

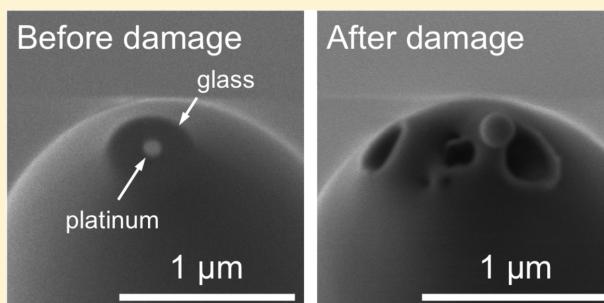
Origins of Nanoscale Damage to Glass-Sealed Platinum Electrodes with Submicrometer and Nanometer Size

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Supporting Information

ABSTRACT: Glass-sealed Pt electrodes with submicrometer and nanometer size have been successfully developed and applied for nanoscale electrochemical measurements such as scanning electrochemical microscopy (SECM). These small electrodes, however, are difficult to work with because they often lose a current response or give a low SECM feedback in current-distance curves. Here we report that these problems can be due to the nanometer-scale damage that is readily and unknowingly made to the small tips in air by electrostatic discharge or in electrolyte solution by electrochemical etching. The damaged Pt electrodes are recessed and contaminated with removed electrode materials to lower their current responses. The recession and contamination of damaged Pt electrodes are demonstrated by scanning electron microscopy and X-ray energy dispersive spectroscopy. The recessed geometry is noticeable also by SECM but is not obvious from a cyclic voltammogram. Characterization of a damaged Pt electrode with recessed geometry only by cyclic voltammetry may underestimate electrode size from a lower limiting current owing to an invalid assumption of inlaid disk geometry. Significantly, electrostatic damage can be avoided by grounding a Pt electrode and nearby objects, most importantly, an operator as a source of electrostatic charge. Electrochemical damage can be avoided by maintaining potentiostatic control of a Pt electrode without internally disconnecting the electrode from a potentiostat between voltammetric measurements. Damage-free Pt electrodes with submicrometer and nanometer sizes are pivotal for reliable and quantitative nanoelectrochemical measurements.



Recently, significant progress has been made for miniaturization of glass-sealed Pt ultramicroelectrodes (UMEs) to submicrometer and nanometer size.^{1–4} These small Pt UMEs offer extremely high spatial and temporal resolutions for electrochemical measurement such as scanning electrochemical microscopy (SECM).^{5,6} Submicrometer- or nanometer-size Pt UMEs can be successfully prepared by heat-pulling a glass-sealed Pt microwire⁷ or by heat-sealing a sharply etched Pt wire into a glass capillary.⁸ The tip end of the Pt–glass composite is mechanically polished to expose the Pt disk surrounded by a relatively thick glass sheath^{9–14} ($3 < RG < 10$, where RG is the ratio of the radius of the glass sheath, r_g , with respect to the electrode radius, a). The heat-pulling/mechanical-polishing approach has been successful also for fabrication of Au¹⁵ and Ag¹⁶ nanodisk electrodes. Moreover, molecularly small Pt UMEs with $a = 1\text{--}3\text{ nm}$ can be obtained by heat-pulling the Pt microwire sealed in a thick-wall glass tube with $RG \gg 10$.¹⁷ On the other hand, a disk UME with $RG < 3$ is often desirable for SECM because such a sharp tip can be positioned closer to a substrate.^{18–21} For this purpose, the tapered end of a glass-sealed Pt UME with $RG > 3$ is heated to melt glass and pull it away from the Pt tip.⁸ The exposed Pt tip is polished mechanically^{8,22} or milled by using focused ion-beam (FIB) technology^{23,24} to obtain a submicrometer-size Pt UME with $RG < 3$.

In this work, we report for the first time that glass-sealed Pt UMEs with submicrometer and nanometer sizes can be readily and unknowingly damaged at the nanoscale to significantly lower their current responses. Such a small UME can be damaged in air by electrostatic discharge (ESD) to recess the Pt tip and, subsequently, contaminate it with removed Pt and glass. In addition, submicrometer- and nanometer-size Pt UMEs can be electrochemically etched in electrolyte solution and contaminated with the Pt nanoparticles removed from the tip at the beginning or end of voltammetric/amperometric measurement when connection of the UMEs to a potentiostat is internally switched on or off, respectively. Recession and contamination owing to electrostatic and electrochemical damage can be a reason why nanoelectrodes often lose a current response¹⁹ or give a low SECM feedback in current-distance curves (i.e., approach curves).²⁵ In fact, a recent atomic force microscopy study showed recession of glass-sealed Pt nanoelectrodes and contamination of both Pt and glass surfaces with nanoparticles.²⁵ An origin of recession or contamination of the nanoelectrodes, however, was not identified.

Received: May 1, 2013

Accepted: June 8, 2013

Published: June 8, 2013



Importantly, nanometer-scale damage to a glass-sealed Pt UME in air can be avoided by employing appropriate ESD protections (Supporting Information), thereby confirming that ESD causes electrode damage. The ESD protections are based on grounding of both a UME and any object that contacts with or exists near the UME. Subsequently, no ESD occurs between the UME and the isopotential object. In our laboratory environments, ESD damage to a Pt UME is seen by scanning electron microscopy (SEM) when an operator does not wear the wrist strap, gloves, and lab coat that are conductive and grounded. Without any ESD protection, a human body accumulates a high electrostatic charging voltage of 10–20 kV.²⁶ Overall, injection of electrostatic charge from an operator into a UME is followed by ESD from the sharp Pt tip to a nearby object, which damages the tip.

We used borosilicate-sealed Pt UMEs with submicrometer size (Figure 1A) to resolve ESD damage on the Pt and glass

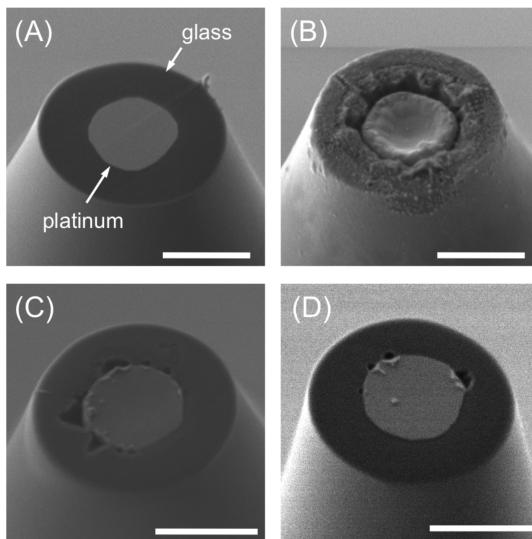


Figure 1. SEM images of a borosilicate-sealed Pt UME (A) before and (B) after ESD damage. Parts C and D show moderately and weakly damaged Pt UMEs, respectively. Scale bars are 1 μm .

surfaces by SEM. These UMEs with a small RG of ~ 2 were fabricated as SECM tips by heat-pulling, heat-annealing, and FIB milling as described above (see also the Supporting Information). We found that ESD damage was made to the Pt UMEs sealed in borosilicate,²⁴ Pb-doped,²³ and aluminosilicate glasses. The damage was less severe with borosilicate glass probably because of its higher conductivity. Noticeably, borosilicate glass has been most widely used to fabricate submicrometer- and nanometer-size Pt UMEs.^{7–9,11,13,15,16,22,24} Quartz-sealed Pt UMEs^{10,13,14} are beyond the scope of this study and were not tested because quartz cannot be heat annealed using a microforge^{23,24} (MF-900, Narishige, Tokyo, Japan) to reduce RG for SECM applications.

ESD damage to a glass-sealed Pt UME cannot be completely avoided without the ESD protections although the damage depends on laboratory environmental conditions and operators. Severe damage was made to the tip end (Figure 1B) when the contact wire of a submicrometer-size Pt UME with well-defined geometry (Figure 1A) was touched by the bare hand of an operator without the ESD protections. The operator does not see, hear, or even feel the ESD, which caused the severe tip damage. The ESD-damaged Pt tip was recessed and its

periphery was deformed. Moreover, the surrounding glass sheath was fractured and deformed. Deformation of glass near the Pt tip suggests that ESD melted glass. The severely damaged boundary between Pt and glass was seen as a dark ring by optical microscopy using a 50 \times objective lens. Less severe damage (Figure 1C) was made during summer because of higher humidity or by an operator with less electrostatic charging voltage, which varies with the type of clothing, shoes, etc.²⁶ The weak damage (Figure 1D) was caused by handling the tip using ESD-protected tweezers without the other ESD protections. The localization of weak damage at glass near the Pt tip suggests that ESD occurs most extensively at the Pt/glass boundary. Severe damage also results from accumulation of moderate or weak ESD damage by repetitive contact with an ESD-unprotected operator.

The severely ESD-damaged UME (Figure 1B) gave a poor SECM approach curve with a low feedback response at a Au substrate (Figure 2) as expected for a recessed UME.^{25,27} The

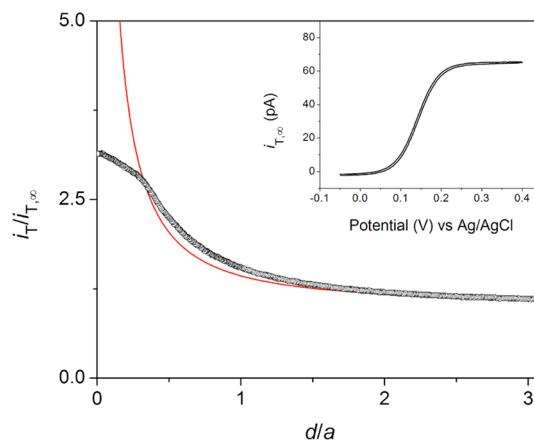


Figure 2. SECM approach curve (circles) at an unbiased Au substrate as obtained using the severely ESD-damaged Pt UME (its SEM image is shown in Figure 1B) with FcMeOH as a redox mediator. The tip potential was 0.35 V against a Ag/AgCl reference electrode. Tip scan rate, 19 nm/s. The red line represents a theoretical positive-feedback curve for an inlaid disk tip with RG = 2.5. The inset shows the CV of 0.5 mM FcMeOH at the damaged UME in 0.1 M KCl. Potential sweep rate, 20 mV/s.

tip current, i_T , based on diffusion-limited oxidation of ferrocenemethanol (FcMeOH) increased only up to ~ 2.5 times of the limiting current in the bulk solution, $i_{T,\infty}$, before the glass sheath of the Pt tip contacted the Au substrate. The contact is indicated by the inflection point of the approach curve. The normalized experimental curve is too broad to fit with the theoretical curve based on diffusion-limited positive feedback at an inlaid disk tip²⁸ (Figure 2). Such a broad approach curve with small positive feedback effect is expected for a recessed UME.²⁷ Noticeably, recession of the damaged tip is not obvious from its excellent steady-state cyclic voltammogram (CV, the inset of Figure 2). Without SEM or SECM characterization, inlaid disk geometry may be assumed to unknowingly underestimate the radius of the damaged electrode from its $i_{T,\infty}$ using the following equation

$$i_{T,\infty} = 4xnFD_w c^* a \quad (1)$$

where x is a function of RG,^{29,30} n is the number of transferred electrons (= 1) in the tip reaction, and D_w ($= 7.8 \times 10^{-6} \text{ cm}^2/\text{s}$)¹¹ and c^* ($= 0.5 \text{ mM}$) are the diffusion coefficient and

concentration of FcMeOH in 0.1 M KCl, respectively. A limiting current at a recessed UME is lower than expected from eq 1 because of the extra diffusion path from the orifice to the recessed surface.³¹ In fact, eq 1 with an $i_{T,\infty}$ value of 64 pA at the damaged UME with RG = 2.5 (i.e., $x = 1.08$) gives a tip radius of 0.39 μm , which is smaller than an approximate radius of 0.47 μm as estimated from the SEM image of this UME before ESD damage (Figure 1A). The underestimated tip radius also contributes to broadening of the experimental approach curve in the normalized form (Figure 2).

Electrostatic damage is not due to the fragility of Pt UMEs after heat-annealing or FIB-milling. Severe ESD damage was also observed with a submicrometer-size Pt UME with a thicker glass sheath (RG ~5 in Figure S-2A, B in the Supporting Information before and after ESD damage, respectively), which was FIB-milled without heat annealing. This result confirms that ESD damage is not due to a thin glass sheath or the fragility of Pt and glass stressed by heat annealing. Moreover, ESD damage was made to a Pt UME without heat annealing or FIB milling (Figure S-2C, D in the Supporting Information before and after ESD damage, respectively). Upon ESD damage, the protrusion of the tapered Pt tip from the glass sheath was completely lost, which resulted in deep recession of the tip. Therefore, ESD damage is not caused by FIB milling although an FIB-milled surface may be more fragile owing to implantation of Ga⁺ from the ion beam.³² Noticeably, a Pt UME was grounded to the sample stage of the FIB instrument to avoid the charging and ESD damage of the tip during milling.

More severe ESD damage was seen with a Pt nanoelectrode (Figure 3A, B before and after ESD damage, respectively). The ~110 nm-diameter Pt UME was prepared by sealing a Pt microwire into a thicker-wall glass tube (RG ~10) to avoid protrusion of an as-pulled Pt tip from the surrounding glass (see above). Then, the small Pt tip was exposed from the glass

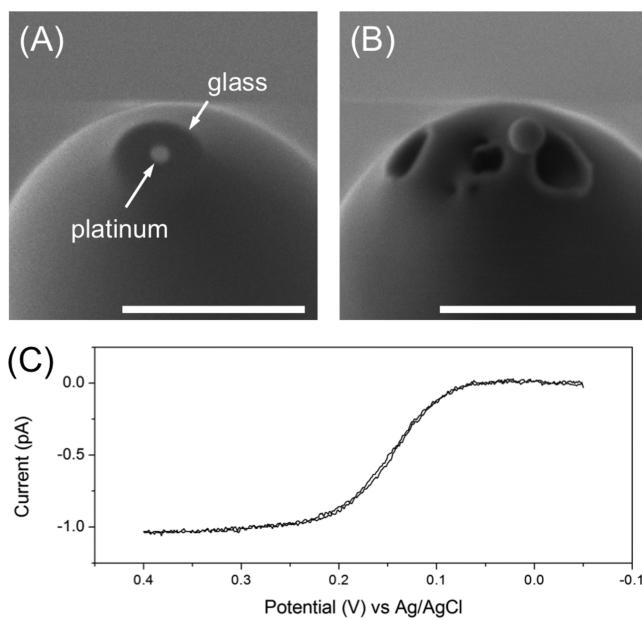


Figure 3. SEM images of a ~110 nm-diameter Pt nanoelectrode (A) before and (B) after ESD damage. Scale bars are 1 μm . (C) Background-subtracted CV of 0.5 mM FcMeOH in 0.1 M KCl as obtained using the ESD-damaged Pt nanoelectrode. Potential sweep rate, 5 mV/s.

sheath by heat-annealing and was FIB-milled (Figure 3A). The ESD-damaged Pt nanotip was completely buried into the glass sheath (Figure 3B). The damaged nanoelectrode gave a $i_{T,\infty}$ value of only 1.0 pA for 0.5 mM FcMeOH in 0.1 M KCl (Figure 3C). When inlaid disk geometry is assumed, eq 1 with this current value gives a tip radius of 6.1 nm, which is ~9 times smaller than the radius of the Pt tip before ESD damage (Figure 3A). This result indicates that the size of a Pt nanoelectrode can be significantly underestimated from its limiting current when the electrode is unknowingly recessed owing to ESD damage.

Finally, we report on the electrochemical damage made to a glass-sealed Pt UME. Specifically, a submicrometer-size Pt tip was etched and recessed during repetitive measurement of the CVs of FcMeOH in 0.1 M KCl at a tip potential between -0.05 and 0.4 V. Such damage was unexpected because even a Pt nanoelectrode is electrochemically stable in this potential range for FcMeOH oxidation.³³ Nevertheless, the SEM image of the Pt UME after measurement of the 38 CVs of FcMeOH (Figure 4A) shows ~250 nm-depth recession of the Pt tip with

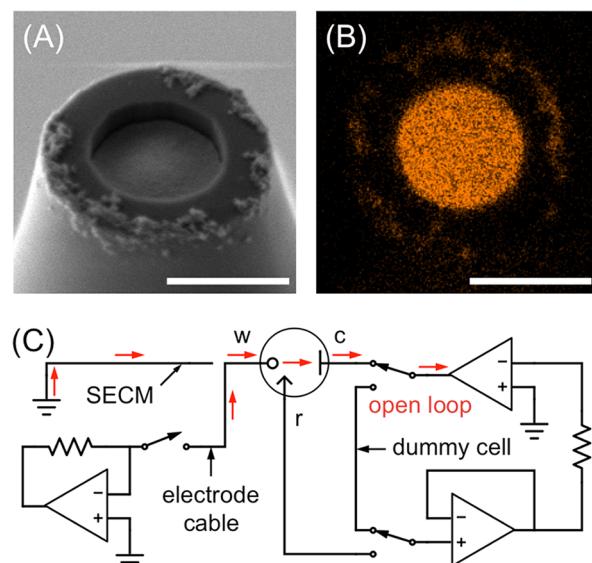


Figure 4. (A) SEM and (B) X-ray EDS images of a Pt UME after measurement of the 38 CVs of 0.5 mM FcMeOH in 0.1 M KCl. Scale bars are 1 μm . In the EDS image, orange dots indicate the presence of Pt. (C) Flow of transient current from a Pt tip to a saturated counter-electrode amplifier under an open-loop configuration at the beginning or end of CV measurement. Red arrows indicate current flow while w, r, and c represent working, reference, and counter electrodes. The tip is attached to the SECM stage using an aluminum holder.

adsorbates on the surface of the glass sheath. X-ray energy dispersive spectroscopy (EDS) of the damaged tip confirmed that the adsorbates are the platinum nanoparticles etched away from the Pt tip (Figure 4B). The spatial resolution of X-ray EDS is high enough to resolve the Pt adsorbates on the glass surface from the central Pt region (see Supporting Information). These adsorbates are located near the Pt/glass boundary after measurement of less CVs. The nanometer-deep recession is not due to ESD because this UME was always handled with the ESD protections. Moreover, the features of ESD damage (Figure 1B–D) contrast to those of electrochemical damage, which shows uniform recession of the whole

Pt surface and no fracture of the glass sheath at the boundary (Figure 4A).

A Pt UME is damaged transiently at the beginning (or end) of each CV measurement when the potentiostat is switched from an internal dummy cell to the electrochemical cell (or vice versa). In fact, electrochemical damage to a Pt UME was dramatically suppressed by maintaining internal connection of the potentiostat to the electrochemical cell between CV measurements. This can be achieved by activating the “cell on between runs” function of the potentiostat (see Supporting Information for details). In contrast, the Pt UME as shown in Figure 4A, B was electrochemically etched only when this function was inactive for measurement of 29 CVs (see also Supporting Information). The resultant electrochemical damage may not be noticeable by SEM after a few potential cycles. An etching depth of ~9 nm per potential cycle is estimated from an etching depth of ~250 nm after 29 CVs.

The electrochemical etching of a Pt UME is due to the transient tip current driven by the saturation of a counter-electrode amplifier upon the switching of the potentiostat from the internal dummy cell to the electrochemical cell (or vice versa). This transition is initiated by turning on relay switches for counter and reference electrodes before the working-electrode switch is turned on (Figure 4C). Since electro-mechanical relays bounce and do not settle down immediately, the counter-electrode amplifier transiently experiences an open-loop configuration to be saturated. The resultant large output voltage of the saturated amplifier transiently drives high current from the Pt tip through the electrolyte solution, thereby electrochemically etching the tip. Even when the working-electrode switch is turned off, the transient current passes through the Pt tip, where electrons are removed during etching to be capacitively stored in the working-electrode cable.^{34,35} Without this cable, a Pt tip was slightly damaged because of its capacitive coupling with the SECM stage. The existence of these capacitive current paths is discussed in Supporting Information.

Noticeably, electrochemical damage is unlikely the unique problem of the potentiostat used in this work because the transient open-loop configuration is intrinsic to any potentiostat for a three-electrode cell. This problem may be readily avoided for a two-electrode cell by internally shorting the noninverting input of the reference electrode amplifier to the output of the counter-electrode amplifier in Figure 4C. SECM, however, often requires an electrochemical cell with more than two electrodes including a macroscopic substrate electrode.²³

CONCLUSIONS

In this work, we reported on the electrostatic and electrochemical origins of nanometer-scale damage to glass-sealed Pt UMEs with submicrometer and nanometer size. Both types of damage are severe with the small UMEs, which are readily charged up by a small number of electrons without potentiostatic control. Importantly, ESD damage to a UME in air can be avoided by protecting the UME from sources of electrostatic charge, most importantly, an operator. The body and cloth of the operator must be grounded by using ESD-safe wrist strap, gloves, and lab coat. Electrochemical damage is likely due to the flow of a transient current driven by a saturated amplifier and can be avoided by maintaining the UME under potentiostatic control in solution. This control can be lost transiently when connection of a potentiostat to the UME is internally switched on or off. Noticeably, the approaches that

were proposed in this study to avoid ESD and electrochemical damage were validated for tip size of >100 nm. More ESD protections or a better potentiostat design may be needed for protecting a smaller Pt UME from damage.

The new concept of nanoscale electrode damage proposed in this work is general and must be considered broadly for reliable nanoelectrochemical measurements and applications. Both electrostatic and electrochemical damage is possible with any submicrometer- or nanometer-size metal UME including an insulated metal tip for scanning tunneling microscopy.³⁶ Moreover, “nano ESD” is a global concern in nanoelectronics³⁶ including the batteries and sensors based on nanostructured electrodes. SECM is useful for detection of a damaged UME with recessed geometry, which gives a low positive feedback while a negative feedback is not sensitive to tip recession.²⁷ Recession and contamination of a damaged UME are not obvious from its well-defined steady-state CV with a lower limiting current, thereby unknowingly underestimating electrode size. In contrast to these metal UMEs, the SECM nanotip based on a nanopipet-supported liquid/liquid interface is apparently free from electrostatic and electrochemical damage.^{37,38} Alternatively, the soft liquid/liquid interface formed at the nanopipet tip may be spontaneously renewable upon damage.

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.

ACKNOWLEDGMENTS

This work was supported by the National Institutes of Health (Grant GM073439) and the National Science Foundation (Grant CHE-1213452). We thank Drs. Melisa Yashinski and Trevor Clark, Materials Characterization Lab, Penn State University, for acquiring X-ray EDS, and Dr. Peixin He, CH Instruments, for helpful discussions. The Petersen Institute of NanoScience and Engineering at the University of Pittsburgh is acknowledged for technical support for FIB milling.

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