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Electrochemical scanning tunneling microscopy examination of the structures of benzenethiol molecules adsorbed on Au(1 0 0) and Pt(1 0 0) electrodes

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Abstract

In situ electrochemical scanning tunneling microscopy (STM) has been used to examine the structures of benzenethiol adlayers on Au(1 0 0) and Pt(1 0 0) electrodes in 0.1 M $HClO_4$, revealing the formation of well-ordered adlattices of Au(1 0 0)-($\sqrt{2} \times \sqrt{5}$) between 0.2 and 0.9 V and Pt(1 0 0)-($\sqrt{2} \times \sqrt{2}$)$R45°$ between 0 and 0.5 V (versus reversible hydrogen electrode), respectively. The coverage of Au(1 0 0)-($\sqrt{2} \times \sqrt{5}$) is 0.33, which is identical to those observed for upright alkanethiol admolecules on Au(1 1 1). In comparison, the coverage of Pt(1 0 0)-($\sqrt{2} \times \sqrt{2}$)$R45°$ – benzenethiol is 0.5, much higher than those of thiol molecules on gold surfaces. This result suggests that benzenethiol admolecules on Pt(1 0 0) could stand even more upright than those on Au(1 0 0). All benzenethiol admolecules were imaged by the STM as protrusions with equal corrugation heights, suggesting identical molecular registries on Au(1 0 0) and Pt(1 0 0) electrodes, respectively. Modulation of the potential of a benzenethiol-coated Au(1 0 0) electrode resulted in irreversible desorption of admolecules at $E \leqslant 0.1$ V (vs. reversible hydrogen electrode) and oxidation of admolecules at $E \geqslant 0.9$ V. In contrast, benzenethiol admolecule was not desorbed from Pt(1 0 0) at potentials as negative as the onset of hydrogen evolution. Raising the potential rendered deposition of more benzenethiol molecules before oxidation of admolecules commenced at $E > 0.9$ V.

Keywords: Scanning tunneling microscope; Adsorption; Benzenethiol; Au(1 0 0); Pt(1 0 0); Solid–liquid interface

1. Introduction

The formation of self-assembled monolayers (SAMs) of thiol molecules on Au(1 0 0) has been examined in ultrahigh vacuum (UHV) and electrochemical environment by using scanning tunneling microscope (STM) to elucidate how the structure of gold substrate influences the organization and the formation mechanism of SAMs at gold surfaces [1–6]. In strong contrast to the cases of SAMs on Au(1 1 1) [7], where a large number of studies are reported, the study of SAMs on Au(1 0 0) is scattering with only a handful of reports addressing the adsorption of *p-tert*-Butylcalix[4]arenedithiol, ethanethiol, butanethiol, decanethiol molecules on Au(1 0 0) [1–6]. It is shown that the structures of thiol molecules on Au(1 0 0) vary with the preparation methods and their molecular structures. For example, ethanethiol was found to arrange in ($1.2\sqrt{2} \times p\sqrt{2}$)$R45°$ ($p = 7.0$ or 8.2), whereas butanethiol forms $c(2 \times 8)$ on a (1×4) reconstructed surface in UHV and produces an

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incommensurate adlattice in ethanol solutions [1,3,5]. This structural variability of SAMs on Au(1 0 0) is partly associated with the complicated atomic structures of the Au(1 0 0) substrate. STM results obtained for ethanethiol and butanethiol molecules show that the hexagonal atomic structure of the reconstructed Au(1 0 0) is lifted to produce a quadratic (1 × 1) structure upon the adsorption of thiol molecules [1,3,5]. Furthermore, adsorbate-induced expansion of the Au(1 0 0) substrate lattice is proposed to account for the extraordinary coverage of 50%, rather than 22%, of protruded islands revealed by STM [8–10]. In addition, pit formation, frequently observed for thiol – modified Au(1 1 1) [11,12], has not been found on Au(1 0 0).

This study is intended to reveal how benzenethiol molecules are adsorbed on quadratic Au(1 0 0) and Pt(1 0 0) electrodes and how electrochemical potential affects the adlayer structures. The present study differs from the previous studies of alkanethiol on Au(1 0 0) in the following aspects. First, benzenethiol admolecules can interact with their neighbors via the π–π stacking interaction [13,14], which can be stronger than the dispersion force due to the alkyl end groups examined previously. Second, in the present study benzenethiol molecules were adsorbed onto Au(1 0 0) and Pt(1 0 0) electrodes at potentials at least 0.4 V more negative than their open-circuit potentials. This can be detrimental to the structure of thiol on Au(1 0 0), as potential is known to control the atomic structure of Au(1 0 0) [8–10]. Third, thiol admolecules, known to donate charges to Au and Pt electrodes [15,16], can influence how much benzenethiol molecules are adsorbed on these electrodes under potential control. Meanwhile, by comparing the results obtained with benzenethiol on Au(1 0 0) and Au(1 1 1) [17–19], one gains insights into SAMs of arylthiol molecules on gold electrodes.

In addition, we examined benzenethiol on Pt(1 0 0) electrode to elucidate the role of adsorbate-substrate interaction in producing SAMs. We recall our previous STM study of benzenethiol molecules adsorbed on Pt(1 1 1), where $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30°$ structures are also identified, as those found for sulfur adatoms [20]. Two nearest neighbor molecules are 0.56 and 0.48 nm apart in these two structures, which are less than the van der Waals diameter of a benzene molecule. Tentatively, the strong Pt–S bond is responsible for the production of these compact molecular adlattices. Now, for Pt(1 0 0), if benzenethiol admolecules also adapt the $(\sqrt{2} \times \sqrt{2})R45°$ structure as sulfur adatoms [21], an even stronger repulsive force is expected among admolecules. It would be interesting then to see if the Pt–S bond is sufficiently strong to compensate for the intermolecular repulsive interaction. It is worthwhile noting that benzenethiol molecule on Rh and Ru(0 0 0 1) surfaces are also examined to elucidate the formation of SAMs at Pt group metal [22,23]. The Ru–S bond again prevails to produce a Ru(0 0 0 1)-$(2 \times \sqrt{3})rect$ – benzenethiol structure, similar to that of sulfur adatoms, and admolecules stand upright on the substrate.

2. Experimental section

Single-crystal bead electrodes of gold and platinum were prepared by using the Clavilier's method described elsewhere [24,25]. The pretreatment of these electrodes involved annealing with a hydrogen torch, followed by quenching in hydrogen-saturated Millipore water (resistivity >18.2 MΩ). The electrode was then quickly transferred into an electrochemical or STM cell under the protection of a thin layer of water. According to previous reports [8–10], the as-prepared Au(1 0 0) surface would presume a reconstructed "hex" structure. As the potential of Au(1 0 0) was held at 0.3 V, 400 mV negative of the point of zero charge of Au(1 0 0) in 0.1 M $HClO_4$, benzenethiol molecules were adsorbed on a reconstructed Au(1 0 0) electrode [10]. For Pt(1 0 0), this annealing-and-quenching pretreatment produced a (1 × 1) surface decorated with square mounds and a thin oxide layer. To remove the oxide layer, the potential was scanned negatively from the open-circuit potential (ca. 0.9 V) to 0 V (vs. reversible hydrogen electrode, RHE) prior to the dosing of benzenethiol admolecules. As reported previously [10,26], ordered Au(1 0 0) and Pt(1 0 0) electrodes both produce well-defined cyclic voltammograms in 0.1 M $HClO_4$, which were used to diagnose the surface state of these as-prepared Au and Pt electrodes.

Ultrapure perchloric acid, and benzenethiol were purchased from Merck Inc. (Darmstadt, Germany). They were used as received without further purification. Triple-distilled Millipore water was used to prepare all solutions, for example the supporting electrolyte of 0.1 M $HClO_4$. The solubility of benzenethiol in water is ca. 7.6 mM at room temperature and this value was used to estimate its concentration in STM and CV experiments [27]. The benzenethiol-containing 0.1 M $HClO_4$ was added directly into a Teflon STM cell which housed the Au(1 0 0) or the Pt(1 0 0) electrode.

The STM was a Nanoscope-E (Santa Barbara, CA) and the tip was made of tungsten (diameter 0.3 mm) prepared by electrochemical etching in 2 M KOH. After thorough rinsing with water and acetone, a tip was further painted with nail polish for insulation. The leakage current of the tip at the open circuit potential was less than 0.05 nA. More than 80% of the as-prepared tips yielded molecular resolution. STM imaging was always in the constant-current mode, which could yield high quality STM images. A reversible hydrogen electrode (RHE) was used as the reference electrode in the electrochemical and STM measurements. All potentials reported herein refer to a RHE scale.

3. Results and discussion

3.1. In situ STM of Au(1 0 0) in benzenethiol-containing $HClO_4$

Fig. 1 shows time-dependent in situ STM images obtained with an Au(1 0 0) electrode in 0.1 M $HClO_4$ + 80 μM