Thiolate Dynamics on Surfaces

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Thiolate-Induced Metal Adatom Trapping at Solid–Liquid Interfaces**

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Organosulfur compounds, in particular thiolates, are one of the most important classes of surface-active species and have very diverse applications. On the one hand, they are extensively employed in molecular self-assembly, for which they may be considered as the archetypal system, with wide ranging applications in nanoscience (for example molecular electronics, immobilization of biomolecules, and stabilization of nanoparticles).[1–3] On the other hand, organosulfur species have been empirically developed and used as additives for a long time in various areas of chemical engineering, including corrosion inhibition and modern galvanic plating, such as the damascene plating process used for the formation of copper interconnects on ultra large-scale integrated microchips.[4] While the structure of ordered self-assembled thiolate monolayers has been studied in great detail,[1–3] much less is known on thiolate adsorbates at low surface coverage, where these species are highly mobile on the metal surface at room temperature. Clarifying the dynamic behavior of thiolates in the low-coverage regime is of great importance for understanding the elementary mechanisms of both molecular self-assembly as well as their influence on the surface chemistry in additive applications, where the surface coverages likewise are often well below saturation densities. Atomic-scale studies of thiolates at low coverage, performed in ultrahigh vacuum (UHV) at cryogenic temperatures, revealed a much more complex behavior than previously anticipated, involving pronounced interactions with metal adatoms.[5–7]

Herein,we present studies on the surface dynamics at solid–liquid interfaces and room temperature; that is, under conditions typically employed in applications, for the most simple organosulfur adsorbate, methyl thiolate, on Cu(100) electrode surfaces in 0.01 M HCl solution. The use of this system not only is interesting in view of the importance of thiol-bound species in an electrochemical environment (for example in copper electroplating), but also allows the dynamic behavior to be influenced by the applied potential, thus providing additional information on the molecular mechanisms. As will be shown by our quantitative in situ high-speed scanning tunneling microscopy (video-STM) studies, interactions with metal adatoms also play a significant role under these conditions, which may have important implications for the surface chemistry of these species.

In the studied potential range, the chloride coadsorbate forms a well-ordered square *c*(2×2) lattice on the Cu(100) electrode surface (lattice spacing $a_0 = 3.6$ Å), which is clearly visible in high-resolution STM images.[8,9] Upon addition of dimethyl disulfide to the solution, distinct isolated adsorbates gradually emerge on the surface, which occupy sites of the *c*(2×2) lattice (Figure 1 a). Based on their small size and their similar appearance in the STM images as adsorbed sulfide,[10,11] these species are identified as methyl thiolate adsorbates (CH_3S_{ad}), formed by dissociative adsorption of dimethyl disulfide at defects within the chloride adlattice. An analoguous dissociative adsorption mechanism, involving splitting of the S–S bond, was proposed for the widely employed additive bis(3-sodiumsulfopropyl disulfide) (SPS) on Cl-covered Cu(100).[12,13]

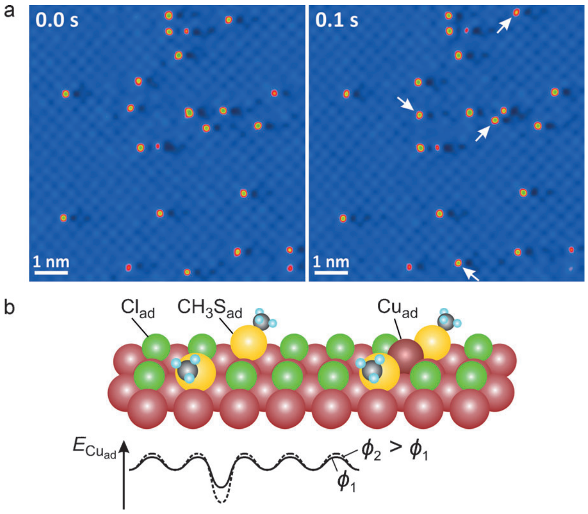

Figure 1. Structure and dynamics of methyl thiolate adsorbates. a) Two subsequent images taken from an in situ video-STM sequence of CH_3S_{ad} on Cu(100) in 0.01 M HCl at −0.32 V_{SCE}, recorded at 10 Hz, showing mobile thiolates and the *c*(2×2) Cl adlattice (arrows indicate CH_3S_{ad} hopping events). b) Structural model of a CH_3S_{ad} "dimer" with and without trapped Cu adatom. For the latter, the energy landscape for a Cu_{ad} is indicated for two electrode potentials ϕ.

At coverages of several percent, only isolated CH_3S_{ad} or small metastable CH_3S_{ad} clusters are present on the surface. Video sequences reveal frequent fluctuations in the adsorbate positions with typical residence times t_{thiol} in a *c*(2×2) lattice site, depending on potential and the presence of neighboring CH_3S_{ad}. For isolated CH_3S_{ad}, t_{thiol} increases exponentially from 0.1 to 5 s between −0.40 and −0.24 V (Figure 2 a). Although ordered CH_3S_{ad} domains are absent, specific local adsorbate configurations are characteristic. In particular, CH_3S_{ad} adsor-

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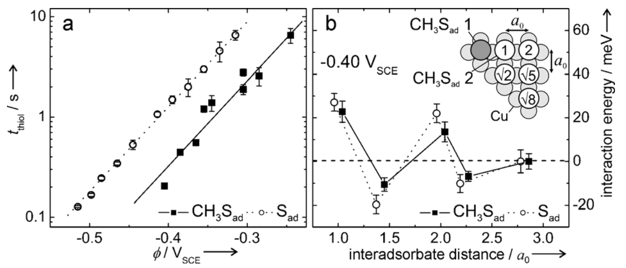

Figure 2. Adsorbate mobility and interaction. a) Residence time t_{thiol} of isolated CH_3S_{ad} in $c(2\times2)$ lattice sites as a function of potential. b) Potential energy as a function of the CH_3S_{ad}–CH_3S_{ad} distance at $-0.40\,V_{SCE}$ (inset: relative CH_3S_{ad} positions), obtained from a quantitative analysis of in situ video-STM data. For comparison, analog data for adsorbed sulfide at the same interface is shown (from Ref. [10,11]).

bates at separations corresponding to the next-nearest-neighbor distances of the $c(2\times2)$ lattice, i.e., at a spacing of $\sqrt{2}a_0 = 5.1$ Å (see model in Figure 1b, left-hand side), are observed with high probability, whereas CH_3S_{ad} on neighboring lattice sites are rarely found. A detailed statistical analysis by the same methodology as in our study of sulfide on Cu(100)[10] provided quantitative data on the pairwise intermolecular interaction between the methyl thiolate adsorbates that support these findings (Figure 2b). Specifically, attractive CH_3S_{ad}–CH_3S_{ad} interactions at a distance of $\sqrt{2}a_0$ are found, whereas CH_3S_{ad} at spacings of a_0 and $2a_0$ interact repulsively. These results are very similar to those obtained for sulfide adsorbates,[10] albeit the positional fluctuations of the latter occur at a factor four lower rate.

Surprisingly, the appearance of those adsorbate configurations where CH_3S_{ad} are separated by the energetically preferred spacing of $\sqrt{2}a_0$ (in the following denoted as "CH_3S_{ad} dimers") fluctuates between two well-defined states (Figure 3), specifically, a state consisting of two well-separated isolated adsorbates and a state where a third maximum appears in between the two CH_3S_{ad}. The latter indicates the presence of an additional adsorbate, which occupies the empty four-fold hollow site between the two CH_3S_{ad} and two Cl_{ad} instead of a $c(2\times2)$ lattice site (see Figure 1b, right-hand side). As will be shown in the following, this additional species can be identified as Cu adatoms (Cu_{ad}) that are transiently trapped in the CH_3S_{ad} dimers.

Similar metal adatom bound thiolate dimers were reported in low-temperature STM studies of methylthiolate self-assembly on Au(111) under ultrahigh vacuum (UHV) conditions at 5 K by Maksymovych et al. and are now regarded as an essential structural component of thiol self-assembly on this surface.[5–7] In those studies, the CH_3S-Au_{ad}-SCH_3 species was extremely stable, even at rather extreme tunneling conditions. In contrast, the corresponding state found in our room-temperature study at the Cu(100)–electrolyte interface exists only for time periods of ≤ 0.5 s before returning to the adatom-free state. This time period is much shorter than the lifetime of the dimer; that is, the time period over which the two CH_3S_{ad} maintain their positions. Despite the relatively high time resolution of our video-STM, we could never detect indications for the approach or departure of the trapped species, such as the presence of another adsorbate in the vicinity of the dimer directly before or after the state with the central protrusion was observed. Either the trapped species approaches the dimer by rapid surface diffusion or it is formed by adsorption from the electrolyte solution. This unambiguously rules out CH_3S_{ad} or S_{ad} as the trapped adsorbate species, which are irreversibly adsorbed and exhibit very slow surface diffusion in the studied potential regime (see Figure 2a). In this context, it is worth mentioning that along with CH_3S_{ad}, a second, highly dynamic adsorbate species was observed in high-quality STM videos. These additional adsorbates change their position in more than 70% of the observations while being scanned, from which residence times of about 1 ms can be estimated. They thus may well correspond to specimens of the trapped adsorbate in the weaker-binding sites of the (CH_3S_{ad} free) $c(2\times2)$–Cl-covered Cu surface.

Further insight is obtained by a detailed analysis of the CH_3S_{ad} dimers dynamics. The probability that a dimer is occupied by an adatom is shown in Figure 4a as a function of potential and dimer lifetime. Obviously, this occupancy is independent of the lifetime or, conversely, the occupation of the dimer center does not noticeably influence the residence times of the involved CH_3S_{ad}. Since trapping and release of adatoms occurs on a much faster timescale and any effect of the adatoms on the dimer stability should therefore affect short- and long-lived dimers to an equal extent, this behavior is expected. Capture and release of adatoms are random events, as corroborated by the approximately exponential decay of the CH_3S_{ad} dimer residence times for staying in the adatom-filled or empty state, respectively (Figure 4b).

All of these data depend strongly on the electrode potential. Of particular interest is the

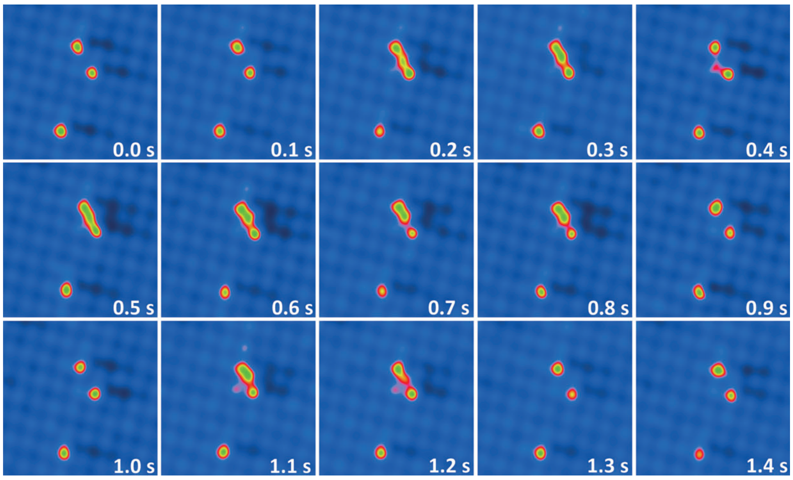

Figure 3. Adatom trapping by thiolate dimers. Subsequent images taken from an in situ video-STM sequence at $-0.24\,V_{SCE}$. The CH_3S_{ad} dimer in the upper part of the image fluctuates rapidly between a state with two separated maxima and a state with an additional maximum located in the dimer center, which is attributed to transient trapping of Cu adatoms in between the two CH_3S_{ad}.

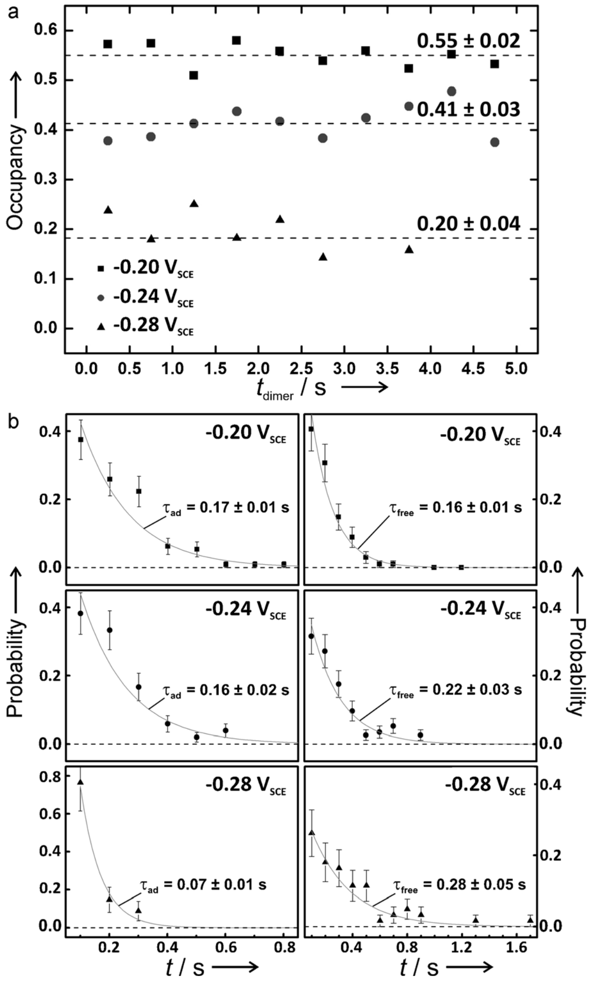

Figure 4. Quantitative dynamics of adatom trapping by isolated CH_3S_{ad} dimers. a) Fraction of CH_3S_{ad} dimers occupied by an adatom as a function of dimer lifetime and potential. Dashed lines indicate the average occupancy at each potential. b) Normalized distributions of the residence times of adatoms in the CH_3S_{ad} dimers (left-hand side) and of the residence times of the adatom-free CH_3S_{ad} dimer state (right-hand side) at different potentials. From fits to an exponential decay function (solid lines), the corresponding average lifetimes of adatoms in the dimer τ_{ad} and of the empty dimer τ_{free} are determined. Only events as in Figure 3, where merely the central protrusion appeared or disappeared within an isolated dimer but no changes in the positions of the two CH_3S_{ad} of the dimer occurred, were considered in this analysis.

pronounced increase of the dimer occupancy towards more positive potentials. This increase can be attributed to an increase in the surface concentration of the trapped species and a correspondingly higher probability of these highly mobile adatoms or adions to encounter a CH_3S_{ad} dimer. Qualitatively, this potential dependence of the concentration is expected for both copper ions, formed by electrochemical dissolution of the electrode, and copper adatoms on the electrode surface. However, in the first case the near-surface concentration of the dissolved ions should increase by approximately one decade per 60 mV potential change for a one-electron transfer process, which is more than three times higher than the occupancy change found in our experiments. Direct copper ion trapping from solution therefore does not seem to explain our observations. To assess the effect of the potential ϕ in the second case, we consider the adatom formation energy, which has a potential-dependent electrostatic contribution of $p_Z \varepsilon_0^{-1} C_d \phi$, where C_d is the differential capacitance and p_Z the dipole moment of the metal adatom.[14] Using $p_Z = 0.092\, e\,\text{Å}$, calculated for Cu adatoms on bare Cu(100)[15] and $C_d = 25\ \mu\text{C}\,\text{cm}^{-2}$,[16] this energy contribution is $0.26\ \text{eV}\,\text{V}^{-1}$. The corresponding change in the Cu_{ad} surface concentration for a potential increase $\Delta\phi$ is $\exp(p_Z \varepsilon_0^{-1} C_d \Delta\phi / k_B T)$, which would result in a 125 % increase for $\Delta\phi = 80$ mV at room temperature. This value is in agreement with our experimental results, corroborating copper adatoms as the trapped species.

From these observations, a physical picture of copper surface transport on the thiolate-covered surface emerges where copper adatoms move by rapid surface diffusion between metastable sites formed within the short-lived CH_3S_{ad} dimers. The increase in residence times τ_{ad} of the adatom in the dimer (Figure 4b, left-hand side) indicates a stronger Cu_{ad} trapping towards more positive potentials; that is, a larger activation energy for Cu_{ad} detachment from the dimer. The characteristic time τ_{free} a dimer remains in the unoccupied state (Figure 4b, right-hand side) depends on the energy barrier for Cu_{ad} hopping into the CH_3S_{ad} dimer site as well as the Cu_{ad} surface coverage. The latter increases with potential, which itself could already account for the decrease in τ_{free} towards more positive potentials. If an additional potential dependence of this energy barrier exists, it has to be significantly smaller than that of the barrier for Cu_{ad} hopping out of the CH_3S_{ad} dimer. Consequently, the Cu_{ad} binding energy in the dimer site has to increase with increasing potential (see energy scheme in Figure 1b).

Since the thiolate binding to the metal surface does not depend significantly on the length of the hydrocarbon group,[1–3] a similar interaction with metal adatoms is expected for other thiolates. Indeed, evidence for this was found in low-temperature STM studies of propane- and phenylthiol on Au(111).[7] Transient trapping of copper adatoms in "dimer" configurations should therefore also occur for other thiolates, including thiolate species with functional terminal groups. Specifically, this behavior is also expected for organosulfur additives, such as SPS, which are commonly used as accelerator species in copper electrodeposition. This has important implications for the role of these organosulfur additives in copper electroplating, and in particular in the technologically important damascene process. Currently, the deposition-accelerating properties of these additives are ascribed exclusively to the terminal groups (for example SO_3^-), which locally displace deposition-inhibiting additives, such as poly(ethylene glycol), from the copper surface and by this provide physical access of copper ions to the electrode.[12,13] The thiol group is mainly thought to provide an anchor that attaches these functional units to the metal. Our results suggest that the thiolate unit plays a more active role, adding additional functionality to organosulfur additives. Specifically, these species provide sites where the copper adatoms are more strongly bound to the metal surface; that is, significantly lower the final state energy for the electrochemical transfer of a copper ion in solution to a Cu_{ad} on the surface. This will also lower the energy of the transition state (by an amount determined by the transfer coefficient) and thus increase the rate of this ion-transfer reaction at thiolate dimer sites. Of course, an additional barrier for copper adatom diffusion away from the thiolate exists, but this will not impede the reaction as long as Cu_{ad} release from the trapping sites occurs faster than the rate-limiting ion-transfer reaction. According to this scenario, the stabilization of copper adatoms by adsorbed thiolates will help to make the energy landscape of the deposition reaction more level; that is, the accelerator acts as a true catalyst. Interestingly, the typical accelerator coverages under conditions used in damascene plating are in the range of 0.1 monolayers,[12] where the density of thiolate dimer configurations is very high. Therefore, the mechanism described above should be very effective.

As exemplified herein for the case of copper plating, the mutual copper adatom–thiolate interactions and resulting surface dynamics found in this study can have substantial implications. More generally, our observations indicate that these effects are not limited to clean surfaces at low temperature, but are a very general phenomenon that influences the surface chemistry of these systems also in complex environments and under real-world conditions, although the adatom trapping is short-term transient rather than permanent in the latter case. These results will also be significant in many other areas of interface and nanoscience. For example, single-molecule conductance measurements, which often employ (structurally uncharacterized) thiolate-tethered species, may be affected by such dynamic metal adatom attachment/detachment, resulting in temporal fluctuations between different states in room-temperature experiments. Understanding and quantifying these processes as well as determining how they are influenced by the surface structure and environment will therefore be vital for a wide range of fundamental studies as well as technological applications.

Experimental Section

All experiments were performed in a self-constructed in situ video-STM using tungsten tips coated by polypropylene.[11] The video sequences were recorded in constant-height mode at image acquisition rates of 10 images per second. The Cu(100) single-crystal substrate was prepared by electropolishing in orthophosphoric acid, rinsing with ultrapure water, and subsequent immersion into the electrolyte prepared from suprapure hydrochloric acid (Merck). Low-coverages of thiolate adsorbates were dosed by adding 5 μL of a 7 μM aqueous solution of dimethyl disulfide (Sigma–Aldrich, 99 % purity) to the electrolyte in the STM cell (total volume ≈ 1 mL).

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