Electrochemistry Communications 11 (2009) 1554

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Corrigendum

Corrigendum to "A gas-diffusion gold-ring tip: Fabrication, characterization, and application in electrocatalysis" [EChem. Comm. 11 (2009) 885–888]

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I wish to add co-authors Jose L. Fernandez and Cynthia G. Zoski who contributed to this research and whose names were omitted by accident. I also wish to make it clear that this work was performed by Grants to New Mexico State University from the National Science Foundation (CHE-0540843, EPS-0447691/NMSU-costshare; ADVANCE).

I regret any inconvenience this oversight has caused the scientific community. Sincerely, H. Liu.

Acknowledgment

The support by the National Science Foundation (CHE-0540843, EPS-0447691/NMSU-costshare; ADVANCE) is gratefully acknowledged.

DOI of original article: 10.1016/j.elecom.2009.02.018
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1388-2481/$ - see front matter
doi:10.1016/j.elecom.2009.04.024

Electrochemistry Communications 11 (2009) 885–888

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

A gas-diffusion gold-ring-tip: Fabrication, characterization, and application in electrocatalysis

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ARTICLE INFO

Article history:
Received 21 December 2008
Received in revised form 8 February 2009
Accepted 11 February 2009
Available online 20 February 2009

Keywords:
Scanning electrochemical microscopy
Micropipette electrode
Ring-tip
Gas dispenser
Electrocatalysis

ABSTRACT

A gas-diffusion gold-ring microelectrode used as scanning electrochemical microscopy tip was fabricated. Compared to the ring-tip for droplet dispensation reported before, the as-fabricated micropipette tip has a larger ring size (ca. 25 μm diameter) that is beneficial to gas dispensation and is more sensitive to electroactive species. This micropipette electrode functioned as both a normal SECM tip and a gas dispenser was demonstrated by imaging $FcMeOH^+$/FcMeOH reaction and electrocatalytic oxygen reduction reaction, respectively.

1. Introduction

Scanning electrochemical microscopy (SECM) is highly efficient in probing electron, ion, and molecule transfers, and other reactions at solid–liquid, liquid–liquid, and liquid–gas interfaces. This allows for the investigation of a wide variety of processes, from metal corrosion to the flux of ions through membrane pores and the activity of living biological cells [1–8]. In most cases, SECM uses an ultramicroelectrode (UME) tip that offers important advantages for electroanalytical applications including greatly diminished ohmic potential drop in solution and double-layer charging current, and the ability to reach a steady-state in seconds or milliseconds.

Micro-disk electrodes were served as the most frequently employed SECM tips because of their relatively facile fabrication methods and stably electrochemical responses. Also, quantitative measurements (e.g., kinetic data) through well-developed and rigorous electrochemical theories were easily available for disk-shaped tips [9–12]. However, for some specific applications, many non-disk UMEs [13,14] employed as SECM probe tips were fabricated and investigated, and the basic theories relevant to conical [15–18], micro-band [2,19,20], hemispherical or sphere-capped [21–23], and ring-shaped [24–26] SECM tips were deduced from disk-shape tip theories with technically approximate treatments. Therein, ring-shaped UMEs used as SECM probes were of special interest in connection with optical fiber probes [27,28] and near-field scanning optical microscopy experiments [24,25]. In fact, the micropipette ring-shaped electrodes provide attractive advantages that they can serve as not only the sensitive probes for electrochemical reactions but also the dispensers to deliver electroactive substances to substrates during the reaction process.

In this communication, we described a gas-diffusion SECM tip fabricated originally from the glass capillary. The gas-diffusion tip is generally produced via a procedure roughly including pulling micropipette, coating conductive layer, insulting surface, and exposing conductive ring-tip. Compared to the ring-tip for droplet dispensation reported before, the as-fabricated micropipette tip has a larger ring size (ca. 25 μm outer diameter) that is more difficult to achieve but more beneficial to dispense gases and will be more sensitive to electroactive species. The as-fabricated micropipette ring-tip was characterized by optical and electrochemical methods, and it functioned as both a SECM tip and a gas dispenser was demonstrated in the SECM imaging and oxygen reduction reaction (ORR) electrocatalytic applications.

2. Experimental

2.1. Fabrication of micropipette gold-ring electrode

The gas-diffusion micropipette tip is fabricated via a series of consecutive processes shown in Scheme 1. All aqueous solutions were prepared with Milli-Q water (18 MΩ cm) and all chemicals used were analytical grade. An eligible micropipette tip should be finally exposed a gold-ring with 13–16 μm ID and 24–30 μm OD.

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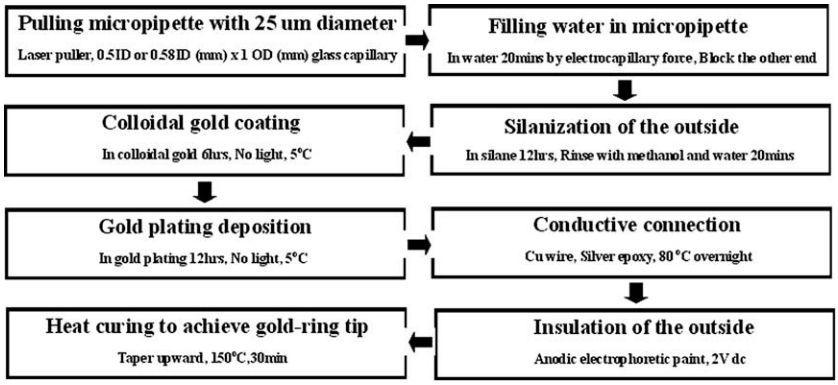
doi:10.1016/j.elecom.2009.02.018



Scheme 1. Fabrication procedure of the gas-diffusion micropipette ring-tip.

2.2. Electrochemical and SECM measurements

The electrochemical and SECM measurements were performed on a CHI900B model (CH Instrument, USA). A traditional three-electrode system was applied. The prepared micropipette tip and a platinum wire were served as the working electrode and the counter electrode, respectively. A Ag/AgCl electrode was used as the reference electrode. Additionally, a 125 μm diameter Pt disk substrate was employed as the second working electrode during the SECM measurements.

3. Results and discussion

As the micropipette was firstly formed from pulling a glass capillary, optical observation under the microscope (Olympus, Japan) was carried out to confirm that there were no cracks at the surface and the taper ring has right size. After completing the two-step gold coat, both the outside and the taper end surfaces should be checked under the microscope to ensure that they were nicely gold-coated (as shown in Fig.1a and b). An incompact gold layer was easily to peel off in the later use. In order to attain a ring-shaped gold tip, the insulated taper had to be heated upwardly to re-expose gold-ring at the very end. Shown in Fig. 1c and d are the images of the eligible gold-ring SECM tip (15 μm ID and 25 μm OD) after the insulating and heating treatments. It could be seen that the outside of the gold layer was coated entirely with the insulating layer but the gold-ring at the taper end surface was fully exposed.

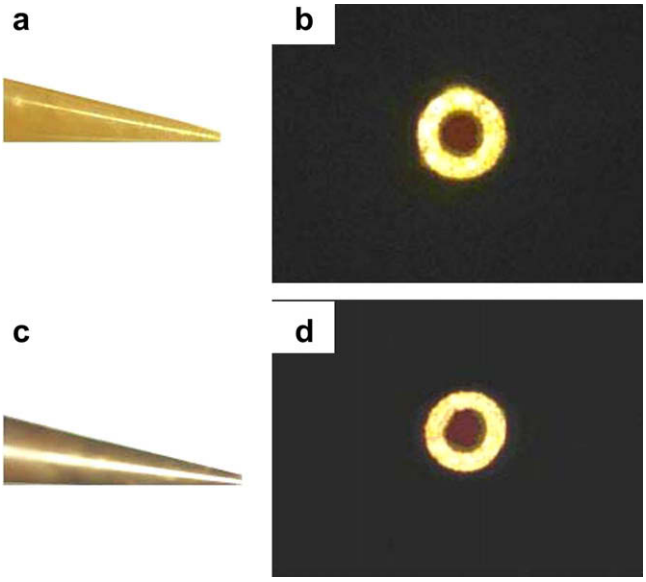


Fig. 1. Optical images of an eligible micropipette electrode (15 μm ID and 25 μm OD) with nice gold coating on both outside wall (a) and tip end surface (b). After insulating coat and heat curing treatments, the wall was entirely insulated (c) but gold-ring at tip end was exposed (d).

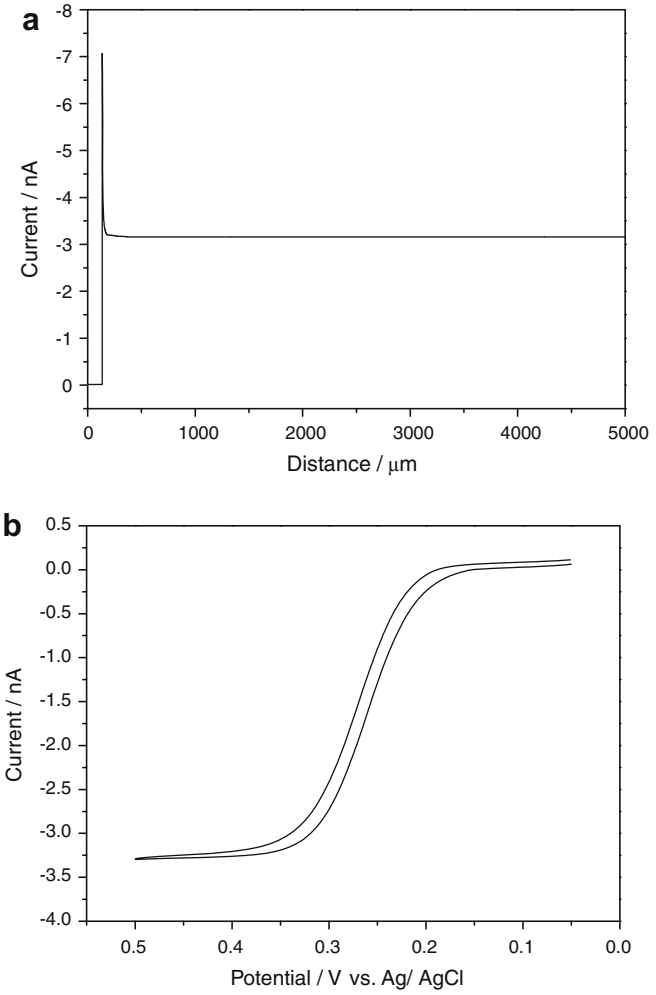


Fig. 2. Electrochemical characterization of the micropipette tip: (a) Approach curve from air to 1 mM FcMeOH and 0.1 M KCl solution with tip potential 0.4 V vs. Ag/AgCl; (b) Steady-state voltammogram in 1 mM FcMeOH and 0.1 M KCl solution with scan rate 50 mV/s.

For obtaining the more detailed information about the as-fabricated micropipette tip, the optically checked gold-ring micropipette electrode was further characterized by electrochemical means. Shown in Fig. 2a is the approach curve. As the gold-ring tip approached from air, zero current flowed at the tip. Once the tip touched the solution, a current was arisen rapidly since the ferrocenemethanol (FcMeOH) was oxidized around the exposed gold-ring. As the tip was immersed into the solution, the current maintained constant, indicating an insulating layer had entirely coated on the micropipette wall. Once it had been confirmed that a well-insulated micropipette probe had been constructed, steady-state voltammetry was performed to estimate the dimension of the exposed gold-ring. A steady-state voltammogram of the micropipette ring-tip in 1 mM FcMeOH and 0.1 M KCl solution (deoxygenated) is shown in Fig. 2b. An approach for estimating the dimensions of ring microelectrodes from steady-state cyclic voltammetry data was reported by Lee [24], in which the ratio of the steady-state currents obtained at disk electrodes to those obtained at ring electrodes with similar radii was calculated for a range of dimensions. Using this approach, we calculate the outer radii for the ring electrode 12.4 μm, and this value agrees closely with that observed using optical microscope (outer radii: 12.5 μm).

Based on the optical observation and electrochemical measurements, the eligibility of the fabricated micropipette ring-tip has been fully confirmed. In order to demonstrate the applicability of the micropipette tip as a SECM probe, a recording tip current SECM imaging experiment was curried out. As shown in Fig. 3a, the electroactive FcMeOH species (R) was oxidized at the Pt disk at a potential of 0.40 V (vs. Ag/AgCl), and the corresponding oxidized-state product $FcMeOH^+$ (O) diffused to the tip and was reduced back to FcMeOH at 0.0 V (vs. Ag/AgCl). Fig. 3b shows the SECM image of this reduction by recording the micropipette ring probe current using SG/TC mode. It can be seen that this SECM image from the ring-tip is not special compared to those classic images from disk tips, even at the relatively high scan rate used here. This result reveals that the fabricated micropipette gold-ring tip can be severed as a normal SECM probe.

In fact, this micropipette gold-ring electrode could function not only as an eligible SECM tip, but also as a gas dispenser that filled with electroactive gases which diffuse to the substrate electrode and occur an electrocatalytic reaction there (as illustrated in Fig. 4a). The micropipette gold-ring tip acted as an oxygen gas dispenser could be demonstrated via the SECM imaging electrocatalysis of ORR at a Pt substrate electrode (Fig. 4b). In order to achieve a definite SECM image for this gas-diffusion controlled ORR reaction at the Pt substrate, the pressure of the oxygen gases dispensed in the micropipette was maintained ~20 psi, and the gap between the tip and the substrate was ~2.5 μm. Actually, the imaging scan rate used here is relatively low considering the slower gas-diffusion in the aqueous solution. However, this will be beneficial to accumulation of the dissolved oxygen species near the substrate and generating a larger catalytic current. It should be noted that there is possibility of increasing the scan rate by adjustment of the oxygen pressure and the dispenser-substrate gap. The experiments to address the issues of gas pressure, species concentration, tip-substrate gap, substrate material, and image rate for high-efficient electrocatalytic applications are undergoing.

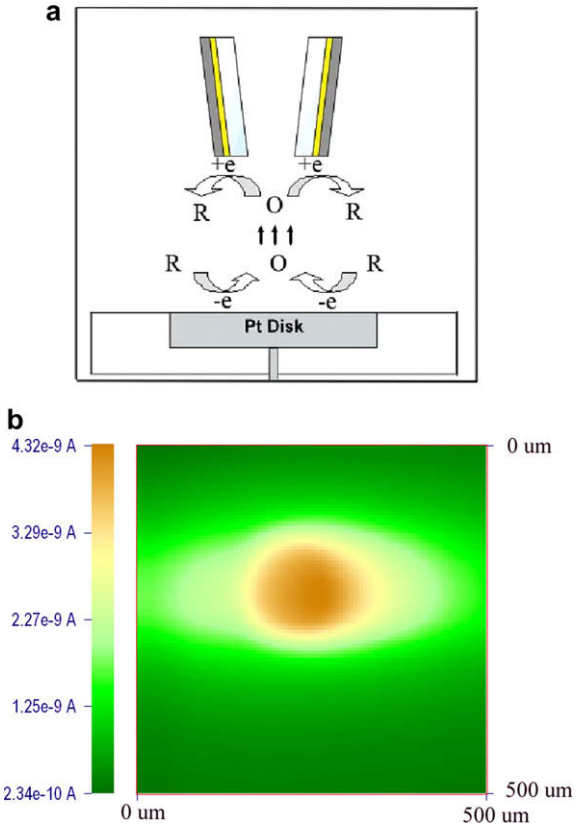


Fig. 3. The micropipette tip as a SECM probe: (a) Cartoons of redox reactions between tip and substrate electrodes; (b) SECM image of $FcMeOH^+$/FcMeOH redox by recording tip current using SG/TC mode. The electroactive mediator solution was 1 mM FcMeOH and 0.1 M KCl, and the tip-substrate separation was 3.75 μm. (Tip potential: 0 V vs. Ag/AgCl, Pt substrate potential: 0.4 V vs. Ag/AgCl, imaging scan rate: 5 μm/0.01667 s, *X* as long travel direction).

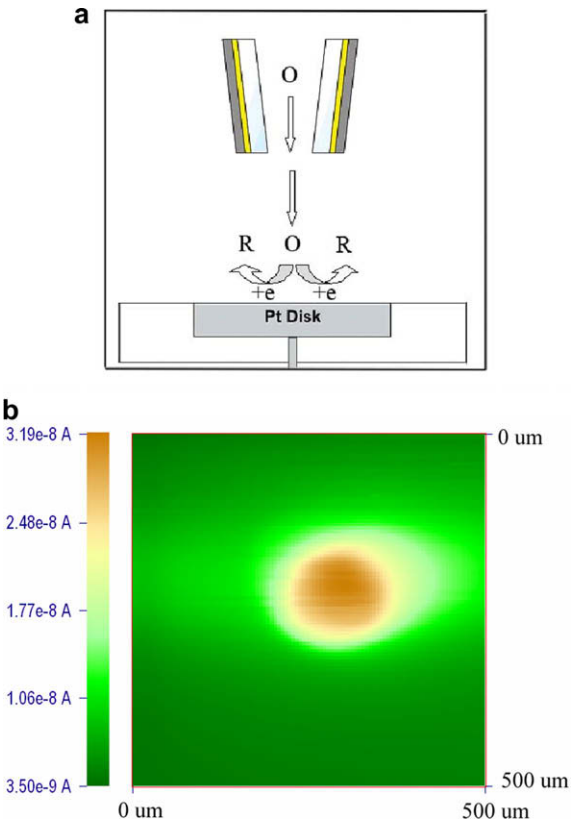


Fig. 4. The micropipette tip as a gas dispenser: (a) cartoons of reactions for the dispensed gas to the other electrode; (b) SECM image of ORR in 0.5 M H_2SO_4 solution by dispensing oxygen through the micropipette ring-tip and diffused to the 125 μm Pt substrate. (Reduction potential: 0.05 V vs. Ag/AgCl, imaging scan rate: 1 μm/0.01667 s, *X* as long travel direction).

4. Conclusions

A gas-diffusion micropipette SECM tip with large ring size was fabricated. Compared to the ring-tip for droplet dispensation reported before, it is more difficult to achieve but more beneficial to gas dispensation and will be more sensitive to electroactive species. This microelectrode could be functioned as both a SECM tip and a gas dispenser. Further optimizing work is addressing to realize high-efficient electrocatalytic applications.

Acknowledgements

The support by National Science Foundation (CHE-0210315) is gratefully acknowledged. I thank Dr. Zoski G.C. very much for the most useful suggestion during experiments and Dr. Jose L. Fernandez for help with adjustment of the used puller.

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