

Electrocatalytic Reduction of Hydrogen Peroxide at Nanoporous Gold Surfaces

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Abstract : We report on the electrocatalytic reduction of hydrogen peroxide at nanoporous gold (NPG) surfaces. Various NPG surfaces with different surface structure were prepared by changing the conditions of electrodeposition for Ag-Au layers such as the concentration ratios of $\text{KAu}(\text{CN})_2$ over $\text{KAg}(\text{CN})_2$ and deposition charges. The effects of different electrochemical conditions on the electrocatalysis of H_2O_2 reduction were investigated. The NPG surfaces exhibited sensitive amperometric responses for H_2O_2 reduction, from which calibration plots with higher sensitivity than a bare Au surface were obtained.

Keywords : Nanoporous gold, Electrocatalysis, Hydrogen peroxide, Amperometric detection

1. Introduction

Over the past decades, there has been a notable progress in the synthesis of gold nanoparticles (AuNPs) of various sizes and shapes, which led their useful applications in various fields such as fundamental physics, electrochemistry, and biology.¹⁾ For AuNPs being utilized in electrochemical applications, they should be assembled on the electrode surfaces; however, the supported AuNPs suffer from sintering and self-aggregation.²⁾ Recently, nanoporous gold (NPG) surfaces attracted much attention due to their unique physical and chemical properties.²⁻⁴⁾ Various applications based on NPG surface structures have been reported including electrocatalysis,⁵⁾ surface-enhanced Raman scattering spectroscopy,⁶⁾ and electrochemical sensors.⁷⁻⁹⁾

NPG structures can be prepared by the selective dissolution of Ag from thin Ag-Au alloy films in a concentrated nitric acid. The NPG surfaces exhibit a high surface area with well-defined pore-ligament structures on the nanometer scale. A commercialized Ag-Au thin foil has been traditionally utilized to produce NPG surface layers,^{3,4)} which were supported on electrode surfaces such as glassy carbon for electroanalytical applications.^{7,8)} In an alternative route to fabricate NPG electrode surfaces, Ag-Au alloy layers are directly electrodeposited on electrode surfaces and then

transferred to a concentrated nitric acid to dissolve Ag to produce NPG surfaces.¹⁰⁾ In addition to the apparent simplicity in the fabrication steps, this method offers an important advantage for electroanalytical applications because the fine control of surface structures of NPG is possible by changing various electrochemical parameters during the electrodeposition of Ag-Au layers. Recently we have showed that the surface structure of NPG electrodes can be finely tuned by controlling the deposition charges during the formation of Ag-Au layers, which in turn regulates the electrocatalytic activity of glucose oxidation.¹¹⁾

In this work, we investigated the electrocatalytic reduction of hydrogen peroxide (H_2O_2) at NPG electrode surfaces. The surface structure of NPG was controlled by changing the composition and total charge of electrodeposition for the formation of Ag-Au layers on Au electrodes. The dependence of electrocatalytic activities toward the reduction of H_2O_2 on the surface structures of NPG was examined by cyclic voltammetric methods, based on which the amperometric detection of H_2O_2 was demonstrated.

2. Experimental Section

All solutions were prepared using purified water (Milli-Q, 18.2 $\text{M}\Omega\cdot\text{cm}$). $\text{KAg}(\text{CN})_2$, $\text{KAu}(\text{CN})_2$, and Na_2CO_3 were obtained from Aldrich and H_2O_2 was obtained from Junsei. H_2SO_4 was obtained from Merck and a 0.1 M solution was

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used as a supporting electrolyte. Electrochemical measurements were conducted using a BAS 100B (Bioanalytical Systems) and the solution was purged with nitrogen prior to use. Pt wire and Ag/AgCl electrodes (3 M KCl) were used as counter and reference electrodes, respectively. Scanning electron microscopy (SEM) characterization was performed using a LEO 1530 Field Emission SEM (Carl Zeiss) with an acceleration voltage of 5 kV.

Au films evaporated onto silicon (Au/Si) wafers (KMAC, Korea) were employed as substrates and cleaned for 1 min in piranha solution. The Ag-Au alloy layers were electrodeposited on the cleaned Au/Si surfaces from solutions containing 15 mM $\text{KAu}(\text{CN})_2$ and various concentration of $\text{KAg}(\text{CN})_2$ in 0.25 M Na_2CO_3 supporting electrolytes such that the concentration ratios of $\text{KAu}(\text{CN})_2$ over $\text{KAg}(\text{CN})_2$ were adjusted from 1 : 1.5 to 1 : 5. A constant potential of -0.95 V was applied and the deposition charge was changed to control the thickness of the Ag-Au alloy layers, which were transferred to concentrated nitric acid to selective dissolution of Ag.¹⁰ The prepared NPG electrode was confined in a Viton O-ring with an inner diameter of 2.9 mm and used as a working electrode.

3. Results and Discussion

3.1. Electrocatalytic reduction of H_2O_2 at NPG surfaces

Fig. 1(A) shows cyclic voltammograms of bare Au and NPG surfaces prepared from solutions containing 15 mM $\text{KAu}(\text{CN})_2$ and 30 mM $\text{KAg}(\text{CN})_2$ measured in 10 mM $\text{H}_2\text{O}_2 + 0.1$ M H_2SO_4 solutions. On bare Au surfaces, no discernible faradaic current for H_2O_2 reduction was observed down to -0.4 V, and a further potential excursion in the negative direction resulted in the hydrogen evolution. On the other hand, a significant cathodic current was measured at NPG surfaces, indicating that the NPG surfaces are electrocatalytically active for H_2O_2 reduction. A typical SEM image of NPG surfaces obtained with a deposition charge of 0.03 C during Ag-Au alloy layer formation steps is shown in the inset of Fig. 1(A). Erlebacher and co-workers also reported that NPG surfaces reduce oxygen via a 4-electron route consisting of a first 2-electron reduction of oxygen to hydrogen peroxide, followed by a second 2-electron catalytic reduction of hydrogen peroxide to water.¹² As the total deposition charge increases, the peak potential gradually shifts in the positive direction and the overall current level increases. This means that NPG surfaces prepared with higher deposition charges becomes more active for H_2O_2 electroreduction. The increase of current level for H_2O_2 reduction

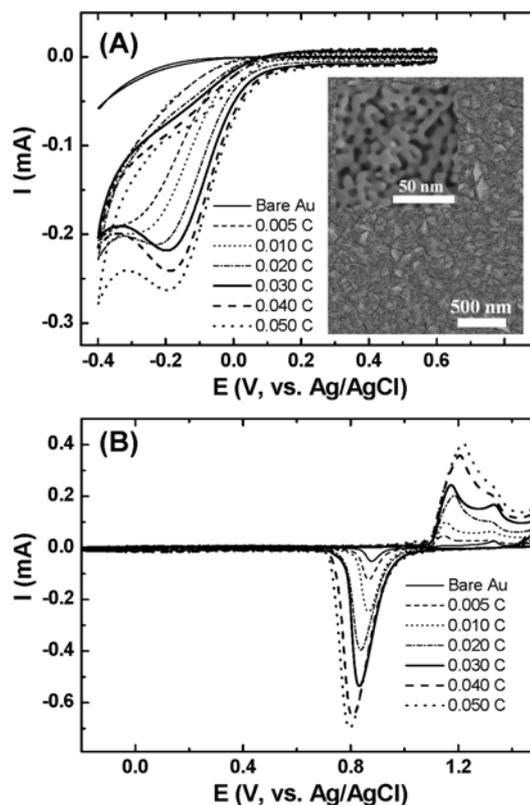


Fig. 1. Cyclic voltammograms of bare Au and NPG surfaces obtained in solutions containing (A) 10 mM $\text{H}_2\text{O}_2 + 0.1$ M H_2SO_4 and (B) 0.1 M H_2SO_4 . Scan rate: 50 mV s^{-1} . The Ag-Au alloy layers were electrodeposited from solutions containing 15 mM $\text{KAu}(\text{CN})_2$ and 30 mM $\text{KAg}(\text{CN})_2$ (conc. ratio = 1 : 2) in 0.25 M Na_2CO_3 with various total deposition charges during the formation of Ag-Au alloys. Inset shows a typical SEM image of NPG surfaces with a deposition charge of 0.03 C.

can be ascribed to the increase of electrochemical surface area (ESA) at NPG surfaces prepared with higher deposition charges. Fig. 1(B) shows the cyclic voltammograms of NPG surfaces in the Au oxide formation and dissolution region, where the cathodic peak current at around 0.8 V increases. This indicates that the ESA of NPG surfaces becomes larger as the deposition charge increases.

Fig. 2 reveals more detailed aspects regarding on the effect of deposition charge on the electrocatalytic activity of NPG surfaces toward H_2O_2 reduction. The ESAs of NPG surfaces were estimated from Fig. 1B by integrating the charge consumed for the reduction of the surface oxide monolayer,¹³ which were normalized with respect to the ESA of bare Au surfaces. As shown by the filled circles in Fig. 2, relative ESAs of NPG surfaces linearly increase with

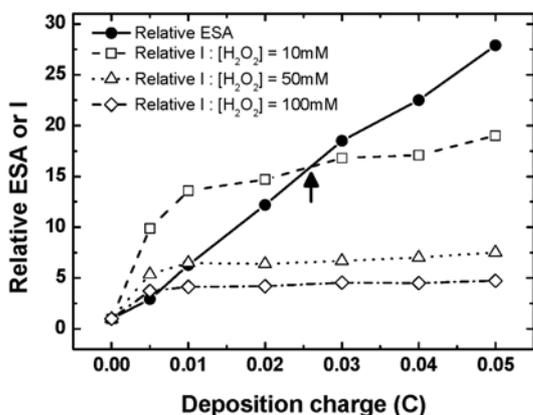


Fig. 2. Relative electrochemical surface area (ESA) or cathodic current for H_2O_2 reduction measured on NPG surfaces as a function of the deposition charge during the formation of Ag-Au alloy layers. The Ag-Au alloy layers were electrodeposited from solutions containing 15 mM $KAu(CN)_2$ and 30 mM $KAg(CN)_2$ (conc. ratio = 1 : 2) in 0.25 M Na_2CO_3 .

deposition charge. Fig. 2 also shows that the current level for H_2O_2 reduction rapidly increases up to around 0.01 C of deposition charge, and thereafter the rate of increase slows down. We have recently reported a similar result for glucose electrooxidation on NPG surfaces, where we ascribed this behavior to the fact that diffusion layer of glucose cannot fully penetrate through all the pores in NPG surfaces with higher ESA.¹¹⁾ At higher concentrations of H_2O_2 , the relative cathodic current level for H_2O_2 reduction on NPG surfaces compared to that on bare Au surfaces became smaller. This might be due to the fact that a higher concentration of H_2O_2 forms a thicker diffusion layer, which results in the less efficient usage of the NPG surfaces.

3.2. Effect of the composition of electrodeposition solution on electrocatalysis

We next examined the effect of composition of $KAu(CN)_2 + KAg(CN)_2$ solutions for electrodeposition of Ag-Au layers on the electrocatalysis toward H_2O_2 reduction. The solid lines in Fig. 3 show that the relative ESAs of

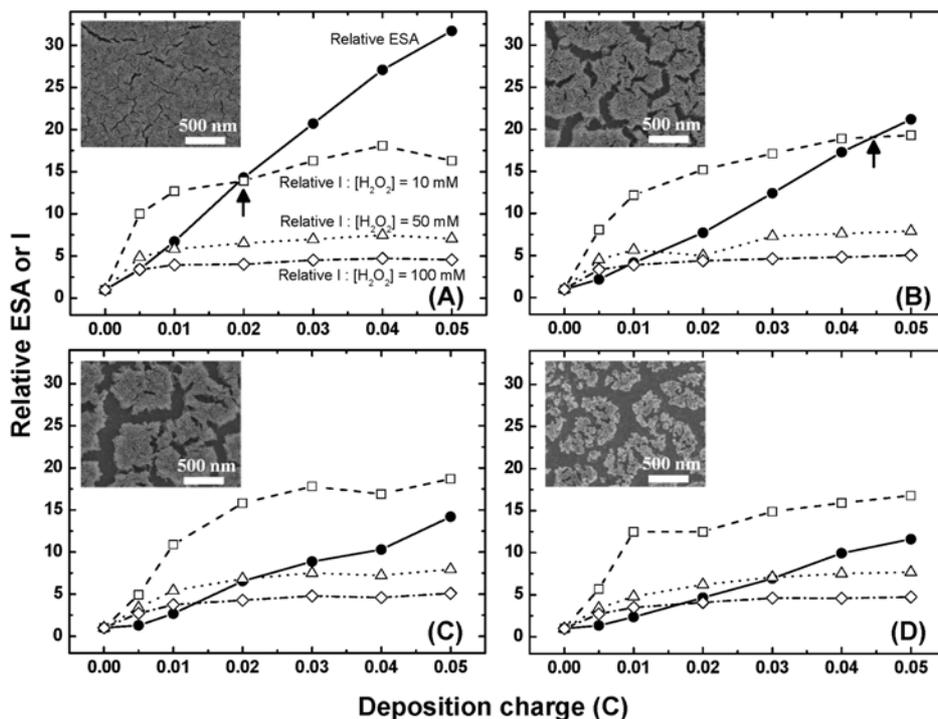


Fig. 3. Relative electrochemical surface area (ESA) or cathodic current for H_2O_2 reduction measured on NPG surfaces as a function of the deposition charge. The Ag-Au alloy layers were electrodeposited from solutions containing 15 mM $KAu(CN)_2$ and (A) 22.5 mM, (B) 45 mM, (C) 60 mM, and (D) 75 mM $KAg(CN)_2$ in 0.25 M Na_2CO_3 . The concentration ratios of $KAu(CN)_2$ over $KAg(CN)_2$ are (A) 1 : 1.5, (B) 1 : 3, (C) 1 : 4, and (D) 1 : 5. Insets show typical SEM images of NPG surfaces with a deposition charge of 0.03 C at each concentration ratio.

NPG surfaces linearly increase with deposition charge for all of the solution compositions. As the concentration ratios of $\text{KAu}(\text{CN})_2$ over $\text{KAg}(\text{CN})_2$ increases from 1 : 1.5 to 1 : 5, the relative ESA gradually decreases. This can be explained by the SEM images of NPG surfaces (insets in Fig. 3) that the nanoporous domains decrease at higher concentration ratios. The dependence of cathodic currents for H_2O_2 reduction on the deposition charge exhibits a similar trend as shown in Fig. 2. Interestingly, the cathodic currents for H_2O_2 reduction were maintained at virtually same level for concentration ratios between 1 : 1.5 and 1 : 4 despite the decrease of ESA of NPG surfaces. The decrease of cathodic currents in the case of 1 : 5 concentration ratio (Fig. 3(D)) might be due to the apparent collapse of nanoporous structures.

It is noteworthy to consider the catalytic efficiency of NPG surfaces toward H_2O_2 electroreduction compared to that of a bare Au surface in terms of the cathodic current per unit ESA. Fig. 2 shows that the relative ESA curve (solid line) and the relative current curve (dashed line for 10 mM H_2O_2 case) cross at the deposition charge of ~ 0.025 C (noted as an arrow). This means that the NPG surfaces prepared with deposition charges less than 0.025 C produce higher cathodic currents than those expected from the increase of ESA. For example, the NPG surface with 0.01 C of deposition charge has 6 times larger ESA than a bare Au surface, while the current at NPG surface is 14 times larger than that observed on the bare Au surface. However, after 0.025 C of deposition charge, the NPG surfaces do not utilize all the increased ESA for electroreduction of H_2O_2 . If we consider the crossing points between the relative ESA and cathodic current (arrows in Fig. 2 and Fig. 3), the position of the crossing points becomes greater as the concentration ratios increases. For the NPG surface with a concentration ratio of 1 : 4 (Fig. 3C), the relative cathodic currents are always higher than the relative ESA up to 0.05 C of deposition charge, indicating all the increased ESA introduced by NPG formation is utilized for electroreduction of H_2O_2 and this NPG surface shows higher catalytic efficiency than other NPG surfaces in terms of the cathodic current per unit ESA.

3.3. Amperometric detection of H_2O_2 at NPG surfaces

Because the NPG surfaces show electrocatalytic activity toward H_2O_2 , we performed the amperometric detection of H_2O_2 on NPG surfaces. Although the electrocatalytic efficiency is better at NPG surfaces with higher concentration ratios, the absolute current level is more important in amperometric detection. In this regard, the NPG surfaces

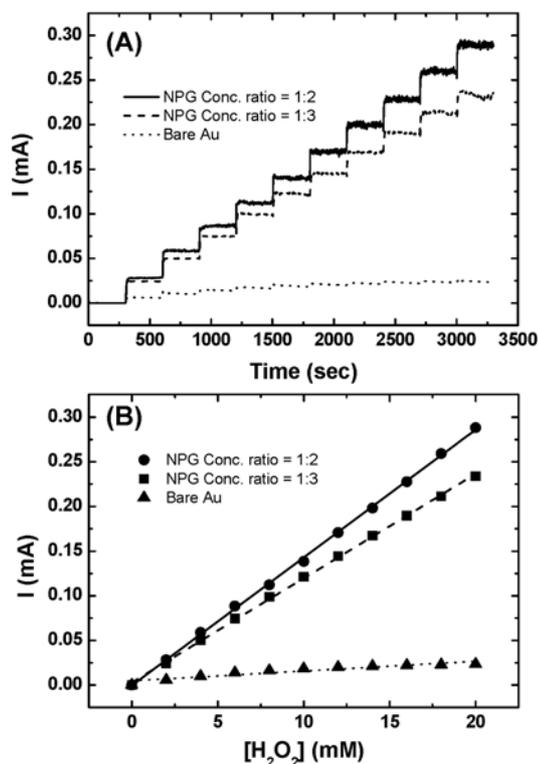


Fig. 4. (A) Amperometric responses of bare Au and NPG surfaces with a successive addition of 2 mM H_2O_2 in 0.1 M H_2SO_4 electrolyte solutions at -0.2 V. NPG surfaces were prepared with a deposition charge of 0.05 C. (B) Calibration plots obtained from (A).

with concentration ratios of 1 : 2 and 1 : 3 were chosen for the amperometric detection. Fig. 4(A) shows amperometric responses of bare Au and NPG surfaces with a successive addition of 2 mM H_2O_2 in 0.1 M H_2SO_4 electrolyte solutions. The applied potential on electrode surfaces is -0.2 V, at which potential negligible amperometric responses are observed on a bare Au surface. On the other hand, NPG surfaces exhibit sensitive amperometric responses upon the addition of H_2O_2 . Fig. 4(B) shows calibration plots obtained from the amperometric responses, where NPG surfaces exhibit an order of magnitude larger sensitivity than a bare Au surface. Considering the amperometric detection of H_2O_2 is important in many bioanalytical applications such as glucose sensors, we expect the NPG surface can be utilized in other electroanalytical fields.

4. Conclusion

Electrocatalytic reduction of H_2O_2 at nanoporous gold

(NPG) surfaces prepared by electrodeposition of Ag-Au alloy layers followed by the selective dissolution of Ag was examined. We found that the NPG surfaces are electrocatalytically active for H_2O_2 reduction compared to bare Au surfaces and the activity depends on the conditions of electrodeposition for Ag-Au layers such as the concentration ratios of $KAu(CN)_2$ over $KAg(CN)_2$ and deposition charges. NPG surfaces prepared with higher concentration ratios showed better electrocatalytic activity in terms of the cathodic current per unit ESA. The NPG surfaces exhibited sensitive amperometric response for H_2O_2 reduction, from which calibration plots with higher sensitivity than a bare Au surface were obtained. The unique electrocatalytic reduction of H_2O_2 at NPG surfaces may find applications in other electrochemical area.

Acknowledgements

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