

Structure of Dithiothreitol Monolayers on Au(111)

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We have investigated the structure and properties of dithiothreitol (DTT) monolayers adsorbed on Au(111). Using scanning tunneling microscopy (STM), and Auger electron spectroscopy (AES), we have compared the properties of DTT monolayers with those of more conventional octanethiol layers. STM measurements indicate that much of the DTT layer is disordered; however, small ordered regions with local $2\sqrt{3} \times \sqrt{3}$ symmetry are observed. STM images of octanethiol films exhibit the characteristic close packed $\sqrt{3} \times \sqrt{3}$ molecular layer with $c(4 \times 2)$ supersymmetry. AES indicates sulfur coverage for both the DTT and octanethiol films is similar. AES studies involving Ellman's reagent, a marker species, suggest a significant fraction of the DTT molecules in the adlayer bind to the gold via two Au–S bonds. On the basis of AES and STM measurements, we propose a structural model in which the majority of DTT molecules bind to the gold surface via two Au–S bonds. The distance between the two Au–S bonds is 5.00 Å, or the same $\sqrt{3}a$ spacing observed between close packed alkanethiol molecules.

Introduction

Self-assembled monolayers (SAMs) of thiol molecules on gold have attracted a great deal of interest due to the potential for far reaching application in a variety of areas.¹ Much work has focused on functionalized SAMs, which allow for microscopic tuning of macroscopic properties at the interface. A considerable part of this work has dealt with dithiols. α - ω dithiols in particular have been used in molecular electronics applications where one end of the molecule is attached to a metal electrode, and the other forms a chemical bond with a second electrode, i.e., a nanocrystal.² This application, like others, relies on an upright alignment of the dithiol molecule. Although this conformation exists for rigid-rod dithiols,^{3,4} it is not always present for more flexible dithiols.^{5–8}

Recently, dithiothreitol (DTT), was used as a base for titanium alkoxide thin films with potential photocatalytic application.⁹ DTT is a four carbon α - ω dithiol with hydroxyl groups on the second and third carbons (Figure 1). Formation of the titanium films requires that DTT bind to the gold surface via two Au–S bonds with hydroxyl groups exposed. In this configuration titanium(IV) isopropoxide molecules attach to DTT and form an alkoxide film. DTT conformation was inferred primarily by measuring surface wetting properties. The authors found the water contact angle was consistent with hydroxyl groups exposed on the outer surface of the DTT monolayer and consistent with previous studies of oxidized DTT.^{10,11}

In this paper, we further address the question of DTT conformation at the Au(111) surface and explore the microstructure of these layers using scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). For comparison, we have performed similar measurements on octanethiol (Figure 1), a more conventional alkanethiol SAM. Alkanethiol SAMs form crystalline layers as a result of both the chemical bond between the molecule and the gold surface, and the van der

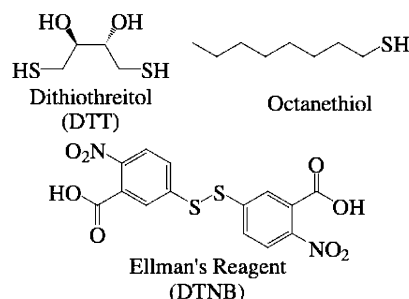


Figure 1. Structures of dithiothreitol, octanethiol, and Ellman's reagent.

Waals interaction between adjacent alkyl chains.¹ These interactions produce an upright ($\sqrt{3} \times \sqrt{3}$)R30° hexagonal lattice of molecules with an alkyl chain tilt angle of 30° from the surface normal.

Experimental Section

The DTT was provided by Diagnostic Chemicals¹² and used as received. Octanethiol was 98.5+% grade purchased from Aldrich.¹³ To address the question of Au–DTT binding, we also used 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB) which is commonly referred to as Ellman's reagent (Figure 1). The DTNB was 99% pure and purchased from Aldrich.¹³ All solutions were prepared in HPLC grade ethanol at a concentration of 1.0 mM.

The substrates were gold films epitaxially grown on mica in a vacuum. Following growth, the films were flame annealed in a natural gas flame. Flame annealing produces large flat Au terraces with (111) termination.¹⁴ The efficacy of the flame anneal step for each sample was determined directly by scanning tunneling microscopy (STM) prior to thiol adsorption. STM measurements were performed in air, and at room temperature using a Besocke^{15–17} style instrument controlled by RHK electronics.¹⁸

The Au films were immersed in thiol solution at 60 °C. The solution was heated prior to gold introduction, and the samples were held at 60 °C for the duration of the exposure. After

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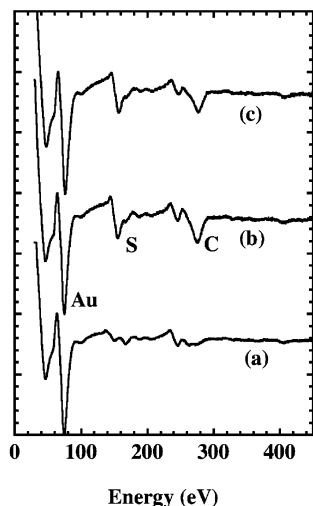


Figure 2. AES spectra of bare gold (a), octanethiol (b), and DTT covered films (c). The major peaks are Au(74 eV), S(153 eV), and C(275 eV). The Au:S ratio (~ 3) is similar for both DTT and octanethiol films.

exposure, the samples were removed from solution and rinsed with copious amounts of ethanol to remove any unbound thiol. Thiol adsorption was verified on selected samples using Auger electron spectroscopy (AES). These samples were introduced into an ultrahigh vacuum (UHV) system via a fast-entry load-lock. Clear carbon and sulfur peaks were observed in AES, indicating the presence of adsorbed thiol species. The Au:S ratio was similar for both DTT and octanethiol covered films (Figure 2).

Given the insulating nature of the alkyl chains, molecular resolution imaging with the STM requires that the tip reside outside the molecular layer. For longer thiols (10 carbon units or more), Bumm et al. found it necessary to scan at very low tunnel currents and maintain a tunneling impedance of 10 or even 100 G Ω to keep the tip outside the SAM.¹⁹ For the shorter chain octanethiol samples we required an impedance in excess of 2.0 G Ω to observe individual molecules. At fixed impedance we observed no bias dependence in the images. Stable images were obtained at both positive and negative sample bias. For DTT-covered films a tunneling impedance of ~ 1.5 G Ω was required to obtain molecular images. In addition, we only obtained molecular resolution for DTT under negative sample bias (tunneling out of filled states). At this time, the nature of the bias dependence remains uninvestigated.

To investigate the nature of the DTT conformation at the surface, both DTT and octanethiol covered surfaces were immersed in a 1.0 mM DTNB solution for 15 min at room temperature (RT). Following DTNB treatment, the films were transferred to the UHV system where AES measurements were performed to look for the presence of a nitrogen peak at 389 eV.

Results and Discussion

Figure 3 is a 500 Å \times 500 Å image of a Au(111) surface following immersion in 1.0 mM octanethiol solution at 60 °C for 4 h. The image includes a 50 Å \times 50 Å inset with single molecule resolution. The figure illustrates several features typical of alkanethiol SAMs on gold. The molecules form a densely packed $\sqrt{3} \times \sqrt{3}$ overlayer of molecules with $c(4 \times 2)$ superstructure.¹ The image also exhibits vacancy islands, or pits (large dark regions), one Au atomic layer (2.5 Å) deep, dispersed about

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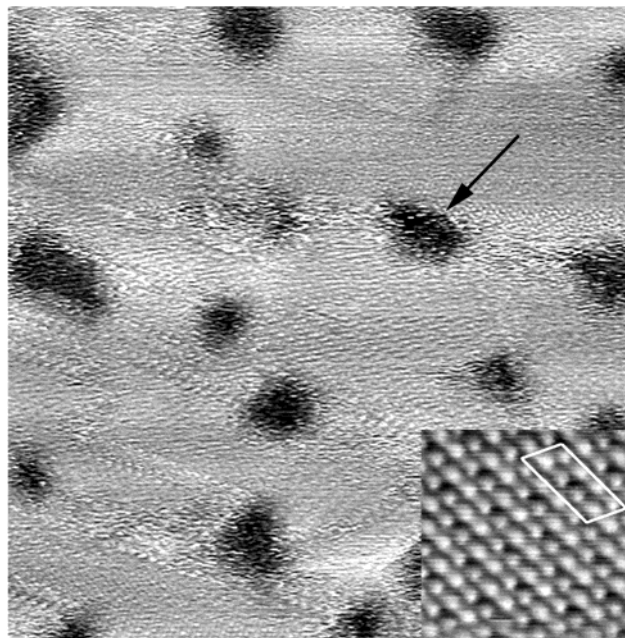


Figure 3. 500 Å \times 500 Å STM image of a gold surface following immersion in octanethiol solution at 60 °C for 4 h. The image was obtained at a sample bias of +1.0 V and a tunnel current of 0.5 nA. The larger dark regions are vacancy islands (example indicated by arrow) as discussed in the text. The image exhibits many of the features characteristic of an alkanethiol-covered surface. The molecules arrange in a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern as evident in the 50 Å \times 50 Å inset. Also evident in the inset is the $c(4 \times 2)$ unit cell (outlined).

the surface. The pits are ubiquitous to alkanethiol adsorption and related to rearrangement of Au surface atoms during chemisorption of the thiol molecules.²⁰

Figure 4 is an STM image of a sample following immersion in 1.0 mM DTT solution at 60 °C for 3 h. Similar to the octanethiol films, the surface exhibits 2.5 Å deep pits. The pits are smaller compared with similarly prepared octanethiol surfaces; however, the fraction of the surface covered with pits is the same in both cases (5–10%).²¹ Unlike octanethiol, the majority of the DTT layer is disordered. Small ordered domains (see inset) that exhibit local $(2\sqrt{3} \times \sqrt{3})$ symmetry are seen. This periodicity is larger than the $\sqrt{3} \times \sqrt{3}$ packing observed on octanethiol, and suggests that DTT does not pack as densely. The packing density suggested by the STM images is consistent with the Auger data. AES of both octanethiol, and DTT exposed films exhibit the same Au:S ratio (~ 3), indicating the same areal density of sulfur at the surface (Figure 2). Because each DTT molecule contains two S atoms, a similar Au:S ratio implies less DTT at the surface.

One question that arises when adsorbed dithiol layers are available is whether the molecules bind to the surface via one or two Au–S bonds.⁸ Tour et al.³ and Shon et al.⁴ find that rigid-rod dithiols form SAMs with one thiol attached to the surface, i.e., upright configuration. For more flexible dithiols both upright and prone (two Au–S bonds) configurations are possible.^{5–8} Previous ellipsometry and contact angle measurements for DTT and oxidized DTT are consistent with molecular adsorption via two Au–S bonds.^{9–11} Banks et al. compared the water contact angles of DTT covered surfaces ($31 \pm 2^\circ$), ω -hydroxyalkanethiol ($\text{HO}(\text{CH}_2)_{11}\text{S}$)–Au interfaces ($22 \pm 6^\circ$), octanethiol films ($98 \pm 2^\circ$), and bare gold ($50 \pm 6^\circ$).⁹ The values

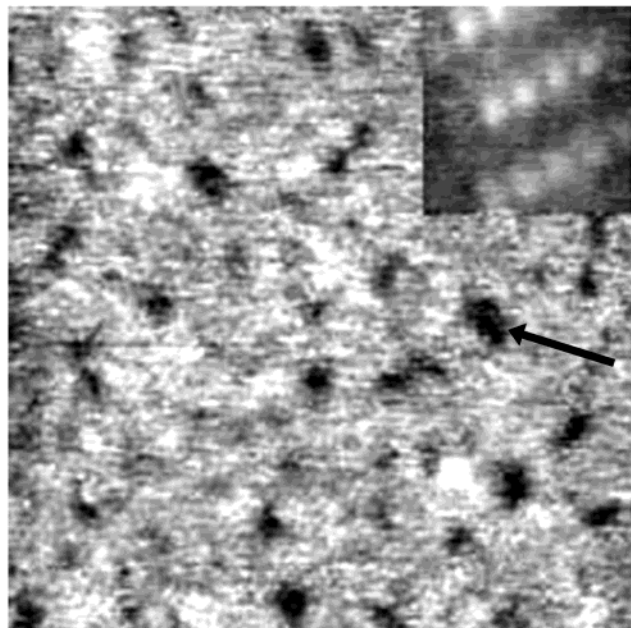


Figure 4. 500 Å × 500 Å STM image of a Au surface exposed to DTT at 60 °C for 3 h. The image was obtained at −0.87 V sample bias and 0.49 nA tunnel current. The 30 Å × 30 Å inset was obtained at −0.67 V and 0.49 nA on a surface immersed at 60 °C for 12 h. Much of the DTT layer is disordered, although regions of local $2\sqrt{3} \times \sqrt{3}$ are observed (see inset). Like octanethiol, the surface exhibits vacancy islands one Au layer deep dispersed about the surface (see arrow). These defects occur during thiol adsorption.

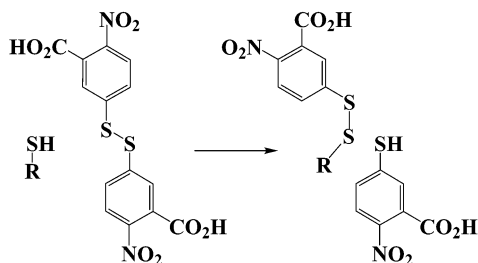


Figure 5. Chemical reaction between DTNB and free thiol. DTNB reacts with exposed thiol (left) to form a complex and liberate TNB (right).

for both DTT and ω -hydroxyalkanethiol films indicate hydrophilic surfaces and suggest DTT, like $\text{HO}(\text{CH}_2)_{11}\text{S}$, has hydroxyl groups exposed at the outer surface of the monolayer.

To further address the question of molecular attachment, we used DTNB. DTNB is commonly used to detect free thiol in solution.²² In solution, exposed sulfhydryl groups react readily with DTNB to form a complex and liberate 5-thio-2-nitrobenzoic acid (TNB). The liberated TNB is detected using UV/vis spectroscopy. In our experiment, the dithiol molecules reside as a monolayer on the Au(111) surface. Even if every dithiol molecule on the surface liberates one TNB molecule into solution, the UV/vis signal would be extremely small. As a result we chose to use AES to look for the presence of the complex at the surface. Specifically, we used AES to look for the presence of nitrogen. Barring steric constraints imposed by adsorption geometry, we expect DTNB to react with exposed thiol at the surface. The resultant TNB–thiol product would contain nitrogen and can be detected in AES (see Figure 5). In Figure 6, the AES spectra of bare Au(111) (a), octanethiol (b), and DTT (c) films following immersion in DTNB at RT for 15 min are presented.

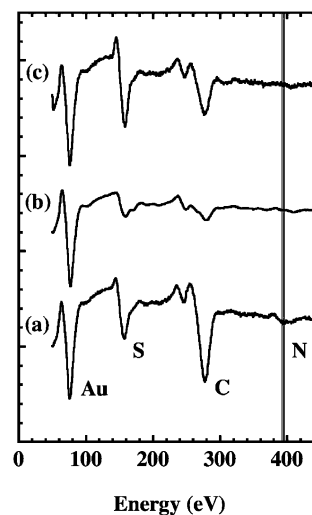


Figure 6. AES spectra of bare gold (a), octanethiol (b), and DTT covered surfaces (c), following exposure to DTNB at RT for 15 min. Only the bare gold substrate exhibits a measurable N peak at 389 eV (vertical line) following exposure to DTNB.

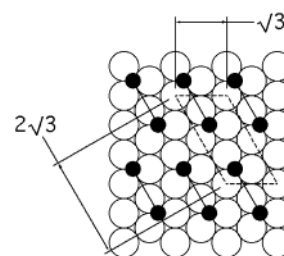


Figure 7. Proposed structural model for DTT adsorbed on Au(111).

Octanethiol and DTT covered surfaces exposed to DTNB do not exhibit any observable nitrogen peak. In contrast, the bare gold film exhibits both nitrogen and sulfur peaks at 389 and 153 eV, respectively. The nitrogen peak is considerably smaller than the sulfur transition. This is primarily due to differences in the Auger sensitivity of the transitions (at 3 keV beam energy the relative sensitivity of N is 1.22, and S 4.76).²³ Allowing for the different peak sensitivities, the curve suggests that nitrogen and sulfur are present in similar amounts at the surface. Although bare gold does not expose free thiol, it appears that the S–S bond in DTNB is broken when adsorbed onto Au(111) and a complete layer of TNB is produced at the surface. Both octanethiol and DTT covered surfaces do not display a N peak following DTNB exposure. The results suggest that both octanethiol and DTT form relatively compact layers (little exposed gold) and that the majority of DTT molecules bind to the surface via two Au–S bonds (no free thiol). Given the rather weak Auger sensitivity of the nitrogen transition, we cannot rule out small voids in the overlayer, or a small fraction of DTT molecules in an upright configuration.

The AES spectra of unreacted octanethiol and DTT films (Figure 2) indicate a similar areal density of sulfur at the surface. Octanethiol forms a compact monolayer with one molecule and Au–S bond per $\sqrt{3} \times \sqrt{3}$ cell,¹ and the AES results suggest the density of Au–S bonds is similar for DTT. STM results also indicate that the majority of the DTT overlayer is disordered, with local regions of $2\sqrt{3} \times \sqrt{3}$ symmetry. In these regions, we propose the structural model shown in Figure 7. In this model, the sulfur atoms are still packed in a $\sqrt{3} \times \sqrt{3}$ arrangement (consistent with AES); however, there are two sulfur atoms per molecule and thus the unit cell is larger. The molecule in this

configuration has both sulfur atoms spaced approximately 5 Å apart and oriented in the same direction, i.e., down.

To investigate the viability of this arrangement, a series of PM3-RHF calculations were carried out on several DTT conformations. The geometries were obtained using the eigenvector following a search algorithm, as described by Baker.²⁴ Two low-energy conformations were found. The distance between the two sulfur atoms in the lowest energy conformation was 5.7 Å (linear configuration). The other low energy conformation was only 0.20 kcal/mol higher in energy and the distance between the two sulfur atoms was 4.8 Å and similar to the spacing we propose for DTT on Au(111). The calculations suggest that there would be little or no conformational barrier toward DTT chemisorbing with the two sulfur atoms fitting nicely onto the (111) Au surface in a $\sqrt{3} \times \sqrt{3}$ configuration (the $\sqrt{3}$ distance on the surface is 5.0 Å).

The prone configuration for DTT is consistent with the behavior of other systems. DTT is a relatively short α - ω dithiol. Our calculations indicate that the molecule is flexible with little conformational barrier between the two bonding configurations. Previous work has shown that unlike more rigid α - ω dithiols, flexible dithiols can arrange in a prone configuration. This is particularly true for shorter molecules. UHV STM measurements of hexanedithiol,^{7,8} and octanedithiol⁶ layers concluded that the molecules lie prone on the surface, whereas XPS measurements of longer octanedithiol molecules adopt an upright molecular alignment.²⁵

In addition to length, molecular conformation can depend on the environment during monolayer formation. Esplandiú et al.⁸ found that the orientation of electrochemically deposited hexanedithiol depends on electrode potential. At 0.1 eV the molecules form a disordered layer with upright alignment; however, at more negative potential the molecules reorient into a prone configuration.

The alkanedithiol systems studied previously by STM exhibit large striped domains.^{7,8} The stripe spacing is consistent with the length of the dithiol molecules studied, and a $\sqrt{3}a_{\text{Au}}$ periodicity along the stripes was observed. The $2\sqrt{3} \times \sqrt{3}$ symmetry we observe for DTT is similar. In particular, the $2\sqrt{3}$ spacing is consistent with the length of the DTT molecule in a prone configuration. Compared with the alkanedithiol layers, however, DTT does not exhibit any large ordered domains. Although the reason for this is not well understood, the presence of hydroxyl groups on the DTT molecule will complicate interactions between adjacent molecules and may prevent long-range order.

Summary

We have used AES and STM to investigate the structure of DTT monolayers on Au(111). Unlike octanethiol, which forms an ordered $\sqrt{3} \times \sqrt{3}R30^\circ$ monolayer, the DTT monolayer forms

a compact but primarily disordered layer. STM measurements do reveal small regions of local $2\sqrt{3} \times \sqrt{3}R30^\circ$ symmetry. Like alkanethiol films, the DTT layer exhibits pits 2.5 Å deep dispersed about the surface which occur during thiol adsorption.²⁰

The symmetry observed in STM, previous contact angle experiments,^{9,10} and our AES experiments involving DTNB (Ellman's reagent), suggest much of the DTT layer binds to the surface via two Au–S bonds, i.e., in a prone configuration.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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