



Fabrication and characterization of nanoporous gold on microelectrode



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ABSTRACT

We fabricated nanoporous gold (NPG) on a microelectrode by oxidation and reduction cycles (ORCs) in acidic media. The typical morphology of the nanostructures comprised tangled thickets of branched nanowires with diameters of 20–30 nm. Furthermore, the surface area was significantly increased compared with the bare electrode. The roughness factor (R_f) of NPG could be controlled by changing the number of ORCs. The NPG-modified microelectrode with a roughness factor of 49 could immobilize 11 times more thiol-modified oligodeoxynucleotides on its surface than a microelectrode without NPG ($R_f = 1.8$). The results suggest that NPG formation is an important method for enhancing the electrochemical sensitivity of microelectrodes.

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1. Introduction

Electrochemical systems with microelectrodes are of high interest owing to their potential application in electrochemical analysis, sensors, and microscopy [1–3]. Microelectrodes are becoming thinner in order to minimize the electrochemical systems and improve the response time and spatial resolution. Thus, the reduction in surface area creates problems, such as low sensitivity and low signal-to-noise ratio [2]. Introducing nanostructures into the electrode surface can increase the effective surface area and considerably enhance the catalytic activity. The methods for introducing nanostructures include the template technique [2,4,5], electrodeposition [6–8], nanoparticle modification [9–11], and alloying of multi-metal compounds followed by selective dealloying. The alloying–dealloying method provides nanoporous gold (NPG)-modified electrode [12–15], which is biocompatible and easily functionalized, as well as colloidal gold nanoparticles [16,17]. Thus, it has been extensively applied to numerous biosensors and biofuel cells [18–20]. Recently, NPG was electrochemically fabricated via the one-step anodization of bare gold in acidic aqueous solutions instead of alloying–dealloying [21–23]. The advantage of this fabrication method is that it is relatively simple to prepare and the metallic material used in the fabrication is pure gold. We have also fabricated NPG-modified electrodes for the direct electrochemistry of cytochrome P450 [24]. On the other hand, the use of oxidation and reduction cycles (ORCs) in acidic electrolytes is a convenient method to fabricate nanostructures on a gold surface [10,25]. We applied the ORC treated electrodes to demonstrate

the direct electrochemistry of oxidoreductases, such as cytochrome P450 [26] and the flavin-containing monooxygenase [27].

Herein, we examined two fabrication methods of NPG microelectrodes: (1) anodization and (2) the ORC treatment. We concluded that the ORC treatment could successfully form NPG with high surface area on the microelectrode. The morphology of the fabricated microelectrode was observed by field emission scanning electron microscopy (FESEM) and the electrochemical behavior was assessed by voltammetry. We further confirmed the increase in the amount of oligodeoxynucleotides immobilized on the microelectrode.

2. Experimental

2.1. Reagents and chemicals

Hexaammineruthenium(III) chloride ($(\text{Ru}(\text{NH}_3)_6)\text{Cl}_3$, 98%) and potassium hexacyanoferrate(II) ($\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, 99.5%) were purchased from Sigma-Aldrich. Interstrand cross-linked oligodeoxynucleotides with a dithiol group (s-ODNs, Fig. S1) were prepared as previously reported [28,29]. All other chemicals were of analytical grade or of the highest purity available and were used without further purification. Double-distilled water was used throughout the experiments. Au wire was purchased from the Nilaco Corporation, Japan (99.95%), and borosilicate glass capillaries were purchased from (#1B150-6) from World Precision Instruments, USA.

2.2. Apparatus

The voltammetry experiments were performed on an HZ-5000 electrochemical analyzer (Hokuto Denko Co. Ltd., Japan). A piece of Pt wire and an Ag/AgCl electrode with saturated KCl were used as the counter

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and reference electrodes, respectively. All potentials were reported relative to the Ag/AgCl reference electrode. All experiments were carried out at room temperature. FESEM images were acquired with a Hitachi S-4300. Energy-dispersive X-ray spectroscopy (EDX) was performed by using an EDAX Genesis system with FESEM capabilities.

2.3. Fabrication of the nanostructures

We first fabricated the bare Au microelectrode by heat-sealing a piece of Au wire (50 μm in diameter) in a borosilicate glass capillary. The diameter of the electrode including the glass sheath was ca. 80 μm . The tip of the Au wire encased in the capillary was polished with #4000 and #15,000 polishing films, and cleaned electrochemically in 0.5 M H_2SO_4 solution by scanning from 0 V to 1.6 V at 100 mV/s for 15 cycles. Then, the NPG was fabricated on the electrode surface by the ORC treatment. Potentials of 1.22 V and 0.28 V were applied for 30 s in 25 mM HCl aqueous solution, and that was repeated between 1 and 14 times. Constant-voltage anodization (CVA) was carried out at 1.22 V for 2 min in 25 mM HCl aqueous solution.

2.4. Measurement procedures

The real surface area of the microelectrodes was electrochemically measured from the amount of charge consumed during the reduction of the gold oxide monolayer on the surface. Voltammetry was carried out in 0.5 M H_2SO_4 solution by scanning from 0 V to 1.6 V at 100 mV/s and the reported value of 386 $\mu\text{C}/\text{cm}^2$ was used in the calculations [30]. The characterization of the microelectrode was performed in 4 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.1 M KCl with a scan rate of 50 mV/s. The s-ODNs modification was performed by dipping the microelectrode in 0.2 μM s-ODNs solution (3 μL , 0.5 M phosphate buffer, pH 7) overnight in a humidity chamber at room temperature, and then washing in stirred distilled water (150 rpm) for 10 min at 30 $^\circ\text{C}$. After the modification, the electrode was masked with 1 mM 6-mercapto-1-hexanol reagent for 1 h and washed in stirred phosphate buffer (150 rpm) for 1 min. The immobilized s-ODNs were quantified with redox-active hexaammineruthenium(III) chloride [31].

3. Results and discussion

3.1. Morphology of nanostructures

We previously fabricated nanoporous gold (NPG) on a macro electrode by CVA [24]. CVA was applied for 2 min in 25 mM aqueous hydrochloric acid (HCl) to form NPG on the microelectrode surface. However,

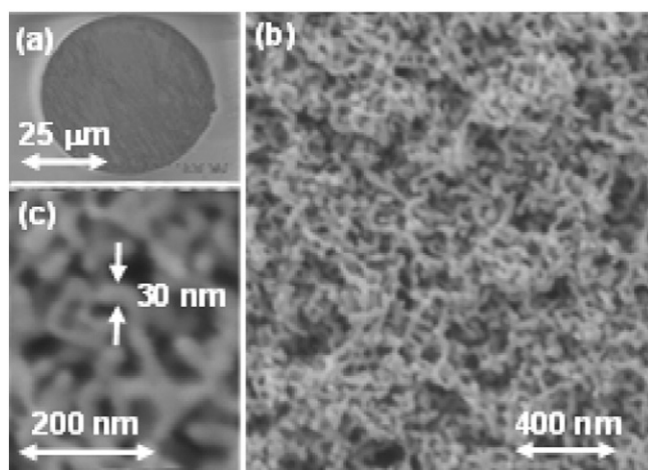


Fig. 1. (a) FESEM images of the tip of microelectrode with 50 μm diameter surrounding glass shield obtained by 10 oxidation and reduction cycles (ORCs) in 25 mM HCl. NPG surface was depressed 3–5 μm from glass shield. (b, c) High-magnification images of NPG.

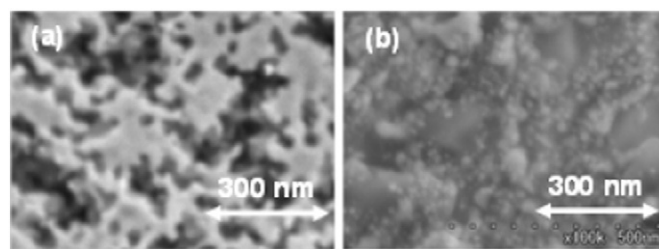


Fig. 2. FESEM images of nanostructures obtained after 10 ORCs in (a) 15 mM and (b) 55 mM HCl.

this yielded thin and heterogeneous NPG on the microelectrode surface (Fig. S2). We have also previously shown that nanoparticles (20–30 nm in diameter) were formed on the macro electrode by the ORC treatment in 100 mM HCl [10]. Next, a microelectrode was subjected to the ORC treatment in 25 mM HCl. Interestingly, NPG actually different from that observed in the CVA treatment was homogeneously formed over an entire area of the microelectrode surface (Fig. 1). The nanostructures were tangled thickets with diameters in the range of 20–30 nm which can be categorized into mesoporous materials. They were completely different from the nanoparticles fabricated by using the ORC treatment for the macro electrodes [10]. Although the NPG could be observed on the microelectrodes from the ORC treatment in 20–50 mM HCl, the polished surface partially remained in 15 mM HCl (Fig. 2a) and the nanoparticles that had been seen in the previous report [10] were observed in 55 mM HCl (Fig. 2b).

Deng et al. explained the formation of the NPG in aqueous HCl [21]. During oxidation, the Au substrate electrochemically dissolves to Cl^- form $[\text{AuCl}_2^-]$ near the electrode surface depending on the concentration of Cl^- (Eq. (1)).



$[\text{AuCl}_2^-]$ immediately transforms to Au^* atoms and $[\text{AuCl}_4^-]$ at the growth site of the nanostructures (Eq. (2)).



According to these equations, the dissolution of the Au substrate proceeds slowly in low concentrations of Cl^- (Eq. (1)). On the other hand, high concentrations of Cl^- disturb the growth of the Au nanostructures (Eq. (2)). These reactions could explain the formation of the Au structures in different Cl^- concentrations. In our results, the ORC treatment could fabricate thicker branched nanowires of NPG than CVA. In the case of ORC treatment, $[\text{AuCl}_4^-]$ is reduced to Au^* atoms at a low potential (0.28 V) (Eq. (3)). This reductive deposition of Au on the nanowires might be the reason behind the thicker nanowires than those fabricated by CVA.



3.2. Characterization of NPG nanostructures

EDX was used to characterize the chemical composition of the NPG that was fabricated on the microelectrode by using 10 ORCs (Fig. 3). The results suggest mass percentages of 91.6% Au, 6.8% C, and 1.6% Al. The carbon was a surface contaminant from the atmosphere and the aluminum was attributed to stray radiation from the specimen holder. Hence, the nanostructures were 99.95% Au.

The NPG on the microelectrode was also electrochemically characterized in aqueous sulfuric acid (H_2SO_4) (Fig. 4a). Because the voltammogram of the NPG provided a nearly identical profile to that of the bare microelectrode, the NPG comprised polycrystalline gold, like the

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