The Adlayers of 6-Anilino-1,3,5-Triazine-2,4-Dithiol Monosodium on Au(111) Electrode in Acidic Solution Studied by Electrochemical Scanning Tunneling Microscopy

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We investigated the electrochemical behavior of the triazinedithiol derivative (TAD), 6-anilino-1,3,5-triazine-2,4-dithiol monosodium (ATDS), on a Au(111) electrode surface in 0.05 M HClO4 using electrochemical measurements and scanning tunneling microscopy (STM). The oxidation of Au was significantly suppressed by modifying Au with ATDS. It was found that each ATDS molecule formed an agglomerate recognized as a set of three bright spots on the Au(111). The agglomerate was also in part linearly ordered along the \( \sqrt{3} \) direction, and no definite phase transition was seen, which was supported by the fact that the CV curve was degenerated by ATDS molecules adsorbed on the electrode in the double-layer region. This result differed from previously reported results of the CV and ECSTM measurements for the 6-octylthio-1,3,5-triazine-2,4-dithiol monosodium (OTDS)-modified Au(111) electrode. The ATDS molecule formed significantly stable adlayer structures on the Au(111). This might contribute to the relatively high corrosion inhibition ability of the ATDS molecule.

Key Words: Triazinedithiol Derivatives, Corrosion Inhibitor, Self-assembled Monolayers (SAMs), Electrochemical STM, Au(111) Electrode

1 Introduction

Reforming on the surface of a solid by organic molecular assemblies has been widely studied.1-3 Especially, the metal-thiol type self-assembled monolayers (SAMs) formed by simply soaking a metallic substrate in a solution containing mercaptan species have attracted attention as a fundamental or an up-to-date element for the construction of an organic-inorganic supermolecular complex at a solid-liquid interface.

Triazinedithiol derivatives (TADs) contain a thiol group which can react with the metal surface. Moreover, TAD is relatively stable in air due to thiol-thione tautomeration. TADs have been widely used in industrial technologies such as anti-corrosion, water-repellency, and adhesives between metals and polymers.4 Although TAD is a widely used material, research concerning the adsorption behavior of the TAD containing two or more sulfur atoms on the surface of a metal has never been reported using a visual approach at an atomic level. Therefore, we have investigated what structure is formed by the adsorption of such a TAD on a metal surface and reported the first example of an adlayer structure of 6-octylthio-1,3,5-triazine-2,4-dithiol monosodium (OTDS) on a Au(111) single crystal electrode in a HClO4 solution using electrochemical scanning tunneling microscopy (ECSTM).5 The OTDS molecule formed an adlayer closely packed along the <112> direction (the so-called \( \sqrt{3} \) direction) due to the van der Waals interaction of the octylthio group.

In this paper, we paid attention to 6-anilino-1,3,5-triazine-2,4-dithiol monosodium (ATDS), which is known as an excellent corrosion inhibitor,6,7 and investigated its adsorption behavior on the Au(111) surface in an acidic solution. Comparing the characteristic of the ATDS molecule with the OTDS molecule, the former easily maintains the thiol form due to an anilino group, whereas the latter easily exists in the thione form due to an octylthio group. If the ATDS molecule exists in the thiol form, the mercapto group in the ATDS molecule will be able to more strongly combine with a Au atom on the Au(111) surface when compared to the OTDS molecule, because the nucleophilicity of the mercapto group in the ATDS on the Au surface is higher than that of the OTDS due to stabilization by the nonlocalization of \( \pi \)-electrons in the triazine ring of ATDS.8 Consequently, it is expected that the ATDS adlayer formed on the Au(111) surface may be more stable than the OTDS adlayer. We studied the adlayer structure of ATDS on Au(111) in an HClO4 solution using cyclic voltammetry and ECSTM, and the adlayer’s stability is described as follows.
Fig. 1 Chemical structure and space-filling model of 6-anilino-1,3,5-triazine-2,4-dithiol monosodium (ATDS).

2 Experimental

ATDS (Nikko Metal Chemical, Zisnet AF, see Fig. 1) was used as obtained. A well-defined Au(111) single crystal electrode was prepared by techniques described in the literature and was annealed in a hydrogen flame under light yellow heat to yield an atomically flat, clean, and reconstructed Au(111) surface. A clean Au(111) electrode was modified by immersion in an aqueous solution containing 50 μM ATDS. The modified electrode was then rinsed with ultrapure water and transferred to the cells for voltammetric and ECSTM measurements. Electrochemical measurements were carried out in a three-compartment glass cell containing 0.05 M HClO₄ deoxygenated by bubbling purified N₂ gas. The ECSTM cell was stored overnight in carboxylic acid (conc. H₂SO₄: 35% H₂O₂: 3:1) and then boiled for at least 2 h in ultrapure water (exchanging the water every 0.5 h) before each measurement. The ECSTM measurements were carried out in 0.05 M HClO₄ using a Nanoscope IIIa (Digital Instruments). A tungsten tip etched in 1 M KOH was used as the probe. To minimize the residual faradaic current, the tungsten tip was coated with nail polish. Pt wires served as the counter and reference electrodes for the STM measurements. The reference electrode was a reversible hydrogen electrode (RHE) in 0.05 M HClO₄.

3 Results and Discussion

Figure 2 shows the cyclic voltammograms (CVs) of bare Au(111) (thin solid line), ATDS-modified Au(111) (thick solid line) and OTDS-modified Au(111) (dotted line) electrodes in a 0.05 M HClO₄ solution. The potential region from −0.10 to 0.90 V is apparently a featureless double-layer region. In order to understand the details of the electrochemical reaction of the ATDS-modified Au(111) electrode, a more detailed CV was measured in the double-layer region. The cathodic current commencing around 0 V is due to the H₂ evolution reaction. In the amplified CV profile of the OTDS-modified electrode in the double-layer region, a redox couple was found. On the negative scan, a cathodic peak was observed at 0.30 V, whereas an oxidative peak appeared at 0.65 V during the anodic scan. These peaks were attributed to the disordered-phase transition of the OTDS adlayer based on the results of the ECSTM observation. On the contrary, the CV profile for an ATDS-modified Au(111) enhanced in the double-layer region was featureless and did not show any remarkable redox peaks in the double layer region. The charging current of the ATDS-modified electrode in the double layer region decreased more than that of a treated electrode. In the case of a bare Au(111) electrode, the oxidation current due to the electrochemical oxidation of the Au surface commenced around 1.30 V. Such an electrochemical oxidation of the Au surface was significantly suppressed for both the ATDS- and OTDS-modified electrodes. The degree of suppression of the electrochemical oxidation of Au for the ATDS-modified electrode is more noticeable compared to the OTDS-modified electrode, suggesting that the ATDS adlayer formed on Au(111) is more stable than the OTDS adlayer. Large peaks were observed around 1.60 V for both modified electrodes. These peaks might be due to the polymerization of ATDS and OTDS or due to the oxidative desorption of these adlayers including the oxidation of the Au surface.

To understand the adlayer features of ATDS on a molecular level, an ECSTM observation was performed in 0.05 M HClO₄. Figure 3 shows in-situ STM images of the ATDS adlayer on Au(111) obtained at various electrode potentials. The ECSTM measurement was started at or near the open circuit potential (0.60-0.80 V). As shown in Fig. 3, triangular-shaped terraces were observed, which were caused by the atomic arrangement of the Au(111) substrate. A number of agglomerates were observed, being in part linearly adsorbed on the terrace (Fig. 3a). Most of the agglomerates were distinguished as a set of three bright spots, and the spot size is ca. 10 nm corresponding to an ATDS molecule (see inset in Fig. 3a). The ATDS molecules constructing the agglomerates seem to be aggregated or dissipated from the ATDS molecule as a nucleus adsorbed on the Au(111) surface according to the change in the electrode potential. The formation of the agglomerates is probably attributed to the π-π interaction between the aromatic rings of the ATDS. The ordered agglomerates marked by the arrows in Fig. 3a were also aligned in the <112> direction, the so-called √3 direction. Such an adsorption mode allowing agglomerate ordering along the √3 direction suggests the existence of adsorption sites where ATDS molecules are selectively...
adsorbed on the Au(111) surface. According to the STM observation of the 4-mercaptopyridine adlayer formed on the Au(111) surface, a similar molecular nucleation was observed along the ordered lines. This is related to the zigzag-like reconstructed structure on the Au(111) surface which is called a “herringbone structure”, where SAM molecules tend to be adsorbed on the corner or edge sites during the initial adsorption stage. Therefore, it is thought that the agglomerative nucleation in the ATDS adlayer is strongly influenced by the herringbone reconstructed structure of Au(111).

Upon stepping the potential to a more positive region than the open circuit potential (Fig. 3b), the agglomerates consisting of three bright spots became unremarkable. These agglomerates were recognized as a larger bright spot when the potential was shifted to a more positive potential. On the other hand, when the electrode potential was returned to the open circuit potential, the assemblies consisting of three bright spots again appeared as shown in Fig. 3a.

Next, the electrode potential was gradually shifted from the open circuit potential to negative potentials. Figures 3c ~ 3e show the sequential STM images of the ATDS adlayers on a Au(111) observed at 0.50 V, 0.44 V and 0.38 V, respectively. As the potential shifts in the negative direction, the entire terrace surface became uniformly covered with the ATDS molecules. The coverage of the ATDS molecules on the Au electrode surface is ca. 85%, which means that one ATDS molecule adsorbs on six Au atoms on the Au(111) surface. However, we could not observe the STM image of the ordered ATDS molecules such as a clear image of an OTDS molecule. This might be attributed to the two-dimensional stability of the adlayers formed by the π-π interaction between the ATDS molecules. The aromaticity of the ATDS molecule containing an anilino group should be higher than that of the OTDS molecule containing an octylthio group, because the ATDS molecule is hard to transfer from the thiol form to the thione form by the nonlocalization of π-electrons in the triazine ring of ATDS compared to the OTDS molecule. Therefore, the ATDS molecule may be able to form a relatively stable adlayer.

When the H2 evolution reaction took place for a while at around 0 V, the adlayer structure was disordered, and the surface roughness of the electrode increased (Fig. 3f). The adlayers were divided into some triangular-shaped islands, which were rotated by 30° with respect to the Au lattice direction. The morphological height of the islands was found to be 0.24 nm corresponding to the height of the Au single atomic step. The formation of such triangular-shaped islands may be related to the surface reconstruction of Au(111). However, the ATDS adlayers as seen in Figs. 3a ~ 3e were quickly regenerated when the electrode potential was returned to a more positive potential value from the 0 V region, and each molecule was linearly arranged in the \( \sqrt{3} \) direction before long.

We previously reported that the disorder-order phase transition in the OTDS adlayer occurs at 0.30 V when the OTDS-modified Au(111) electrode was prepared by immersing the electrode in 200 \( \mu \)M OTDS solution. During the surface modification with the 50 \( \mu \)M ATDS solution, however, no clear phase transition in the adlayers was found, as shown in Fig. 3, which corresponds to the CVs of ATDS (Fig. 2). Namely, these results indicate that the ATDS molecule forms more stable adlayer structures on Au(111) compared to the OTDS molecule. This also seems to contribute to the relatively high corrosion inhibition ability of the ATDS molecule.

4 Conclusion
The first example of the adlayer structure of ATDS on a Au(111) single crystal electrode in an HClO4 solution was visually reported using ECSTM. The ATDS molecules were attracted to each other to form an agglomerate recognized as a set of three bright spots probably due to the π-electron attraction between the molecules. The assembly was in part linearly ordered, implying that the ATDS adlayer is strongly influenced by the herring-
bone reconstructed structure of the Au(111). In conclusion, the ATDS molecule was found to form significantly stable adlayer structures on Au(111).

References