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Scanning Tunneling Microscopy Studies of the Electrochemical Reactivity of Thiourea on Au(111) Electrodes

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In situ scanning tunneling microscopy (STM) is proposed as an option to investigate the electrochemical reactivity of nontrivial systems. For this purpose the controversial electro-oxidation and electro-reduction of thiourea at Au(111) surfaces under potential control and constant temperature are considered. Sequential STM imaging show thiourea adsorption in striped arrays that evolve to a hexagonal close-packed (hcp) structure when the electron surface charge density is decreased. The transient hcp structure is electro-oxidized to formamidine disulfide (FDS) that slowly yields adsorbed sulfur. These results show that STM is a powerful tool to understand the reactivity of adsorbed molecules at conducting surfaces, by sequential imaging at the molecular level.

Since the advent of high-resolution local probes such as scanning tunneling microscopy (STM), a large number of solid surface structures, including those of adsorbed layers, have been firmly established. However, the potential of STM to discriminate the reactivity of complex species adsorbed on well-defined solid surfaces, one of the most important and attractive areas of heterogeneous physical chemistry, has not been explored until now. Access to this option requires high-quality real-time imaging at atomic and molecular levels, a highly stable setup (instrument), and rate processes compatible with the instrumental response. Only very recently these techniques have been used to study the kinetics of heterogeneous reactions in real time,[1] under a somewhat limited environment such as ultrahigh-vacuum (UHV). Experiments with the same low level of impurities as UHV, and accurate control of applied potential (E) and temperature (T), can be performed at well-defined metal/electrolyte-solution interfaces. In these cases, slight changes in

the electron charge density at the metal surface, produced by small changes in E, can induce adsorption from solution, chemical and structural changes of adsorbed species, and charge-transfer reactions. We explore the possibility of investigating these processes at the nanometer-scale using single-crystal surfaces under well-controlled conditions.

STM studies of sulfur and organic S-containing molecules adsorbed on Au(111) have attracted considerable attention in recent years.[2] At present, the atomic level structures of both the substrate and the S adlayers are well-known under different experimental conditions.[3-4] Therefore, electrochemical surface reactions involving these species on Au(111), offer the opportunity of testing STM techniques to elucidate the electrochemical reactivity of a nontrivial adsorbed molecule. Among S-containing molecules, thiourea (TU) is specially attractive since TU reactions at metal surfaces are not yet completely understood[5,6] despite the fact that TU is widely used as an additive in electroplating to improve coating quality,[7] and to inhibit corrosion.[8] TU at the Au(111)/electrolyte interface
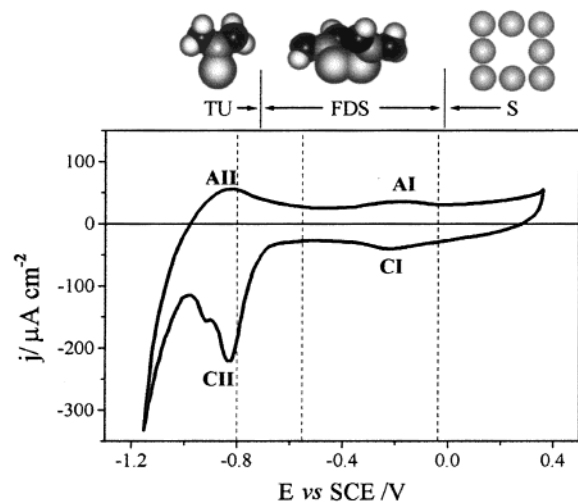
Figure 1. Cyclic voltammogram of Au (111) in 0.05 M NaClO$_4$ + 0.05 mM TU run at 100 mV/s (T = 298 K). Dashed lines indicate E values for sequential in situ STM images presented in Figures 2−4. Dynamically preponderant adsorbate in each potential region (this work) is drawn schematically above.

Figure 2. STM images (constant current mode, T = 298 K). (a) 26 × 50 nm^2, and (b) 7 × 7 nm^2 image (E = −0.55 V, I_t = 3 nA, V_{bias} = 100 mV) showing TU striped phase. Probable adsorption sites are depicted in (c). Arrows (b, c) point to 0.44 nm features zigzagging along [110] direction. Bottom row of (c) shows 0.50 nm array. (d) Top view of TU molecule.

Figure 3. (a) 1.8 × 1.4 nm^2 STM image of hcp TU adsorbed perpendicular to Au(111) (E = −0.05 V, I_t = 3 nA, V_{bias} = 100 mV). Square inset: Fourier transform; round inset: hcp TU obtained after cycling cathodically through −1.2 V (see text). (b) Top view of proposed scheme for close-packed TU adlayers on Au(111). (c) High electron density centers associated with the scheme depicted in (b).

therefore appears to be a good model system to explore the use of in situ STM to investigate reaction pathways at molecular level.

Voltammetric experiments were run in a conventional glass cell[9] with a Au(111) working electrode,[10] a platinum counter electrode, and a saturated calomel reference electrode (SCE) utilizing a PAR 362 potentiostat. For in situ STM imaging with a Nanoscope III electrochemical STM setup (Digital Instruments Inc.), a Au(111) working electrode,[10] a large area gold counter electrode, and a palladium/hydrogen reference electrode were used, although all values of E in the text are given in the SCE scale. High-purity chemicals and Milli-Q*-water were used to prepare oxygen-free aqueous 0.05 M NaClO$_4$ + 0.05 mM TU solutions.

A typical voltammogram of Au(111) in the working solution (Figure 1) shows, in agreement with earlier reported data,[6] two conjugated pairs of broad current peaks at $E \cong$ −0.20 V (peaks AI/CI) and $E \cong$ −0.80 V (peaks AII/CII). For E < −1.10 V, the hydrogen-evolution-reaction cathodic current is observed. Peak AI has been related to the one-electron surface electro-oxidation of TU yielding either formamidine disulfide (FDS), or direct sulfur formation.[6] On the other hand, FDS can also be formed from the hydrolysis of TU and its subsequent decomposition in solution.[11] Decomposition products may also be adsorbed on Au(111). Peak CI corresponds to the electroreduction of the as yet unidentified surface species formed in the potential range of peak AI. Peaks AII/CII have been tentatively assigned to the electro-adsorption/electrodesorption of S species produced by anodic desulfurization of adsorbed TU,[6] by somewhat limited conventional techniques.

To elucidate the electrochemical reactions associated with peaks AI/CI and AII/CII, we have performed sequential in situ STM imaging at different values of E, in the range of each peak. Figures 2−4 show a representative sequence of images taken at the E values indicated in Figure 1.

At E = −0.55 V (Figure 2a), striped surface structures that are similar to those found for alkanethiol[12] or head-on ethanethiol[13] adsorbates on Au(111) are first observed after 10 min. The striped structures are stable for more than 10 min, and present slight bunching and lengthening of these 10 ± 5 nm long, 0.07 ± 0.02 nm vertical corrugation stripes, that upon initial observation are separated by between 1.5 and 4.5 nm. By
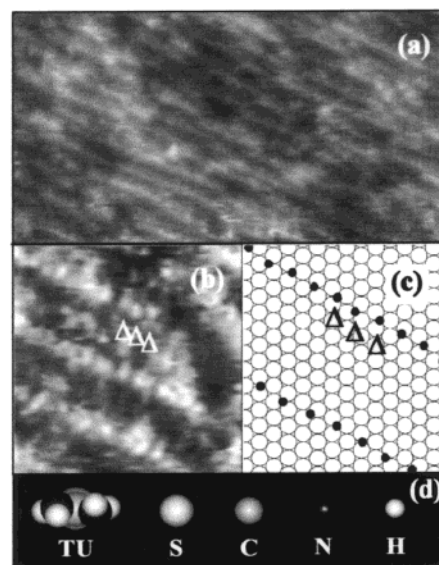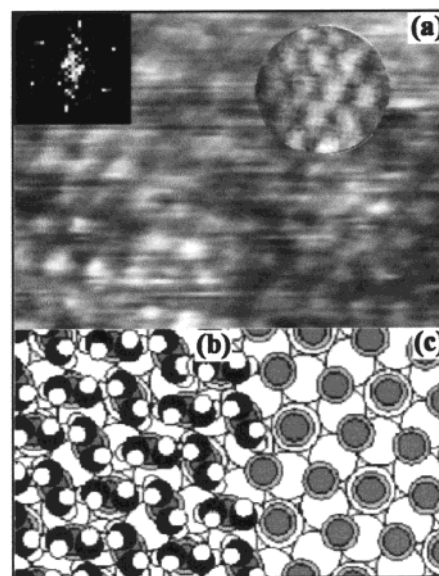
analogy, perpendicular S-head on TU electroadsorption[14] should involve its tautomeric forms,[15] i.e., with S and C atom singly bonded to each other. Bright spots separated by as little as 0.50 and 0.44 nm along stripe directions (Figure 2b, arrows) are frequently resolved. Probable adsorption sites are depicted in Figure 2c. We associate each bright spot with one perpendicular adsorbed TU molecule (Figure 2d) with the high electron density at the S-atom position.[16]

Packing of the adsorbed molecules is increased by changing E from −0.55 V to −0.05 V. After approximately 8 min at this potential, hexagonal patterns with d = 0.33 ± 0.01 nm are observed (Figure 3a). Figure 3b shows our model, with TU molecules closely packed on alternating hollow-top-hollow Au-
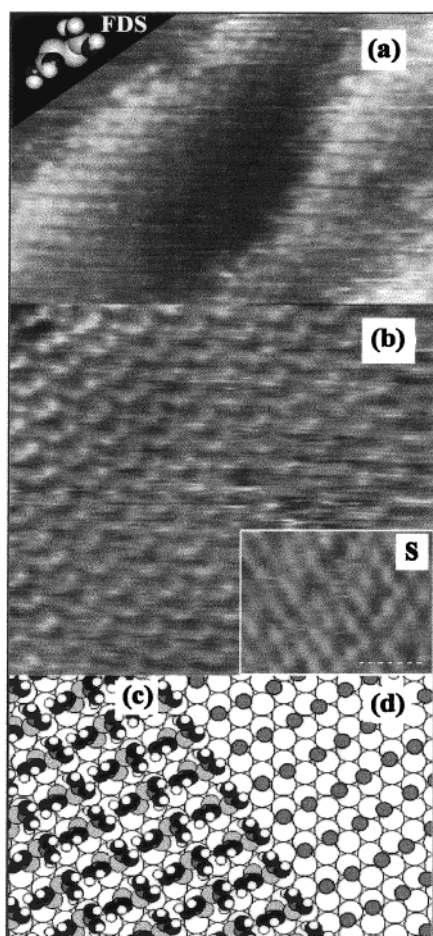
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Figure 4. (a) 8.0×10.0 nm^2, and (b) 6.5×6.5 nm^2 STM image of FDS adlayers on Au(111) ($E \cong 0$ V, $I_t = 40$ nA, $V_{bias} = 50$ mV). FDS inset in upper left corner in (a). (c) Scheme of FDS arrangement in upper left corner of (b). (d) High electron density centers associated with the scheme depicted in (b). Inset in lower right corner of (b) shows 2.0×3.0 nm^2 image of S octomers on Au(111) ($E = -0.05$ V, $I_t = 40$ nA, $V_{bias} = 18$ mV).

(111) sites. Figure 3c shows respective high electron density centers, which clearly rule over topography in resulting image contrast, much as in S[3,4] (inset in Figure 4b) and Se[17] octomers adsorbed on Au(111). Raman spectroscopy experiments indicate that hydrogen bonding plays an important role in stabilizing this structure.[15] Hydrogen bond stabilization has also recently been reported for self-assembled monolayers.[18]

However, while keeping $E = -0.05$ V, the close-packed hexagonal (hcp) arrays become unstable after approximately 11 min, as evidenced by blurred images. About 4 min after losing molecular resolution, a striped array spontaneously reappears. Ordered regions within stripes show up about 1 min later, and rapidly propagate throughout the stripes (Figure 4a). Figure 4b shows ladder-like structures in the upper left corner, and other periodic arrangements where bright rungs are slightly tilted with respect to their orientation in the upper left corner. Striped arrangements (Figure 4a) are unmistakably different from the "dilute adsorbed-TU phase" shown in Figure 2a; and order within (Figure 4b), different from TU arrangements, S trimers,[19] and S octomers[3,4] (inset in Figure 4b). We made blank experiments by adsorbing FDS on Au(111) and observed STM images similar to those depicted in Figure 4b.

FDS tilted TU-subunits (inset in Figure 4a) no longer have their maximum electron density atop S atoms, but rather closely associated with N atoms.[16] Assuming, as for TU, that only high

electron density is imaged as bright spots, the model presented in Figures 4c, d accounts for FDS ladder-like adsorption on Au(111). The exact FDS adsorption site cannot be discerned from our experiments, however, the separation between bright spots suggests that the 0.19 nm bond distance of the S—S group in the FDS molecule is maintained. For the same FDS surface coverage, different structures are observed depending on the choice of three rotationally equivalent Au(111) hollow pairs for FDS adsorption, and two nonequivalent molecular FDS configurations. Note that upon going from the hcp TU to the FDS surface structure, soluble FDS species are also expected.[5]

The change of E from -0.05 V to values in the range of the potential of peak CII results in the desorption of the FDS lattice, whereas upon changing E to potentials lying near that of peak AII, the hcp TU lattice on Au(111) with $d = 0.32$ nm reappears (circular inset in Figure 3a). For $t < 1$ h, we failed to observe the typical $(\sqrt{3} \times \sqrt{3})$R30° lattice of S atoms that is expected for $E < -0.80$ V.[3] The close resemblance between peaks AII/CII and those found for ethanethiol adsorption on Au(111)[15] indicates that they involve the electro-adsorption and electrodesorption of TU and not only the electro-adsorption and electrodesorption of S species produced by TU anodic electrooxidation, as already suggested.[6] The latter process might, however, predominate at longer adsorption times and/or for aged solutions.

FDS structures left alone are slowly oxidized to polymeric sulfur. After 6 h at $E \cong -0.10$ V (inset in Figure 4b), typical S-octomers with $d \cong 0.3$ nm are observed, i.e., the fingerprint of adsorbed S atoms on Au(111).[4] The same result is obtained (i) by electro-oxidizing adsorbed TU at potentials positive with respect to peak AII, (ii) upon first adsorption on Au(111) but from aged TU-containing solutions, and (iii) upon S adsorption from sulfide blanks.[3] With sufficient aging, S-octomers with $d \cong 0.2$ nm atop S multilayers are observed. S octomers have been observed in all runs performed where (i)−(iii) were satisfied.

Many images of TU stripes, hcp TU, FDS ordered structures, and S octomers have been obtained, both from in situ and from ex situ experiments. Some noise appears in all images, due to the dynamics of the electrochemical process itself. However, we have been able to image, in conclusive and reproducible form, sequential TU electro-adsorption, packing, and further oxidation to FDS (Figures 2a, 3a, 4b); FDS electro-oxidation to sulfur (inset in Figure 4b); and reappearance of hcp TU (round inset in Figure 3a) following electro-reduction potential scans starting from FDS covered Au(111). Typical times for TU-adsorption, TU-packing, and TU-dimerization to FDS under the experimental conditions presented herein are in the order of minutes, whereas oxidation of FDS to sulfur takes hours. Therefore, the preponderant species associated with voltammetric peaks AI and AII (Figure 1) are FDS and TU, respectively.

Finally, from our sequential STM imaging, in conjunction with conventional electrochemical methods, we have gained much insight on earlier controversial results concerning the reactions and dynamic behavior of these systems. While the incorporation of other techniques, such as FTIR spectroscopy,[20] can improve the knowledge of the system, the potential of in situ STM imaging to derive the electrochemical reactivity of molecules for relatively slow processes is clearly demonstrated.

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