



Bench-top fabrication and electrochemical applications of a micro-gap electrode using a microbead spacer



Seungjin Park ^a, Jun Hui Park ^{b,*}, Seongpil Hwang ^{c,*}, Juhyoun Kwak ^{a,*}

^a Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

^b Department of Chemistry Education, Institute of Fusion Science, Chonbuk National University, Jeonju 54896, Republic of Korea

^c Department of Advanced Materials Chemistry, Korea University, Sejong 339-700, Republic of Korea

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ABSTRACT

Large-area micro-gap electrodes were fabricated employing uniform-sized spherical beads as spacers to precisely control the gap thickness ranging from 500 nm to 8 μm for large amperometric signal by the combination of electrochemical amplification by redox cycling and the large area of the electrodes. As a biosensor application, dopamine oxidation with an Au–Au (4 μm) gap showed selective and sensitive amplification of dopamine in the presence of ascorbic acid.

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1. Introduction

Generator–collector [1,2] electrode systems have drawn much interest due to the electrochemical amplification by redox cycling; where one electrode cautiously conducts a forward (e.g., oxidative) reaction with help from a backward (e.g., reductive) reaction at the other electrode and vice versa. Generator–collector systems consisting of a gap electrode [3–6], interdigitated array (IDA [7]), and surface interrogation SECM (SI-SECM) [8] have been demonstrated for various applications [9–11].

A gap electrode provides highly amplified steady-state currents through efficient collection of the redox cycling [12–15]. Gap systems have been applied to study the mechanisms of chemical reactions and to determine the kinetic rate-constant [16]. Various methods using the classical micrometer [17], polymers [3,4,6,18,19] and e-beam lithography [20] have been reported for the fabrication of small gap and disposable sensors. Precise control of gap thickness in hundreds of nm, however, is still challenging while expensive nano-lithography enables such a small gap.

A bench-top fabrication of gap electrodes might play significant roles in electrochemical sensors originated from signal amplification, electrochemical selectivity and small sample volume. The state-of-the-art SECM-based and lithographically fabricated nanogaps have some limitations such as cost and accessibility for sensor applications. As a

bench-top process, commercially available thermoplastic sealing films ranging in the tens of micrometers have been widely used for dye-sensitized solar cells [21]. They are not suitable in electrochemistry because of their large thicknesses (> 25 μm) and irregular changes in thickness during the curing process. Recently, Compton and co-workers introduced a useful method for gap electrodes; Epoxy was employed as a sticky spacer, which simultaneously blocks electrical contact and maintains parallel spacing between the electrodes with tens of μm [3–6,12]. However, benchtop fabrication of gap also has still been a challenge in terms of reproducibility, precision in gap distance, large area.

Herein, we introduce a new strategy for large-area ($\sim 1 \text{ cm}^2$) gap fabrication ranging from 500 nm to 8 μm . This method uses spherical micro-beads as uniform spacers. Commercially available micro-beads in various diameter enable precise controls in various gap distance by monodispersed beads. The smallest gap by ours is ca. 500 nm, which is smaller than previous benchtop method in the order of magnitude [3–6,18,19]. Moreover, large area of electrode was successfully fabricated in spite of difficulty in leveling. Fabricated gaps were characterized by SEM and cyclic voltammetry to confirm redox cycling. The fabricated gap electrode was applied to dopamine detection using an Au–Au (4 μm) gap system. Selective and sensitive detection of dopamine in the presence of interfering ascorbic acid was achieved by measuring the collector current. A gap electrode has a large current originating from the large area of the electrodes and from the redox cycling of the electroactive species, even in the presence of trace amounts of analytes, which enables detection through low-cost electronics. Additionally, the gap thickness, which controls the turn-over rate of redox cycling, can be

* Corresponding authors.

E-mail addresses: echem@jbnu.ac.kr (J.H. Park), sphwang@korea.ac.kr (S. Hwang), Juhyoun_Kwak@kaist.ac.kr (J. Kwak).

precisely controlled by altering the bead size. Hundreds of nL of the sample solution is sufficient to fill the cavity of the gap, which is effectively pulled up by capillary forces. Because of the precise gap thickness and the versatility of the electrode materials, the kinetic constant will be investigated in future works.

2. Experimental

All chemicals (obtained from Aldrich) were analytical or better grade. Silica beads (SS03N, 0.54 μm , Lot# 9473, BangsLab), latex beads (L3030, 2 μm , Sigma-Aldrich), dynabeads (M450-epoxy, 4.5 μm , Invitrogen) and magnetic beads (6.2 μm , 8.18 μm , UMC3N, UMC4N, respectively, BangsLab) were used as spacers. Epoxy was purchased from Henkel Corporation. The buffer solution for Dopamine/Ascorbic acid experiments was composed of 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4 (pH 3).

Electrochemical measurements were performed using a CHI 900B bipotentiostat with a conventional three- or four-electrode system. Pt wire and Ag/AgCl (3 M KCl) were served as counter electrode and reference electrode, respectively.

To fabricate the gap electrode, ITO glasses (1.1-mm-thick, resistivity = 15 Ω , 30 mm \times 10 mm for lower electrode, 15 mm \times 10 mm for upper electrode) were cleaned with piranha solution (3:1 = H_2SO_4 : H_2O_2 ; WARNING: *this solution is highly aggressive*) for 20 s followed by rinsing with water, isopropyl alcohol and subsequent drying with N_2 , and then, the surface of the electrode was treated with O_2 plasma making it hydrophilic (Fig. 1A). Next, a dropping solution of diluted beads (e.g., 4 μm beads were used in a 0.2% v/v bead solution which was the minimum concentration used to prevent the two electrodes from shorting) was prepared with an ethanol solvent. Both the complete wetting of the

hydrophilic surface and the low surface tension of ethanol block multilayer formation. After evaporation, ca. 10% bead surface coverage was attained (Fig. 1B). Upper ITO was carefully aligned face-to-face upon the beads (electroactive area of 10 mm \times 10 mm) (Fig. 1C). The temporary assembly held together by Kapton tape (3 M, US, 3 mm \times 30 mm, to block the penetration of epoxy into the gap) was sealed with epoxy on each side under pressure using a 10 g weight (Fig. 1D) followed by thermal curing (50 $^\circ\text{C}$ for 30 min.). After removing the weight, additional epoxy was applied to the uncovered top surface with the same thermal treatment (Fig. 1E). For gold-gold gap, fabrication follows the identical procedure except Au on Si (100 nm Au, 5 nm Ti on Si) instead of ITO.

3. Result and discussion

3.1. Characterization of micro-gap electrode

The micro-gaps consist of two parallel macro-electrodes with micro-beads located between them. The large-area electrodes (1 cm^2) are effectively separated by pillar beads (2 μm , 4 μm , 6 μm , and 8 μm in diameter), as shown in Fig. 2. Note that the smallest gap of 500 nm was fabricated in spite of low yield (~15%) probably caused by the electrode being short-circuited (Fig. 1). Efforts to fabricate tens of nm gap by our method are underway using flat electrode.

Fabricated gap is served as thin layer electrochemical cells (TLCs), where electrochemical redox cycling is observed when electroactive species are oxidized (or reduced) at the generator electrode (GE); product diffuse toward the collector electrode (CE) where they are reduced/oxidized back to reactant electrochemically (Fig. 3A). Thus, diffusion layer of redox molecules keeps thin leading to the steady-state current

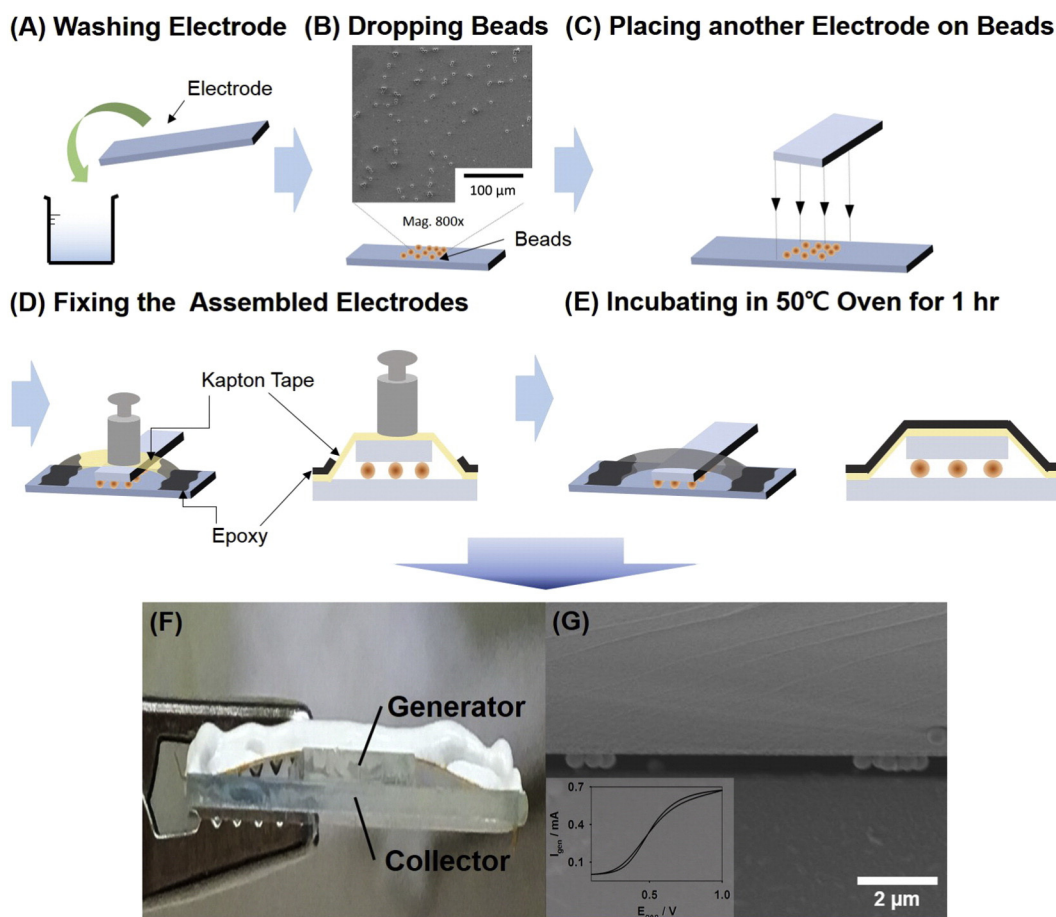


Fig. 1. Illustration of the fabrication process using beads (A)–(E). (F) is a picture of the fabricated gap. (G) is the SEM image of the 500 nm gap. Inset: CV was obtained at the 500 nm gap in the presence of 100 μM FeMeOH and 2 M KNO_3 at 100 mV/s.

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