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3-Mercapto-1-propanesulfonic acid and Bis(3-sulfopropyl) Disulfide Adsorbed on Au(111): In Situ Scanning Tunneling Microscopy and Electrochemical Studies

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Received September 9, 2008. Revised Manuscript Received October 23, 2008

3-Mercapto-1-propanesulfonic acid (MPS) and bis(3-sulfopropyl) disulfide (SPS) adsorbed on a Au(111) electrode were studied by using in situ scanning tunneling microscopy (STM). Although the adsorptions of MPS and SPS are known to be oxidative and reductive, respectively, on an Au(111) electrode, these two ad molecules behave similarly in terms of phase evolution, surface coverage, potential for stripping, and characteristics of cyclic voltammetry. However, different adsorption mechanisms of these molecules result in different structures. Raising electrode potential causes more MPS and SPS molecules to adsorb, yielding ordered adlattices between 0.67 and 0.8 V (vs reversible hydrogen electrode). The ordered adlattices of MPS and SPS appear as striped and netlike structures with molecules adsorbed parallel to the Au(111) surface. Switching potential to 0.9 V or more positive still does not result in upright molecular orientation, possibly inhibited by electrostatic interaction between the end group of $-\text{SO}_3^-$ and the Au(111) electrode. Lowering the potential to 0.4 V disrupted the ordered adlayer. Stripping voltammetric experiments show that MPS and SPS ad molecules are desorbed from Au(111) at the same potential, suggesting that these molecules are both adsorbed via their sulfur headgroups. The S–S bond in SPS is likely broken upon its adsorption on Au(111).

Introduction

Self-assembled monolayers (SAMs) of organosulfur molecules on metal surfaces have attracted much interest because SAMs can be used to modify and tailor the properties of metal surfaces. SAMs are always formed by specific thiol/substrate interaction which anchors organic molecules to a metal surface. Furthermore, the van der Waals force existing among adsorbed molecules renders a close-packed arrangement of ad molecules, which can be highly ordered on a single crystalline surface such as Au(111).^{1–7}

The formation mechanism and the structures of SAMs on metal surfaces have been extensively examined.^{2,7–14} These studies are either performed in vacuum where SAMs are prepared by vapor deposition or in ambient atmosphere by dipping a

substrate in a thiol-containing solution. For the solution approach, electrochemical methods can be used to study the effect of potential on the adsorption, the structure, and the stability of a SAM. Alkanethiol SAMs adsorbed on a Au(111) surface have received the most attention, while organosulfur compounds with terminal groups of $-\text{CH}_3$, $-\text{OH}$, and $-\text{COOH}$ are also examined.^{1,7,15,16} Meanwhile, studies on SAMs with different chain length and on metal surfaces under potential control in various electrolytes are also reported.^{17–20}

Among the applications of SAMs, their uses as surfactants for metal deposition in both vacuum^{3,7,15,16,21} and electrochemical systems are well documented.^{17,19,22} The interaction of metal atoms with the terminal groups of a SAM,^{7,16,17,23,24} as well as the permeability of a SAM, are shown to affect the growth mode of a metal deposition. For electrochemical deposition, the charge transport across a SAM also plays an important role in the deposition of metal atoms. In an industrial electroplating bath, short chain alkanethiols or disulfides are frequently used as additives to render desired characteristics of the deposited films. Bis(3-sulfopropyl) disulfide (SPS) and 3-mercapto-1-propane-

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sulfonic acid (MPS) are commonly used additives which allow a smooth copper film. These two compounds also accelerate Cu deposition to induce a superconformal electrodeposition of copper in a via-hole plating of printed circuit boards.^{25–30} Despite their important uses in Cu deposition, a fundamental understanding of how these additives work is still lacking.

MPS and SPS are organosulfur molecules with a terminal group of sulfonate. Their adsorption on a metal substrate can influence how Cu is plated subsequently on a substrate. It is surprising to learn that the adsorption of alkanethiol containing a sulfonate functional group has been largely overlooked. This study illustrates how in situ scanning tunneling microscopy (STM) can be used to study the adsorption of MPS and SPS on a Au(111) electrode. While the adsorption of MPS is believed to result in thiolate species as reported for typical organosulfur compounds, molecules with disulfide linkage like SPS could have their S–S bond cleaved before the thiolate species was adsorbed on Au(111).

Experimental Section

Ultrapure sulfuric acid was purchased from Cica-Merck. Bis(3-sulfopropyl) disulfide (SPS) and 3-mercaptopropionic acid (MPS) were obtained from Raschig (Germany) and Aldrich, respectively, and were used without further purification. Millipore triple-distilled water (resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$) was used to prepare all solutions used in this study. Au(111) single-crystal electrodes were prepared by the Clavilier method, and they were annealed in a hydrogen flame and quenched in ultrapure water saturated with hydrogen before use.^{31,32} The as-prepared Au(111) electrode was transferred to the electrochemical cell or mounted in the scanning tunneling microscope.

The STM experiments were performed using a NanoScope E (Digital Instruments, Santa Barbara, CA) equipped with an electrochemical system and a high-resolution scanner. The tips for STM were made of tungsten wire (diameter 0.25 mm) and prepared by electrochemical etching in 2 M KOH. A Pt wire was used as a quasi-reference electrode in the STM cell, and the measured potential was calibrated to the RHE in this work. The STM imaging was operated in the constant-current mode throughout this study.

Results and Discussion

Cyclic Voltammetry Study. Figure 1 shows the cyclic voltammograms (CVs) of a bare Au(111) electrode in a 0.1 M H_2SO_4 solution and the electrode modified by MPS or SPS in a solution containing 0.1 M H_2SO_4 and 1 mM MPS or SPS. For the bare Au(111) electrode, the voltammogram resembles those reported in the literature,^{17,31,32} confirming the presence of a well-defined Au(111) surface. For the MPS- and SPS-modified electrodes, the Au(111) electrode was held at 0.4 V for about 20 min to induce molecular adsorption, followed by sweeping potential negatively at a scan rate of 50 mV/s.

The MPS and SPS adlayers are found to be stable in the potential range between 0.35 and 0.8 V. In the negative potential sweeping, a main reductive peak (C2 and C2') appears near 0.05 V, accompanied by a minor peak C1 at a more positive position of

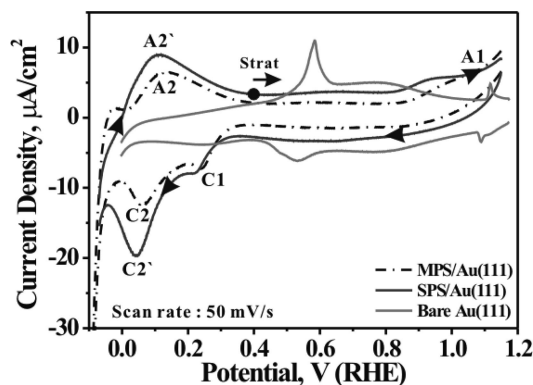


Figure 1. Cyclic voltammograms for a bare Au(111) electrode in a 0.1 M H_2SO_4 solution, and the MPS- and SPS-modified electrodes in a solution containing 0.1 M H_2SO_4 and 1 mM MPS or SPS at a scan rate of 50 mV/s.

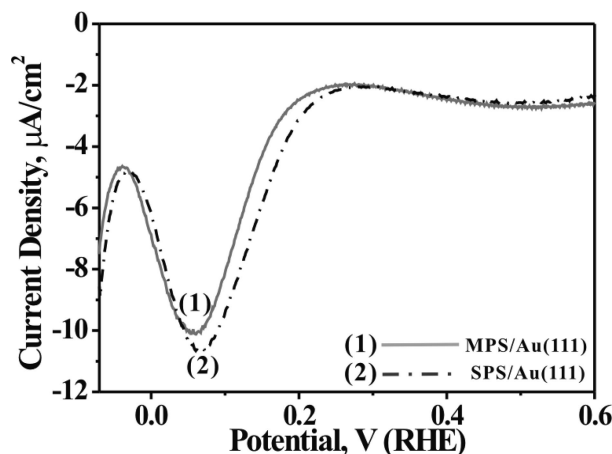


Figure 2. Cyclic voltammograms for the Au(111) electrodes modified by MPS and SPS adlayers. The measurements were performed in a thiol-free solution containing only 0.1 M H_2SO_4 at a scan rate of 50 mV/s.

0.25 V. In the following reversal scan to the positive direction, a broad oxidation peak appears near 0.08 V. In general, the morphologies of the CV features obtained for Au(111) modified with MPS and SPS are similar, which implies that the two adlayers have similar characteristics. In other words, the disulfide (SPS) ad molecule has turned into thiolate (MPS) by breaking the S–S bond and coupling with the Au surface in the adsorption process.

Tentatively, the major reductive peaks of C2 and C2' are attributed to the reductive desorption of molecular adlayers from the Au(111) electrode, but the origin of the minor peak C1 is unclear at the present stage. These characteristics resemble those reported by others, which are proposed to stem from stepwise reduction of 3-mercaptopropionic acid (MPA) and other alkanethiol SAMs on Au(111).^{33,34} To further substantiate this issue, a CV experiment was performed with a Au(111) electrode modified with MPS or SPS in thiol-free 0.1 M H_2SO_4 . The CV profiles shown in Figure 2 contain no minor peak at 0.25 V for both SPS and MPS, while the major peaks shift slightly. This result implies that the minor peak is associated with MPS or SPS molecules in the electrolyte. Two possible reasons are inferred for the appearance of the minor peak: (1) There were multilayers of thiol adsorbed on Au(111) if the electrolyte contained thiol

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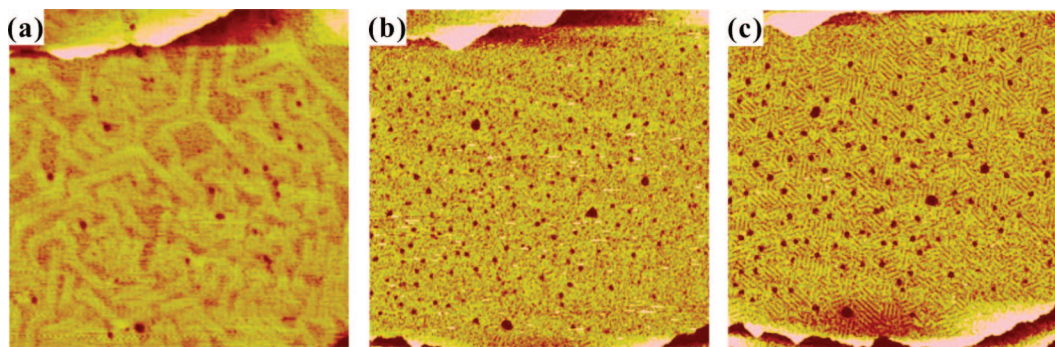
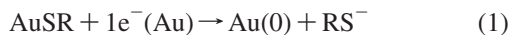


Figure 3. In situ STM images ($200 \times 200 \text{ nm}^2$) showing the adsorption behavior of MPS on Au(111) surface in a solution containing 0.1 M H_2SO_4 and 1 μM MPS. These images were acquired (a) at 0.4 V, 8 min after MPS introduction, (b) 6 min after elevation the potential to 0.54 V, and (c) at 0.67 V.

molecules. Admolecules not attaching to Au(111) directly could be adsorbed more weakly and were desorbed at more positive potentials than those directly adsorbed on Au(111). (2) The reductive reaction of the thiol molecules in the electrical double layer contributes to the minor reductive peak. Further studies are required to resolve this issue.

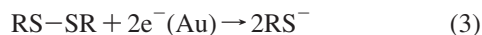
One distinctive difference in the CV features of MPS- and SPS-modified Au(111) seen in Figure 1 is their peak current densities for the major reductive peaks of C2 and C2'. This difference cannot be ascribed to different coverage of these two compounds on Au(111) because identical reductive current densities were observed in a thiol-free electrolyte (Figure 2). For a thiol adlayer, the reductive desorption reaction is



This reaction occurs for both MPS and SPS adlayers, giving rise to the major reductive peaks in Figure 2. The charges integrated from these two peaks are almost identical, indicating the coverage of these molecular adlayers are roughly the same. This result supports our view that SPS molecules dissociated and were adsorbed in the form of MPS as the reaction shown below^{35,36}



When SPS is present in the electrolyte solution, another reductive reaction corresponding to the breaking of S–S bond of the disulfide molecule (eq 3) is involved, which contributes to a higher reductive current to the peak at 0.05 V.



In the subsequent positive-going scan, an oxidation peak appears at about 0.08 V, ascribable to the readsorption of desorbed thiol molecules. It was reported that the adsorption of a disulfide on metal surface was a reductive process as shown by eq 2.^{35,36} This adsorption scheme could hold for SPS/Au(111) in this study. When the potential of the Au(111) electrode is held at 0.15 V, a transient reductive current appeared after the injection of SPS into the electrolyte (Figure S1). Therefore, the oxidative readsorption peak (A2') in SPS solution is not a result of SPS dissociation but is attributed to the readsorption of desorbed anionic ion (RS^-) in the electrical double layer. The close positions of oxidative peaks for MPS and SPS (A2 and A2') sustain this inference.

In Situ STM Study. *Adsorption of MPS on Au(111).* Before the introduction of MPS or SPS into the STM cell, the herringbone

feature of the reconstructed Au(111) electrode was observed at 0.4 V in a 0.1 M H_2SO_4 solution, confirming the formation of a well-defined Au(111) surface.^{7,17a,32b,37} Shortly after adding about 1 μM MPS at 0.4 V, nanometer-scale pits ascribable to the sites of molecular adsorption appeared shortly. The STM image in Figure 3a was acquired 8 min after MPS was added. In this image, herringbone rows, as well as adsorbed domains of nonordered structure are present simultaneously. Furthermore, several pinhole defects, or etching pits, caused by thiol adsorption on gold substrate are also observed in this stage.^{15–17,38,39}

More MPS molecules were adsorbed to displace the herringbone structure, but these processes were very slow at 0.4 V. The herringbone feature of Au(111) was not completely eliminated. To promote the adsorption of MPS, the potential was raised to 0.54 V, prompting the expansion of MPS domains at the expense of the herringbone rows. The Au(111) surface was finally saturated with MPS after a potential at 0.54 V for 6 min (Figure 3b). Apparently, the more positive potential promoted the oxidative adsorption of MPS, leading to a further adsorption of MPS. Although no ordered domain was found in Figure 3b, the randomly distributed etching pits on the surface indicate the presence of a MPS adlayer. No appreciable change of the adsorption structure was noted after prolonged STM imaging at this potential (0.54 V). However, an ordered adlayer structure appears shortly after shifting the potential to 0.67 V (Figure 3c). The ordered adlayer exhibits striped patterns, shown in Figure 3c.

The fact that a MPS adlayer formed at 0.54 V was disordered may imply that the coverage of MPS on the Au(111) surface was not high enough to form an ordered adlattice. In addition, the van der Waals (VDW) interaction among the adsorbed MPS molecules could be weak also because a MPS molecule contains only three methylene units.^{7,16} These two key factors needed to produce ordered SAM were both missing, leading to poorly organized MPS adlayer at 0.54 V. On the other hand, at 0.67 V or more positive potentials, in situ STM revealed an ordered striped structure of MPS, as Figure 4 illustrates. Striped phases similar to that of MPS have been found for alkanethiol SAMs with $-\text{CH}_3$ or $-\text{OH}$ terminated groups, which are converted into more compact phases, dubbed the “saturation phase”, at more positive potentials.^{7,15,17,22} In contrast, the striped phase of MPS did not undergo such a phase transition when the potential was shifted positively until the onset of molecular oxidation at 1.05 V. Because this phase transformation is frequently associated

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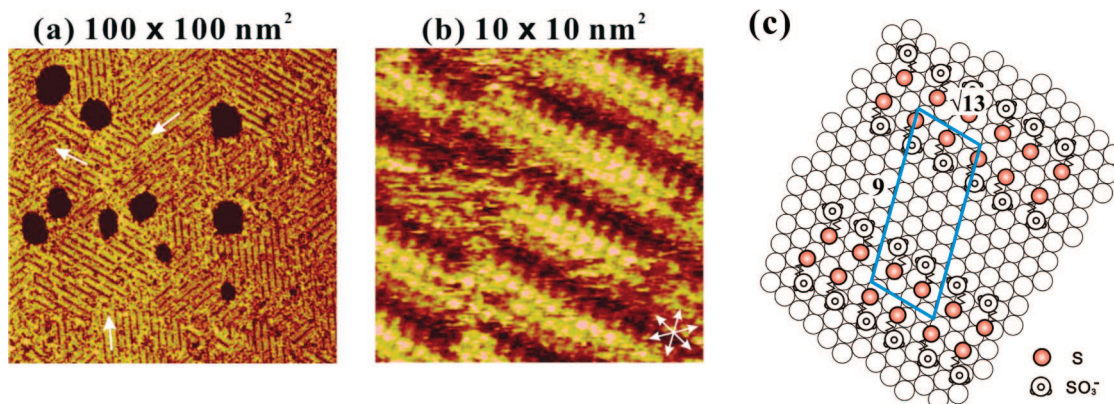


Figure 4. High-resolution STM images (a, b) and the corresponding ball model proposed (c) for the striped phase of the MPS adlayer on the Au(111) surface. The images were acquired at 0.8 V.

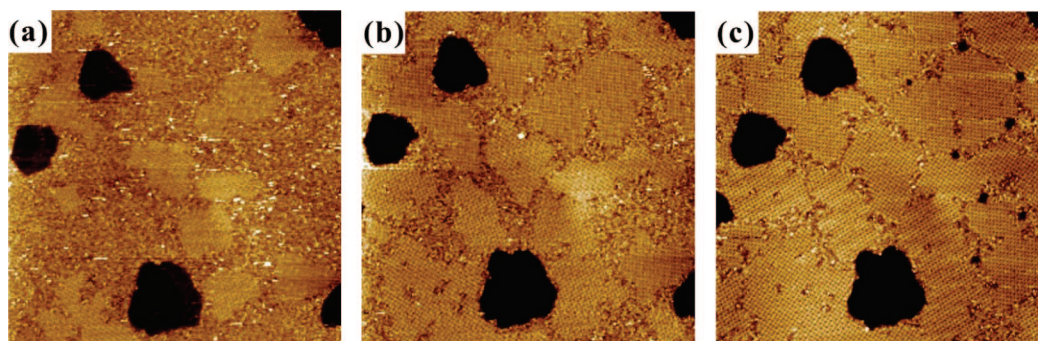


Figure 5. In situ STM images ($100 \times 100 \text{ nm}^2$) showing the phase evolution of SPS adlayer from disordered to ordered structure after elevating the potential to 0.8 V. The imaging was performed in a solution containing 0.1 M H_2SO_4 and 1 μM SPS.

with reorientation of adsorbed thiol molecules, from horizontal to vertical configuration, the stability of the striped MPS structure against anodic polarization indicates that MPS molecules were adsorbed preferentially parallel to the Au(111) surface. This could result from a substantial electrostatic interaction between the terminal sulfonic group of MPS molecules and the positively charged Au(111) electrode.

In a $100 \times 100 \text{ nm}^2$ scale image (Figure 4a), three rotational domains, oriented 60° or 120° with respect to each other, are found and denoted by the arrows. The molecular-resolution image (Figure 4b) shows that the molecules lying along the close-packed direction (the $\langle 110 \rangle$ direction) of the Au(111) surface are aligned in a head-to-head fashion. Similar to the striped phase of other alkanethiols, the brightest spots located at the center of a striped row are attributed to the S headgroups which chemically bonded to the Au substrate. The end groups of $-\text{SO}_3^-$ located outward in the striped row did not give rise to clear protrusions. The distance between two striped rows was measured to be $2.61 \pm 0.1 \text{ nm}$, equivalent to ~ 9 times that of the gold diameter (0.298 nm). The striped rows run parallel to the $\sqrt{13}$ direction of the Au(111) lattice, and the distance between every other MPS molecule in this direction is $1.04 \pm 0.1 \text{ nm}$. These STM results are evidence of an ordered adlattice of $(9 \times \sqrt{13})$, and a corresponding model is given in Figure 4c. The coverage of this MPS adlattice is estimated to be 0.11 (MPS molecule for every gold atom).

Adsorption Behavior of SPS. The adsorption of SPS was examined by using STM in a manner the same as that for MPS. STM results show that SPS molecules were adsorbed on Au(111) but in disarray between potentials 0.4 and 0.55 V. The potential was then elevated positively, and ordered adlayer lattices gradually emerged. These STM findings are parallel to those observed

with MPS. The onset potential for the formation of ordered SPS adlayer was ca. 0.8 V, slightly more positive than that found for MPS. Ordered domains gradually expanded at this potential and eventually covered the entire Au(111) surface in about 10 min. The progressive evolution of the ordered adlayer was monitored by the STM, and the results are shown in Figure 5.

Although the adsorptions of MPS and SPS are known to be oxidative and reductive reactions, respectively, the progression of the adsorption phases seems to be similar for the two compounds. However, there are apparent differences in the STM results. First, a higher positive potential is required for SPS to induce the phase transformation to ordered adlayer. Second, no striped phase was observed for SPS. Furthermore, the etching pits seen in the SPS adlayer were much larger with lower density in comparison with that for MPS. Apparently, these differences relate to the different adsorption mechanisms between MPS and SPS. For the adsorption of SPS, it involves a reductive dissociation of disulfide (eq 3) into thiolate (RS^-) and a simultaneously oxidative adsorption of the thiolate on the Au electrode.



Although the final adsorbed species are identical for MPS and SPS, the different molecular structures of the two compounds in the initial adsorbed state trigger the distinct properties mentioned above.

To further address this issue, in situ STM was used to follow the SPS adlayer on Au(111) while the potential was swept from 0.8 to 0.05 V first to strip the adlayer, followed by a positive sweeping to allow readsorption of the desorbed molecules at close proximity of the electrode. A series of STM images were collected at different potentials in this process and are shown in

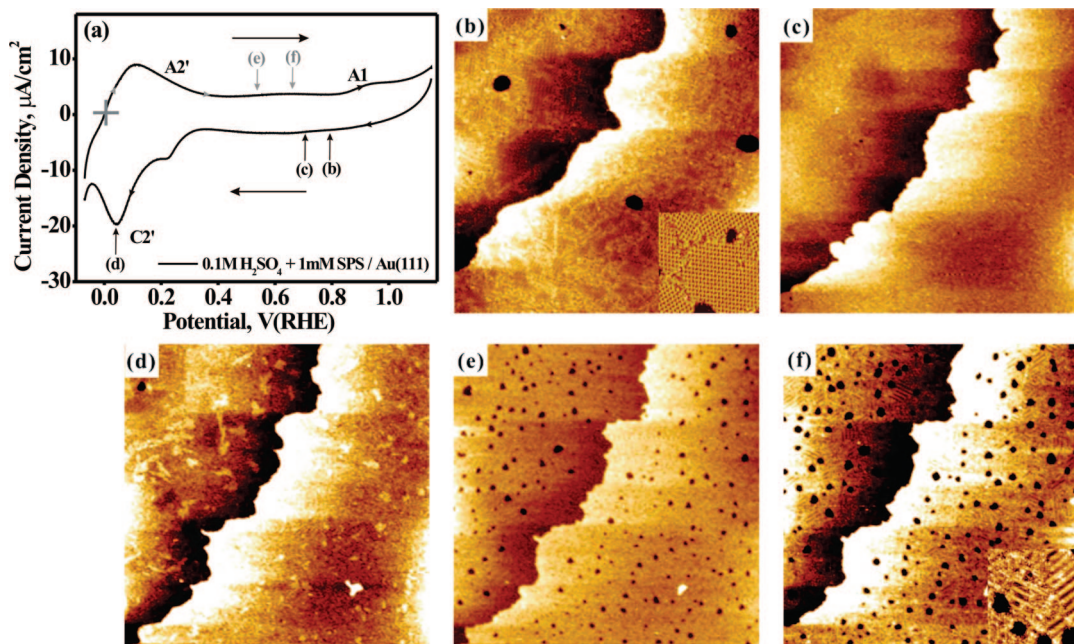


Figure 6. In situ STM images showing the phase evolution of an ordered SPS adlayer in an electrochemical desorption (negatively sweeping from panels b to d) and a followed readorption (positively sweeping to panels e and f). The high-resolution lattice images before (b) and after (f) this action are shown in the insets. These images correspond to the states indicated in the CV profile (a).

Figure 6. Ordered domains as well as the etching pits can be observed at potential 0.8 V (Figure 6b), but these features disappear at 0.7 V (Figure 6c). At 0.05 V where the SPS adlayer was largely desorbed, the Au(111) electrode seemed roughened (Figure 6d), probably due to the desorption of adlayer and adsorption of protons and other ions. In the reversal sweep, a disordered adlayer appears accompanying by distributed pits of etching defects at 0.55 V (Figure 6e), which looks similar to that of MPS-modified Au(111) shown in Figure 3b.

When the potential reached 0.65 V, the disordered adlayer was displaced by an ordered structure exhibiting a well-defined striped feature (Figure 6f). A higher resolution image shown in the inset of Figure 6f reveals that this structure is the same as that of MPS. These results support the model proposed in the literature,^{35,36} as well as our view in the previous discussion, that the S—S bond of SPS was cleaved upon its adsorption on Au(111) and it was MPS molecules that were actually adsorbed.

A higher resolution STM image ($70 \times 70 \text{ nm}^2$) taken for the SPS adlayer indicates two lattice structures (phases I and II) as shown in Figure 7. The STM molecular images revealing phases I and II are shown in panels a and b of Figure 8, respectively. Both images reveal ordered arrays made of elongate rods measured to be 1.4 nm from end to end (marked by the dash cycle in Figure 8a). Because this dimension is two times larger than that of a MPS molecule, it is thought that each rod is made of two MPS molecules. The difficulty to differentiate each individual MPS molecule could be associated with the possibility of other structures. The shape of this elongated unit leads us to propose two MPS molecules (dissociated from SPS) lying on the substrate with head-to-head configuration of thiolate in the center and outward exposing of sulfonic groups.

Around each unit are four neighboring units which cross-intersect with the center one, forming a network structure for both phases. The unit cells marked in the STM images indicate $(2\sqrt{21} \times 6)$ and $(3\sqrt{13} \times 6)$ structures for phases I and II, respectively. The structure models proposed for the two phases are schematically shown below the STM images. According to these models, the coverages of thiolate on the Au(111) surface

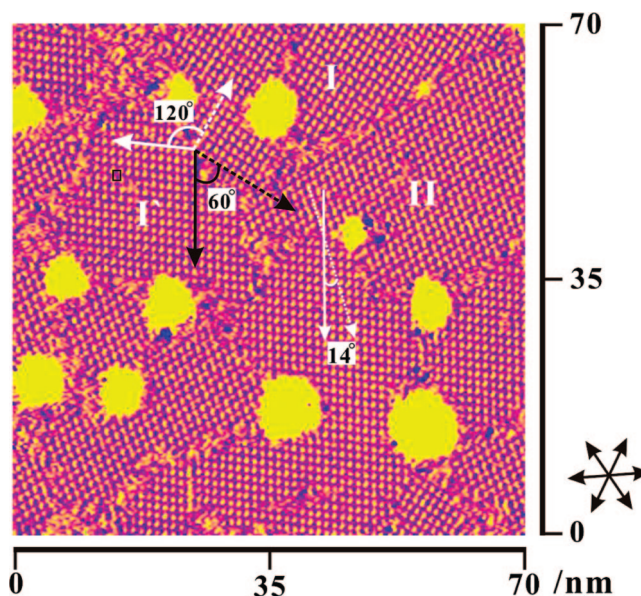


Figure 7. High-resolution STM image of SPS adlayer on Au(111) surface. The tip potential and the tunneling current were -0.62 V and 2.3 nA , respectively.

were estimated to be 0.09 and 0.11, respectively. Stripping voltammetric experiments can be performed with Au(111) electrodes coated with alkanethiol molecules in 1 M KOH. These electrochemical measurements can yield information concerning the strength of Au—S bonds and the coverage of thiolate species adsorbed on Au(111).^{17,40} We adapted this method on MPS- and SPS-modified Au(111), and the results are shown in Figure 9. A sharp reductive peak appears at about -0.75 V (vs Ag/AgCl) for both MPS and SPS. The charges contained in the reduction peaks of MPS and SPS were $38 \pm 0.5 \mu\text{C}/\text{cm}^2$ and $40 \pm 0.5 \mu\text{C}/\text{cm}^2$, respectively. These values translate into coverages of

(40) (a) Esplandiù, M. J.; Hagenstrom, H.; Kolb, D. M. *Langmuir* **2001**, *17*, 828. (b) Loglio, F.; Schweizer, M.; Kolb, D. M. *Langmuir* **2003**, *19*, 830.

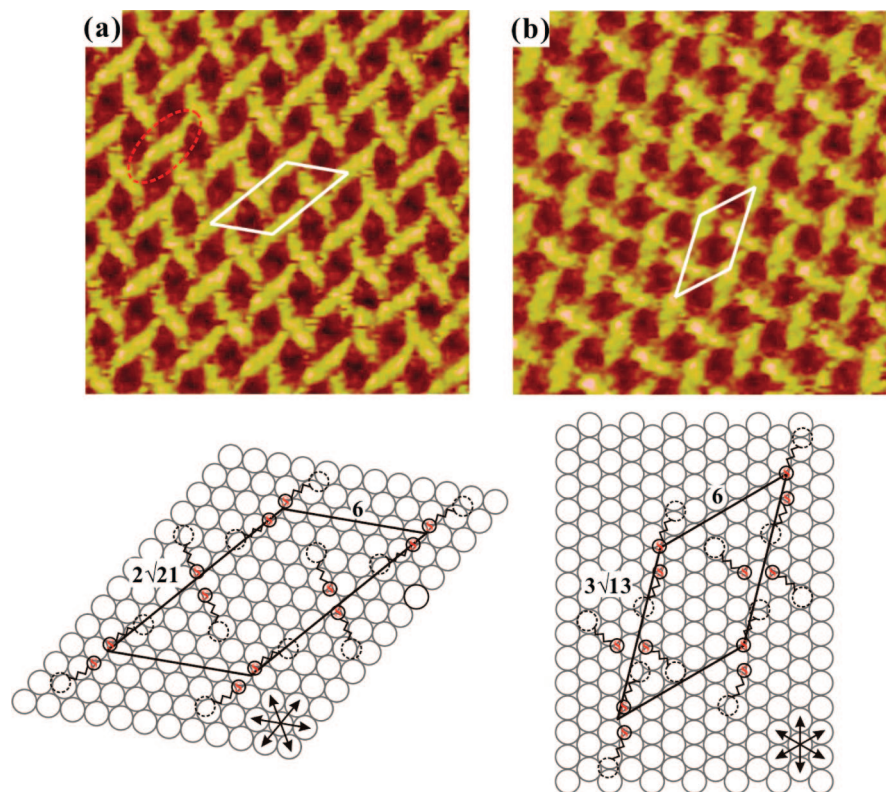


Figure 8. Molecular resolution STM images of SPS adlayer of structures I (a) and II (b) on Au(111) surface (scan size $10 \times 10 \text{ nm}^2$). The corresponding molecular models proposed for the two structures are shown below the STM images.

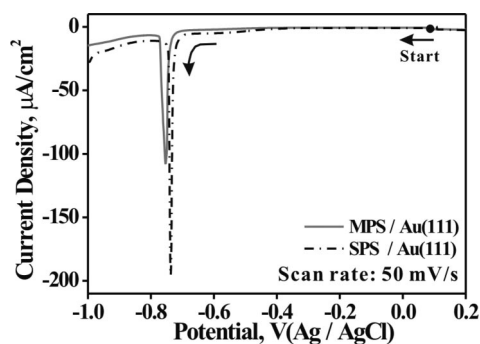


Figure 9. Cyclic voltammograms for MPS- (solid line) and SPS-modified (dash line) Au(111) electrodes recorded at 50 mV/s in 1 M KOH.

0.158 and 0.166, assuming a reduction scheme of $\text{RS}-\text{Au} + \text{e}^- \rightarrow \text{RS}^- + \text{Au}$. Compared with the coverage deduced from the STM images in Figures 3 and 8, these values are slightly larger, probably caused by the unaccounted molecules adsorbed at surface defects of steps, domain boundary, etc.

Although MPS and SPS have different adsorption mechanisms and adlayer structure, the two adlayers exhibit similar characteristics in terms of the phase evolution, surface coverage, striping potential, and CV behavior. These results are consistent with the facts that both MPS and SPS act similarly as additives in the copper-plating process. It is noteworthy that the presence of other additives in a practical copper plating bath may lead to an adsorption behavior different from the present result.^{25–30} Further

studies are required to elucidate the effect of other components in the practically complicated system.

Conclusion

The present study demonstrates that MPS and SPS are adsorbed similarly on a Au(111) surface. SPS molecules dissociate to MPS molecules as they are adsorbed on Au(111). The resultant lateral molecular arrangement however differs from that made by direct adsorption of MPS. Ordered striped and netlike structures are found for adsorbed MPS and SPS molecules at ca. 0.67 and 0.8 V, respectively. Disordered adlayers were observed at more negative potentials for both molecules. When the SPS adlayer was subjected to an electrochemical desorption–readsorption process, it transfers to an adlayer resembling that of MPS. The present results indicate that SPS molecules were adsorbed through dissociation of S–S bonds and present in a form of MPS thiolate on the substrate.

Acknowledgment. This work was sponsored by the National Science Council of Taiwan under Contract No. NSC 96-ET-7-006-001-ET and NSC 96-2221-E-006-058 and is gratefully acknowledged.

Supporting Information Available: A figure showing the current density response on a Au(111) electrode after addition of MPS or SPS in a 0.1 M H_2SO_4 solution at 0.15 V (RHE). This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA8029598