Electrochemical Surface Plasmon Resonance Measurement of Electrocatalytic Oxidation of Glucose on Gold Electrode

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The electrochemical reaction of glucose on a thin gold film electrode was investigated using the surface plasmon resonance (SPR) method. A cyclic voltammogram of glucose on a thin gold film electrode showed anodic current in both anodic and cathodic scans. The potential dependence of the refractive index change was simultaneously measured by SPR and showed that the change in the gold electrode surface status switched the catalytic reaction. In addition, a potential step experiment revealed that the SPR signal showed the underlying electrode status whereas the electrode current showed the overall catalytic oxidation of glucose.

**Key Words**: Surface Plasmon Resonance, Glucose, Gold, Electrocatalysis

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1 Introduction

The performance of electrochemical sensors is strongly influenced by the electrode material and surface conditions. Therefore, it is important to monitor the surface status under experimental conditions with a view to realizing reproducibility and better performance. For example, electrochemical oxidation can be used for detection in sugar analysis. Gold, copper, nickel, and mercury exhibit catalytic activity for the oxidation of sugar. The glucose oxidation rate on a gold electrode is greatly influenced by the electrolyte, crystal orientation, and the oxidation states of the gold and the adsorbed anions. The oxidation mechanism has been investigated by voltammetry and spectroscopy and it is reported that the adsorbed anions catalyze the oxidation of glucose and the gold oxide inhibits this reaction.\textsuperscript{[1–5]} When analyzing the electrochemical glucose reaction, it is desirable to monitor the electrode status in-situ and in real-time without disturbing the surface condition and diffusion of bulk species. Adsorption spectroscopy combined with electrochemical methods have been used for analyzing the surface species. Spectroscopy uses the imaginary part of the refractive index or dielectric constant and can be used to identify the molecular species, but the sensitivity is insufficient for transparent molecules. The real part of the refractive index can be used to quantify a transparent species on a surface. Surface plasmon resonance (SPR) has been used to measure small changes in real part of refractive index. SPR is now widely used for monitoring biological intermolecular interactions.\textsuperscript{[5]} SPR gives the refractive index of the thin gold film surface within a few hundred nm from the surface depending on the wavelength and refractive index of the prism being used. The sensitivity as regards a refractive index change is high enough to allow us to detect the sub-monolayer adsorption of small molecules. When an electrode surface is modified with redox active molecules, the potential dependent change in the redox state and the induced change of density (conformation) can be measured by SPR.\textsuperscript{[5–9]} The SPR configuration has many advantages for in-situ electrochemical experiments. An inert gold thin film electrode is used as a working electrode and this electrode is easily modified with thiole-terminated functional molecules. The optical path does not go through the solution, therefore the electrochemical cell can be designed freely. It has been shown that SPR measurement of a gold surface under electrochemical conditions reflects the surface state with high potential resolution, and the quantitative relation was obtained as a current measurement as in cyclic voltammetry (CV).\textsuperscript{[10–12]}

In this work, we used this technique to analyze the electrocatalytic oxidation of glucose and we were able to measure the catalytic reaction from the current and surface status separately by SPR.

2 Experimental

We measured the refractive index as the SPR reflection minimum angle (SPR angle) in the Kretschmann configuration optical setup as previously described.\textsuperscript{[10]} We used an LED light source (870 nm). The electrochemical cell was mounted on the surface of a BK7 cylindrical prism. A sputtered gold thin film on BK7 glass was used as the working electrode. Titanium was used as an adhesion layer. The thickness of the metal layer was 45 nm, which gave the best signal to noise ratio for the SPR angle measurement at 870 nm. An electrochemical experiment was conducted with the gold thin film electrode as a working electrode and a platinum counter electrode. A KCl saturated Ag/AgCl reference electrode was used and all the potentials in this report refer to this electrode. A HECS 990 potentiostat (Fuso, Kawasaki) and a digital recorder were used to synchronize the voltam-
Fig. 1 Cyclic voltammograms (CV) (upper panel) of a gold thin film electrode deposited on a BK7 substrate, and the potential dependence of the SPR signal (lower panel) measured simultaneously with CV. The solid lines indicate the presence of 0.5 mM glucose in 0.1 M phosphate buffer pH 6.8. The dotted lines indicate results obtained in phosphate buffer. The scan rate was 2 mVs⁻¹.

metry and the SPR measurement data. d-Glucose was obtained from Kanto Chemical (Tokyo), and the other chemicals were of the highest grade available.

3 Results and Discussion

The glucose was oxidized above 0.1 V in the anodic scan on the thin film gold electrode and this current was suppressed above 0.4 V as shown in Fig. 1. Simultaneously measured SPR angle shift showed large and staircase like increase in the higher potential range (0.7 to 1.3 V). This corresponds the stepwise oxidation of gold. The observed current response for glucose is the same as previously reported for bulk electrodes. In the cathodic scan, a positive current was observed. Also a positive current was observed in the anodic scan in the same range. These were common responses of the gold surface to glucose oxidation. Because this reaction occurred in a limited potential range, and the species adsorbed on the gold electrode is potential dependent, the catalysis would be facilitated by adsorbed species, such as hydroxide. The potential dependent change of the adsorbed species can be monitored as refractive index change of the surface. This potential dependent change of the gold surface was observed from simultaneously measured SPR as shown in Fig. 1 lower panel.

Fig. 2 Chronoamperometry (upper panel) of 24 mM glucose in 0.1 M phosphate buffer on a gold thin film electrode and the simultaneously measured SPR angle shift (lower panel). The potential was stepped from 0.2 V to 0.6 V at time zero and back at T = 0.5.

Although the current responses were totally different with presence and absence of glucose, the SPR signals were almost same for both conditions. Therefore the SPR signal reflected the surface state of the gold electrode even though the glucose oxidation was in progress. The refractive index difference between glucose and its oxidized form will not be as large as difference of an ion complex because the reaction involves the transfer of hydrogen, and their spectra are transparent. Also the glucose and gluconolactone charges are the same, and counter ion relocation would not occur during the oxidation, therefore the refractive index change after the reaction will be small compared with the reaction on typical redox molecules, and other ion complexes involving a center metal charge change.

In the potential range over 1.2 V, a small SPR angle shift and a large current increase was observed. This reaction is a electrochemical reaction of water. The refractive index change of this reaction will be small as for the glucose. The SPR signal exhibited a large change at 0.45 V and a kink at 0.3 V. It is expected that the adsorbed species replaced at this potential. The glucose oxidation current was observed below 0.4 V, and the positive current peaks were observed around 0.3 V in both scan directions. Therefore, the observed refractive index reflected the catalytic ability of gold surface. In other word, we can observe the switching of the catalysis by SPR.
We carried out a potential step experiment to determine the glucose oxidation effect on SPR in more detail (Fig. 2). The potential was stepped between 0.2 V and 0.6 V. At these potentials, the glucose oxidation was suppressed in CV. In the voltammogram shown in Fig. 2, the current responses were almost the same with or without 24 mM of glucose, therefore the oxidation current was not observed. The SPR signal was different under these conditions because the glucose solution had a higher refractive index. However, the time courses of the SPR angle change were the same regardless of the glucose concentration. In the oxidation step, the SPR angle increased and it took 200 ms to reach a steady state. It took less than 10 ms to restore the original SPR angle level in the reduction step. Because oxidation was not observed from the current response and the SPR signal showed the potential dependent refractive index change, the SPR signal under these conditions showed the surface status of the gold electrode. As the oxidation reaction would involve the reconstruction of the adsorbed molecules and the reduction step would involve the random removal of the adsorbed molecules, the observed relative reaction rate was faster during reduction than oxidation.

4 Conclusion

We analyzed glucose oxidation by using electrochemical SPR measurements. The current signal showed the overall catalytic reaction and the SPR signal showed the underlying status of the gold surface. Although electrochemical measurements are relatively easy and can be carried out at a small cost, it is not very easy to investigate the in situ status of the surface. As SPR measurements are relatively easy to perform and the setup is simple, this method can assist in situ analysis of many electrochemical processes.

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References