# Preparation and Characterization of Metal Monolayer Prepared by Using Ionic Pair of Anionic Self-assembled Monolayer with Cationic Metal Ammine Comlex

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## 1. Introduction

In recent years various types of ad-atom electrodes were studied from view points of understnnding the deposition process and application to catalytic reactions.In this paper we will report that characterization and preparation of metal monolayers prepared by using ionic pair of cationic metal ammine complexes with a 3-mercaptopropionic acid (MPA) SAM. The schematic representation for preparation of metal monolayer was shown in Fig. 1.

## 2. Experimental

Au (111) single crystal electrodes were prepared by the flame annealing method. $[Ag(NH_3)_2]$/MPA modified Au(111) and $[Cu (NH_3)_4]$ / MPA / Au (111) electrodes were prepared by dipping the MPA - modified Au (111) electrode into 10 mM $Ag_2SO_4$ or $CuSO_4$ solution containing 50 mM $NH_3$ for 10 min, respectively. Electrochemical measurements were carried out by a BAS 50W electrochemical analyzer.

## 3. Results and discussion

Figure 2a shows a Cyclic Voltammogram(CV) for reductive desorption of a MPA-modified electrode in 50 mM $NH_3$ . A sharp peak at -0.7 V corresponds to the desorption of MPA was clearly observed. The surface excess of MPA calculated from the area of the CV was $6.2 \times 10^{-10}$ mols/cm$^2$. In contrast, as shown in Fig. 2b, the peak was shifted to – 1.1 V for $[Ag (NH_3)_2]$ / MPA electrode. This suggests that $[Ag (NH_3)_2]^+$ as a conterion for the MPA SAM was reduced to form Ag sub-mono layer under the MPA SAM, since the interaction of silver-sulfur is stronger than that of gold-sulfur. MPA was removed from the Ag/Au(111) surface 1.82 x10$^{-10}$ mol/cm$^2$, was almost 1 / 3 of full coverage during the process.

Fig. 2c shows a CV for reductive desorption of $[Cu(NH_3)_4]$/MPA. In this case, the desorption peak potential was equal to that of the MPA SAM. However, additional reversible redox waves at – 0.1 V corresponds to the reaction of $[Cu(NH_3)_4]^{2+}$ was observed. The peak current was proportional to the scan rate, which indicates that the $[Cu(NH_3)_4]^{2+}$ species were fixed to the electrode surface. Also, the observed reversible redox waves are stable for over 20 cycles between – 0.2 to 0.2 V (Fig. 2d). The surface excess of $[Cu (NH_3)_4]^{2+}$ calculated form the oxidation wave was $2.4 \times 10^{-10}$ mol / cm$^2$.

This technique can be applied to prepare various the ad-atom monolayers on polycystal gold electrodes as well.
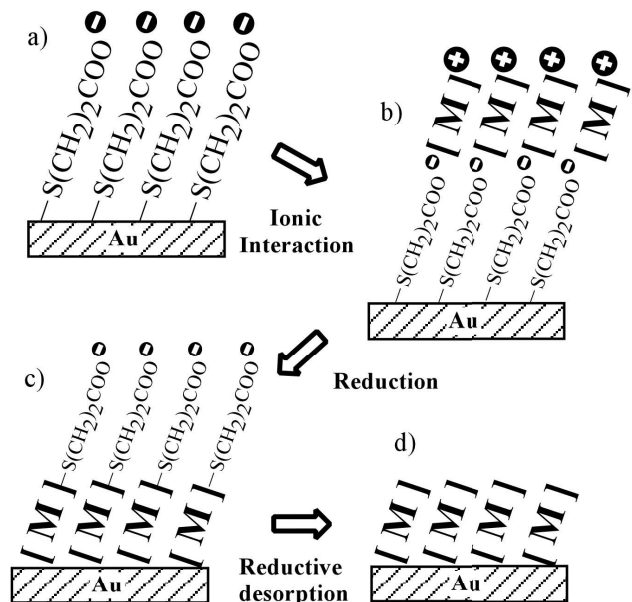


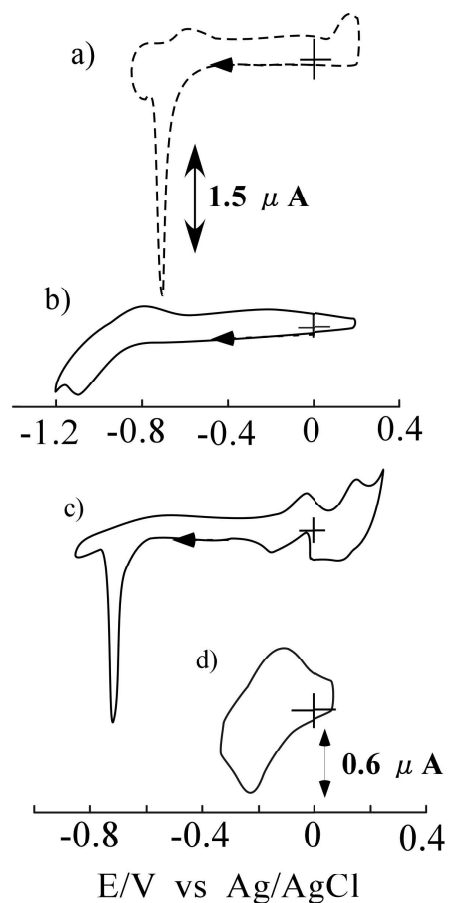Fig.1 Schematic representation for preparation of metal monolayer using MPA SAM.



Fig.2 Cyclic voltammograms of a) MPA (from +0.2 V) ,b) MPA/ [Ag(NH3)2]+ (from ＋0.15 V. ) , c) MPA/[Cu(NH3)4]$^{2+}$ (from 0 V), d) MPA /[Cu(NH3)4]$^{2+}$ (from0.05 V) on Au(111)in 50 mM NH$_3$ solution.