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Self-Powered Hydrogen Peroxide Sensor and Its Biosensor Application

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Abstract

Simple and robust properties are the important aspects for biosensing chip. The combination of Prussian blue modified Au and Pt electrodes produces an electric current by H_2O_2 in the solution. We fabricated an interdigitated microarray electrodes using this combination (Au/PB-Pt IDEs) which showed a linear current generation to H_2O_2 concentration. The glucose oxidase (GOx) immobilized Au/PB-Pt IDEs exhibited a glucose sensor action in which the H_2O_2 produced by GOx's enzymatic reaction was detected through the IDEs. The phenomenon demonstrated that oxidative enzyme immobilized Au/PB-Pt IDEs provides a simple amperometric biosensor without an external potential source nor a reference electrode.

1. Introduction

H_2O_2 is a common product of general oxidative enzymes. Many biosensors based on oxidative enzymes detect H_2O_2 for the evaluation of substrates (analytes) concentration. For this detection, amperometry measurement with the three electrode system (working, counter and reference electrodes) is commonly used experimental setup, where a constant potential (approx. 0.6 V vs Ag/AgCl) is applied to the working electrode versus the reference electrode then the oxidation current between the sensing electrode and the counter electrode is measured [1]. This current is related to the H_2O_2 production, thus the analyte concentration can be estimated. Although this method is very classical way, many biosensors still employ the same principle (e. g. glucose, cholesterol, and lactic acid sensors) [2]. Accordingly improvement of H_2O_2 detection is crucial for biosensor field.

Simple and robust properties are important aspects for biosensing chips. The above mentioned amperometry measurement, however, requires a complicated experimental parts such as potentiostat and the reference electrode. Therefore, several types of self-powered biosensors were developed that generated electrical power proportionally to the concentration of the analyte. Since self-powered biosensor only requires a simple two electrode system together with an ammeter for current measurement [3]. To improve the sensitivity, one may also fabricate a chip type biosensor based on IDEs (interdigitated electrodes) design for this simple system, because it is well known that a large enhancement of electrochemical reaction at the narrow electrode gap can be obtained for IDEs [4].

In this study, we fabricated intergiditated electrodes of Au and Pt (Au-Pt IDEs) consisting a series of parallel microband electrodes. After an electrodeposion of Prussian blue ($Fe^{III}_4[Fe^{II}(CN)_6)]_3$) on the Au electrode forming Au/PB-Pt IDEs, a spontaneous electrical current generation between Au/PB and Pt electrodes was observed under a H_2O_2-containing solution. Mechanism of current generation was investigated and characterizations of H_2O_2 response current were performed. In addition, we immobilized glucose oxidase (GOx) on Au/PB-Pt IDEs and observed current generation depending on the glucose concentration.

2. Experimental and results

Au-Pt IDEs (157 pairs of fingers, 10 μm periodicity, 7 mm length) was fabricated on a glass plates (1×2×0.05 cm) using photolithography technique. Electrodeposition of PB on the Au electrode was carried out with a cyclic voltammetric condition (0.35-0.75 V vs. Ag/AgCl, 100 mV/sec, 30-70 cycles) in a growing solution (1 mM $K_3[Fe(CN)_6]$ and 1 mM $FeCl_3$ in a mixture of 0.1 M HCl and 0.1 M KCl). Fig. 1 shows a laser scanning image of 70 cycle sample. The green colored PB thin layer was grown on the Au electrode. The size of deposited PB clusters was confirmed 200 - 500 nm by scanning electron microscope.

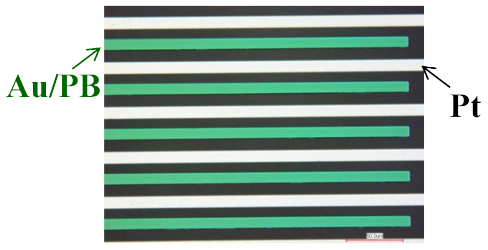

Fig. 1 A laser scanning image of Au/PB-Pt IDEs.

A short-circuit electric current was monitored for the water-immersed sample under the successive injection of a H_2O_2 solution. As shown in Fig. 2, the short-circuit current

increased at the each moment of injection, which demonstrates that a current is certainly generated by H_2O_2 introduction. The calibration curve derived from the amperometric result is shown in Fig. 3. A linear relationship between the H_2O_2 concentration and current density was observed below the range of 0.2 mM.

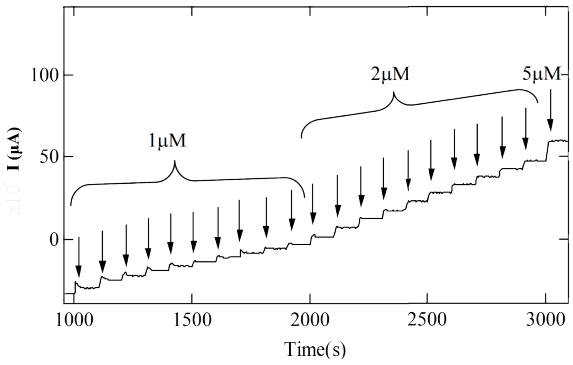

Fig. 2 Current response of Au/PB-Pt IDEs to H_2O_2 injections. Arrows indicate the timing of H_2O_2 injections with the amount corresponding to increase the indicated concentrations.

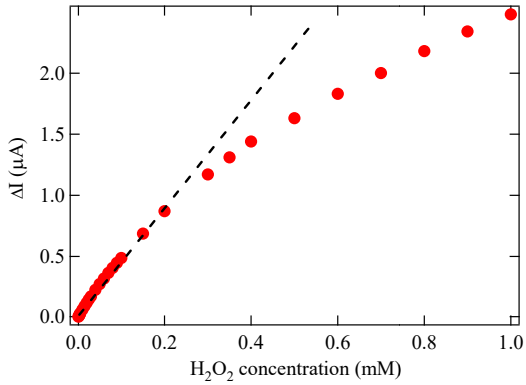

Fig. 3 Calibration curve for the Au/PB-Pt IDEs.

Fig. 4 illustrates the mechanism involved in detection of H_2O_2 by Au/PB-Pt IDEs. This is based on an electrocatalytic conversion of H_2O_2 to H_2O and 1/2 O_2. During this reaction the Gibbs free energy is decreased (-206 kJ/mole of O_2 produced), which corresponds to the driving force of current production [5]. At the Pt cathode side, two protons and O_2 are generated by oxidation of H_2O_2. These protons are consumed by the reductive reaction of H_2O_2 on the PB anode side.

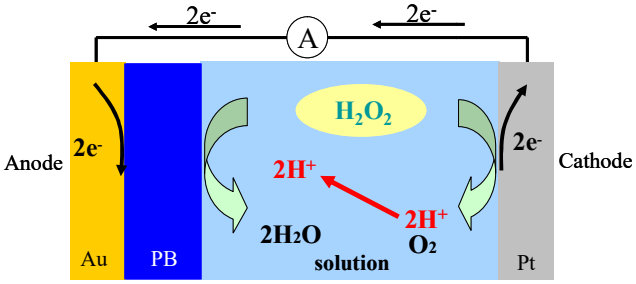

Fig. 4 Mechanism of current generation by H_2O_2.

H_2O_2 is the common product of oxidative enzyme family. The combination of Au/PB-Pt IDEs and oxidative enzyme will provide the simple sensor system. To demonstrate this idea, we immobilized GOx through the cross-linking with glutaraldehyde. Fig. 5 shows the amperometric response of GOx immobilized Au/PB-Pt IDEs to glucose injections. Occurrence of current generation by glucose is clearly revealed. This phenomenon indicates that H_2O_2 was produced through the enzymatic reaction of GOx, then the H_2O_2 generated the electric current through the reaction on Au/PB-Pt IDEs. The analytical curve of current versus glucose concentration confirms the linear range below 5 mM.

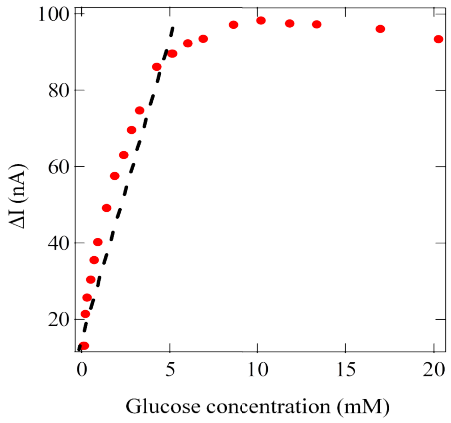

Fig. 5 Calibration curve of the GOx immobilized Au/PB-Pt IDEs.

3. Conclusions

Selective PB deposition on the Au surface of Au-Pt IDEs was successfully carried out by electrodeposition. The obtained Au/PB-Pt IDEs revealed current generation between the Au/PB and Pt electrode by H_2O_2 injection. The calibration plot demonstrated that Au/PB-Pt IDEs produced a current linearly below 0.2 mM H_2O_2 concentration range. This phenomenon can be applied to the fabrication of a simple and robust biosensor based on amperometry. The idea was examined using the GOx immobilized Au/PB-Pt IDEs. We found that GOx immobilized Au/PB-Pt IDEs exhibited a clear amperometric response upon glucose injection. This result indicates that Au/PB-Pt IDEs can be used as a simple amperometric biosensor without the requirement for a potential source or a reference electrode. Finally, this study was supported by NIMS Nanofabrication Platform in Nanotechnology Platform Project sponsored by MEXT.

References

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