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Electrochemical STM Investigation of 1,8-Octanedithiol Self-Assembled Monolayers on Ag(111) in Aqueous Solution

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It is well-known that organic films adsorbed at metal surfaces are widely applied for corrosion inhibition and lubrication. Nowdays, the availability of sophisticated techniques for structural investigation at a molecular level, such as scanning tunneling microscopy (STM) and different spatially averaging diffraction techniques, has allowed the investigation and characterization of highly ordered monolayers; among these, self-assembled monolayers (SAMs) of alkanethiols are undoubtedly the most investigated, thanks to their stability and ease of spontaneous organization on metal surfaces.[1,2] Fundamental research on SAMs has also been encouraged by their potential applications such as microcontact printing,[3] nanolithography,[4] and biosensing.[5]

The self-assembly mechanism of alkanethiols was initially justified by the strong affinity between surface metal atoms and the sulfur head groups promoting adsorption up to an upper limit imposed by close packing of the aliphatic chains in a hexagonal phase. Subsequently, however, the application of more refined experimental techniques revealed that this picture of the self-assembly process is rather simplistic. Early STM studies of SAMs on Au(111) revealed the presence of pitlike defects in the scanned images. Different explanations were provided for these pits, that is, modification of the tunneling barrier,[6] chain disorder,[7] and two-dimensional islands of Au vacancies.[8–10] The latter interpretation, based on the observation that, as a rule, the pit depth corresponds to the Au(111) single-atom step height and is not related to the length of the alkyl chain, is now generally accepted. The formation of the pits has been ascribed to etching of Au in the alkanethiol solutions,[10] adsorbate-induced reconstruction of the gold surface[11] by shrinkage of the surface lattice constant,[8] or lifting of reconstruction with creation of vacancies that nucleate islands in the terraces.[12]

The observation of appreciable pit formation even for assembly by gas-phase transport[11,13] has been regarded as evidence against a predominant Au-etching mechanism. It is interesting to observe that these pits can be healed at temperatures only slightly above room temperature (50–70 °C);[14,15] this denotes an appreciable enhancement of the lateral mobility of surface atoms induced by the adsorption of alkanethiols, which might be explained by their well-known tendency to form mercaptide complexes with the noble metals.

STM investigations of alkanethiol SAMs on Ag(111) have also revealed the presence of vacancy islands[14] or, alternatively, monatomic silver islands,[16] with ordered hexagonal structures of alkanethiol molecules on the islands as well as off. Both sulfide ion and methanethiol were reported to give rise to a $(\sqrt{7} \times \sqrt{7})$R10.9° structure,[17] whereas longer chain alkanethiols exhibit incommensurate close-packed hexagonal structures.[16,17] Thermal annealing of alkanethiol SAMs was found to annihilate substrate vacancy islands on both Au(111) and Ag(111).[14] The main differences between the two substrates stem from the higher surface mobility and reactivity of silver with respect to gold,[14,16] which cause silver to be more easily etched in alkanethiol solutions.

Recent STM investigations at very low surface coverages both in UHV[12,13] and in situ[18] have revealed the presence of striped features consisting of alkanethiol molecules lying flat on the Au(111) surface. Accurate low-energy helium diffraction measurements showed that the periodicity of the stripes is nearly equal to twice the thiol length; this was tentatively interpreted as a head-to-head dimerization of the molecules due to strong sulfur–sulfur interactions.[19] The importance of these interactions also emerged from a structural investigation of a decanethiol SAM on Au-(111) by grazing incidence X-ray diffraction;[20] this reveals a S–S spacing of 2.2 Å, which strongly implies a dimerization of the sulfur head groups.

Besides metal–sulfur interactions, which play a major role in stabilizing the structure of alkanethiol SAMs on noble metals, other interactions are therefore important, that is, metal–metal interactions for pit formation, intra- and intermolecular interactions for packing and defect healing, and sulfur–sulfur interactions for sulfur dimerization in striped phases and, possibly, in some close-packed SAMs.[20] With the aim of gaining further insight into the role of sulfur–sulfur interactions in the structure of thiol SAMs, we investigated the adsorption of 1,8-alkanedithiol on Ag(111). In fact, the presence of two terminal sulfur head groups is expected to enhance this role. SAMs of 1,6-hexanedithiol and 1,10-decanethiol on gold have been extensively employed for attaching CdS, CdSe, and PbS nanoparticles on top of them (see ref 21 and references therein).

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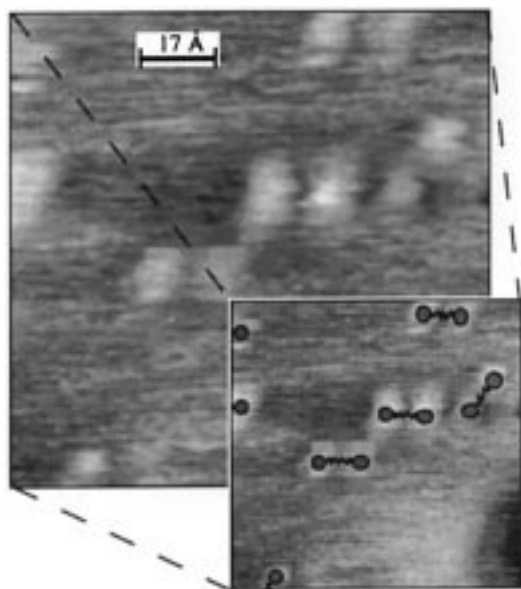
Figure 1. STM image (11.5 nm × 11.5 nm) of Ag(111) in an aqueous solution of 25 μM 8DT + 10 mM NaF. Electrode potential = −1.3 V/SCE; bias voltage = 0.8 V; tunneling current = 1.0 nA. The position of the individual 8DT molecules is indicated in the inset.

Figure 2. STM image (65.1 nm × 65.1 nm) of Ag(111) in an aqueous solution of 0.5 mM 8DT + 10 mM NaF. Electrode potential = −1.25 V/SCE; bias voltage = 0.74 V; tunneling current = 2.0 nA.

Measurements were carried with a Topometrix TMX2000 system, modified for in situ measurements as already described.[22] For the STM cell and the experimental procedure, the reader is referred to ref 23. 1,8-Octane-dithiol (8DT) from Aldrich was used without further purification. Small aliquots of a freshly prepared solution of 1 M 8DT in 99.8% ethanol (Fluka, puriss p.a.) were added to an aqueous NaF solution to attain the desired 8DT concentration. The resulting 8DT solution was then introduced in the STM cell. All STM images were obtained in the constant-height mode and are unfiltered. All potentials are referred to the saturated calomel electrode (SCE).

The behavior of the dithiol on Ag(111) could only be investigated between −1.4 and −0.9 V/SCE. Potentials negative to −1.4 V caused catalytic hydrogen evolution, with a faradaic current increasing in time; potentials positive to −0.9 V caused the irreversible formation of large and irregular bumps of deposited material, which spoiled the surface as imaged by STM and shifted hydrogen evolution toward more positive potentials by a few hundred millivolts. It is possible that at potentials positive to −0.9 V the adsorbed 8DT molecules tend to reorganize slowly into a phase of higher density, with the intermediate formation of 3D islands.

In the proximity of −1.3 V and at low dithiol concentrations, the STM images in Figure 1 reveal the presence of pairs of bright spots at a constant distance of 13 ± 1.0 Å, which compares favorably with the length, 12 Å, of an 8DT molecule, calculated by estimating the first-nearest-neighbor C−C and C−S distances along the molecular axis at 1.27 and 1.5 Å.[24] This strongly suggests that the pairs of bright spots are adsorbed terminal sulfurs of 8DT molecules lying flat on the Ag(111) surface.[25] The flat
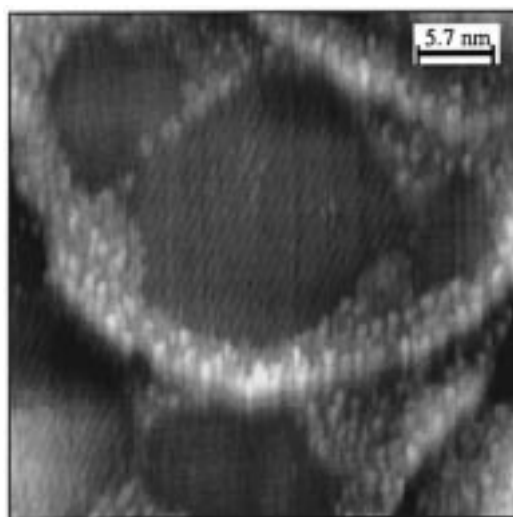
hydrocarbon chains joining the terminal sulfurs cannot be distinguished from the water molecules adsorbed on the substrate, thus indicating that their intrinsic resistances in the tunneling gap are comparable. In principle, these 8DT molecules may be either chemi- or physisorbed, since alkanethiols can both physisorb through van der Waals interactions and chemisorb through the sulfur bond. Temperature-programmed desoption measurements in UHV carried out by Lavrich et al.[26] on alkanethiols of different chain length indicate that, for chain lengths greater than 14 carbons, the physisorption enthalpy is greater than the chemisorption enthalpy; alkanethiols not longer than octanethiol show both a physisorption enthalpy and a chemisorption enthalpy. The above authors[26] also found that hexanedithiol chemisorbs on Au(111) so rapidly that a value for the physisorption enthalpy could not be obtained. In view of the latter result, chemisorption of 8DT on Ag seems more probable than physisorption, independent of the parallel or vertical orientation of the adsorbed molecules.

Shifting the potential from −1.3 to −0.9 V/SCE causes the dithiol molecules to be notably adsorbed. The adlayer is initially disordered, in the form of clusters of variable size and shape: these features are similar to those reported on gold in UHV at low surface coverages of alkanethiols.[4] These clusters are mobile on the surface and can be entirely removed by scanning the surface at high tunneling currents (say, >3 nA). Keeping the polarization constant for more than 100 s causes the appearance of dark patches, due to depressions (see Figure 2), which maintain a limited mobility, albeit lower than that of the structureless clusters from which they originate. A closer inspection of the patches reveals the presence of striped structures, as shown in Figure 3. They form preferentially in the middle of terraces, disordered adsorption being a maximum in the proximity of steps, as also observed in HS− adsorption.[27] Two different types of striped structures are observed: one (structure **a** in Figure 3) has a corrugation period of 4.6 ± 0.5 Å along the stripes and a periodicity of the stripes of 20 ± 2.0 Å; the other (structure **b** in Figure

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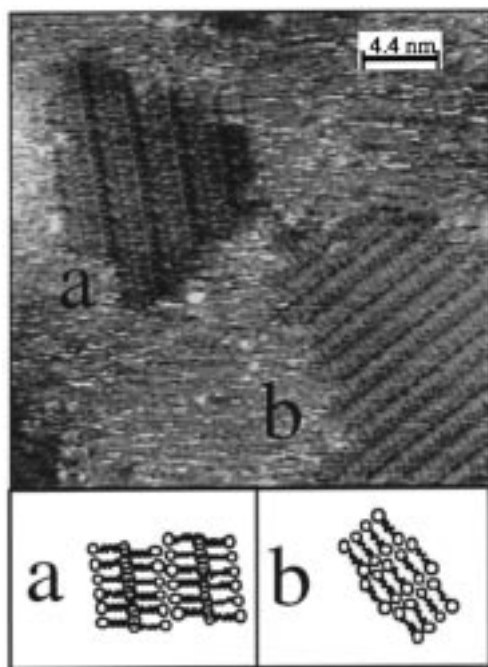
Figure 3. STM image (28.3 nm × 28.3 nm) of Ag(111) in an aqueous solution of 0.4 mM 8DT + 10 mM NaF. Electrode potential = −1.2 V/SCE; bias voltage = 0.64 V; tunneling current = 1.0 nA. The inset shows the proposed molecular models for the two striped features.

3) has a corrugation period of 4.9 ± 0.5 Å and a periodicity of 12 ± 1.2 Å. The molecular models that we propose tentatively for the two striped features are depicted in the insets of Figure 3. Structure **a**, whose period is about twice the length of the 8DT molecule, involves a zipper-like interlocking of the sulfur atoms, with strong S−S interactions similar to those in disulfides, as also proposed by Fenter et al.[20] for alkanethiols on Au(111), or in the S_3 trimers resulting from SH^- adsorption on Ag(111).[27] Structure **b**, whose period is about equal to the length of the 8DT molecule, involves a head-to-head packing arrangement with weaker S−S interactions, such as those proposed by Poirier et al.[13] for striped structures of alkanethiols on Au(111). The simultaneous presence of both structures on the same STM images indicates that they have about the same stabilization energy. The various striped domains are rotated by 60 ± 3° or 120 ± 3° with respect to each other. These rotations, together with corrugation periods close to $2.89\sqrt{3}$ Å, where 2.89 Å is the Ag−Ag nearest-neighbor distance, suggest an epitaxial matching of the striped domains with the substrate.

The surface coverage by the striped structures tends to increase as the potential approaches the positive limit of −0.9 V/SCE, beyond which irreversible and disordered 8DT deposition takes place. 8DT concentrations > 0.1 mM are required for the striped domains to cover the electrode surface completely. The growth of the different domains stops when they come into contact, as shown in Figure 4a, where the orientation mismatch prevents their merging. On the other hand, the formation of large domains is favored by more negative potentials, close to the desorption limit, as shown in Figure 4b. This is probably due to the lower density of nuclei at these negative potentials.

Topographic profiles across the 8DT-coated silver surface reveal that the depth of the pits within which the striped structures are imaged is close to 1 Å and, hence, definitely less than the height of a silver monatomic step, 2.35 Å.[14] Additional insight into the nature of these
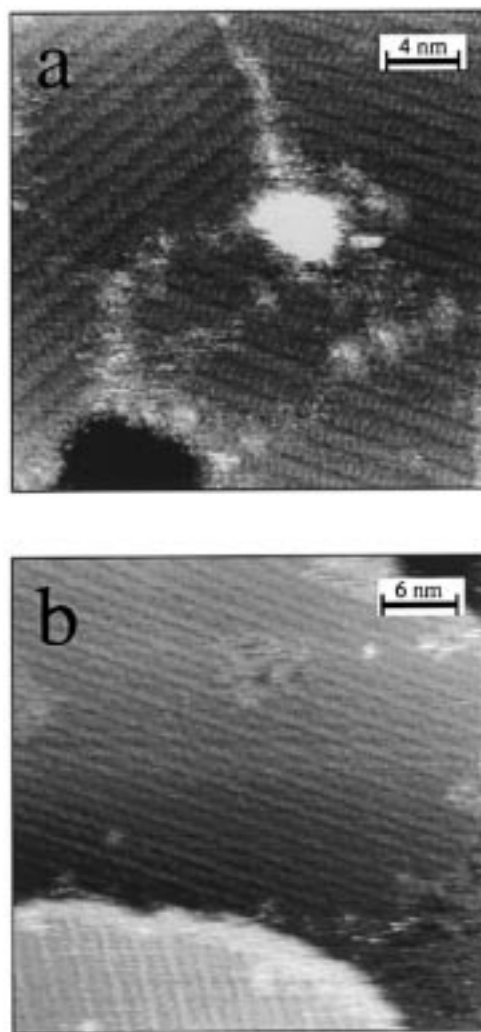

Figure 4. STM images of Ag(111) in an aqueous solution of 0.5 mM 8DT + 10 mM NaF. Image a is 25.6 nm × 25.6 nm; electrode potential = −1.0 V/SCE; bias voltage = 0.5 V; tunneling current = 1.6 nA. Image b is 38.6 nm × 38.6 nm; electrode potential = −1.2 V/SCE; bias voltage = 0.74 V; tunneling current = 1.5 nA.

depressions can be gained from the sequence of images in Figure 5, which illustrate the dynamics of the dithiol adsorption on a surface with pre-existing holes one atomic step high. It is apparent that the latter holes are deeper than the striped structures. Moreover, while the size of the striped structures increases regularly in time, that of the pre-existing holes decreases. Healing of the Ag(111) surface in nonspecifically adsorbed electrolytes was already reported,[22] even though it is expected to proceed at lower rates at potentials negative to the point of zero charge. The above behavior can be tentatively explained by assuming that the disordered 8DT adsorption that precedes stripes formation is characterized by dithiol molecules anchored by only one end to the surface, the other end forming some silver mercaptide complex by chemical erosion of the substrate. Once these further ends are also anchored to the substrate with formation of the striped structures, the silver ions released by the mercaptide complex are returned to the substrate, thus healing the pre-existing holes. The slight depression of the striped domains may be just the effect of a modest electronic conductivity along the alkyl chains of the 8DT molecules anchored by only one terminal sulfur, which molecules are assumed to surround the domains. This effect may be
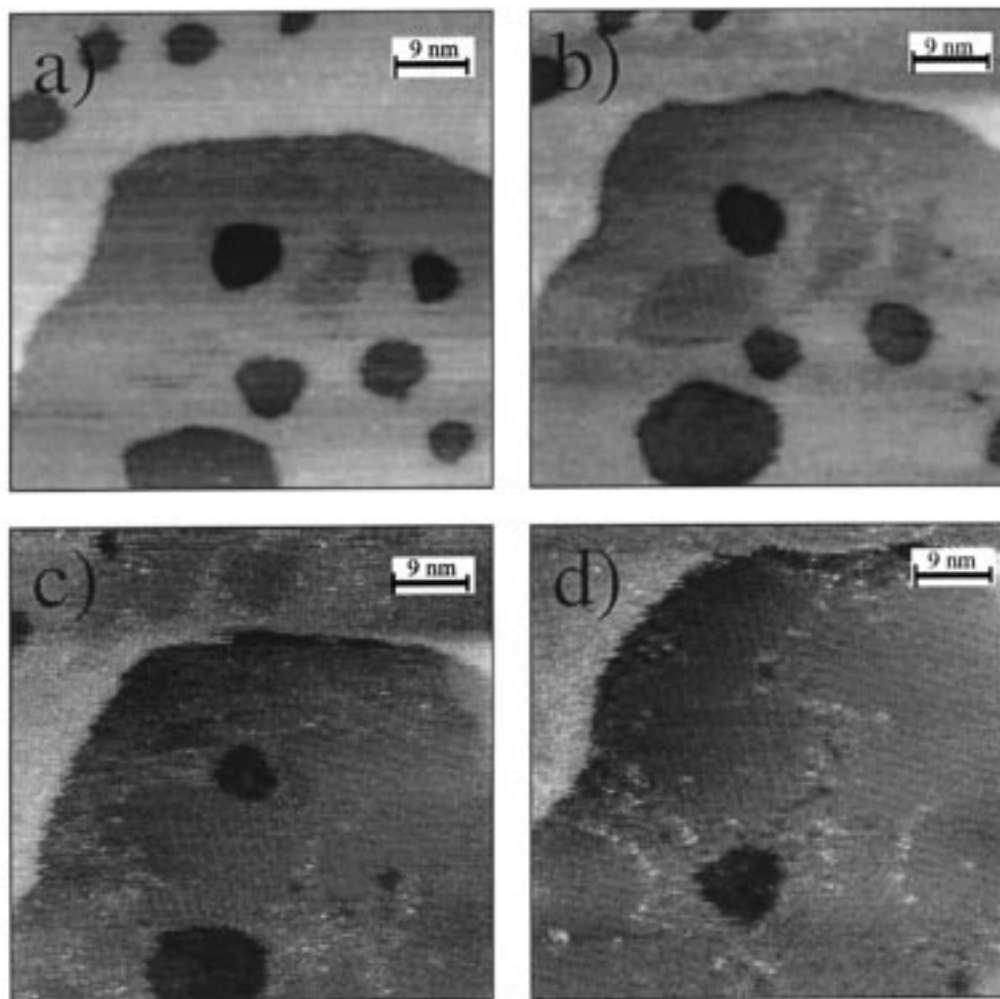
Figure 5. Sequence of STM images of Ag(111) in an aqueous solution of 25 μM 8DT + 10 mM NaF. Electrode potential = −1.00 V/SCE; bias voltage = 0.5 V; tunneling current = 2.0 nA. The images are 57.8 nm × 57.8 nm and were obtained immediately after a potential step from −1.3 to −1.0 V/SCE (a), and after 45 (b), 82 (c), and 173 s (d).

analogous to that causing the area of an Au(111) surface covered by an ordered $\sqrt{3} \times \sqrt{3}$ structure of vertically adsorbed decanethiol molecules to appear larger than the areas covered by the corresponding striped structure.[18] Incidentally, a roughly vertical orientation for adsorbed alkanedithiol molecules on Ag(111) was reported by Nakanishi et al.[21]

In conclusion, dithiol adsorption on Ag(111) gives rise to close-packed SAMs of molecules lying flat on the electrode surface. The striped structures of these SAMs are strongly influenced by intra- and intermolecular sulfur−sulfur interactions, just as are the striped phases of alkanethiols on Au(111).