

Preparation and Characterization of Pt Ad-Layer on Au Electrode Using Ionic Pair of Cationic SAM with  $\text{PtCl}_6^{2-}$   
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## 1. Introduction

The purpose of this study is developing the new method to prepare the Pt ad atom on Au electrode using an ion pair of the cationic SAM with anionic metal complexes. The procedure for preparation was schematically shown in Fig. 1. In this paper the effect of the chemical structure SAM on Pt ad-layer was discussed.

## 2. Experimental

Structures of four thiols or disulfide studied, together with estimated surface structures at an Au electrode were shown in Fig. 2. 2- and 4-pyridinethiol (2-PySH, 4-PySH) were purchased from Tokyo Kasei Co., (Tokyo Japan) and used as received. 5,5'-pyrimidinedisulfide (5,5'-PymSSPy) and 2-mercaptopyrazine (2-PyZSH) were synthesized and identified by NMR and elemental analysis. Cyclic voltammetry was performed on a BAS 50 W electrochemical analyzer. A gold disk electrode polished with 0.3  $\mu\text{m}$  of aluminum powder was used as a working electrode. A Pt plate and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The gold disk electrode was modified with thiol and the prepared thiol-modified electrode was dipped into in 10 mM  $\text{H}_2\text{PtCl}_6$  / 0.1 M  $\text{H}_2\text{SO}_4$  for 20 min and rinsed with 0.1 M  $\text{H}_2\text{SO}_4$ .

## 3. Results and discussion

Fig. 3 shows that Cyclic voltammograms (CVs) in 0.1 M  $\text{H}_2\text{SO}_4$  obtained at various electrodes. Since hydrogen overpotential of Au is higher than that of Pt, at an Au electrode no reduction wave was observed in this scan region (Fig. 3(a)). In contrast, at a Pt/4-PySH/Au electrode (Fig. 1(b)), clear reduction wave of  $\text{H}^+$  was observed at  $-0.35$  V. This means that Pt was deposited on the electrode surface and acted as a catalyst for  $\text{H}_2$  evolution. In addition, after reductive desorption of 4-PySH (shown in Fig. 1(c)), the reduction wave shifted positively and the reduction current increased compared with the curve (b). Although the current for desorption of  $\text{H}_2$  was less than that on pure Pt plate (Fig. 3(d)), the clear desorption current of  $\text{H}_{\text{ad}}$  was observed in Fig. 3(c).

In order to control the amount of deposited Pt, similar experiments using 2-PySH, 2-PyZSH, and 5,5'-PymSSPy were carried out. The charges for  $\text{H}_{\text{ad}}$  desorption obtained at Pt-modified Au electrodes were summarized in Table. 1. The desorption charge depended on the structure of modifier used. When 5,5'-PymSSPy was used as a modifier, the charge was 84 % of that at Pt disk electrode, while only 32 % when 2-PySH was used.

By this technique Pt ad-layer on the Au polycrystal electrode was shown to be deposited and the amount of ad-atom was controlled by selecting the modifier for the SAM.

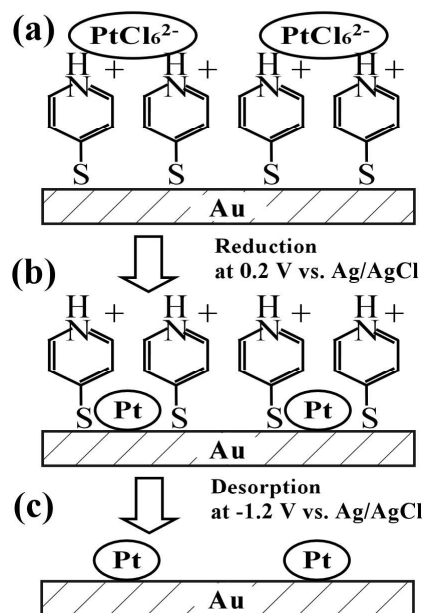


Fig. 1. Schematic representation for preparation of metal monolayer using self-assembled-monolayer (SAM) of 4-PySH

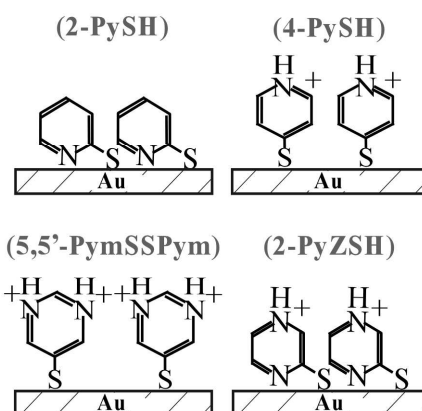


Fig. 2. Possible structure of modified electrodes

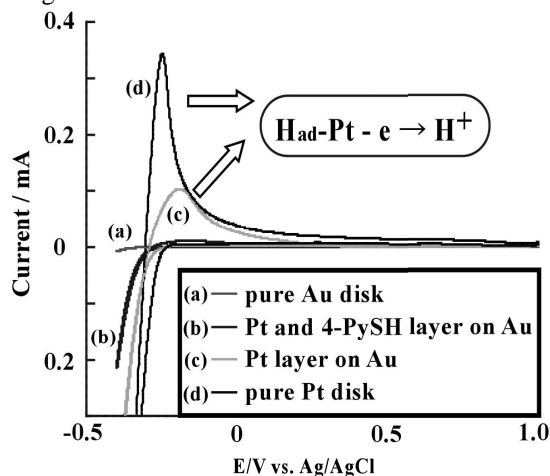


Fig. 3. Cyclic voltammograms in 0.1 M  $\text{H}_2\text{SO}_4$ . Scan rate : 50 mv/s

Table 1. Charge for desorption of hydrogen obtained from cyclic voltammograms in 0.1 M  $\text{H}_2\text{SO}_4$  at Pt-modified Au electrodes prepared by the method shown in Fig. 1.

Pure Pt Disk electrode		$6.2 \times 10^{-4}$ C (100 %)	
$2.0 \times 10^{-4}$ C (32 %)	$3.0 \times 10^{-4}$ C (48 %)	$4.3 \times 10^{-4}$ C (70 %)	$5.2 \times 10^{-4}$ C (84 %)