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Fabrication of Nanoscale Gold Disk Electrodes Using Ultrashort Pulse Etching

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A novel method for preparing a nanometer-sized gold disk electrode is described. The electrode was fabricated by electrochemical etching of a gold wire, insulating the etched wire with a varnish with the exception of the apex, and cutting down the apex by applying ultrashort (40 ns) etching pulses in an HCl solution. Cyclic voltammograms of a 0.10 M ferrocyanide solution recorded at the electrode showed that a series of etching pulses gradually reduced the diffusion-limited current at the electrode by etching its apex. Characterization by cyclic voltammetry and scanning electron microscopy revealed the transformation of a cone-shaped apex into a disk-shaped electrode with a radius of typically between 50 and 250 nm.

In recent years, fabrication of electrodes with ultrasmall geometric dimension, the so-called ultramicroelectrode (UME), has received increasing attention from the electrochemists. UMEs have small capacitances and reduced ohmic voltage (*IR*) drops thanks to their small areas and small currents, respectively, enabling electrochemical measurements with small cell time constants, reduced double layer charging, and high mass transport to the electrodes. As such, UMEs have been used in measurements of fast heterogeneous electron-transfer rates, transient electrochemical experiments, voltammetric experiments in low-conductivity media, and probing neurochemical microenvironments.[1−3] UMEs of hemispheric shapes fabricated to the nanometer sizes have also been used as scanning tips for various scanning probe microscopies.[4−7]

UMEs are fabricated usually by insulating an electrochemically etched metal wire with coatings with the exception of its apex. Various materials have been used to insulate metal wires, including glass, varnishes, wax, epoxy, paraffin, polymers, and electrophoretic paints.[3,8,9] A UME fabricated by electrochemically etching a wire is often assumed to have a hemispherical apex, but the electrode shape is difficult to control during the fabrication process and is usually not well defined on the nanometer scale. It is desirable to develop a means to fine-control the shape and size of a UME. Well-defined shapes of UMEs are important for electrokinetic and scanning electrochemical microscopic (SECM) measurements, in which the currents are assumed to be evenly distributed over the electrode surface. In this paper, we report a novel technique to trim the protruded part of an electrode surface by applying ultrashort etching pulses to make a disk-shaped electrode. It is shown that the pulse etching method changes a cone-shaped apex of a gold UME into a flat disk electrode. The method should be applicable to fabricate UMEs of various metals including gold.

Materials and Electrochemical Apparatus. Potassium chloride, hydrochloric acid, sulfuric acid, hydrogen peroxide (all reagent-grade from Samchun Pure Chemical), and potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$; Aldrich, 99%) were used as received. Solutions were prepared with deionized water having a specific resistivity of 18 MΩ·cm. Gold wires (Nilaco, 99.95%, 0.3- or 0.25-mm diameter) for gold UMEs, platinum wires (Nilaco, 99.97%, 0.5-mm diameter), and a homemade Kel-F electrochemical cell were cleaned with piranha solutions (mixtures of 30% H_2O_2 and 70% H_2SO_4) for 5 min. (Warning: Piranha solutions are strong oxidants and react violently with organic impurities, especially when hot!)

A potentiostat in an electrochemical scanning tunneling microscope (NanoScope IIIa, Veeco Instruments) was employed to perform cyclic voltammetric experiments. A three-electrode Kel-F cell was used for cyclic voltammetry, with Ag/AgCl (in saturated KCl) reference and platinum counter electrodes. A field emission scanning electron microscope (JSM-6330F, JEOL) was used to characterize the nanometer-sized gold disk electrodes.

Fabrication of UMEs. We prepared UMEs from gold wires in three steps, which are conceptually presented in Figure 1. In the first step (Figure 1a), a gold wire was etched in a 3.6 M HCl solution by electrochemical oxidation according to the reaction,[10]

$$Au(s) + 2Cl^- \rightarrow AuCl_2^- + e^- \qquad E^\circ = 1.154\ V \quad (1)$$

where E° is the standard electrode potential for the reaction. A

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(1) Penner, R. M.; Heben, M. J.; Longin, T. L.; Lewis, N. S. *Science* **1990**, *250*, 1118.

(2) Forster, R. J. *Chem. Soc. Rev.* **1994**, 289.

(3) Zoski, C. G. *Electroanalysis* **2002**, *14*, 1041.

(4) Fan, F.-R.; Kwak, J.; Bard, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 9669.

(5) Macpherson, J. V.; Unwin, P. R. *Anal. Chem.* **2000**, *72*, 276.

(6) Bach, C. E.; Nichols, R. J.; Beckmann, W.; Meyer, H.; Schulte, A.; Besenhard, J. O.; Jannakoudakis, P. D. *J. Electrochem. Soc.* **1993**, *140*, 1281.

(7) (a) Wipf, D. O.; Bard, A. J. *J. Electrochem. Soc.* **1991**, *138*, 469. (b) Bath, B. D.; Lee, R. D.; White, H. S. *Anal. Chem.* **1998**, *70*, 1047.

(8) Conyers, J. L., Jr.; White, H. S. *Anal. Chem.* **2000**, *72*, 4441.

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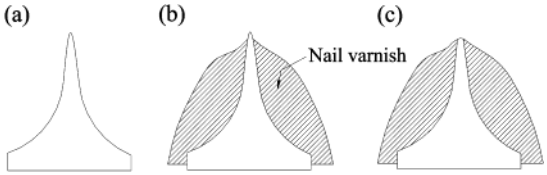

Figure 1. Schematic illustration of the fabrication procedure of a gold UME: (a) an electrochemically etched gold wire, (b) a gold electrode with a nail varnish coating, and (c) a gold UME produced by pulse etching of the apex.

dc voltage of 1.7 V applied between a gold wire and a platinum counter electrode provided a sufficient overpotential to drive the reaction. The etching setup similar to the ones reported in the literature[11,12] was used, in which a counter electrode was a platinum wire ring, so that the electrochemical etching eventually cut the gold wire into two pieces, both with cone-shaped tips. A homemade electronic circuit was used to automatically terminate the etching as soon as the current became close to zero. To detect this, the etching current was monitored using a current-to-voltage converter (OPA620, Texas Instruments), whose output was fed into a comparator (LM306, Texas Instruments). The comparator detected the termination of electrolysis by monitoring a sudden decrease of the etching current due to gold wire breakage. The comparator controlled an analog switch (MAX4609, Maxim Integrated Products) to stop the etching. The response times of the comparator and the switch were 28 and 150 ns, respectively. With this method, gold tips whose radii of curvature were smaller than 100 nm were routinely produced.

In the second step (Figure 1b), an etched gold tip was coated with nail varnish containing nitrocellulose (transparent color, Royal Manicure, Daewon Cosmetics) except at its apex. Since gold is a soft metal, the coating material must be very soft as well like a varnish. A harder material such as wax easily destroys the sharp gold apex. The varnish coating was made according to the standard procedure:[13] dipping of a wire into the varnish, pulling it out, and drying it in air with its apex pointing upward. This procedure was repeated a few times to improve the sealing between the gold surface and the varnish. The shape and size of the uncoated apex are determined by the viscosity and adhesiveness of the varnish and the gravity force. Because these parameters are not well controllable on a nanoscopic level, UMEs prepared in this way usually had an asymmetric shape, with an irregular borderline at the apex rim between the gold and the varnish coating. The success rate for obtaining a properly shaped UME was relatively low at this stage.

Usually, the UMEs thus prepared were not treated further, and the electrode surface has been assumed to be of a hemispherical or disklike shape in many applications.[1,8,9,14,15] This assumption, however, may lead to a possibility of erroneous analysis in UME measurements. For example, an irregularly shaped UME may lead to incorrect rate constants in electron-transfer kinetic measurements.[16,17] The faradaic current profile recorded as a function of the distance between the UME and the substrate depends on the geometry of the UME in SECM measurements.[16] The planar UME is assumed to face the substrate in SECM, and the irregular-shaped UME facing the substrate asymmetrically causes the current distribution to become uneven. Thus, UME tips require further refinements.

In the final step (Figure 1c), a UME prepared as described above was further etched to form a disk-shaped electrode by applying ultrashort voltage pulses. For this, a gold UME was immersed in an HCl solution of a very low concentration (typically 1 mM), and voltage pulses were applied to the UME to etch away the uncoated part of the gold apex little by little. The pulse duration was programmed to be very short (40 ns), so that one such pulse would provide only thin stripping of the gold surface and that the degree of etching could be fine-controlled by the number of applied pulses. Schuster et al.[18] have demonstrated that ultrashort (<100 ns) voltage pulses can be used for controlling the rate and the spatial resolution during electrochemical etching by locating the electrodes very closely to each other. In our present work, a nanosecond pulse etching is possible solely because of the ultrafast charging time of UMEs.[2] For a UME with a diameter of 100 nm, the double layer capacitance is estimated to be ~1.6 fF using a typical capacitance value of ~20 μF/cm^2 for the gold electrode in aqueous electrolytes. The uncompensated resistance, R_u, is estimated from the equation,[19]

$$R_u = \rho/4\pi r \qquad (2)$$

where ρ is the specific resistivity of the solution and r is the radius of the spherical electrode. With ~100 nm of diameter and a specific conductance of 0.0016 Ω^{-1} cm^{-1} for 1.2 mM HCl solution,[20] an R_u value of 9.9 MΩ is obtained. This gives a charging time constant of ~16 ns, resulting in mostly faradaic currents leading to effective etching of the surface during the pulse duration. Thus, most of the faradaic current flowing would be localized at the dendritic sites during the electrolysis when the electrode shape is hemispheric. As the pulse etching proceeds, however, the electrode becomes more of a disk shape and the uncompensated resistance becomes larger as can be seen from the equation,[19,21]

$$R_u = \rho/4r \qquad (3)$$

which gives a time constant of as long as 50 ns. At this point,

(9) Sun, P.; Zhang, Z.; Guo, J.; Shao, Y. *Anal. Chem.* **2001**, *73*, 5346.
(10) Bard, A. J. *Encyclopedia of Electrochemistry of the Elements*; Marcel Dekker: New York, 1975; Vol. 4, Chapter 3.
(11) Christoph, R.; Siegenthaler, H.; Rohrer, H.; Wiese, H. *Electrochim. Acta* **1989**, *34*, 1011.
(12) Ibe, J. P.; Bey, P. P., Jr.; Brandow, S. L.; Brizzolara, R. A.; Burnham, N. A.; DiLella, D. P.; Lee, K. P.; Marrian, C. R. K.; Colton, R. J. *J. Vac. Sci. Technol. A* **1990**, *8*, 3570.
(13) Gewirth, A. A.; Craston, D. H.; Bard, A. J. *J. Electroanal. Chem.* **1989**, *261*, 477−482.
(14) Slevin, C. J.; Gray, N. J.; Macpherson, J. V.; Webb, M. A.; Unwin, P. R. *Electrochem. Commun.* **1999**, *1*, 282.
(15) Chen, S.; Kucernak, A. *J. Phys. Chem.* **2002**, *106*, 9396.
(16) Shao, Y.; Mirkin, M. V.; Fish, G.; Kokotov, S.; Palanker, D.; Lewis, A. *Anal. Chem.* **1997**, *69*, 1627.
(17) (a) Oldham, K. B. *Anal. Chem.* **1992**, *64*, 646. (b) Baranski, A. S. *J. Electroanal. Chem.* **1991**, *307*, 287.
(18) Schuster, R.; Kirchner, V.; Allongue, P.; Ertl, G. *Science* **2000**, *289*, 98.
(19) Wightman, R. M.; Wipf, D. O. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1986; Vol. 15.
(20) Bockris, J. O. M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum: New York, 1977; Vol. 1, Chapter 4.
(21) Michael, A. C.; Wightman, R. M. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York; 1996; Chapter 12.

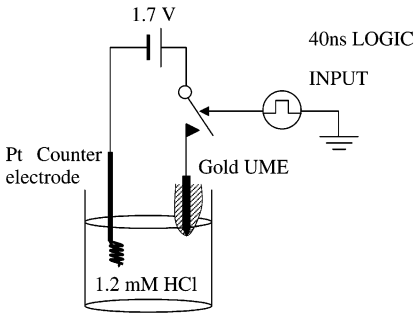

Figure 2. Schematic diagram of the ultrashort pulse etching setup. A 40-ns logic input drives a switch to apply a 1.7-V pulse between a gold UME and a Pt counter electrode immersed in 1.2 mM HCl.

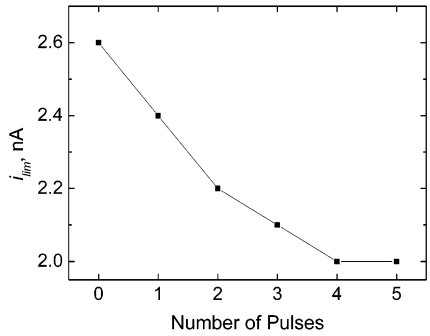

Figure 3. CV limiting currents (i_{lim}) plotted as a function of the increasing number of 40-ns, 1.7-V pulses applied in 1.2 mM HCl. The limiting current was obtained in a 0.10 M $K_4Fe(CN)_6$ with 1.0 M KCl as a supporting electrolyte. The scan rate was 50 mV/s.

most of the currents flowing would be used to charge a double layer capacitor and the electrode tip would not be etched effectively any more.

Figure 2 shows a schematic diagram of the pulse etching apparatus. A 40-ns logic input from a pulse generator (PG-1990, ED Engineering) switched on a 40-ns, 1.7-V pulse to the gold electrode. The time response of the switch (MAX4614, Maxim Integrated Products, Inc.) was 5 ns. After the pulse etching, the electrode was transferred to an electrochemical cell, in which the progress of the etching process was monitored by cyclic voltammetry (CV). The etching and electrochemical characterization cycle was repeated until a satisfactory electrode shape was attained.

Characterization of UMEs. Pulse etching of an uncoated apex of a gold tip reduces the apex size, which in turn decreases the uncoated surface area of the tip. The change in the gold surface area was monitored by cyclic voltammetry. Figure 3 presents the results of the cyclic voltammetric limiting currents (i_{lim}) recorded in a 0.10 M $K_4Fe(CN)_6$ solution with 1.0 M KCl as a supporting electrolyte. The limiting current gradually decreases from 2.6 to 2.0 nA as the number of etching pulses increases from zero to four, indicating that the area of uncoated gold apex decreases. The limiting current does not decrease noticeably after the fourth pulse and reaches a constant value. This implies that the sharp apex has changed to a nearly flat surface on which an additional etching pulse does not significantly alter the surface area, with the rim of the electrode being protected by the coated varnish from etching (see Figure 1c). The number of pulses needed to reach this constant limiting current depends on the initial size of the exposed apex and the pulse-etching condition. It also depends on how close the initial apex shape is to a hemisphere; the limiting current observed at the pulse-etched disk electrode would be ~64% of that obtained from the original hemispherical tip if the original tip before the pulse etching had the same radius as the disk. This is because the steady-state current at a UME has an expression,[19,21]

$$i_{\mathrm{lim}} = 2\pi nFDCr \tag{4}$$

for an ideally hemispherical electrode, whereas it is

$$i_{\mathrm{lim}} = 4nFDCr \tag{5}$$

for a disk electrode.[22] Here n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, and C is the bulk concentration of electroactive species. Thus, our result, in which the limiting current decreases from 2.8 to 2.0 nA, is in reasonably good agreement with theoretical prediction. One can estimate the amount of gold atoms removed from the limiting current data in Figure 3, if one assumes that the electrode apex maintains an approximately conical shape with its angle being progressively widened by the etching pulses. It is estimated that each pulse removes $\sim 2 \times 10^7$ atoms on the average during the initial four shots. For the experimental procedures described above, a flattened surface flush to the vertical axis of the wire was obtained by applying usually fewer than 10 pulses, and the limiting currents at times decreased to as much as about half of those observed at the sharp tips without pulse etching. This indicates that many tips reported in the literature, which had been prepared by only the first electrochemical etching step, had distorted hemispherical shapes.

Figure 4a shows a typical CV obtained at a UME formed by initial etching of a gold wire into a sharp tip and varnish coating, but without subsequent pulse etching. The curve exhibits a somewhat distorted sigmoidal shape. The hysteresis of the CV shown during forward and reverse sweeps, as well as the distorted sigmoidal shape, suggests that the shape of the exposed apex of the electrode deviates significantly from that of an ideal disk-shaped UME or the sealing between the varnish and the gold surface is poor.[3,16] Figure 4b shows a CV at a UME prepared by trimming its apex with four etching pulses to the point at which a limiting current plateau is observed as shown in Figure 3. The reversible sigmoidal curve indicates that the electrode has characteristics of well-behaved UMEs. UMEs prepared in this way exhibited improved characteristics in electrochemical measurements over the ones that were not treated with etching pulses.

The surface area of the UME was estimated from the i_{lim} values measured in CV experiments using eq 5 with a D value of 5.2×10^{-6} cm^2/s for 0.1 M $K_4Fe(CN)_6$ in 1.0 M KCl,[22] assuming a flat surface of the electrode. From the limiting current of 2.0 nA in Figure 4b, the effective radius of the gold UME is estimated to be 100 nm. UMEs prepared by the present method usually had an effective radius of 50−250 nm. UMEs of a smaller size could be made as well, if the initial size of the gold apex was made small by controlling parameters in steps 1 and 2. A UME with an

(22) Dayton, M. A.; Brown, J. C.; Stutts, K. J.; Wightman, R. M. *Anal. Chem.* **1980**, *52*, 946.

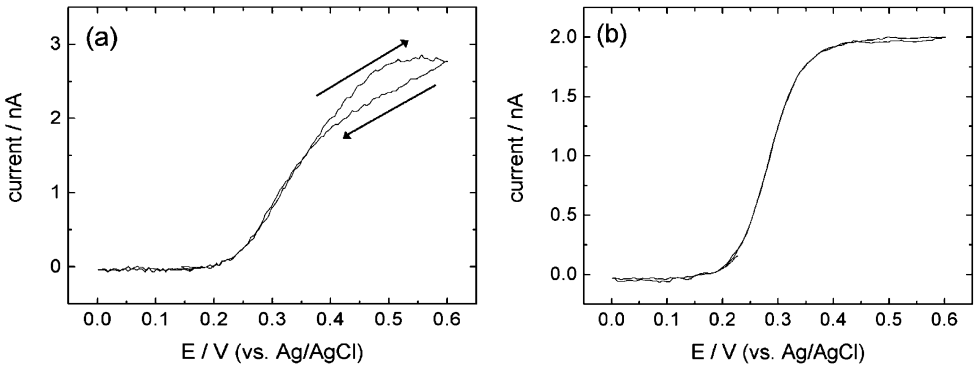

Figure 4. CVs for 0.10 M $K_4Fe(CN)_6$ at a gold UME in 1.0 M KCl as a supporting electrolyte: (a) before the pulse etching and (b) after the fifth pulse etching. The scan rate was 50 mV/s.

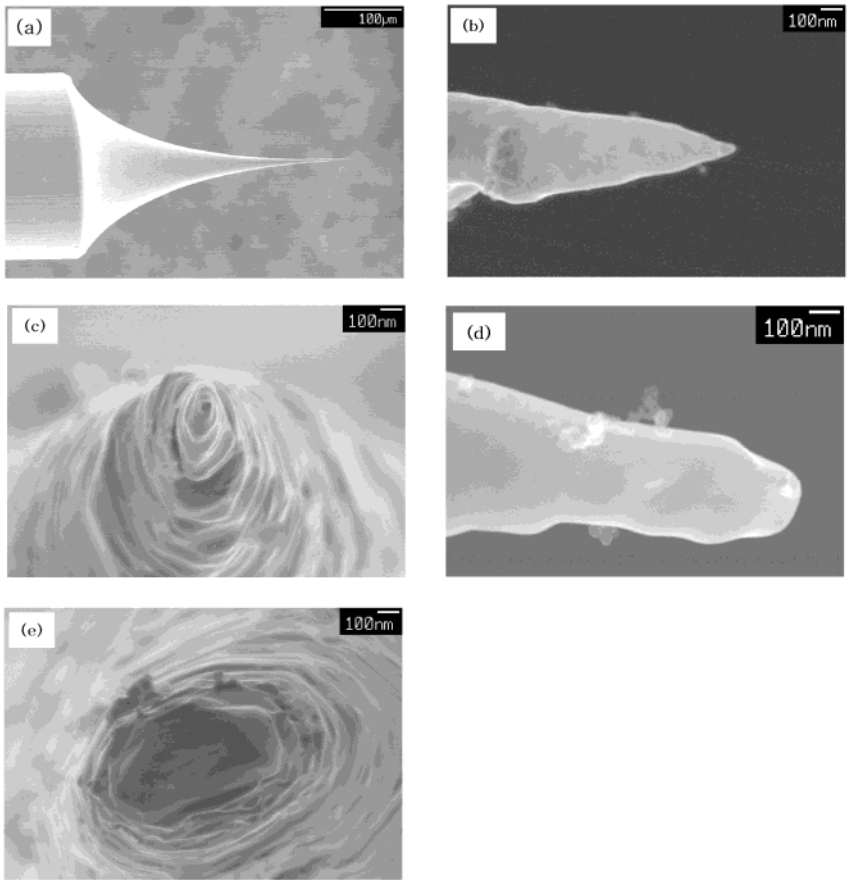

Figure 5. SEM images of (a) the whole shape of an electrochemically etched gold tip and (b) its apex in a side view and (c) in a top view. The radius of curvature at the apex is ~25 nm. The flattened apex of a gold UME after steps 2 and 3 is shown in (d) from the side and in (e) from the top. The images a−c are from the same tip, and (d) and (e) are from different tips.

effective radius of as small as 10 nm was constructed after pulse etching by this method.

We examined the shape of the UME by scanning electron microscopy (SEM). Figure 5a shows a low-magnification SEM image of an electrochemically etched gold tip prepared in step 1. The curved etched surface and the sharp apex are characteristic features obtained from dc electrochemical etching, much resembling the shape of a tungsten tip prepared by the dc-etching method.[12] Figure 5b magnifies the apex region of the etched gold tip in a side view, and Figure 5c shows the same tip in a top view, in which the apex is recognizable as a dark spot located near the center. The apex has a radius of curvature of ~25 nm in these figures. An etched wire like that shown in panels a−c was prepared into a UME through steps 2 and 3 and then characterized by recording CVs. To examine the shape of the UME with SEM, we stripped off the varnish coating by dissolving it in acetone. Figure 5d shows the SEM image of the electrode with the coating removed, and this is the one we used for obtaining the CV in Figure 4b. The apex of the UME has become flattened after the pulse etching, and the apex has a radius of ~100 nm, which agrees well with the radius estimated from its CV scan. Figure 5e shows a top view of another UME prepared through steps 2 and 3. It clearly shows a wide, flat terrace formed at the UME apex. The terrace boundary is elliptical rather than perfectly circular, which implies that the wire etching occurs somewhat asymmetrically under the usual conditions, a feature also visible in the dc-etched

wire shown in Figure 5c. These SEM images confirm the change of a conical apex to a disk-type electrode, which was suggested by the CV results.

It should be pointed out that the etching pulses did not always flatten an electrode surface. The gold apex could become either flattened or sometimes even sharper by the voltage pulses during an intermediate stage of etching, as we found by examining several etched apexes with SEM. However, when the CV limiting current reached a plateau, the conical apex of the original tip was trimmed most probably to a disk-type flat surface. Such a shaping process occurs apparently due to protection of the electrode rim from etching by the varnish coating. The preferential etching at the dendritic sites can also assist transformation of the sharp apex into a flat surface. When an electrode surface was overetched by application of more than necessary voltage pulses, the surface could also be made recessed. Sometimes the limiting current was observed to jump after a voltage pulse, which may have been caused by removal of a chunk of coated varnish at the verge of the electrode during the etching process. This effect was severe when low-viscosity varnish materials, which produced thinner coatings on gold wires, were used.

The CV and SEM results presented here suggest that the UMEs prepared only by the coating step without fine trimming may not have a well-defined apex, although the size determined by CV can be as small as a few nanometers.[1,8,9,14,15] The disk-shaped UMEs made after rough polishing are as large as several hundred nanometers depending on the size of the polishing materials.[23,24] In this case, the UMEs can also be contaminated by the polishing material. In this respect, the pulse etching method improves the reproducibility of UME fabrication, both in fine-shaping the electrodes and in attaining a desired electrode size.

(23) Lee, C.; Miller, J. C.; Bard, A. J. *Anal. Chem.* **1991**, *63*, 78.
(24) Tschuncky, P.; Heinze, J. *Anal. Chem.* **1995**, *67*, 4020.

SUMMARY AND CONCLUSION

It is demonstrated that ultrashort etching pulses can be used for trimming an etched gold apexes into planar UMEs. The steady-state voltammetry and SEM images reveal that the apex size decreases and its surface flattens out as the number of etching pulses increases. The UMEs prepared in this fashion exhibit the following characteristics in contrast to the UMEs fabricated with no trimming procedure or mechanical polishing: (i) a disklike shape with an effective radius of 50−250 nm, (ii) better reproducibility in fabricating UMEs of a desired size, and (iii) better electrochemical performance than conventional UMEs due to its well-defined shape. The principle underlying the pulse etching appears to be simple and quite general, and therefore, the method is considered to be extendible to fabrication of UMEs made of other materials.

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