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A facile method for fabricating carbon fiber-based gold ultramicroelectrodes with different shapes using flame etching and electrochemical deposition

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ABSTRACT

In this study, we developed a simple, cost-efficient, and time-saving approach for producing gold (Au) ultramicroelectrodes (UMEs) with different shapes and sizes ranging from one micron to several microns in diameter. A microneedle, in combination with a flame-etched carbon fiber (CF), acts as a template for electrochemical fabrication of Au electrodes. To fabricate spherical and disk-shaped electrodes, a small gap at the tip of the microneedle was formed using CFs whose tips were flame-etched to a size larger than that of the microneedle tip opening. The gap was then electrochemically filled with Au using chronoamperometry. However, to fabricate rod-shaped electrodes, the size of the CF tip was flame-etched to a size smaller than the microneedle tip opening, which resulted in CF to protrude from the microneedle tip opening. Then, the CF surface was electrochemically modified with Au. The whole fabrication process for each electrode took less than 15 min. The fabrication method is quite useful for researchers with limited resources, and the fabricated UMEs have great potential to be used in various applications ranging from constructing nano-/micro-biosensors to single-cell analysis.

1. Introduction

An ultramicroelectrode (UME) is operationally defined as an electrode that has at least one dimension, known as the critical dimension, less than 25 μm [1,2]. This critical dimension can be the diameter of a disk electrode or the width of a band or a ring electrode. The production of UMEs enables micro- and nanoscale analysis [3–5]. Unlike millimeter-sized electrodes, UMEs have features that increase sensitivity, such as low ohmic potential drop, low double-layer charge current, and high molecular transport [6,7]. Small-sized electrodes have become powerful tools for electrochemistry and are used in a wide range of applications including electrochemical imaging by scanning electrochemical microscopy [8], study of single molecules and nanoparticles [9], chemical sensing in cells [10], understanding of electron-transfer kinetics [11], and double-layer effects [12]. They are also used in the construction of nano-/micro-biosensors, which enables achieving high temporal and spatial resolution, local detection, and detection in small volumes.

Au is preferred as the electrode material for electrochemical sensors, especially for affinity-based electrochemical biosensors, because of its high stability in body fluids [13]. Utilizing the extremely strong Au–thiol interaction, target molecules can readily be immobilized on the gold electrode. Au microelectrodes are usually made of micron-sized Au wires using a laser-based micropuller; however, depending on the large difference between the melting points of Au (1064 °C) and quartz (1710 °C) or even borosilicate (1640 °C), fabrication of Au UMEs is extremely difficult. Electrochemical deposition of Au has been utilized as an alternative to develop such small-sized electrodes. For instance, Lai et al. modified the surface of a recessed Pt nanoelectrode with Au for fabricating a probe-based electrochemical DNA biosensor [14]. In their study, a sharp, long, and tapered Pt nanoelectrode was first fabricated using a laser puller, and then, the electrode tip was chemically etched to form a nanopore, which was then filled with Au through electrochemical deposition. In another recent study, Zhang et al. developed an approach for fabricating nanopipette-based electroplated nanoelectrodes. In this approach, a quartz nanopipette drawn by a laser puller was used as a template [15]. The nanopipette was immersed in a liquid gallium-indium alloy electrode for electrochemical deposition of Au, and thereby, the fabrication of the nanoelectrode in the pipette. Subsequently, the nanopipette was further filled electrochemically with a conducting polymer (polypyrrole) to develop an electrical contact between the deposited Au nanoelectrode and a metal wire. The introduced fabrication process took over 14 h and the probe tip was required to be rinsed following the electrochemical deposition process to remove the residues of the metal alloy. In the present study, a rather simple, low-cost, and time-saving approach was developed for

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fabricating ultra-small-sized Au electrodes, where a microneedle along with a flame-etched carbon fiber (CF) served as a template for electrochemical fabrication of Au electrodes. The fabricated UMEs have great potential to be used in various applications ranging from constructing nano-/micro-biosensors to single-cell analysis.

2. Materials and methods

2.1. Materials (10-point font with single spacing)

Patch clamp glass capillary (OD/ID: 1.65/1.1 mm) – PG10165-4 (World Precision Instruments, USA), silver paste (Sigma Aldrich, USA), chloroauric acid ($HAuCl_4 \cdot xH_2O$) (Sigma Aldrich, USA), sulfuric acid (H_2SO_4) (Sigma Aldrich, USA), phosphate-buffered saline (PBS) (Sigma Aldrich, USA), hydrogen chloride (HCl) (Sigma Aldrich, USA), ferrocenemethanol ($FcCH_2OH$) 97% (Sigma Aldrich, USA), glucose oxidase from *Aspergillus niger* (Sigma Aldrich, USA), D(+)-glucose (Sigma Aldrich, USA), H_2O_2 (Sigma Aldrich, USA), H_2SO_4 (Sigma Aldrich, USA).

CFs with a diameter of ~6 μm were kindly provided by Prof. Hitoshi Shiku (Tohoku University, Japan).

2.2. UME fabrication

The fabrication of the UMEs with different shapes is illustrated in Fig. 1. First, a single CF was fixed to a copper wire that was only exposed at the tips using a silver paste, and then, the connection was made permanent by baking and solidifying the silver paste at 180 °C. Then, the tip of the CF was flame-etched using simple lighter in a process that took only a few seconds. A glass capillary (PG10165-4, World Precision Instruments, LLC, USA) was pulled using a micropuller (PC-10 micropulling machine, Narishige, Japan) to produce two microneedles using the following parameters: option: 2, first-pull position adjustment plate: 6 mm, second-pull position adjustment plate: 2 mm, weights: 2 (one type light and one type heavy), no. 1 heater level: 65 and no. 2 heater level: 37 [16]. The flame-etched CF fixed to the copper wire was inserted in one of the glass microneedles by using the wire, which was fixed on the glass tubes with heat-shrinking rollers to prevent any damage to the CFs in the subsequent operation. In order to fabricate disk-shaped and spherical Au electrodes, the fiber was not flame-etched to nanosize, so it did not protrude from the tip of the microneedle but instead formed a gap. Afterward, the probe with an obvious gap at the tip was immersed in a solution containing 2 mM $HAuCl_4$ (0.1 M NaCl, 1.5 wt% HCl) to electrochemically fill the gap with Au. Chronoamperometry was used for electrochemical deposition of Au for which the potential was held at − 0.1 V (vs Ag/AgCl) using a potentiostat (Autolab PGSTAT204, Metrohm, Switzerland). The change in current with respect to time was recorded to control the fabrication process and the size of the electrodes. For the rod-shaped Au electrodes, first a cone CF electrode was produced, for which the CF tip was flame-etched down to nanolevel using a simple lighter so that it could protrude from the tip of the microneedle. Afterward, the surface of the conical CF electrode (CFE) was first cleaned in acetone and milli-Q water, and then, modified with Au in the same way as that described for disk-shaped and spherical electrodes.

2.3. Electrochemical characterization of the probes

Following the production of UMEs, the computer-assisted SEM/EDS analysis was performed to confirm Au electrochemical deposition on a Carl Zeiss 300VP scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) system using EDAX TEAM (Texture and Elemental Analytic Measurement) software. Prior to analysis, the sample was coated with a 5-nm-thick gold film, and then, the electrochemical deposition was confirmed by EDS analysis in a small area at 45×10^3 magnification. Next, the electrochemical behavior of these probes was analyzed in a PBS solution containing 1 mM $FcCH_2OH$. At this point, CV curves were obtained by sweeping the potential of the working electrode between 0 and + 0.6 V (vs. Ag/AgCl) at a scan rate of 50 mV/s. In the case of rod-shaped electrodes, CV curves both before and after surface modification were obtained to observe the change in size.

2.4. Simulation

Basically, the electrochemical behavior of each UME was simulated for validation of the experimental results. First, a 3D model for each UME was designed in 1000 × 1000 × 1000 μm spaces by using the electrode dimensions shown in respective SEM images; i) microdisk UME; inner radius: 0.6 μm and outer radius 0.65 μm (dimensions obtained from the SEM image of a typical micropipette, Fig. 2A_I), ii) sphere UME; 5.3 μm - the radius of the dashed circle in Fig. 2A_{III} was used for simulation and iii) rod UME: radius: 2 μm and length: 28 μm (Fig. 3A_{II}). A free triangular mesh was used for each active electrode surface with the minimum and maximum element sizes specified to be 0.01 and 0.02 μm, respectively. COMSOL Multiphysics 4.4 was used to

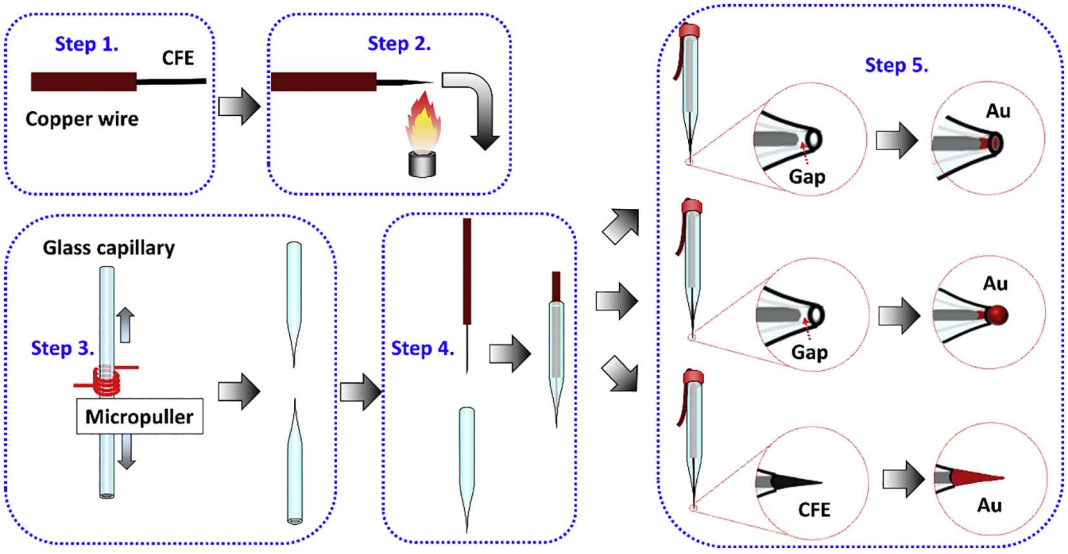

Fig. 1. The fabrication process used for UMEs with different shapes; disk, spherical and rod. The process consists of five simple steps; (i) fixation of a CFE to a copper wire, (ii) flame-etching the tip of the CFE, (iii) production of microneedles using a micropuller, (iv) insertion of the flame-etched CFE in a microneedle and (v) electrochemical deposition of Au.