# Platinum Layer Formation on a Self-assembled Monolayer by Electrochemical Deposition

Deyu Qu and Kohei Uosaki*
*Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810*

(Received November 25, 2005; CL-051461; E-mail: uosaki@pcl.sci.hokudai.ac.jp)

A platinum metal-self-assembled monolayer (SAM)–gold substrate sandwich structure without a short circuit between the two metals was successfully constructed by electrochemical deposition of platinum on top of a 1,4-benzenedimethanethiol (BDMT) SAM-covered Au(111) substrate. Deposition of Pt was carried out by electrochemical reduction of Pt ions, which were adsorbed on free thiol end groups of the BDMT SAM, in a Pt ion-free sulfuric acid solution. Electrochemical measurements and X-ray photoelectron spectroscopy (XPS) showed the reduction of the adsorbed Pt ions to metallic platinum on top of the SAM. After a cathodic potential scan of the Pt–SAM–Au electrode to −1.25 V in 0.1 M KOH solution, a typical cyclic voltammogram of the Au(111) electrode was obtained, showing that the BDMT SAM was reductively desorbed with a Pt layer and that no platinum was deposited directly on the Au(111) surface.

Metal-layer formation on an organic monolayer has been an important research subject in recent years because of its connection with an attractive field of molecular electronics in which an organic monolayer will be used as electronic components. Self-assembled monolayers (SAMs) of thiols are good candidates to be used as molecular layers for this purpose because of their ease of preparation, highly ordered structure and well-documented characteristics. A metal–SAM–metal sandwich structure without a short circuit between the two metals is used to determine the electrical properties of the molecules and is also an essential component of molecule devices. However, most attempts to electrochemically deposit a metal on top of an SAM have failed.[1–13] The reasons of the failures are the existence of defect sites in the SAM and presence of metal ions in solution. Even if some metal ions are immobilized on top of an $\omega$-functional thiolate SAM, excess amounts of free metal ions in the bulk solution can still penetrate the organic film through these imperfections and metal deposition occurs underneath the SAM not on top of it. Recently, Kolb and co-workers proposed a new approach to form a metal layer on an organic surface by electrochemical reduction of Pd(II) ion pre-adsorbed on a 4,4′-dithiodipyridine-modified Au(111) surface.[14–16] In their system, however, the formed metal layer was only weakly adsorbed on the SAM.

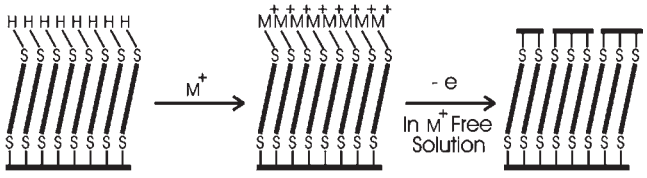


**Figure 1.** Schematic illustration of metal-layer formation on top of a SAM.

In this study, we propose another approach for metal-layer formation on top of an SAM with strong interaction between the SAM and the formed metal layer as shown in Figure 1.

At first, a Au(111) electrode was modified with a self-assembled monolayer of BDMT in a 1 mM ethanolic BDMT solution.

After a full monolayer of BDMT was formed on the Au(111) surface with a free thiol end group face up, the SAM-covered electrode was then immersed in an aqueous solution containing 5 mM of $PtCl_4^{2-}$ ions for 20 min. The Pt ions in the solution was expected to bound to free SH end groups on the SAM surface.[17–19] The presence of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks at 72.9 and 75.6 eV, respectively, and Cl2p peak at 200.1 eV in XP spectra with the relative amount of Pt and Cl of 3.8 confirmed that the platinum ions were adsorbed on the SAM in the form of platinum tetrachloride complex ($PtCl_4^{2-}$). The binding energy of Pt $4f_{7/2}$ negatively shifted from 73.4 eV of Pt $4f_{7/2}$ of $K_2PtCl_4$.[21] This suggests that Pt was coordinated with the S end group and that the oxidation state of Pt was changed from +2 to +1.[17,19] After adsorption of Pt ions, the S2p peak seemed to be broadened with decreased intensity of the peak at 164 eV and a slight shift to lower binding energy of the shoulder around 162.5 eV. This suggests that thiol was converted to thiolate after the Pt ion adsorption, indicating that the free thiol groups on the surface were coordinated with platinum complex ions.

Finally, the electrode was transferred to a platinum ion-free 0.05 M $H_2SO_4$ solution and the adsorbed Pt ions on the BDMT SAM-covered Au(111) electrode were reduced electrochemically by holding an electrode potential at +0.4 V, which is more negative than the redox potential of $PtCl_4^{2-}$/Pt (ca. +0.55 V),[20] to form a Pt layer on top of the SAM.

A cyclic voltammogram (CV) of the resulting electrode recorded in a 0.05 M $H_2SO_4$ solution was in good agreement with a typical CV of a platinum electrode with waves of adsorption and desorption of hydrogen. This proves that a platinum layer was formed. The charge associated with the desorption of hydrogen was found to be 61 $\mu C\,cm^{-2}$, which is equal to about 28% of the desorption of one full monolayer of hydrogen on a Pt surface. This is reasonable as the amount of thiolate on Au(111) surface, i.e., Pt adsorption site, is only 1/3 of the surface Au atoms of the Au(111) substrate.

XP spectra of a Pt–BDMT–Au(111) electrode showed peaks of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ at 71.7 and 75.2 eV, respectively, which are shifted from 72.9 and 75.6 eV obtained before the reduction, respectively, confirming that a metallic platinum layer was formed. The Cl2p peak totally disappeared after electrochemical reduction of Pt ions. This result also shows that the Pt complex ions were reduced to metallic platinum. The C1s signal and the position of the S2p peak were found to be the same before and after the electrochemical reduction.

Angle-resolved XPS was applied to a Pt–BDMT–Au(111)

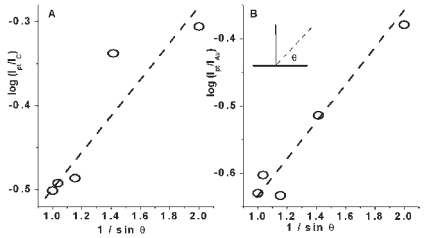


**Figure 2.** Dependencies of relative intensities of (A) $I_{Pt}/I_c$ and (B) $I_{pt}/I_{Au}$ on a take-off angle. $I_{Pt}$, $I_{Au}$, and $I_C$ represent the intensities of XP spectra of Pt $4f_{7/2}$, Au $4f_{7/2}$, and C1s peaks, respectively.

electrode to determine the position of Pt. The relationship between the relative intensities of Pt4f over Au4f and C1s and the take-off angles was shown in Figure 2. The figure clearly shows that the relative intensities of Pt4f to those of Au4f and C1s increased as the take-off angle decreased. This proves that Pt was indeed deposited not underneath but on top of the BDMT SAM.

The results of electrochemical measurements also provide evidence that the platinum layer formed only on top of the SAM. A solid line in Figure 3 shows a current response when the potential of the Pt–BDMT SAM-modified Au(111) electrode was scanned negatively from 0 to −1.25 V. The cathodic current increased significantly when the potential became more negative than −1.0 V and a shoulder was observed at −1.18 V. The large cathodic current is due to hydrogen-evolution reaction (HER) and the shoulder is due to desorption of the Pt–BDMT SAM. The reductive desorption took place at more negative potential than the reductive desorption potential of the BDMT SAM (−1.13 V), showing that the presence of Pt on BDMT made the desorption more difficult. The dashed line in Figure 3 shows the current response of the electrode during the reverse scan from −1.25 to 0 V. It must be noted that the HER current at a given potential decreased in the scan. The inset of Figure 3 shows the CV of the electrode in the potential region between −0.6 and +0.6 V after above mentioned negative potential scan. This is a typical CV of a clean Au(111) electrode in a 0.1 M KOH solution as reported in the literature,[22] showing the removal of the BDMT layer and recovery of the clean Au(111) surface by potential cycling. The HER current decreased further in the following scans.

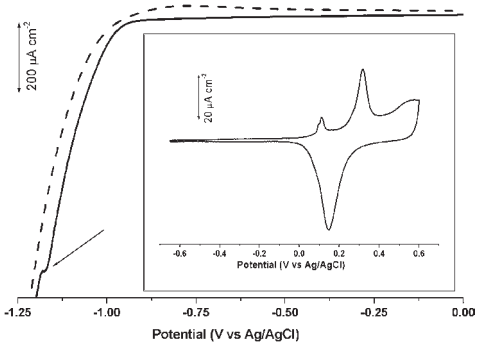


**Figure 3.** CV of a Pt/BDMT/Au electrode in 0.1 M KOH solution. Scan rate: 20 mV $s^{-1}$. Solid line: potential scan from 0 to −1.25 V. Dashed line: reverse scan from −1.25 to 0 V. Inset: CV of the electrode in potential region between −0.6 and +0.6 V after above mentioned scan.

Furthermore, the XP spectra obtained after the negative scan to −1.25 V in a 0.1 M KOH solution showed the disappearance of Pt4f and S2p peaks. These results clearly show that platinum was removed with BDMT by the cathodic scan in alkaline solution, indicating that a Pt was not deposited on the Au(111) surface but only on top of the SAM.

In summary, a novel method to construct a Pt/SAM/Au sandwich structure without a short circuit between two metals was proposed. XPS and electrochemical measurements confirmed that metallic platinum only deposited on top of the SAM and that no metallic platinum existed on the Au(111) surface. The metal deposition on Au underneath the SAM through defect site was avoided because electrochemical deposition was carried out in a platinum-ion free solution. In this way, no platinum ions penetrated through imperfections in the course of electrochemical reduction of Pt ions and only Pt ions pre-adsorbed on the BDMT SAM were reduced.

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