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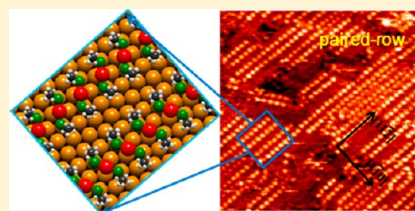
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Adsorption and Electron-Induced Dissociation of Ethanethiol on Au(111)

Fangsen Li,^{†,‡} Lin Tang,[‡] Jianzhi Gao,[‡] Wancheng Zhou,[§] and Quanmin Guo^{*,‡}[†]State Key Laboratory of Low-Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, China[‡]School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT, U.K.[§]State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

ABSTRACT: Dissociation of ethanethiol and the formation of Au-adatom-diethylthiolate rows on the Au(111) surface were investigated using scanning tunneling microscopy (STM) at low temperature. Ethanethiol molecules physisorb on Au(111) at 120 K by sequentially occupation of the elbow site, the fcc domain before covering the whole surface with a semiliquid layer without long-range order. Scanning the physisorbed layer with a sample bias higher than +1.2 V leads to dissociation via cleaving the H–S bond. One of the dissociation products, ethylthiolate, forms a double-row structure with the rows aligned in one of the $\langle 11\bar{2} \rangle$ directions. These double rows arise from the Au-adatom-dithiolate species: $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{SCH}_2\text{CH}_3$.



INTRODUCTION

Self-assembled monolayers (SAMs) of alkanethiol molecules on the Au(111) surface have been extensively studied for more than three decades.¹ Although the concept of a dense molecular layer self-assembled above a metal surface is clear and simple, a thorough understanding of the atomic structure at the molecule–substrate interface has not yet been achieved. Early studies of this system assumed that alkanethiolate species directly bond to a nearly perfect Au(111) surface^{2–10} with the S atom occupying one of the high symmetry sites, hence giving rise to the experimentally observed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.^{10–14} However, since the molecule–Au(111) interface is buried beneath the alkane chains, most of the surface sensitive techniques are unable to provide a direct image of the interface. Thus, a vigorous test of the existing models based on the thiol–Au bonding had not been available until the important discovery of the Au adatoms.^{15–20} Although the initial experimental verification of the Au adatoms was achieved by STM imaging of low-coverage methylthiolate at low temperature,¹⁵ subsequent studies confirmed the existence of such adatoms at room temperature within a complete monolayer of octanethiols.^{21,22} By taking into consideration of the Au adatoms, several new structural models for alkanethiol SAMs on Au(111) have been proposed.^{18,20,23–25}

The majority of the structural studies aim at explaining the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase and the associated $3 \times 2\sqrt{3}/c(4 \times 2)$ phase. In order to simplify the system, short-chain alkanethiols such as methanethiol and ethanethiol are introduced by assuming that the structure of alkanethiol SAMs on Au(111) is independent of the chain length. There is a clear advantage of using methanethiol in theoretical modeling. This is because van der Waals interaction cannot be modeled accurately, and in the case of methanethiol the van der Waals interaction between two methyl groups can be ignored with little effect on the overall outcome.^{8–10,23,25,26} However, the

assumption that methanethiol would form the same structure on Au(111) as the longer chain alkanethiols, albeit logical, has been seriously questioned according to recent investigations. Kondoh et al. were the first to report the observation a 3×4 phase for methylthiolate at full coverage.²⁷ Because they only observed such a phase at cryogenic temperatures; it has been assumed that this is not a stable phase at room temperature. Since then, a similar 3×4 phase has been reported for methylthiolate monolayer prepared in solution on Au(111)²⁸ and in vacuum,²⁹ ethylthiolate monolayers prepared in solution,³⁰ and in electrochemical cells,³¹ all at room temperature. A more recent study carried out in our laboratory using high-resolution STM imaging at both RT and low temperature on methylthiolate and ethylthiolate monolayers prepared in vacuum shows that the 3×4 phase is the thermodynamically stable phase at room temperature for both monolayers.³² The $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase and its $3 \times 2\sqrt{3}/c(4 \times 2)$ variants for the longer chain alkanethiols do not exist for methanethiol and ethanethiol monolayers.

In view of the nonexistence of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase for methyl and ethylthiolate monolayers and the presence of Au adatoms, new investigations need to be conducted as well as re-examination of previously reported works, including some of our own work.^{33–35} What is reported here forms part of our recent study of this controversial system. Here we present findings from an STM study of ethanethiol adsorbed on Au(111). We prepare a physisorbed ethanethiol monolayer at 120 K. We then apply a sample bias greater than +1.2 V to induced S–H bond breakage. This is then followed by the formation of $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{SCH}_2\text{CH}_3$ which is observed in organized rows. Our finding is comparable to the structures

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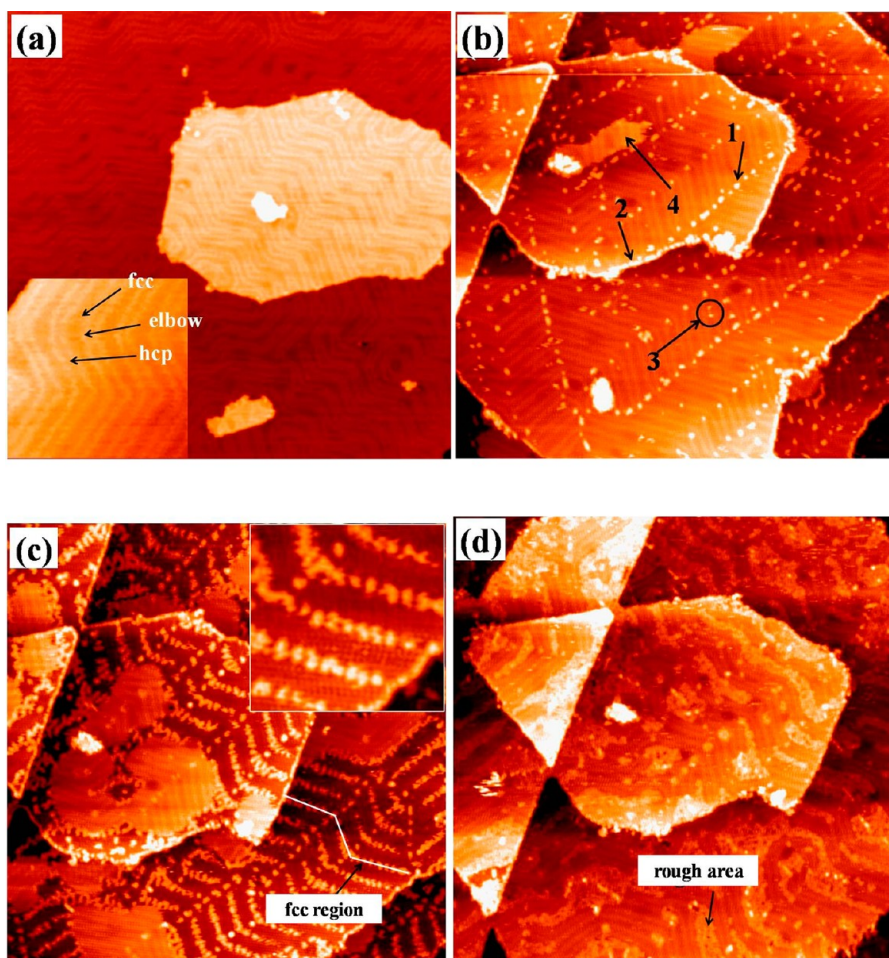


Figure 1. (a) Clean Au(111) surface before dosing ethanethiol molecules at 120 K. Image size: 200 nm \times 200 nm. Inset highlights the fcc and hcp stacked regions and the elbow site. (b) STM image, 150 nm \times 150 nm, showing the surface at the early stage of adsorption. Arrow 1 points to a molecules at an elbow site; arrow 2 points to molecules at step edges; arrow 3 points to molecules within the fcc region; arrow 4 points to a dense molecular island. (c) Selective population of the fcc stacked regions by well-spaced molecules. (d) Completion of the first molecular layer. The herringbone reconstruction could be observed through the molecular layer. All images were obtained at 120 K with $V_b = -1.20$ V and $I_t = 0.05$ nA.

observed after exposing Au(111) to diethyl disulfide³⁶ and can be explained rather well using the Au-adatom-dithiolate model.

EXPERIMENTAL SECTION

The experiments were conducted in an ultrahigh vacuum (UHV) chamber with a base pressure of 5.0×10^{-10} mbar. The gold sample was a thin film prepared by thermal evaporation of gold onto a highly oriented pyrolytic graphite substrate in a BOC Edwards Auto 306 deposition system. Such an Au thin film exposes large (111) oriented atomic terraces which are used for the adsorption of ethanethiol. The sample, once transferred into the UHV system, was cleaned with cycles of Ar^+ ion (1 keV energy) sputtering and thermal annealing to 950 K until atom-resolved herringbone reconstruction was observed. Ethanethiol (ET) molecules were introduced into the UHV chamber via a leak valve connected to a glass tube containing the ET (97%, Aldrich) liquid. The Au sample was cooled down to 120 K using liquid nitrogen during dosing under 5.0×10^{-7} mbar of ethanethiol vapor. STM imaging was performed continuously as the surface coverage of the ET molecules increased to a full layer. A built-in PBN heater in the sample holder was used to vary the sample temperature from 120 K to room temperature (RT). All STM images were acquired, using electrochemically etched tungsten tips, under a sample bias voltage of -1.2 V with a tunneling current of 0.05 nA.

RESULTS AND DISCUSSION

Short-chain alkanethiol molecules have low adsorption energies on Au(111). Single-layer methanethiol thermally desorbs from Au(111) at 160 K, and for single-layer *n*-propanethiol the desorption temperature is 210 K.³⁷ The desorption temperature for ethanethiol is thus estimated to be between 160 and 210 K. When ethanethiol is dosed to Au(111) at room temperature, a dissociation probability of $\sim 5 \times 10^{-5}$ is measured.³² Here we focus on the formation of a non-dissociated physisorbed layer at 120 K.

Figure 1a shows an STM image of the clean Au(111) surface with its usual herringbone reconstruction pattern. Initially, ethanethiol molecules are found only at the elbow sites and step edges (Figure 1b). Once the elbow sites are taken by the molecules, the fcc region becomes populated (Figure 1c). This is similar to what happens when methanethiol molecules are dosed at 100 K.³⁷ As more molecules land onto the surface, a complete layer is eventually formed (Figure 1d). Figure 2 shows a sequence of STM images from the same area of the sample as the molecular coverage increases.

Inset in Figure 1c shows that molecules within the fcc region keep a certain distance from each other. This is probably due to an electric dipolar repulsive interaction between ET molecules. The preferential occupation of the fcc region suggests that at

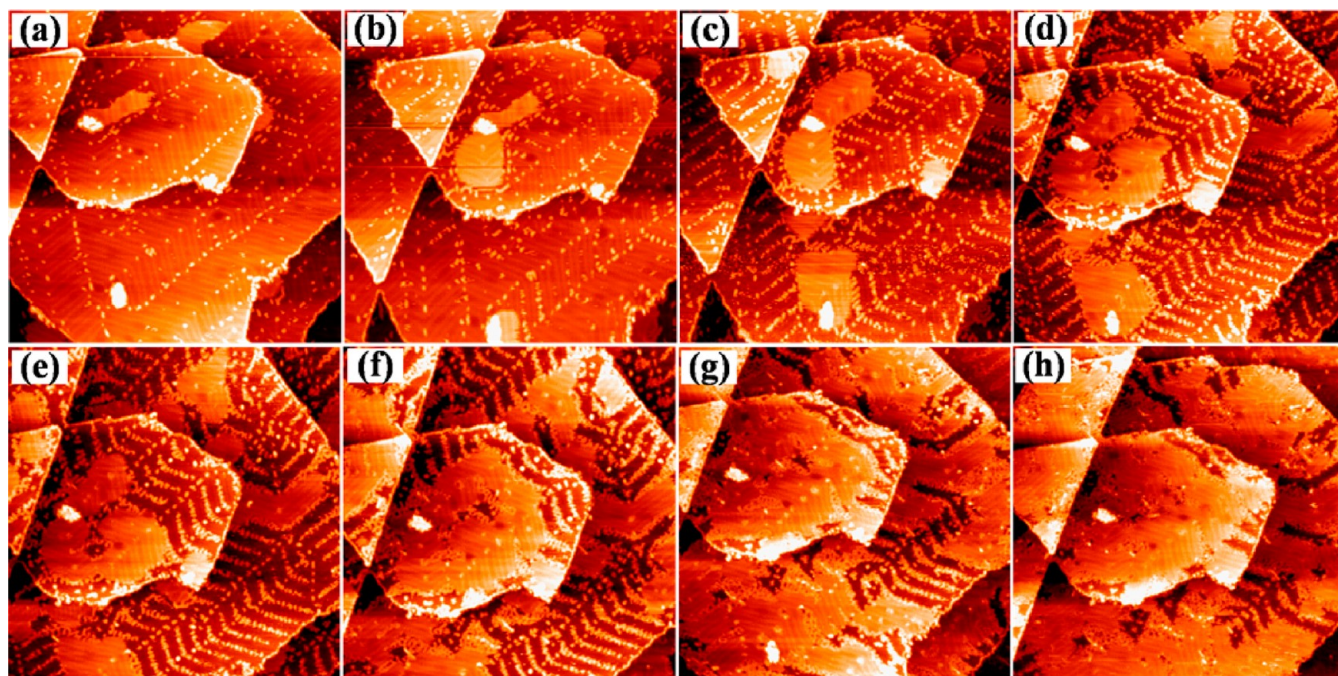


Figure 2. Time-lapsed STM images, 150 nm \times 150 nm, showing how the evolution of the physisorbed overlayer. All images were obtained at 120 K with $V_b = -1.20$ V and $I_t = 0.05$ nA.

120 K ET molecules can easily jump from the hcp region over the discommensuration line to the fcc region. Well before the completion of the molecular layer, some dense-looking molecular islands are found on the atomic terrace, such as the one pointed by black arrow 4 in Figure 1b. The formation of a dense island at less than saturation coverage would suggest an attractive interaction between the molecules. This contradicts the obvious repulsive interaction observed for molecules inside the fcc region. The dense islands shown in Figures 1 and 2 have no special topological features and they appear very smooth in the images. Height profiles shown in Figure 3 provide some evidence that the dense islands consists of the same molecular species as those attached to the elbow site.

A possible explanation for the observation of the dense islands is that these islands are not actually condensed islands. Instead, they arise from fast moving molecules. Apart from the molecules fixed at the elbows, molecules on the surface at 120 K are mobile. However, their movement is either confined by the fcc region or by some other boundaries such as steps. Therefore, a small number of fast diffusing molecules confined to a local area would produce a “ghost island”. As more and more molecules are deposited onto the surface, more islands appear and the density of each island increases. At full layer coverage (Figure 1d), the molecules are still mobile, albeit their movement is impeded by neighboring molecules. In Figure 1b, there is a small bright patch at the left corner of molecular island 4; this is due to a pre-existing small Au island. In a previous study of physisorbed *n*-propanethiol using temperature-programmed desorption (TPD),³⁸ Rzenicka et al. found that, apart from a multilayer desorption peak, there are more than one desorption peak from the first monolayer, indicating that the first molecular layer is inhomogeneous. The different structural phases observed in our STM imaging for ethanethiol are thus consistent with their TPD results. One expects a low-temperature desorption peak from the liquidlike phase, followed by at least one more peak due to molecules

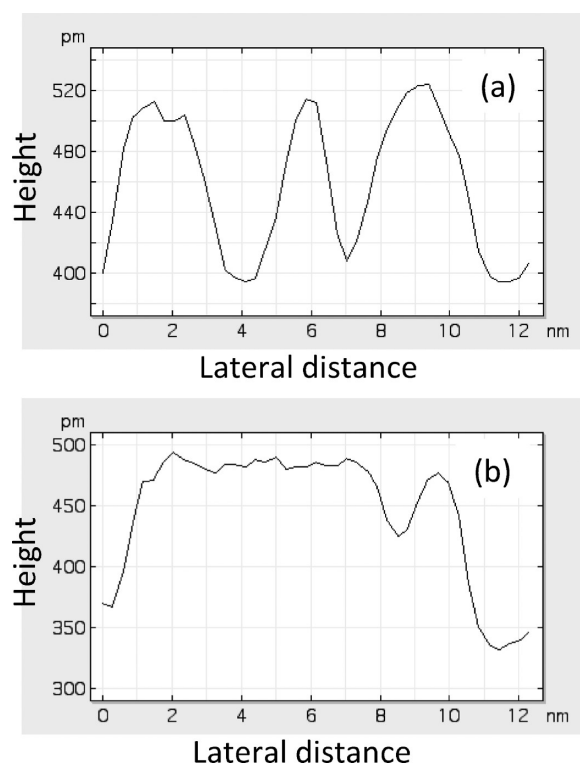


Figure 3. (a) Height profile across bright features at the elbow sites. They are 0.12 nm tall measured from the Au(111) substrate. (b) Height profile across a dense molecular island and one bright feature at an elbow site. The molecular island has the same height as the individual bright features.

desorbing from the fcc region and the elbow sites. The complete layer as shown in Figure 1d does not seem to have a uniform structure. Some areas appear smooth and “transparent” with the underlying herringbone pattern seen through the

molecular layer. Other areas consist of loosely packed molecules and appear grainy. All the molecules are physisorbed without dissociation. This is proved by raising the sample temperature to RT at which point all molecules are found to have desorbed leaving behind a clean Au(111) surface.

We have tried two different ways to induce molecular dissociation: (i) slow thermal annealing to 220 K and (ii) scanning with a large enough sample bias voltage or applying a voltage pulse. While annealing is found to be hardly effective, we find that scanning the sample with +1.2 V or higher can lead to rapid electron-induced dissociation similar to that found for adsorbed propanethiol molecules.¹⁹ Scanning with −1.2 V does not seem to affect the molecules, suggesting that electron injection from the tip into the molecule is required for dissociation. Under both positive and negative bias voltages, there is a strong electric field beneath the STM tip. Field induced effect cannot be ignored although we have not performed any detailed study on such an effect.

Figure 4a shows an STM image of the Au(111) surface covered by a smooth layer of ethanethiol. We performed a few

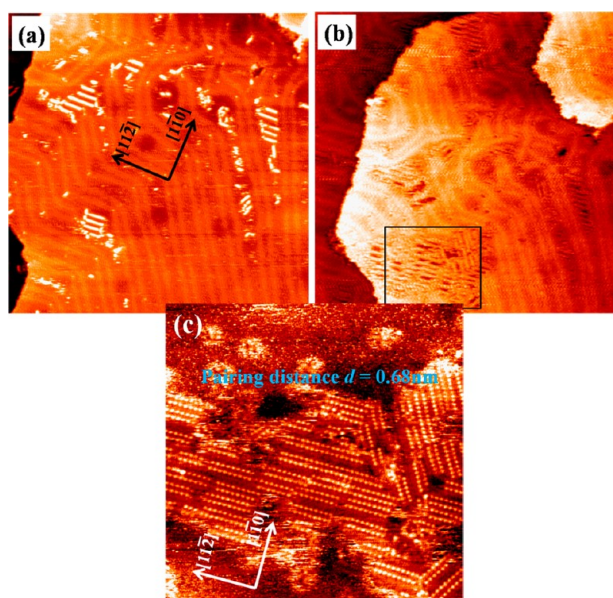


Figure 4. A series STM images showing ethanethiol adsorbed on Au(111) at 120 K. (a) STM image, 80 nm × 80 nm, showing striped-like phases nucleated exclusively inside fcc regions. (b) The striped-like phases grow under STM scanning. This STM image is 90 nm × 90 nm. (c) High-resolution STM image of the stripes, 30 nm × 30 nm, from the area inside the black rectangular box in (b), showing each bright row in (a) and (b) actually contains two paired rows.

bias voltage ramps from −3 to +3 V. This resulted in the appearance of bright stripes within an otherwise featureless molecular layer. These bright stripes are located in the fcc region of the herringbone reconstructed surface and they are parallel to the $[11\bar{2}]$ direction. Figure 4b shows an image where larger patches of stripes are found. From this image it can be seen that the formation of the stripes has lifted the surface reconstruction. This is a clear signal that some sort of chemical bonding has been formed between the stripes and the Au(111) substrate. Since a similar electron injection process has already been demonstrated to be able to dissociate *n*-propanethiol on Au(111),¹⁹ we thus deduce that the stripes are a direct result of ethanethiol dissociation.

Figure 4c shows a high-resolution STM image for the striped-like phase inside the black box in Figure 4b. Comparing the image in Figure 4b with that in Figure 4c, we find that each bright row in the low-resolution image in Figure 4b actually consists of two individual rows of bright spots. In Figure 4c, the rows always appear in pairs with the vertical distance between the two paired rows equal to 0.68 ± 0.03 nm. The distance between adjacent bright spots along each row is 0.50 ± 0.03 nm. Because of the 3-fold symmetry of the (111) plane, rows are found to be parallel to one of the three $\langle 11\bar{2} \rangle$ directions. The characteristic of the paired-rows are very similar to the Au-atom-diethylthiolate rows appeared on Au(111) after exposing the sample to diethyl disulfide.³⁶ Moreover, in our study of ethylthiolate monolayer formed on Au(111) at RT, similar paired-rows have also been identified.³² Therefore, the paired-row structure shown in Figure 4c arises from ordered Au-atom-diethylthiolate chains. A ball model for such ordered Au-atom-diethylthiolate chains is shown in Figure 5a. In Figure 5a, there are three rows of Au-atom-diethylthiolate or three paired rows of CH_2CH_3 . The local bonding environment involves an Au adatom at the bridging site with S forming a chemical bond with the Au adatom. The S atom also bonds atop an Au atom in the substrate. This structural motif has been confirmed by a number of recent investigations.^{15,20,32}

Obviously, Au atoms are required to form the Au-atom-diethylthiolate unit. The lifting of the surface reconstruction releases Au atoms equivalent to 0.045 ML. There is also the possibility that some Au atoms are dropped off from the STM tip during the bias voltage ramp. The STM tip, after scanning the Au(111) surface, is always coated with Au atoms. Based on the above analysis, the appearance of the paired rows can be explained as follows. Electrons from the STM are injected into the adsorbed ET molecule breaking the S–H bond. Two ethylthiolate species combine with a single Au atom forming a $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ unit. The $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ units pack into ordered rows as shown in Figure 5a. Within each row, an S atom from one $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ is located next to the Au adatom of the neighboring $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ unit. The negatively charged S atom and the positively charged Au adatom are held together by electrostatic attraction. This is the key driving force for the formation of the rows. Similar bonding scheme is also found in the 3×4 phase of the both methyl and ethylthiolate monolayers.³²

In the STM images, the terminal methyl groups appear as bright protrusions with the Au adatom invisible. For Au-atom-dimethylthiolate, both the methyl group and the Au adatom appear as bright protrusions.^{15,32} Thus, for Au-atom-diethylthiolate, the CH_3 group is sticking out away from the gold surface. The raised height of the CH_3 group makes it much more visible in the STM. The measured distance between two paired spots in the images, 0.68 ± 0.03 nm, also agrees with the above conclusion.

The magnified STM image in Figure 5b highlights the positional correlation of the bright protrusions. In this image, three paired-rows are labeled (i), (ii), and (iii). For rows (i), the solid black line marks out two CH_3 groups in a single $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ unit. The same is done for rows (ii). By doing this, we can determine that the $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ units in these two paired-rows take the same azimuthal orientation. The $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ units in rows (iii) are oriented differently as shown by the different direction of the solid yellow line. These two different

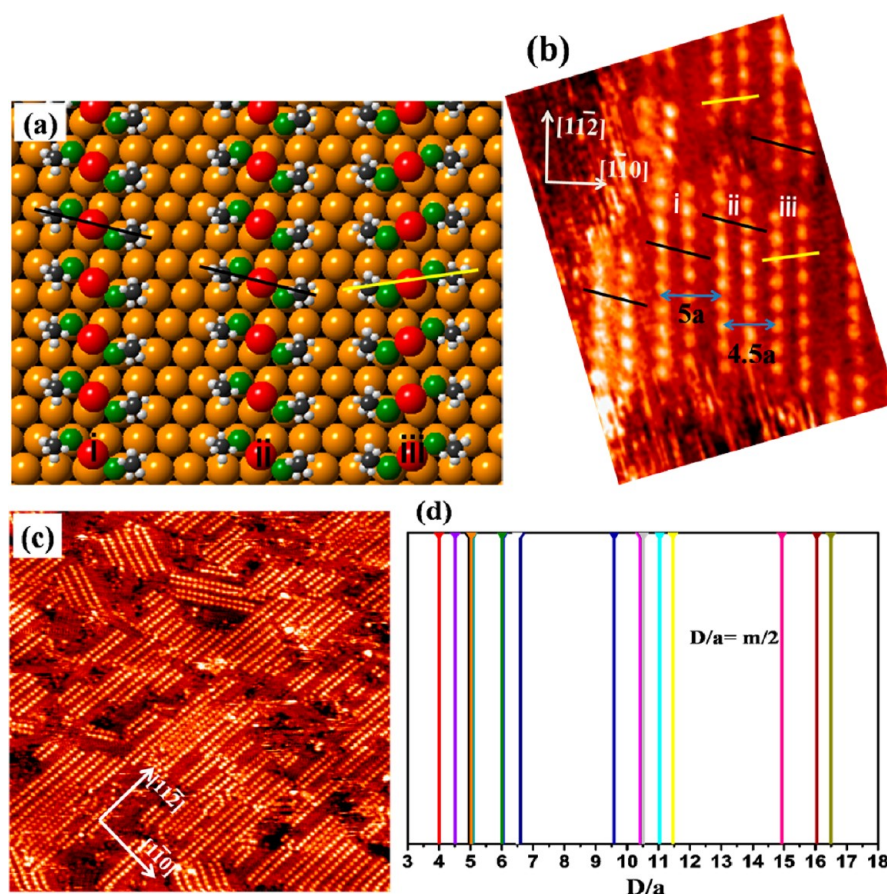


Figure 5. (a) Proposed model for the paired-row structure. The red balls represent Au adatoms, and the green ones represent the S atom. The bright spots in the STM images correspond to the CH_3 groups. (b) A cut-out image from Figure 4c, showing two different orientations of the paired-rows and the different spacing between adjacent pairs. (c) STM image, $35 \text{ nm} \times 35 \text{ nm}$, showing that after heating to 195 K the whole terrace is covered by paired rows. (d) Distance, D , between one paired rows and its next-door neighbor, plotted as D/a where a is the nearest-neighbor distance for surface gold atoms.

orientations are illustrated in the ball model in Figure 5a. From STM images, we find that the two orientations appear with equal probability. The interaction between S and the Au adatom ensures that within each paired rows $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ takes either one or the other orientation, but not both. In this particular case, the distance between rows (i) and rows (ii) is $5a$ where $a = 0.288 \text{ nm}$ is the nearest-neighbor distance of surface Au atoms. The distance between rows (ii) and rows (iii) is $4.5a$. The distance between neighboring paired rows varies; hence there is no standard period in the direction perpendicular to the rows. According to the ball model in Figure 5a, two neighboring pairs can take a number of different distances depending on the local coverage of the $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ unit.

The image in Figure 5c shows a more extensive formation of the $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ rows. In this case, the rows are formed at 195 K. At this temperature, one expects a thermally enhanced electron-induced dissociation as well as more abundant diffusing Au atoms on the surface. In this image, variation of the spacing between neighboring $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ paired rows is clearly seen. We measured the distances between adjacent pairs and plot the data in Figure 5d. This simple procedure leads to the finding that the distance is $ma/2$ where m is an integer. The minimum pair–pair distance found is $4a$ which is controlled by the surface coverage and the van der Waals interaction between the ethyl groups.

Too close a distance between two pairs would lead to greater repulsion between the ethyl group of one pair and that of the next pair. Because of the nonuniform pair–pair spacing, the structure seen in Figure 5c lacks long-range order in the direction perpendicular to the rows. At RT, we have observed a shorter pair–pair spacing of $3.5a$ within a $(5\sqrt{3} \times \sqrt{3})R30^\circ$ phase.³² This $(5\sqrt{3} \times \sqrt{3})R30^\circ$ phase has a regular two-dimensional lattice. Along the direction perpendicular to the rows, the spacing between adjacent pairs alternates between $3.5a$ and $4a$. As the coverage of $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ increases, the average pair–pair spacing will decrease. The $(5\sqrt{3} \times \sqrt{3})R30^\circ$ phase with 0.267 ML of ethylthiolate ($\text{CH}_3\text{CH}_2\text{S}$) corresponds to the highest coverage striped phase before the formation of the final 3×4 phase at 0.33 ML. As a comparison, the coverage for the image shown in Figure 5c is less than 0.2 ML.

CONCLUSIONS

Ethanethiol molecules adsorb nondissociatively at 120 K on Au(111). Electrons injected from the STM tip can induce S–H bond breaking and produce ethylthiolate. Two ethylthiolate species combine with a Au atom to form a Au–adatom–diethylthiolate ($\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$) unit. $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-\text{CH}_2\text{CH}_3$ units organize into rows parallel to the $[1\bar{1}2]$ direction with nonuniform row–row spacing. There are two different azimuthal orientations for the $\text{CH}_3\text{CH}_2\text{S}-\text{Au}-$

CH₂CH₃ units. Within a particular row, all CH₃CH₂S–Au–CH₂CH₃ take the same orientation, i.e., no orientation mixing.

AUTHOR INFORMATION

Corresponding Author

*E-mail Q.Guo@bham.ac.uk; Fax +44 121 414 7327.

Notes

The authors declare no competing financial interest.

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