

Characterizing UME Surface Topography. To observe a microelectrode surface, the electrode must be linearly aligned with respect to the lens of the VSI microscope. This requires a large working distance of at least several centimeters between the lens and the stage of the microscope. Figure 1 shows both side and top views of a homemade device to vertically hold the UME. A small hole fitted to the electrode was cut in the middle of a Teflon cylinder, and the lower part of the electrode was pushed through this hole. Then, this Teflon cylinder was placed on an empty bottle where the rest of the electrode could be kept without suffering any damage.

With a gold UME with a = 25 μm, one could clearly observe the recessed metal inside the insulating sheath and measure its depth. This electrode was polished to produce an RG (the ratio of the radius of the insulating material to that of the metal wire) of ~2 and during polishing the gold became recessed because its hardness (2.5−3 on the Mohs' Scale) is lower than that of the borosilicate glass (5.5−6.5 Mohs' Scale). The two-dimensional image of the electrode surface obtained from VSI (Figure 2b) is in good agreement with an image taken with an optical microscope (Figure 2a). The image shown in Figure 2b incorporates x, y, and z coordinates, where the z value represents the relative height of the surface and is shown as a color gradient ranging from yellow (high) to dark blue (low value). Note that the relative height of the gold surface was lower than that of the borosilicate glass surface. The depth of the recessed hole was estimated from measuring the maximum height of the glass surface and an average height of the gold surface along the x direction with a constant y value (X profile) and along the y direction with a constant x value (Y profile). An example of an X and Y profile is shown in Figure 2c,d. In the X profile at y = 50 μm (white line shown in Figure 2b), the metal portion encompasses 40 ≤ x ≤ 90 μm and the glass portion, x > 90 μm, x < 40 μm. The maximum relative height of the glass was 0.70 μm at x = ~100 μm, and the average relative height of the gold surface was −0.45 μm. The depth of the hole, therefore, was estimated to 1.15 μm. Likewise, an estimated depth at x = 65 μm (blue line shown in Figure 2b) in the Y profile in Figure 2d was ~1.23 μm. The average depth of the hole, estimated by measuring depths from 20 different X-profiles (40 ≤ y ≤ 85 μm) and Y-profiles (25 ≤ x ≤ 70 μm), was determined to be 1.12 μm.

Electrodeposition of Gold on a Recessed UME and SECM Measurements. A gold microelectrode with a = 5 μm was polished to an RG of ~1.5. As discussed, this results in an electrode that is recessed as shown by VSI (Figure 3a,c). The average depth of the recessed hole was about 910 nm. To fill the hole, gold was electrodeposited onto the microelectrode. The electrodeposition was performed using a two-electrode configuration with the gold microelectrode as the cathode and a platinum mesh electrode as the anode with a constant applied current of 8.95 nA (10.8 mA/cm^2) in a commercial gold plating solution at 59 °C. All electrodeposition conditions were identical to the operating conditions provided by the manufacturer of the gold plating solution.[5] The deposition time was calculated by determining the theoretical total charge required to deposit enough gold to fill the recessed space (7.87×10^{-11} cm^3). By this method, the deposition time was determined to be ~90 s. However, in order to account for the nonideality of the current efficiency and allow for a slight protrusion of the gold over the insulation sheath, the actual deposition time used was 115 s. Figure 3b,d shows the electrode surface after the electrodeposition of the gold. The recessed hole was now filled with gold with a small variation because of the nonuniformity of the deposit thickness. This thickness variation is probably related to the current distribution during electrodeposition; however, the estimated average depth of the hole was reduced to 202 nm.

An SECM experiment was performed in a positive feedback mode with FcMeOH, which shows an essentially Nernstian wave, as the mediator. The electrodeposited gold microelectrode and another gold microelectrode with a = 25 μm, RG =2 were used as a tip and substrate, respectively. A potential of 0.4 V, where FcMeOH is oxidized at a diffusion-controlled rate, was applied to the tip while the substrate was held at 0 V, where the oxidized FcMeOH was reduced and a positive feedback curve was obtained as shown in Figure 4a (hollow circles). This could

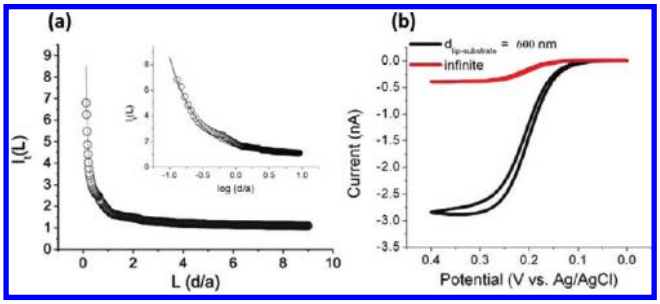

Figure 4. (a) A positive feedback curve (inset is $I_t(L)$ vs log L) in 0.3 mM FcMeOH + 0.1 M $NaNO_3$ on the gold microelectrode after electrodeposition of gold and (b) CVs at d = 600 nm (black) and ∞ (red).

be carried out until the tip was ~600 nm above the substrate electrode ($L = d/a$ = 0.12, where d is the distance between the tip and substrate), resulting in a positive feedback amplification factor, $i_T/i_{T,\infty}$ of about 7. The curve fit the theoretical curve that assumed a flat disk electrode coplanar with the insulating sheath (black line), even though the actual geometry of the electrodeposited electrode surface did not conform exactly to this geometry. As shown in many previous studies, disklike behavior results, even when the "disk" region is irregular or when it protrudes slightly from the insulation sheath.[8] The electrodeposition can thus be used to renew the surface and even produce a very slightly hemispherical protrusion that will allow a close approach with subsequent measurement of fast heterogeneous electron transfer or homogeneous reactions with the SECM.

■ CONCLUSIONS

Vertical scanning interferometry (VSI) is a useful and rapid technique for characterizing ultramicroelectrodes (UMEs) with excellent topographic resolution in the z direction. It allows depths of metal recessions to be determined within several nanometers. The electrodeposition of gold on recessed UMEs can fill the recessed hole to make the electrode more planar or even overfill to obtain a slight protrusion. With such tips and proper alignment, very close approach to a conducting substrate is possible, allowing measurement of reactions with fast kinetics.

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■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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