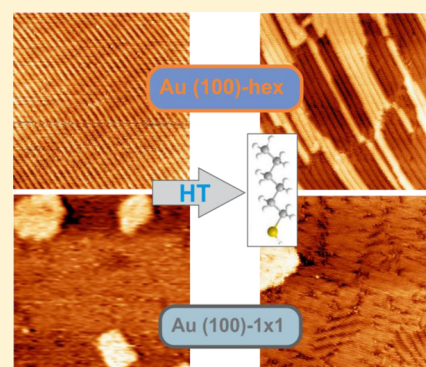


Thiol Adsorption on the Au(100)-hex and Au(100)-(1 × 1) Surfaces

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ABSTRACT: Alkanethiol adsorption on the Au(100) surfaces is studied by using scanning tunneling microscopy, X-ray photoelectron spectroscopy, and electrochemical techniques. Adsorption of hexanethiol (HT) on the Au(100)-hex surface results in the formation of elongated Au islands following the typical stripes of the reconstruction. Ordered molecular arrays forming hexagonally distorted square patterns cover the stripes with surface coverage ≈ 0.33 . On the other hand, HT adsorption on the Au(100)-(1 × 1) surface shows the absence of the elongated island and the formation of square molecular patterns with a surface coverage ≈ 0.44 . The core level shift of thiolates adsorbed on the Au(100)-(1 × 1) and Au(111) is only 0.15 eV, suggesting that chemistry rather than surface sites determines the binding energy of the S 2p core level. These results are also important to complete our knowledge of the chemistry and surface structure for small thiolated AuNPs where the Au(100) together with the Au(111) are the dominant faces.



■ INTRODUCTION

Gold has been used in many technological applications in the field of nanotechnology due to its large chemical stability, interesting optical properties, and biocompatibility.¹ Thus, gold surfaces have been used as platforms for building different devices based on the bottom up approach either from the gas phase or from liquid media under ambient conditions. In particular, self-assembly of thiols becomes the simplest and most efficient route for functionalizing all kinds of substrate topographies: single crystal, polycrystalline, and nanoparticle (NPs). This strategy allows us not only to design surfaces with controlled physical and chemical properties but also to perform additional chemical reactions for building complex molecular systems with specific activity. Today, the wide range thiol-based applications of gold surfaces comprise medicine, biochemistry, catalysis, and electronics.²

Most of the present knowledge for thiol modification of gold surfaces relies on the extensively studied alkanethiol–Au(111) system.³ It is well-known that thiol adsorption on the Au(111) surface produces the lifting of the herringbone reconstruction leading to the (1 × 1) surface structure. On this surface thiols form self-assembled monolayers (SAMs) that at saturation coverage organize in crystalline structures with molecules in standing up configuration, thiol–thiol nearest-neighbor distances $d = 0.499$ nm, 21.65 \AA^2 area per alkanethiolate molecule, and surface coverage $\theta = 1/3$. The thiol–Au interaction is a

covalent thiolate–Au bond that firmly attaches the molecule to the substrate as revealed by X-ray photoelectron spectroscopy (XPS). Also van der Waals forces (vdW) stabilize the SAMs⁴ adding ≈ 0.1 eV per C atom and aligning the alkyl chains parallel to each other in a nearly all-trans configuration and tilted $\alpha \approx 26\text{--}37^\circ$ to the substrate normal. However, small alkanethiol molecules can exhibit $\alpha \approx 50\text{--}60^\circ$ due to molecule–substrate interactions.

Scanning tunnelling microscopy (STM) data for alkanethiolates (RS) on Au(111) reveal different lattices depending on the number of C atoms in the molecules (n). Methanethiol ($n = 1$), ethanethiol (ET) ($n = 2$), and propanethiol ($n = 3$) organize in (3×4) lattices formed by the RS–Au_{ad}–SR complexes (Au_{ad} = Au adatom) in a *trans*-configuration.⁵ Alkanethiols with $n > 3$ form $c(4 \times 2)$ lattices with the RS–Au_{ad}–SR complexes in a *cis*-configuration. The surface coverage by RS–Au_{ad}–SR species ($\theta = 0.33$) needs $\theta_{ad} \approx 0.165$ provided by Au adatom uptake from step edges or from Au surface atoms at terraces, a process that leads to the typical vacancy islands.⁶ Also a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface structure is frequently observed with the $(\sqrt{3} \times \sqrt{3})R30^\circ/c(4 \times 2)$ surface coverage ratio increasing with n .

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In contrast to our detailed knowledge on alkanethiol surface structure and chemistry on Au(111), little is known about molecule organization on the Au(100) surface. This fact is important for understanding the behavior of thiols on polycrystalline and nanostructured gold. For instance, about 30% of gold nanoparticle surfaces greater than 3 nm is composed by {100} faces, while the remaining 70% consist on {111} faces.⁷ The small number of studies on the alkanethiol–Au(100) system provides complex and contradictory information. Earlier He diffraction data on the terminal methyl groups of long alkanethiolate SAMs⁸ indicate the presence of an incommensurate oblique array $\approx 20\%$ denser chain packing than alkanethiolate SAMs on Au(111). On the other hand, based on transmission electron diffraction measurements, it was proposed that alkanethiols arrange into a $c(10 \times 10)$ lattice with $d = 0.454$ nm and $\alpha = 6-12^\circ$.⁹ However, molecular dynamics calculations using the MM2 force field and at a constant temperature of 50 K did not support this surface structure since the alkyl chains undergo distortions of the C–C–C bond angles to reduce the free energy of packing of the all-trans chains.¹⁰ In contrast, low-energy electron diffraction (LEED) studies of short chain alkanethiols ($n < 7$) appear to be consistent with a $c(2 \times 2)$ surface structure, but the lattice constant ~ 0.407 nm in this structure is believed to be too small to accommodate the long chain thiols, exhibiting additional diffraction spot splittings.¹¹ The possibility of a qualitatively different packing arrangement of the chemisorbed sulfur atoms, the alkyl chains, and the terminal methyl groups were investigated by using He diffraction and synchrotron X-ray scattering techniques.¹² Their results show that the structure of the thermally equilibrated RS/Au(100) surface consists of a (1×4) thiolate/Au interface and a distorted hexagonal alkyl chain array. Also, STM in air investigations for decanethiol on the Au(100) surface reveal a $c(2 \times 8)$ with a (1×4) missing row on the Au(100)-hex and an incommensurate oblique structure on the Au(100)-(1 \times 1) surfaces.^{13,14} On the other hand, STM images taken in electrolyte solutions for different alkanethiols on the Au(100) surface show two different phases: the α phase, a quadratic arrangement with $d = 0.44$ nm, assigned to thiol adsorption on the unreconstructed Au(100)-(1 \times 1) surface, and the β phase, consisting of distorted squares with $d = 0.48/0.5$, assigned to thiol adsorption on the hex-reconstructed surface.^{15–17} These images also reveal Au islands with a surface coverage close to that expected from the lifting of the hexagonal reconstruction of the Au(100) surface to form the Au(100)-(1 \times 1) surface. Therefore, it is evident that a more detailed study of alkanethiolate self-assembly on the Au(100) surface deserves more experimental and theoretical work.

This work reports the self-assembly of hexanethiol (HT) on the reconstructed Au(100)-hex and unreconstructed Au(100)-(1 \times 1) surfaces from ethanolic solutions. STM operating in UHV, XPS, electrochemical techniques, and density functional theory calculations (DFT) allow us to obtain a description of the surface structures that are compared with those found for the same thiolate on the Au(111) under the same experimental conditions.

EXPERIMENTAL SECTION

Substrate Preparation. The Au(100) single-crystal substrate (MaTeck) was cleaned by repeated cycles of sputtering with Ar⁺ ions and annealing at 825 K. The cleanness of the sample was characterized in a STM operating in UHV. The Au(100)-(1 \times 1) surfaces were electrochemically

generated¹⁸ by starting from the Au(100)-hex substrate and then lifting the reconstruction in 0.5 M H₂SO₄ by applying a potential $E = 1$ V vs Ag/AgCl for either 300 or 1800 s. Occasionally, evaporated Au on chromium-coated glass plates (Arrandee) was used as Au(111) substrates. These plates, after flame annealing, consist of micrometer-sized Au(111) preferred-oriented single crystals with atomically smooth terraces.

Hexanethiol (HT) (Aldrich, 95%) and absolute ethanol (BASF 99%) were used as received. After UHV preparation and characterization of both Au(100)-hex and Au(100)-(1 \times 1) substrates, the samples were brought to air by using a transfer system between UHV and air and immersed for 24 h in 10^{-4} M HT containing ethanolic solutions. After that, the samples were removed from the solution, rinsed with ethanol, and dried under Ar.

STM Imaging. After sample preparation or SAM formation, the samples were introduced back in the UHV chamber to be characterized in a homemade STM operating at room temperature. Electrochemically etching W tips were used with tunneling currents in the 0.5–1 nA range and 1 V bias voltage. WsXM software was used for image analysis.¹⁹

Electrochemical Experiments. A home-built sample transfer system between UHV and electrochemical environment was used.²⁰ After UHV sample preparation and characterization, the sample was moved to the transfer chamber at 1 bar argon atmosphere.

Cyclic voltammetry was made with an Autolab PGSTAT30 potentiostat and a three-electrode conventional electrochemical cell. A large area Pt plate was used as a counter electrode and a silver/silver chloride (3 M KCl) as the reference electrode (RE). All the potentials in the text are referred to those RE. Aqueous 0.1 M NaOH solution was prepared using NaOH pellets from Sigma-Aldrich (99.99% trace metals basis) and Milli-Q water (18.2 M Ω). Argon gases were 5.0 purity.

Thiol reductive electrodesorption was performed by scanning the potential from -0.3 V to -1.4 V at 0.05 V s⁻¹ in the 0.1 M NaOH solution at room temperature. In each case the charge density (q) involved in the reductive peak desorption was calculated by integration of the peak area. The total electrode real area was measured through the gold oxide reduction peak after the complete electrodesorption of the thiol. This figure was taken as an indication of the surface coverage by the thiol SAM. The q values for each SAM resulted from an average of at least six electrodesorption curves.

XPS Measurements. The photoemission experiments for the adsorption of HT on Au(100) and Au(111) surfaces were carried out in a commercial ultrahigh vacuum chamber with a double anode X-ray source. The base pressure was in the range of low 10^{-10} mbar. The XPS spectra were collected after exciting the sample by an unmonochromatized MgK α radiation at 1253.6 eV, with a 150 mm hemispherical electron energy analyzer (SPECS Phoibos 150). The binding energy (BE) scales for the SAMs on Au surfaces were calibrated by setting the Au 4f_{7/2} BE to 84.0 eV with respect to the Fermi level. The high-resolution S 2p and Au 4f_{7/2} spectra were acquired using the fixed analyzer transmission (FAT) mode with analyzer pass energy of 10 eV.

The S 2p spectra were fitted with a Shirley-type background and two elemental component 2p_{3/2}–2p_{1/2} doublets, each composed of two combinations of Lorentzian and Gaussian (Voigt) functions. The spin–orbit doublet separation of the S 2p signal was fixed to 1.18 eV and the intensity ratio to 2:1. To achieve the best adjustment, the positions, intensities, and

Gaussian widths of these components were modified during the fittings, and the Lorentzian width was fixed at 0.15 eV.

Computational Calculations. Density functional calculations have been performed with the periodic plane-wave basis set code VASP 5.2.12.^{21,22} We have followed the scheme of nonlocal functional proposed by Dion et al.,²³ vdW-DF, together with the optimized Becke88 exchange functional optB88-vdW²⁴ to take into account van der Waals (vdW) interactions. The electronic wave functions were expanded in a plane-wave basis set with a 420 eV cutoff energy. The projector augmented plane wave (PAW) method has been used to represent the atomic cores²⁵ with PBE potential. Core level shifts (CLSs) of the S 2p levels have been calculated within the final state approximation^{26,27} following the Slater–Janak approach²⁸ in which only a half electron is excited from the core level to the valence region and placed in the lowest unoccupied orbital.

RESULTS AND DISCUSSION

Au(100)-hex and Au(100)-(1 × 1) Samples. The STM images (Figure 1a) of the clean Au(100) substrate show

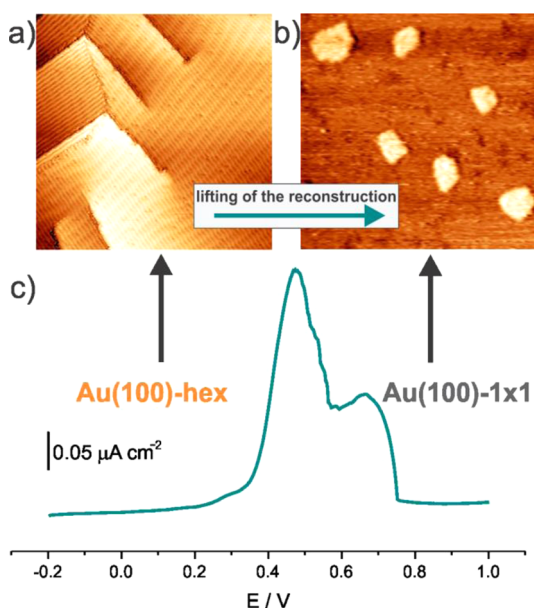


Figure 1. $100 \times 100 \text{ nm}^2$ STM images of (a) a thermally reconstructed Au(100)-hex surface and (b) electrochemically unreconstructed Au(100)-(1 × 1) surface after applying 1 V for 300 s in 0.05 M H_2SO_4 . (c) Current density vs potential (E) profile for the thermally reconstructed Au(100)-hex surface recorded at 0.02 V s^{-1} in 0.05 M H_2SO_4 . The lifting of the reconstruction is indicated.

atomically smooth terraces separated by monatomic high steps that intersect, forming 45° or 90° angles. The typical stripes corresponding to the Au(100)-hex thermally induced reconstruction with an interstripe distance of 1.45 nm and about 0.06 nm in height are clearly visible in the image.¹⁸ These stripes run parallel to the steps which exhibit kinked edges. On the other hand, not all stripes are straight but bent by a few degrees, originating a superperiodicity as shown in Figure 1a.

The Au(100)-(1 × 1) surface was then electrochemically generated by immersing the Au(100)-hex substrate in 0.5 M H_2SO_4 and applying $E = 1 \text{ V}$ for 300 or 1800 s (Figure 1c). The lifting results in the progressive elimination of the typical stripes from the Au surface and the formation of nanometer-sized Au

islands as shown in Figure 1b. It is well-known that the surface free energy of the Au(100)-hex is lower than the Au(100)-(1 × 1) when the surface is neutral, but it increases when the surface is positively charged so that the lifting of the reconstruction takes place.²⁹ However, even at the longer polarization times (1800 s) we observed some stripes of the Au(100)-hex. It has been shown that the kinetics of the hex to (1 × 1) surface reconstruction in electrolyte solutions depends on the number of surface defects.³⁰ Therefore, in the case of well-prepared surfaces with extended terraces, this process can be slow.

Chemical Characterization of Thiol SAMs on Au(100). The chemical nature of the HT SAMs on Au(100) surfaces has been assessed by XPS and compared with that obtained for the same thiol on the Au(111) surface prepared under the same experimental conditions. Figure 2 shows the S 2p region of the

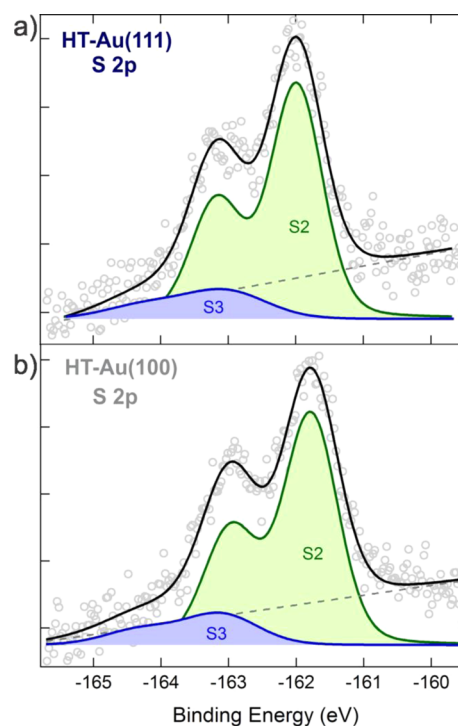


Figure 2. S 2p spectra of (a) Au(111) and (b) Au(100) substrates prepared by immersion for 24 h in ethanolic solutions of HT molecules. The best fits (black lines) and the two elemental components are also shown.

XPS spectrum for HT-covered Au(111) and HT-covered Au(100)-(1 × 1) prepared by electrochemical lifting of the hex phase as shown in Figure 1. The absolute value of the BE of the S $2p_{3/2}$ peak is important to obtain information about the chemical bonding of the S atoms to the Au surface. It is well-known that the S $2p_{3/2}$ core level peak for SAMs of thiols on Au can be usually decomposed into three different components, S1 and S2 at BE $\sim 161 \text{ eV}$ and $\sim 162 \text{ eV}$, respectively, and S3 at BE $\sim 163\text{--}164 \text{ eV}$. The S1 component is associated with atomically adsorbed sulfur. The S2 component is usually assigned to the S atoms chemisorbed on the metal surface through a thiolate bond in the thiol–Au interface and the S3 component to the S atoms in either unbound thiol (free terminal–SH groups) or disulfide species (in S–S bonds formed between neighboring HT chains). In general, the spectra in our samples contain two main S 2p doublets with the $2p_{3/2}$ peaks located at around 162 (S2) and 163.5 eV (S3), the one corresponding to thiolate

being the more abundant one. This component is located at a BE of -161.96 ± 0.02 eV for HT on the Au(111) surface (Figure 2a), while it is placed at a BE of -161.81 ± 0.01 eV for the same thiol on the Au(100)-(1 × 1) substrate (Figure 2b). It means that the difference in the core level shift is only 0.15 ± 0.02 eV.

This low core level shift (CLS) difference between HT adsorbed on both surfaces deserves more attention. The S 2p CLS can be produced either by differences in the chemical state or by being located at different adsorption sites. Recently, some controversy has appeared about the assignment of the S1 component for thiol adsorption on the Au(111) surface to a thiolate^{31,32} instead of to the commonly accepted assignment related to atomically adsorbed sulfur. In our case the small CLS difference for HT on Au(111) and Au(100)-(1 × 1) can be assigned to HT adsorbed on different surface sites. In fact, density functional calculations^{21–23} including van der Waals interactions³³ indicate that the most stable site for the HT S head on the Au(100)-(1 × 1) surface is the 2-fold coordinated bridge irrespective of the coverage,³⁴ while it is well-known that the S heads of HT staples on the Au(111) surface are placed at top sites.⁴ The theoretically estimated difference of CLS²⁸ between these sites in our calculations is ≈ 0.2 eV, in good agreement with the 0.15 eV experimentally measured. Our results show that, despite that the S heads of the thiolates are placed at different adsorption sites on the Au(100) surface (2-fold coordinated bridge) compared to the Au(111) surface (top sites), the binding energy value of the S 2p core level peak is determined by the formation of a strong covalent bond between the sulfur atoms and the gold surface (thiolate–Au bond).

Thiol Adsorption on the Au(100)-hex Surfaces. UHV-STM images taken after immersion of the Au(100)-hex substrate in HT containing ethanolic solution show elongated rectangular features with typical height ~ 0.2 nm, a figure consistent with gold islands (Figure 3a).¹⁴ The rectangular islands, which are completely absent in the clean Au(100)-hex surface, are nucleated on terraces as shown in Figure 3a. The terraces show serrated steps indicating extensive Au atom removal (inset in Figure 3a). The elongated islands are connected by narrow features smaller than 5 nm in width.

Terraces and rectangular islands exhibit a striped structure with 1.6 nm strip width and 0.08 nm interstrip depth which run parallel to the steps. Also, in this case the stripes are not straight and gently bent by a few degrees (Figure 3a,b). Thus, these stripes closely resemble those observed in the clean Au(100)-hex substrate, although they are slightly wider and deeper. A detailed analysis also shows that the islands are nucleated on interstripe regions of the terraces. Interestingly, there is no evidence of vacancy island formation on the HT-covered surface which is characteristic of alkanethiol adsorption on the Au(111) surface.

Molecular resolution on the striped structures indicates that HT molecules arrange into hexagonally distorted square patterns (Figure 3c and FFT inset) with the molecules oriented $\approx 45/50^\circ$ with respect to the stripes and $\approx 80^\circ$ between them. The nearest-neighbor distance results in $d \approx 0.4–0.5$ nm, while the distance along the square diagonal, aligned parallel to the stripes, results in $d \approx 0.6$ nm. The presence of angles smaller than 90° suggests that thiol molecules adopt a quasi-hexagonal arrangement on the stripes (inset in Figure 3c) following the hex-reconstructed substrate. Similar structures have been reported for butanethiol,¹⁷ propanethiol,¹⁶ HT^{15,35} and

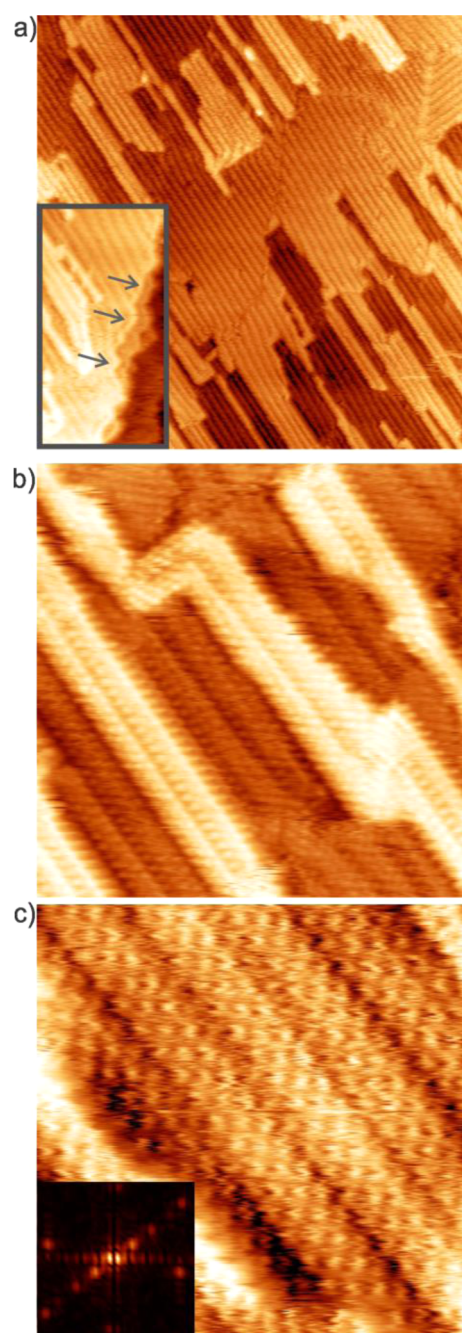


Figure 3. (a–c) STM images of the Au(100)-hex after HT adsorption. (a) 84×84 nm² STM image. Rectangular islands nucleated on terraces. 21×40 nm² inset in (a) shows the serrated steps (arrows). (b) 21×21 nm². Typical stripes on the HT-covered substrate. (c) 8.4×8.4 nm² STM image of HT molecules on the stripes (raw data). Inset in (c) shows the fast fourier transform (FFT) of the molecular surface structure showing the distorted hexagonal pattern (β phase).

decanethiol^{13,14} on the Au(100) surface by in situ STM in electrolyte solutions and referred as the β phase.

However, in contrast to that reported in ref 16 after propanethiol adsorption on the Au(100)-hex, we can not observe the typical islands (Figure 1b) produced by the lifting of the hex reconstruction to form the (1 × 1) surface. Instead, we always image the elongated rectangular islands shown in Figure 3a,b. Then, we propose that these islands do not result from a thiol-induced lifting of the Au(100)-hex to form the

Au(100)-(1 × 1) surface but are produced by a different process involving Au adatom removal from step edges, surface diffusion of Au adatoms on the terraces, and the nucleation and growth of Au islands. The elongated island shape reveals anisotropic surface diffusion,³⁶ supporting the idea that the hex stripes are still present in the surface. The preferred island nucleation at the interstripe regions is also evidence that they are channels for Au adatom flux. Therefore, we can conclude that the stripes of the Au(100)-hex substrate act as templates for thiolate organization as their morphology exhibits only small changes upon SAM formation. This observation contrasts to that found for S adsorption on this face that induces the complete lifting of the hex-reconstruction and the formation of a (2 × 2) lattice.³⁷

Thiol Adsorption on the Au(100)-(1 × 1) Surface.

Clean Au(100)-hex substrates were subjected to 300 s polarization at 1 V to induce the formation of the Au(100)-(1 × 1) phase (Figure 1). STM images after HT adsorption on this surface (Figure 4a) show no evidence of the characteristic

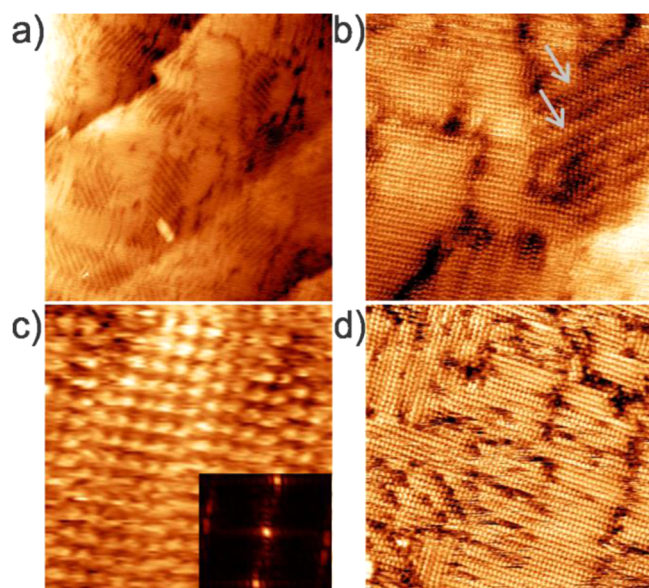


Figure 4. (a–d) STM images of the Au(100)-(1 × 1) after HT adsorption. (a) 90 × 90 nm². Terraces with smooth and some striped domains are shown. (b) 25 × 25 nm². Details of these two different domains. The stripes are indicated by arrows. (c) 6.5 × 6.5 nm² STM image of HT molecules on the smooth domains (raw data). Inset in (c) shows the fast Fourier transform (FFT) of the molecular surface structure showing the square pattern (α phase). (d) 25 × 25 nm² STM image showing stripes with square patterns.

rectangular islands resulting after HT adsorption on the hex-reconstructed Au surface (Figure 3a), thus indicating that they are associated with the reconstructed hex surface. The images reveal planar regions coexisting with some striped domains (Figure 4a). Inside the stripes the molecular arrangement corresponds to the β phase (Figure 4b) indicating that for 300 s polarization time the lifting of the reconstruction is incomplete as already discussed for the electrochemical lifting. Interestingly, the images reveal that some of these stripes become wider than 1.6 nm (≈ 2 nm), and others tend to vanish into planar domains which correspond to the Au(100)-(1 × 1) (Figure 4b, arrows).

On the other hand, molecular resolution smooth regions reveal a nearly square structure (Figure 4c and FFT inset) with

thiolate–thiolate distance $d = 0.44/0.50$ and an 87° angle between the molecules. These patterns have been also observed for longer alkanethiols¹³ and should correspond to the α phase already described for alkanethiol adsorption on the Au(100)-(1 × 1) surface.¹⁶ Interestingly, the α phase is not only present in planar domains (Figure 4c) but also in some “stripe-like” patterns (Figure 4d) in agreement with that observed for propanethiol adsorbed on the Au(100)-hex.¹⁶ Typically, the Au(100)-(1 × 1) domains (shown in Figures 4b,c) exhibit short-range order involving only 2–8 perfectly aligned squares of molecules that are displaced in relation to the next squares. In particular, we observe that a row of molecules bends (Figure 4c, parallel to the x -axis) as the stripes shown in Figure 1a. We also observe that the rows of molecules in the square patterns intercept the steps forming $\approx 45^\circ$ angles (not shown).

STM images taken after thiol adsorption on Au(100)-hex substrates that have been polarized at 1 V for 1800 s reveal a decrease in the number of stripes indicating that the lifting of the reconstruction and the formation of the Au(100)-(1 × 1) surface are improved but also that some hex-reconstructed surface still remains on the surface.

Note that values of $d = 0.45$ nm were also observed for square patterns of long alkanethiols ($n = 20$) by diffraction measurements, and they were assigned to a $c(10 \times 10)$ lattice.⁹ However, molecular dynamic calculations have shown that chain organization produces a significant distortion of the planar packing from the simple square lattice arrangement of the S atoms toward pseudohexagonal close-packing of the outer methyl groups.

Reductive Desorption. The electrodesorption curve for HT SAMs formed by immersion of the reconstructed Au(100)-hex substrate in 10^{-4} M HT for 24 h is shown in Figure 5. The

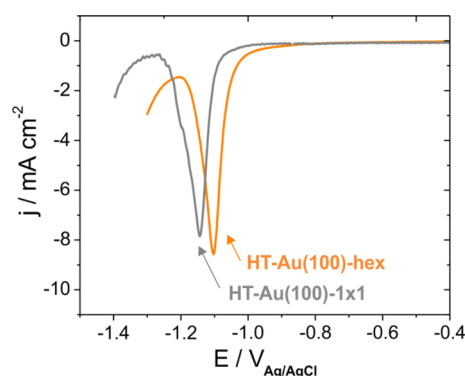


Figure 5. Electrodesorption curves for HT on Au(100)-hex (orange line) and on Au(100)-(1 × 1) (gray line).

cathodic current is related to the HT desorption according to the well-known reaction $\text{HT-Au} + e = \text{HT}^- + \text{Au}$. The peak potential appears at $E_p = -1.10$ V with a charge density $q \approx 80 \pm 16 \mu\text{C cm}^{-2}$, a figure which corresponds to $\theta_{\text{HT}} = 0.33$ considering a complete monolayer on the Au(100)-hex, which has 25% of Au atoms more than the (1 × 1) surface, and one electron transfer process involves $q = 240 \mu\text{C cm}^{-2}$.

On the other hand, the reductive desorption of HT SAMs formed by adsorption on the Au(100)-(1 × 1) substrate leads to similar results (Figure 5). First, the peak potential of the main is $E_p = -1.14$ V, while the charge density is close to $q \approx 85 \pm 10 \mu\text{C cm}^{-2}$, a figure that yields $\theta_{\text{HT}} = 0.44$ considering that the charge density for the Au(100)-(1 × 1) complete monolayer on this surface is $q = 192 \mu\text{C cm}^{-2}$. Note, however,

that θ_{HT} on a Au(100)-(1 × 1) surface should be slightly greater since some domains of the Au(100)-hex (lower coverage) are still visible in the STM images. Similar measurements for HT SAMs on the Au(111) surface result in $E_p = -1.07$ V, $q = 75 \mu\text{C cm}^{-2}$, and $\theta_{\text{HT}} = 0.33$.

The greater θ_{HT} value for the Au(100)-(1 × 1) than those found for the Au(100)-hex and Au(111) surfaces can explain the enhanced electrochemical stability (≈ 0.04 V) against desorption since it is largely dominated by vdW interactions. In fact, it has been shown that for alkanethiols on different Au surfaces E_p is negatively shifted as the number of carbon atoms in the hydrocarbon chains (n) is increased.³⁸ Also, the slope of the E_p vs n straight line is ≈ 1 kcal mol⁻¹ per C unit, a figure close to that observed for vdW forces in solid alkanes.³⁹

CONCLUSIONS AND OUTLOOKS

We found that the adsorption of HT on Au(100)-hex maintains the striped features of the hex reconstruction. The formation of elongated Au islands following the stripe directions and nucleated at interstripe regions reveals anisotropic surface diffusion of Au adatoms which are provided from step edges. On the stripes thiol molecules organize into the β phase already described for shorter thiols.

The electrochemical lifting of the hex reconstruction was not complete under our experimental conditions so that HT proceeds on a surface containing (1 × 1) domains with some amount of hex domains. The more important feature of thiol adsorption on the Au(100)-hex domains is the complete absence of the elongated islands observed for thiol on the reconstructed surface. Thiol adsorption on Au(100)-(1 × 1) domains exhibits the α phase present on both smooth and stripe-like domains.

The HT surface coverage is $\theta \approx 0.33$ and 0.44 for the hex and (1 × 1) surfaces, respectively, this difference in coverage arising from the larger number of Au surface atoms in the hex reconstruction ($\approx 25\%$). Interestingly, we can not observe on the Au(100)-(1 × 1) domains the denser $c(2 \times 2)$ lattice ($\theta_{\text{HT}} = 0.50$) that, based on density functional calculations, exhibits a thermodynamic stability even larger than the thiol “staple” containing the $c(4 \times 2)$ phase on the Au(111) surface.³⁴ This point deserves special attention to find the reasons that hinder the formation of the stable and dense $c(4 \times 2)$ lattice and to propose models for the α and β surface structures based on thermodynamic stability.

The CLS of the thiolates on the Au(111) and (100), where the S heads are placed at different adsorption sites, differs only in 0.15 eV, suggesting that chemistry rather than surface sites determines the BE of the S 2p level. Finally, we think that these results are also important to complete the chemistry and surface structure knowledge for small thiolated AuNPs where the Au(100) together with the Au(111) are the dominant faces.

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Notes

The authors declare no competing financial interest.

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