

Adsorption Behavior of 6-Octylthio-1,3,5-triazine-2,4-dithiol Monosodium on Au(111) Investigated by Electrochemical Scanning Tunneling Microscopy

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An electrochemical STM study revealed that the ordered adlayers of 6-octylthio-1,3,5-triazine-2,4-dithiol monosodium (OTDS) were formed on a Au(111) electrode surface in HClO₄, resulting in the formation of stripe structure by stacking along the $\sqrt{3}$ direction.

The self-assembled monolayers (SAMs) of organic molecules have been extensively studied owing to their potential applications in reforming a solid surface.¹⁻³ In most cases, SAMs are formed using alkanethiol derivatives. Triazinedithiol derivatives (TADs) also contain a thiol group which can react with the metal surface. Moreover, TAD is relatively stable in air due to tautomerization. TADs have been widely used in industrial technologies such as anti-corrosion, water-repellency, and adhesives between metals and polymers.⁴

To understand the self-organization behavior of those materials at a solid-liquid interface at an atomic or molecular level, electrochemical scanning tunneling microscopy (ECSTM) techniques are now recognized as powerful and direct measurement methods.⁵⁻⁸ For example, the ECSTM observations of benzene adsorbed on the clean surfaces of Pt(111) and Rh(111) were succeeded in an electrolyte solution by Itaya and co-workers.⁸ Internal structure depending upon the adsorption site, i.e., the differences in electronic state of benzene molecule were clearly visualized in the high-resolution ECSTM image.⁸ Although TAD is a material generally used, the research on the adsorption behavior of the TAD containing two or more sulfur atoms has never been reported on the surface of the metal using a visual approach at an atomic level. Therefore, we have investigated so far what structure is formed by the adsorption of such TAD on the metal surface.

In this paper, the first example of the adlayer structure of 6-octylthio-1,3,5-triazine-2,4-dithiol monosodium (OTDS, see inset in Figure 1) on an Au(111) single crystal electrode in an HClO₄ solution is visually reported using ECSTM.

OTDS was synthesized by our group.⁹ A well-defined Au(111) electrode was prepared by techniques described in the literature.¹⁰ A clean Au(111) electrode was modified by immersion into an aqueous solution containing either 20 or 200 μ M OTDS. The modified electrode was then rinsed with ultrapure water, and transferred to the ECSTM cell. ECSTM measurements were carried out in 0.05 M HClO₄ using a Nanoscope IIIa (Digital Instruments). Tungsten tip etched in 1 M KOH was used as a probe. To minimize the residual faradaic current, the tungsten tip was coated with nail polish. STM images were recorded

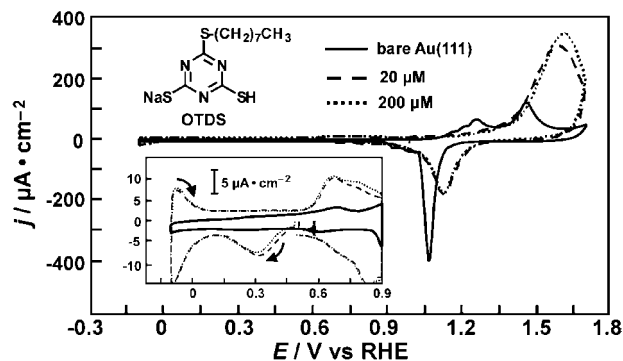


Figure 1. Cyclic voltammograms of bare (solid line) and OTDS-modified Au(111) electrodes in 0.05 M HClO₄ recorded at a scan rate of 50 mV s⁻¹ at 25 °C. The electrodes were prepared by immersing into 20 μ M (dashed line) and 200 μ M (dotted line) OTDS aqueous solutions for 60 s. The inset shows an enlarged CV in the double-layer region.

in the constant-current mode. All potential are referred to the reversible hydrogen electrode (RHE).

Cyclic voltammograms (CVs) of the bare and OTDS-modified Au(111) electrodes were measured in a 0.05 M HClO₄ solution. Figure 1 shows the CVs of a bare Au(111) (solid line) and two kinds of OTDS-modified Au(111) electrodes in a 0.05 M HClO₄ solution. It was found that the electrochemical reaction of the gold surface is considerably suppressed by the modification with OTDS molecules. It seems that the potential region from -0.10 to 0.90 V is apparently a featureless double-layer region. To understand the details of electrochemical reaction for the OTDS-modified Au(111) electrode, the enlarged CV was measured in the double-layer region. In the amplified CV profile (inset in Figure 1), a redox couple was found. During the negative scan, a cathodic peak was observed at 0.30 V, whereas oxidative peak appeared at 0.65 V during the anodic scan. The commencing cathodic current around 0 V is due to the desorption of OTDS molecules and H₂ evolution reaction. In contrast, an oxidation current was commenced at 1.35 V. The oxidative current of Au surface observed around 1.25 V was suppressed, indicating that OTDS adlayer inhibits the electrochemical oxidation of Au surface. The large peak observed at 1.60 V might be due to the polymerization of OTDS or due to the oxidative desorption of OTDS adlayer including the oxidation of Au surface.

To understand the adlayer of OTDS at molecular level, ECSTM measurement was examined in 0.05 M HClO₄.

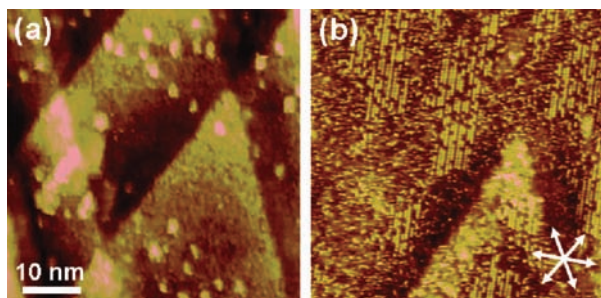


Figure 2. ECSTM images of OTDS adlayers formed on Au(111) electrodes after immersion in 200 μM OTDS aqueous solution in 0.05 M HClO_4 as electrolyte solution. (a) $E = 0.66$ V, and $E_{\text{tip}} = 0.22$ V, (b) $E = 0.32$ V, and $E_{\text{tip}} = 0.22$ V. The set of three arrows indicates Au lattice direction.

Figure 2 shows STM images of OTDS adlayer on Au(111). The observation was started at or near open circuit potential (0.60–0.80 V). At the potentials, disordered structure was seen on the terrace (see Figure 2a). When the potential was swept to 0.20 V, several ordered domains were formed, as shown in Figure 2b. The ordered molecular rows were aligned to the $\langle 112 \rangle$ direction, the so-called $\sqrt{3}$ direction. The reductive peak observed at 0.30 V shown in Figure 1 might be therefore due to the disorder–order phase transition in the OTDS adlayer. Interestingly, no etching pits were seen, while several defects were found in each ordered molecular row. The ordered OTDS adlayer was stably observed at or near 0 V. At potentials more negative than 0 V, STM image of the OTDS adlayer became unclear (not shown).

Furthermore, to investigate dependence upon the concentration of modifier, the OTDS adlayer was prepared under two different modification conditions. Figures 3a and 3b show high-resolution ECSTM images of the OTDS adlayer structures. We found that the threefold-symmetric OTDS adlayers were observed along the $\sqrt{3}$ direction on the Au(111) surface in the potential region between 0.45 and 0 V. In the case of the electrode modified in a 20 μM OTDS solution (Figure 3a), the adsorbed OTDS molecules formed relatively long-range molecular rows running to the $\sqrt{3}$ direction. Each molecular row was rotated by 30° with respect to the Au lattice direction. On the contrary, when the modification was carried out in 200 μM OTDS solution (Figure 3b), the OTDS molecules dominantly formed a characteristic structure like a zigzag network. The average intermolecular distance (the distance between neighboring triazine rings of the OTDS molecules in each row) was found to be 0.49 nm, implying that the formation of the stacked OTDS molecular rows is attributed to the π – π interaction between the triazine rings of OTDS as seen in common heterocyclic compounds.^{7,11–13} We estimated the surface concentration and the molecular diameter of OTDS from a result of the CV measurements of the Au(111) electrode in 0.5 M KOH in the presence of OTDS (not shown here). The electronic charge consumed by the reductive desorption reaction of OTDS was calculated to be ca. $42.7 \mu\text{C cm}^{-2}$, leading to the surface concentration of $4.42 \times 10^{-10} \text{ mol cm}^{-2}$ if one electron reduction takes place. Judging from the value, the molecular diameter of the OTDS is estimated to be ca. 0.6 nm.¹⁴ This value is consistent with the triazinedithiol unit

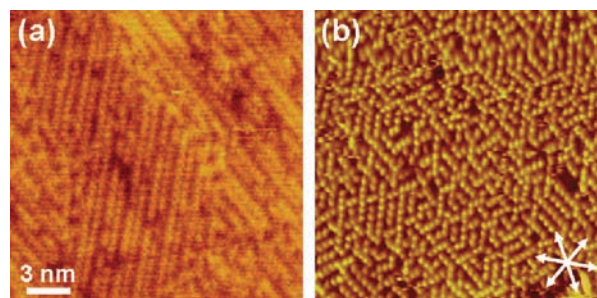


Figure 3. High resolution ECSTM images of OTDS adlayers formed on Au(111) electrodes in 0.05 M HClO_4 . The images were observed for modified electrodes after immersion in (a) 20 μM and (b) 200 μM OTDS aqueous solutions. (a) $E = 0.40$ V, and $E_{\text{tip}} = 0.22$ V, (b) $E = 0.06$ V, and $E_{\text{tip}} = 0.22$ V.

of the OTDS molecule adsorbed on the Au(111). We also found from the ECSTM images that the triazine ring in the OTDS was vertically adsorbed and stacked along the $\sqrt{3}$ direction of Au(111) in the case of the surface modification at lower concentrations of OTDS solutions such as 20 μM . Thus, a clear difference in adlayer structure of OTDS was found on Au(111) in HClO_4 . Further examination is needed to clarify the OTDS adlayer structures depending on the modification condition. The details will be published in a separated paper.¹⁵

In conclusion, an electrochemical behavior and adlayer structures of OTDS were indicated on a Au(111) electrode by using ECSTM.

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