Pt ad-Atom Modified Au Electrode Prepared by Using Ionic Pairing of PtCl₆²⁻ with Cationic SAM Hideaki Kusuda, Hiroyuki Hanazono, Katsuhiko Nishiyama, and Isao Taniguchi Department of Applied Chemistry and Biochemistry, Kumamoto University 2-39-1, Kurokami, Kumamoto 860-8555, Japan

Introduction

Recently, ad-atom modified electrodes were studied extensively from both basic and applied aspects. Here we will report a new technique to prepare ad-atom modified electrodes by using ion-pair of cationic SAM with anionic metal complexes. This technique is schematically shown in Fig. 1. The prepared Pt/Au electrodes were used for catalytic oxidation of sugar and reduction of oxygen.

Experimental

Gold disk and plate electrodes were used as working electrodes for cyclic voltammetry and XPS, respectively. Pt plate and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. 4-pyridinethiol (4-PySH) was used as a modifier. Cyclic voltammetry was carried out using a BAS 50 W electrochemical analyzer.

Results

Elements on the surface determined by XPS were summarized in Table 1. At step 2, the surface concentration of N was almost equal to that of S, indicating 4-PySH was immobilized on the Au surface. At step 3, the ratio of N to Pt was almost 2:1, which suggests that at the electrode surface two 4-PySH molecules form ionic pair with one $PtCl_6^{2-}$ ion. Fig. 2a shows CVs of glucose oxidation in an alkaline solution. At a bare Au electrode, oxidation of glucose started around -0.5V. At the Pt/Au electrode the oxidation potential was shifted forward to negative direction by ca. 0.1 V, and the oxidation current became higher than at an Au electrode, showing on a Pt/Au electrode higher catalytic activity.

On the other hand, at a Pt/Au electrode, reduction of oxygen current was larger than that at an Au electrode, but smaller than at Pt electrode. We succeeded in prepare the Pt/Au having catalytic ability for oxidation of glucose and reduction of oxygen.



Fig.1. Schematic representation of new preparation method of Pt modified Au electrode

Table 1. XPS data for surface elements

sample	Elements (%)				
	Au(4f)	Pt(4f)	N(1s)	S(2p)	Cl(2p)
step2	78.04	-	10.95	11.01	-
step3	77.66	1.83	7.25	7.41	5.85
step4	64.95	3.9	15.35	8.37	7.43
step5	81.09	2.98	6.83	4.68	4.42



Fig. 2(a) Oxidation of glucose(10mM) in 0.1M NaOH,and (b) Reduction of O_2 in 0.1 M NaOH.(Pt/Au : _______; Au : - - - - - ; Pt : ______)