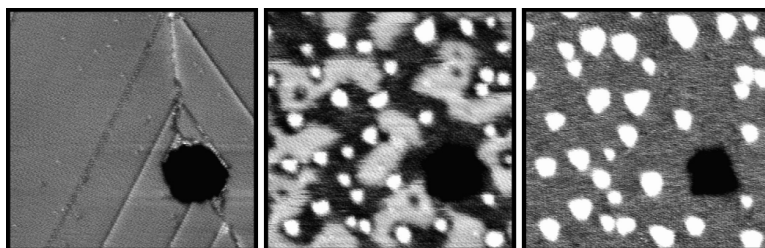


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Alkanethiol/Au(111) Self-Assembled Monolayers Contain Gold Adatoms: Scanning Tunneling Microscopy before and after Reaction with Atomic Hydrogen

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Self-assembled monolayers (SAMs) on Au(111) are some of the most thoroughly studied functionalized surfaces.^{1–3} However, the exact arrangement and configuration of molecules on the surface has long been debated.^{4–15} Recent studies have proposed several new structures that involve sulfur bonding to gold adatoms on the surface, deduced from experimental measurements (X-ray standing wave experiments, electron and X-ray diffraction, and scanning tunneling microscopy) and theoretical calculations (density functional theory and molecular dynamics).^{16–23} In this communication, we report the observation of gold atoms that remain behind after an octanethiol self-assembled monolayer on Au(111) is removed from the surface. We confirm that gold atoms are incorporated into alkanethiol monolayers at a 1:2 gold adatom/alkanethiol ratio.

The experimental approach is to react hydrogen atoms with octanethiol monolayers under vacuum conditions; details are provided in the Supporting Information. Briefly, a thermal gas cracker is attached to an ultrahigh-vacuum scanning tunneling microscope (STM), and images are taken of the same area of the surface before and after incremental dosing with hydrogen atoms. Using this method, changes in monolayer features are monitored over increased hydrogen atom exposure time.

Initial exposure to hydrogen atoms removes single octanethiol molecules, followed by the creation of larger defects and the reorganization of the monolayer.²⁴ In this communication, we use longer periods of hydrogen atom bombardment, which remove octanethiol molecules within close-packed regions of the monolayer, facilitate the formation of lower-density octanethiol phases, and eventually result in the complete removal of adsorbates from the surface. As the monolayer is removed, we observe large bright features that begin to appear in STM images.

Figure 1 shows changes that occur in the octanethiol SAM as a result of exposure to hydrogen atoms. Figure 1a shows the surface prior to hydrogen atom exposure, with features typical in STM images of alkanethiol SAMs: areas of close-packed molecules separated by domain boundaries, along with steps and vacancy islands in the gold substrate. After extensive hydrogen atom exposure (Figure 1b), the monolayer has been removed and large bright islands remain. Changes in the size and shape of the terraces are also observed. The areas of the vacancy islands have become smaller, while those of the terraces have increased, and step edges have become more faceted. Figure 1c–e shows the progression of the surface reaction in the center of the area imaged in panels a and b in Figure 1. We observe that, as the close-packed monolayer is removed, small bright features are formed in the vacated areas. These features then grow in size as more of the monolayer reacts, and there is a simultaneous decrease in the area of the gold vacancy island in the center right of the images.

X-ray photoelectron spectroscopy results reported by Gorham et al. show that, after long periods of hydrogen atom exposure,

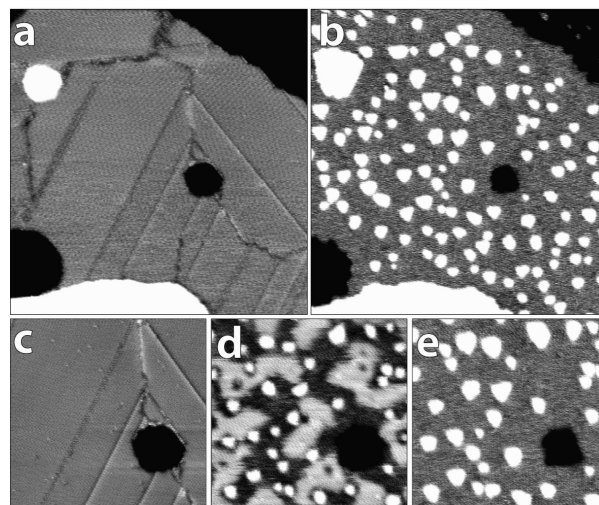


Figure 1. A $1290 \text{ \AA} \times 1320 \text{ \AA}$ octanethiol monolayer (a) before exposure to hydrogen atoms and (b) after 576 s hydrogen atom exposure. (c–e) A $320 \text{ \AA} \times 310 \text{ \AA}$ central area at higher resolution. As the monolayer is removed, bright island features appear and increase in size while the gold vacancy island shrinks (c–e).

short-chain alkanethiol monolayers are completely removed, with no detectable sulfur remaining on the surface.²⁵ We can further confirm this result, as in some cases after extended hydrogen atom exposure we observe the $23 \times \sqrt{3}$ “herringbone” reconstruction characteristic of the clean Au(111) surface in vacuum. We conclude that the bright features observed in STM images after hydrogen atom exposure are single-atom-thick gold islands, and Figure 2 presents additional evidence in support of this conclusion. The image in Figure 2a allows us to compare these gold islands to a nearby step, and the cross section in Figure 2b shows that the islands that appear after hydrogen bombardment have the same height (2.35 \AA) as the gold step. Islands also have flat tops and are frequently triangular in shape, which indicates that they are part of the crystalline gold surface. Finally, we observe that island shape and height do not vary with STM bias voltage and conclude that the islands have the same electronic structure as the underlying gold substrate; this is shown in Figure 2c and is described in greater detail in the Supporting Information.

The formation of new gold islands on the surface, as well as the shrinking size of vacancy islands in the gold surface after monolayer removal, is the result of an apparent increase in the total number of gold atoms in the image. Because hydrogen atom exposure is constant over a much larger area than is imaged, these atoms cannot be coming from other areas of the surface, and the remaining plausible explanation is that they are incorporated into the alkanethiol monolayer and released when the monolayer reacts away.

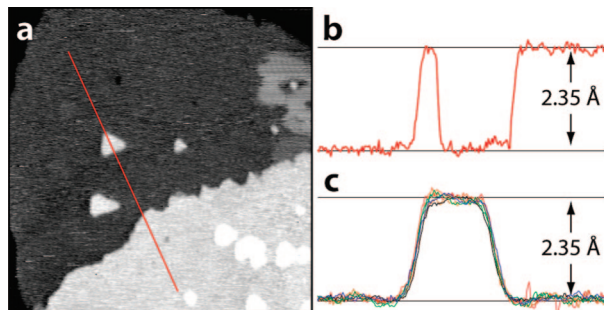


Figure 2. A 1340 \AA^2 octanethiol SAM that has been exposed to hydrogen atoms for 253 min. Large triangular islands have formed in areas where the monolayer has been removed. These islands have the same apparent height as neighboring terrace steps, as seen by the cross section in panel b. Panel c presents seven topographic cross sections recorded at STM bias voltages from -1 to 2 V.

We conclude and confirm that the native octanethiol monolayer structure includes gold adatoms. As octanethiol molecules are removed, the gold adatoms form into islands and deposit along step edges, resulting in the changes we observe: bright, flat, triangular islands; decreasing vacancy island size; and faceting of gold steps.

STM is sensitive to both topographic and electronic features of the surface. DFT calculations of simulated STM images show that electronic effects dominate over topographic ones, and that surface vacancies and adatoms result in small modulations in molecular feature intensities consistent with the monolayer superstructure usually observed in STM of alkanethiols.²³ Our results show that a newly formed gold island appears brighter than the remaining monolayer that surrounds it. This indicates that the electronic perturbation caused by the Au–S bond is stronger than the apparent topographic height added by the alkane chain; the magnitude of this effect is surprising, though the result is consistent with that of Wang et al.²³

We also observe that gold islands initially form along domain boundaries, and that upon further exposure form in areas of the monolayer where the octanethiol monolayer has been removed. As more of the monolayer is stripped from the surface, gold islands grow in size, as can be seen in panels d and e in Figure 1. This is a process of nucleation and growth: as octanethiol is removed, the gold atoms become mobile and can diffuse across the surface. They are more likely to nucleate in domain boundaries and areas free of octanethiol molecules and appear to be excluded from the remaining close-packed regions of the monolayer. We observe that monolayers that are quickly removed using very large hydrogen atom fluxes result in many small islands, as nucleation is favored over growth when large numbers of gold atoms are mobile on the surface at the same time. Conversely, low hydrogen atom fluxes result in few, large gold islands. We cannot say whether the two-dimensional gas-like phase is composed of mobile gold atoms or gold–alkanethiol complexes, though both are plausible at room temperature.²⁶

Analysis of our images shows a 0.143 ± 0.033 increase in gold coverage after monolayer removal by hydrogen atoms (see Supporting Information for details). This is the quantity of gold (fraction of a monolayer) that is “freed up” when the alkanethiol monolayer reacts away; thus, the octanethiol monolayer is accompanied by extensive reconstruction of the gold surface that requires 0.143 additional layers of gold when compared to a bulk-terminated surface. The $c(4 \times 2)$ structure of alkanethiol monolayers contains four molecules and has a unit cell 12 times the area of the Au(111) primitive cell. There are thus 1.7 ± 0.4 additional gold atoms in

each $c(4 \times 2)$ unit cell; that is, there is one additional gold adatom for every two alkanethiol molecules. This is consistent with a number of structural models, including those proposed by Maksymovych et al.,²⁰ Mazzarello et al.,²¹ and Nagoya et al.²² However, we do not observe sufficient gold on the surface for other adatom-based models, which predict 1:1,^{16–19} 2:1,¹⁹ and 0:1²³ gold adatom/alkanethiol ratios, to be correct.

Our study does not provide a direct confirmation that the reconstruction of the gold surface is adatom-based. Complex rearrangements involving adatoms, vacancies, and multiple surface layers would also be consistent with our data, though any such rearrangement must have a net surplus of one gold atom per two alkanethiol molecules, compared to the bulk termination.

Previous adatom-based models have tended to concentrate on small alkane chains (primarily methane-, ethane-, and butanethiol), and the possibility remains that the gold reconstruction observed for these short-chain alkanethiols is different from the intermediate-length octanethiol used in our experiments. We are currently studying the exposure of ethanethiol monolayers to atomic hydrogen, and preliminary results suggest a similar gold reconstruction to that reported here.

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Supporting Information Available: Background discussion, experimental detail, gold island analysis, and structural models presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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