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Gas-assisted focused ion beam fabrication of gold nanoelectrode arrays in electron-beam evaporated alumina films for microfluidic electrochemical sensors

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ABSTRACT

This work reports the fabrication details used to prepare gold nanoelectrode arrays as working electrodes in a microfluidic electrochemical sensor system. We emphasize on the design criteria and the methods used to construct the nanoelectrode arrays for the purpose of enhancing mass transport of the redox species to the electrodes. The fabrication techniques include electron-beam evaporation of Ti and Au to create the electrode platform on a glass substrate, followed by electron-beam evaporation of thick alumina films as a passivation layer. I_2-assisted focused ion beam (FIB) milling is employed to produce high-aspect-ratio pores in the alumina films. The final nanopores with diameters around 60–120 nm are achieved by ion beam sculpting after the initial milling process. The nanopores are filled with Au via electrodeposition to obtain a nanoelectrode structure. The current responses of $Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$ redox species measured at three-electrode cells in polydimethylsiloxane (PDMS) microfluidic chips are investigated by cyclic voltammetry (CV). The current density obtained at the nanoelectrode arrays is increased by two orders of magnitude compared to that obtained from the microelectrode system. In addition, due to the effect of enhanced mass transport, the voltammetric response curve acquired from the nanoelectrode array exhibits large deviations from the classical diffusion-limited current transport theory.

1. Introduction

The potential to realize microfluidic electrochemical sensors is recognized as a promising solution for miniaturized analytical systems to provide manipulation and detection of chemical reactions in nano/micro-liter fluid samples. Because of the small volume, microfluidic devices are ideal for handling costly and difficult-to-obtain samples and reagents. A microchannel platform also offers fast analysis time due to reduced diffusion distance between the sensing units and the target species to be detected. Not only do microfluidic devices make complex analyses simpler to be performed, but they also have other distinct advantages such as low power, decreased cost and waste production, portability, and disposability. Integrated electrochemical microfluidic systems are considered to offer important benefits to an extensive range of applications, including biological research, real-time detection and monitoring of biological threats, and disease diagnosis in point-of-care medical tests.

While miniaturization of fully integrated microfluidic electrochemical sensors is the ultimate goal for decentralized analysis, there is a tradeoff between the sample size and the detection limit. When the volume of the solution is reduced, in a fixed concentration, the total number of molecules available to be detected in a minute volume is also reduced. In some cases, the measured current can be as low as sub-picoampere. Transducing such extremely low-level signal requires a highly sensitive detector. This limitation is circumvented by employing highly efficient electrodes of nanometer sizes in microfluidic systems. These electrodes possess unique properties which create the possibility of acquiring such low-level electrochemical signals. Theoretical studies have shown that the electrochemical behavior of nanoscale electrodes deviates significantly from the predictions of traditional theories. The departure is found to be dependent on the electrode size as it approaches values of molecular dimensions. Those deviations are, for example, the high electric field generated near the electrode surface that causes an enhancement or inhibition of the flux of the electroactive species to the electrode surface [1], the departure of the steady-state current response from that under the classical

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diffusion control theory [2], and the shift of the half-wave potential due to the increase in the current density [3]. Such deviations can be observed from the shape of the voltammetric response curves.

As the electrode size decreases, radial diffusion becomes dominant. When a net current flows across the electrode/solution interface, a depletion layer close to the electrode surface is developed. The thickness of the depletion layer around the electrode with at least one dimension smaller than 10 μm becomes hemispherical and is given by Eq. (1) [4]:

$$\frac{1}{\delta(t)} = \frac{1}{\sqrt{\pi Dt}} + \frac{1}{r} \quad (1)$$

where δ is the thickness of the depletion layer, D is the diffusion coefficient of the species, t is the time scale of the experiment, and r is the radius of the electrode. As the electrode decreases in size, the depletion layer thickness approaches the size of the electrode dimension. Besides, the steady-state diffusion-controlled limiting current is proportional to the inverse of the depletion layer thickness as shown in Eq. (2) [4]:

$$i(t \to \infty) = \frac{nFDAC^*}{\delta(t \to \infty)} \quad (2)$$

where n is electron stoichiometry, F is faraday constant, A is the electrode surface area, and C^* is the bulk concentration of the redox species. According to Eq. (2), smaller electrode provides higher measured current density due to thinner depletion layer. This phenomenon is called enhanced mass transport, which is the primary reason to employ nanoscale electrodes in low-level signal detection. Furthermore, the electric field and charge within the near-electrode layers become significant influences on the mass transport and electron transfer kinetics at the nanoscale electrodes. The region close to the electrode surface where a high electric field exists is described as the electrical double layer whose thickness is characterized by the Debye length, κ^{-1}. The Debye length is proportional to the inverse square root of the ionic concentration, $C^{-1/2}$, as predicted in the Debye–Huckel theory [5] as shown in Eq. (3):

$$\kappa^{-1} = \frac{1}{zF}\sqrt{\frac{\varepsilon_0 \varepsilon_r RT}{2C}} \quad (3)$$

where z is the charge magnitude of each ion in a (z, z) electrolyte, ε_0 is the permittivity of vacuum, ε_r is the static dielectric constant of the medium, R is the gas constant, and T is the temperature. The electric field established at equilibrium is found to be contained within a distance of at most $3\kappa^{-1}$ [5]. For electrodes having radius about a few tens of nanometers, the electrical double layer begins to occupy an appreciable fraction of the depletion layer. The electrostatic force within the double layer will accelerate or retard the flux of the charged species to the electrode surface. Therefore, migration resulting from the high electric field within the double layer will be added to the mass transport equation. The small feature size of the nanoelectrodes also makes their use desirable because the measured currents at the nanoelectrodes exhibit low background noise owing to minimal charging current that is proportional to the surface area of the electrode. Therefore, nanoscale electrodes are desirable in low-level signal measurements to improve the signal-to-noise ratio and to enhance the sensitivity of the microfluidic electrochemical sensors.

Taking into account that the preceding unique properties of nanoelectrodes give rise to the measured current density, research activities in the development of innovative electrochemical sensors have been focusing on the fabrication and characterization of nanoscale electrodes. However, the field of nanoelectrochemistry still remains in its infancy considering the difficulty to produce especially well-aligned and low-packing-density nanoelectrode arrays that yield multiple responses of that obtained from a single nanoelectrode. Approaches used to produce nanopore array electrodes include electron beam lithography [6], nanoimprint lithography [6], and focused ion beam technique [7]. To maximize the signal-to-noise ratio, the concerns for the nanoelectrode array fabrication are rather with the inter-electrode distance, which should be sufficiently large compared to the electrode radius in order to prevent overlapping of the depletion zones [8–10]. In addition, the choice of materials used for the nanoelectrodes' passivation layer is also crucial such that the films should have high density to prevent any leakage current paths, as well as they should be thick enough to minimize parasitic coupling. In this work, we report detailed fabrication steps used to construct the nanoelectrode arrays employed as the working electrodes in the microfluidic electrochemical sensor system. We also show an experimental evidence of the enhanced mass transport effect occurred at the nanoelectrode array.

2. Experimental

2.1. Fabrication of the electrode platforms and the alumina insulation layer on a glass substrate

The fabrication process consists of preparation of dense alumina films as the insulating layer via electron-beam evaporation, fabrication of a high-aspect-ratio nanoscale pore structure in the insulating layer through I_2 gas-assisted focused ion beam (FIB) milling, followed by ion beam sculpting, and electrodeposition of Au to fill the nanopores. Fig. 1 illustrates the fabrication steps used to prepare a nanoelectrode array in a three-electrode cell, consisting of a working electrode (WE), a reference electrode (RE), and a counter electrode (CE), embedded in a polydimethylsiloxane PDMS microchannel.

The electrode platforms composed of 20-nm Ti as adhesion layer and 300-nm thick Au are prepared on a cleaned glass slide using UV lithography, electron-beam evaporation, and lift-off. To prepare the electrodes utilized in aqueous solutions, dense films for the insulating sheath are preferred because they are chemically resistant. Besides, the leakage current of the porous insulation may affect the current response when the films are used for the passivation layer of nanoelectrodes. Electron-beam evaporated alumina (Al_2O_3) is developed as an insulating layer in this work because the fabrication method is compatible with the

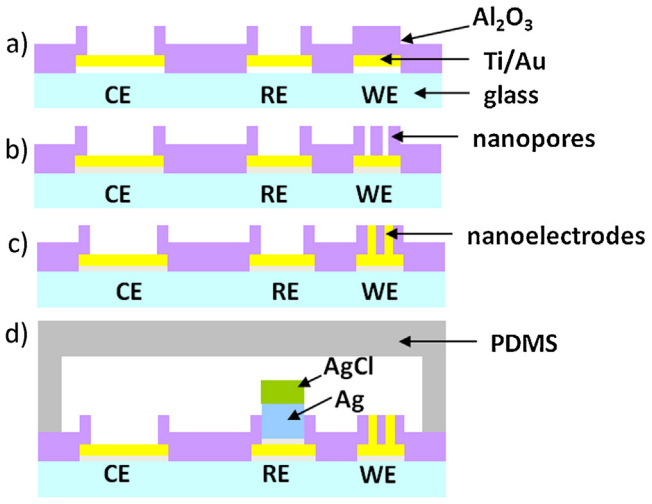

Fig. 1. The fabrication steps used to prepare a nanoelectrode array in a three-electrode cell embedded in a PDMS microchannel. (a) Patterning of the electrodes and the alumina insulating layer using photolithography, e-beam evaporation, and a lift-off method. (b) I_2-assisted FIB milling and unfocused ion beam sculpting of the pore openings. (c) Electrodeposition of Au into the FIB milling nanopores. (d) Ag/AgCl electrode fabrication and assembly with a PDMS microchannel network.