Fabrication of nanoporous gold microelectrode via electrochemical alloying-dealloying

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Nanostructured microelectrodes with high surface areas have recently received much attention due to their excellent electrochemical properties such as fast mass transfer, low Ohmic resistance, low residual currents and high signal-to-noise ratio. Gold is one of the most frequently used materials for microelectrode fabrications and biosensor support because of its chemical resistance to most reagents, high electron transfer rate in heterogeneous reactions, unique catalytic activity and wider potential window compared to Pt. However, the fabrication of nanostructured Au microelectrodes is challenging. Electrochemical alloying/dealloying has demonstrated it as a promising technique for the preparation of free-standing nanoporous Au films from commercially available Au thin films.[1,2] During the electrochemical alloying, highly reactive component Zn is electrodeposited onto the Au film and alloys with Au to form AuZn alloy phase. During the electrochemical dealloying, the reactive Zn is selectively removed from the alloyed layer leading to the formation of porous Au layer. In this present work, we have developed the electrochemical alloyin-dealloying approach to prepare nanopore Au (NPG) microelectrodes. A NPG microelectrode has been successfully prepared by simply applying potential steps to a conventional microdisc electrode in a nonaqueous solution of $ZnCl_2$ in benzyl alcohol at 120 ^oC.[3] Because the electrochemical alloying/dealloying is normally operated under mild conditions, it provides a low-cost and convenient approach for the preparation of the NPG microelectrodes.

The nanostructuring of a 50-μm diameter Au-disc microelectrode was performed by applying periodic potential steps to the microdisc electrode in a nonaqueous solution of $ZnCl_2$ and benzyl alcohol at 120 ^oC with Zn strips as the counter and reference electrodes. During cathodic polarization, the interaction of electrodeposited Zn and the gold substrate results in the formation of a AnZn alloy layer. The following anodic polarization drives selective dissolution of Zn component from the alloy layer, leading to the formation of initial NPG layer. The NPG layer can grow thicker back along the gold wire by repeating the potential steps. The scanning electron microscope (SEM) and energy dispersive X-ray (EDX) microscope measurements were performed using a LEO 5800 scanning electron microscope operating at 20 kV equipped with a NORAN energy-dispersive X-ray detector.

Figure 1(A) shows cyclic voltammograms for the polycrystalline Au-disc microelectrode in 1.6 mol dm^{-3} $ZnCl_2$ and benzyl alcohol. In the negative-going scan, the nucleation-growth of Zn occurs at -0.25 V vs the Zn reference electrode. A current hysteresis which is a nucleation-growth signature is seen upon reversing the scan at -0.62 V. In the positive-going scan, the dissolution of Zn commences at around 0 V and generates an oxidation peak at 0.36 V until it is completed at 0.88 V. Based on this voltammetric behavior, the electrochemical alloying-dealloying process is tuned using double-potential-step chronoamperometry, in which the potential is held at -0.62 V for 10s and then at 1.38 V for 10 s. Typical current-time transients are shown in Figure 2(B). During the first cathodic polarization, the current growth with increasing time indicates continuous Zn deposition. The dissolution of Zn is fast, demonstrated by a sharp oxidation current drop after stepping the potential from -0.62 V to 1.38 V.

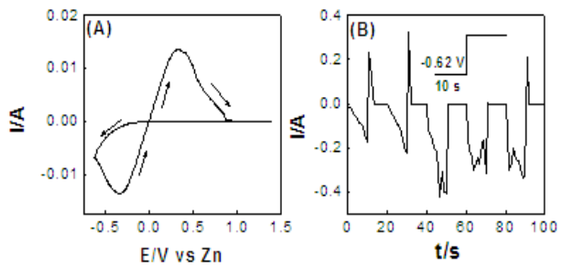

Figure 1 (A) Cyclic voltammograms measured at 100 mV s^{-1} for a polycrystalline Au-disc microelectrode in 1.6 mol dm^{-3} $ZnCl_2$ + benzyl alcohol. (B) Current-time transients for initial 5 double-potential steps.

Figure 2(A) reveals that the NPG microelectrode has a cookie-like appearance characteristic of curved macro-cracks and isolated islands. Its average geometric diameter is 62.2 μm. The islands separated by the cracks display honeycomb-like texture constructed by regular nanopores with sizes ranging from around 50 to 200 nm separated by the walls of approximately 100 nm in thickness, as shown in Figure 2(B). These microstructures facilitate the utilization of pore surfaces and reduce the limitation of reactant mass transport within the porous layer.

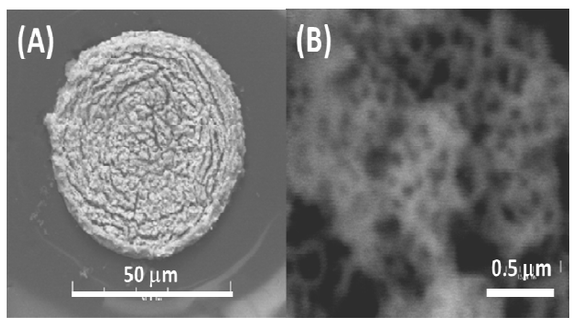

Figure 2 SEM images at different magnification.

In summary, the NPG microelectrode has been successfully prepared from the traditional Au-disc microelectrode through the electrochemical alloying and dealloying in the nonaqueous electrolyte.

References

1. F. Jia,C. Yu, Z. Ai,and L. Zhang, Chem. Mater., **19**, 3684 (2007).
2. F. Jia, C. Yu, K. Deng, and L. Zhang, J. Phys. Chem., **111**, 8424 (2007).
3. J. Jiang, and X. Wang, ECS Electrochem. Letts. **1**, H21(2012).