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Fabrication and characterization of an innovative integrated solid-state microelectrode

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ABSTRACT

Currently, most commercial microelectrodes cannot be used for *in vivo* or *in situ* measurements due to size constraints of the reference and counter electrodes. Thus, integrated miniature microelectrodes are highly desirable. In this work, an integrated needle-type microelectrode consisting of a solid Ag/AgCl reference electrode, a gold counter electrode, and a gold working microelectrode was prepared using a microfabrication technique and an electrochemical modification method. The electrochemical performance of each electrode was characterized using cyclic voltammetry. The effects of chloride ion concentration on the potential of the Ag/AgCl reference electrode were also evaluated. The results showed that the integrated microelectrode displayed high stability, reproducibility, repeatability and reliability, and that it can be used to determine constituents, profiles and functions *in situ*.

1. Introduction

Microelectrodes are one of the most powerful tools for microscale analysis and have been used in physiology, medicine, neuroscience, microbial ecology, and environmental monitoring [1,2]. Microelectrodes offer several advantages over conventional macroscale electrodes, such as rapid response, high signal-to-noise ratio, high current density, small double-layer capacitance, low i–R drop, high spatial resolution, and minimal sample destruction [3]. Thus, microelectrodes are especially suitable for *in vivo* and/or *in situ* analyte detection and may be used for large-scale and extensive applications. Intensive research on microelectrode fabrication is currently under way, and several novel synthetic procedures have recently been proposed to improve the performance of microelectrodes and to extend potential applications [4–9]. Due to their high electrochemical stability, long lifetime, and simple structure, various metal and metal–metal oxide microelectrodes have been employed for the detection of analytes in chemical, biological, environmental, and medical samples [10–12]. Many methods for the fabrication of microelectrodes are currently available [10]. For example, inserting a tapered metal wire into a glass micropipette is a common method used to produce microelectrodes. Alternatively, a glass micropipette can be filled with an alloy that has a low melting-point. Although a considerable amount of research has been conducted to improve these fabrication methods, several problems remain unsolved, including poor reproducibility and the synthesis of multisensor devices [10,13–15]. Thus, to expand potential applications, innovative microelectrode fabrication methods must be developed.

Previously, we synthesized a novel solid gold microelectrode via microfabrication and showed that the electrode could be used to determine the concentration of dissolved oxygen [16]. The addition of Pt–Fe nanoparticles into the microelectrode allowed the successful detection of nitrite ions [17]. Furthermore, the simultaneous detection of dissolved oxygen and nitrate ion was achieved by coating a three-dimensional silver nanostructure on the surface of the microelectrode [18]. Nevertheless, there are still limitations to the practical application of microelectrodes. For example, although the working microelectrode can be inserted into samples for *in vivo* or *in situ* micromeasurements, the conventional reference and counter electrodes must be placed outside the sample, which significantly affects detection. Therefore, to improve *in vivo* and *in situ* micromeasurements, a novel microelectrode was developed by integrating a reference, working, and counter microelectrode. Unlike previous microelectrodes that contain conventional reference and counter electrodes, a completely integrated configuration of microscale electrodes did not require a shielded electrode, which allowed the miniaturization and integration of test units [19].

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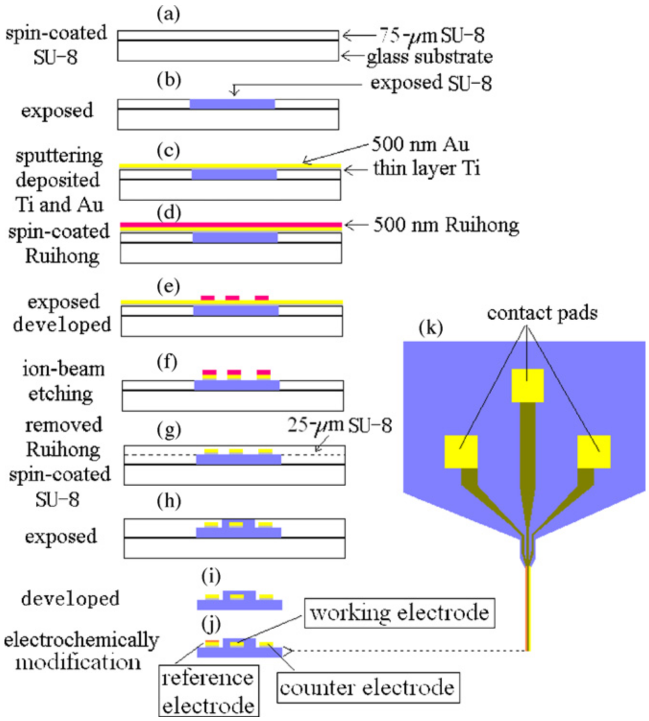

Fig. 1. Schematic of the IME microfabrication procedures (for clarity, only one IME is shown).

In this work, an integrated needle-type solid microelectrode was prepared by microfabrication and electrochemical modification, and the electrochemical performance of the microelectrode was evaluated. The integrated microelectrode (IME) consisted of a gold working microelectrode, a gold counter microelectrode, and an Ag/AgCl reference microelectrode. Gold was selected as the electrode material due to its superior performance in the direct measurement of a variety of analytes such as dissolved oxygen [20,21], inorganic arsenic [22], salbutamol [23], and mercury (II) [24]. After appropriate modifications, the IME produced in this study may be used to detect other substances [25,26].

2. Experimental

2.1. Chemicals

OmniCoat, an SU-8 series negative photoresist, and SU-8 developer were purchased from MicroChem Co., USA. Ruihong, a positive photoresist, was purchased from Suzhou Ruihong Co., Ltd., China. Silver conductive adhesion was purchased from SPI Co., USA. Analytical grade ethanol, acetone, isopropanol, ammonium chloride, silver nitrate, sodium chloride, potassium chloride, potassium ferricyanide, and potassium ferrocyanide were purchased from Shanghai Chemical Reagent Co., China. Deionized water was used in all experiments.

2.2. Microfabrication of the IME

To facilitate mass production, each glass plate was patterned to contain six IMEs. The microfabrication procedure employed in this study is described below (Fig. 1).

Fabrication of the SU-8 layer: a glass plate (60 mm × 60 mm × 2 mm) was washed with detergent, rinsed with water and acetone, and dried at 110 °C for 30 min. To apply an adhesive, the glass was spin-coated with a thin layer of OmniCoat at 2000 rpm for 30 s and was baked at 200 °C for 2 min on a hot plate. Upon cooling, a 75 μm-thick layer of SU-8 (SU-8 2075) was applied, and a two-step soft-bake process (65 °C for 10 min and 95 °C for 60 min) was performed on a level hot plate (Fig. 1a). The photoresist was patterned using a photomask containing the shape of the IME (i-line, 175 mJ/cm^2). An oven was used to conduct postexposure baking (PEB) (65 °C for 5 min; increase to 95 °C at a heating rate of 2 °C/min; 95 °C for 30 min) (Fig. 1b). After baking, the substrate was cooled to ambient temperature on the hot plate or in the oven to relieve stress.

Formation of the gold track: a thin layer of titanium and a 500 nm-thick layer of gold were deposited on the SU-8 layer by sputtering (Fig. 1c). Subsequently, a 600 nm-thick layer of positive photoresist was spin-coated on top of the gold layer and soft baked in an oven (Ruihong, 65 °C for 5 min; increase to 95 °C at a rate of 2 °C/min; 95 °C for 5 min; Fig. 1d). The substrate was aligned and exposed to a photomask containing the desired pattern of metal tracks (exposure: g-line, 58 mJ/cm^2; development: 0.4% NaOH, 1 min; Fig. 1e). After development, ion-beam etching was conducted until the metal uncovered by the positive photoresist was completely removed (Fig. 1f). Subsequently, the remaining positive photoresist was removed with ethanol and the substrate was cleaned in an oxygen plasma for 1 min.

Fabrication of SU-8 upper layer: a second 25 μm-thick layer of SU-8 (SU-8 2025) was spin-coated (soft baked in oven: 65 °C for 5 min; increase to 95 °C at a rate of 2 °C/min; 95 °C for 5 min; Fig. 1g) and patterned with a photomask containing contract pads and an outline of the upper layer (i-line, 90 mJ/cm^2). PEB was performed for an extensive period of time to achieve the desired cross-linking density (65 °C for 5 min; increase to 95 °C at a rate of 2 °C/min; 95 °C for 75 min; Fig. 1h). Upon completion, the substrate was stored under ambient conditions for 5 d to relieve stress and was developed in the SU-8 developer for 1 h. During the development process, the IMEs automatically detached from the glass plate. After development, the IMEs were immediately rinsed with isopropanol (Fig. 1i).

Packing: during the final step, the insulation at each end of the coated copper wires was sanded off. The wires were attached to the contact pads with silver conductive adhesive, and the pads were insulated with silicon rubber.

2.3. Preparation of the reference microelectrode

As shown in Fig. 1i and k, the middle tip of the gold track was embedded in cross-linked SU-8 and was used as the working microelectrode. One of the two gold tracks at the edge of the tip was used as the counter microelectrode, while the other track was modified with Ag/AgCl and was used as the reference microelectrode. To obtain the reference electrode, the following two-step modification was performed.

Modification with Ag: to deposit silver on the gold electrode, 30 cycles of cyclic voltammetry (CV) were conducted in a solution of 10 mmol/L $Ag(NH_3)_2OH$ at a scan rate of 50 mV. At a potential less than 0.1 V (vs. Ag/AgCl, 3 M KCl) (Fig. 2), silver (I) was reduced to atomic silver, which was deposited on the gold surface. Alternatively, silver was oxidized to silver (I) at a potential greater than 0.2 V (vs. Ag/AgCl, 3 M KCl). In the initial solution, silver was not present on the gold surface; thus, the current at the beginning of the first cycle was equal to zero. In the Ag deposition process, silver ion was reduced and deposited on the Au electrode. Subsequently, atomic silver was reoxidized and allowed to dissolve into solution. However, the silver deposited on the Au electrode was not readily oxidized and remained bound to the surface of the electrode. As a result, loosely bound silver dissolved into solution, while tightly bound silver accumulated on the electrode. After several cycles, a layer of tightly packed silver was deposited on the surface of the Au electrode. Alternatively, when a constant potential was applied,