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M. Rohwerder · K. de Weldige · M. Stratmann

Potential dependence of the kinetics of thiol self-organization on Au(111)

Abstract The self-assembly of thiol molecules from ethanolic solution on Au(111) depends significantly on the electrode potential. Especially at cathodic potentials, chemisorption of thiol molecules and the development of the highly ordered structure are slowed down significantly. At potentials near the point of zero charge, first a disordered thiol film of already high thiol density is formed, and then domains of the highly ordered phase develop and grow together. At cathodic potentials, first a disordered film of very low density of predominant flat adsorbed thiol molecules is formed; the formation of ordered domains takes time three orders of magnitude longer than at potentials near the point of zero charge.

Key words Thiols · Self-organization · Electrochemistry · Organic electrolytes · Scanning tunneling microscopy

Introduction

The motivation for this study stems from the aim to improve the adhesion of polymeric coatings for corrosion protection on metal surfaces by means of functionalized thiol monolayers [1, 2, 3] and from the experience that the preparation of stable thiol monolayers on iron turned out to be unexpectedly difficult. In this context it is important to know that thiols do only adsorb on oxide-free iron surfaces, i.e. the iron surface has to be held at a sufficiently cathodic potential to enable adsorption from the liquid phase.

All attempts to prepare stable thiol monolayer films on iron surfaces so far having failed, the question of the reason for this arises. One possible explanation could be

that, for some reason, the thiol adsorption on iron is hindered at the cathodic potentials that are required to keep the iron surface oxide-free.

It is known from gas phase deposition experiments that, though the iron-sulfur bond is a very strong one, it is impossible to prepare stable thiol films on bare iron surfaces in UHV also, but the thiol molecules adsorb well when carbon monoxide or water are predeposited [4]. The explanation for this is that the thiol molecules adsorb flat onto the iron surface where the high reactivity of the iron causes cracking of the sulfur-alkyl bond. In the presence of coadsorbed H_2O or CO the thiol molecules adsorb in a more upright position, and hence they are not cracked. So the question arises whether thiol adsorption from solution at cathodic potentials could be compared to gas phase adsorption under UHV conditions, i. e. whether the thiol molecules adsorb flat onto the surface.

Because of the complexity of the system thiol/iron, as a first step the effect of electrode polarization has been investigated for the well-known system thiol/gold.
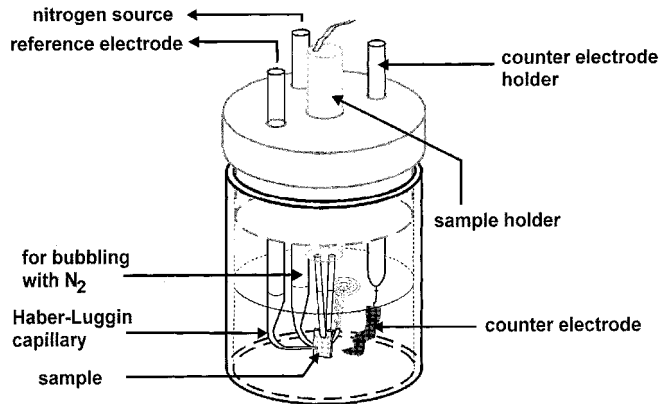
Experimental

The kinetics of thiol adsorption and the evolution of molecular structure during the self-organization process have been investigated as a function of the electrode potential for the system of decanethiol on Au(111) by in situ monitoring of the capacity change and with STM.

The self-organization was performed in an ethanolic solution of 2×10^{-5} M thiol and 0.1 M $LiClO_4$ concentrations. Reference electrode was an Ag/AgCl wire immersed in an ethanolic 0.1 M $LiClO_4$ solution in a reference electrode glass compartment separated from the adsorption solution by a glass frit. This leads to a very low equilibrium concentration of chloride in this compartment, so that the amount of chloride penetrating through the frit into the adsorption solution is negligible. Nevertheless, the concentration is sufficient to guarantee a quite stable reference potential. The stability of this reference electrode was tested by regularly measuring the potential difference vs the ferrocene (I)/(0)-redox sytem, which yielded to $E[\text{Fc(I)/(0)}] \approx +290$ mV (± 10 mV on a time scale of weeks) vs this reference electrode.

M. Rohwerder (✉) · K. de Weldige · M. Stratmann
Max-Planck-Institut für Eisenforschung,
Max-Planck-Strasse 1, D-40237 Düsseldorf, Germany

Fig. 1 Special beaker for adsorption experiments. The modular design allows thorough cleansing of all parts that come into contact with the adsorption solution

Fig. 2 Normalized capacity change vs adsorption time for adsorption of ODT from 2×10^{-5} M, nitrogen-purged ethanolic solution

Flame-annealed gold-coated glass samples (250 nm Au/1 nm Cr/Tempaxglass) were used as substrates [5]. Annealing for about 5 min in a hydrogen flame resulted in surfaces featuring a high density of Au(111) terraces, as has been verified by STM. The samples were clamped between two glass rods, one of which featured a small gold bead that made electrical contact to the gold surface. The other side of the bead was a gold wire, fused into the glass rod and passing out of it at the upper end of the rod well outside the electrolyte, enabling electric contact to the electrode (Fig. 1).

The adsorption solution was purged with pure nitrogen to suppress the oxygen content in the solution. The purging was continued throughout the adsorption experiments. The ethanol was Rothipuran from Roth, and the decanethiol was purchased from Fluka.

STM investigations were carried out with the Nanoscope III equipment from Digital Instruments and the STM A head. The bias and tunneling current for the *ex situ* images were 1.2 V and 50 pA.

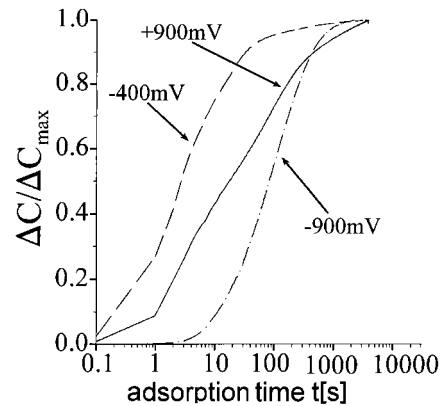Sample preparation included the following steps:

1. Fast immersion of the sample into the solution, which already contained the thiol (under potential control)
2. Adsorption of the thiol and *in situ* monitoring of the capacity change
3. Withdrawing the samples from solution and immediately washing them with pure ethanol, after which they are immediately dried in a nitrogen stream.

The uncertainty in adsorption time for steps 1 and 3 was below 0.5 s. This procedure has proven to be the best way to measure the adsorption kinetics at the different potentials. Immersing the sample first at a fixed potential and stepping to the desired one did not prove to be suitable because of immediate adsorption of thiols even before the step could be applied. After this procedure, the samples were investigated by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS).

The change of capacitance was measured by modulating the electrode potential by 10 mV peak to peak at a frequency of 10 Hz and detecting the 90° phase-shifted component of the current signal by the lock-in amplifier technique.

Results

The first researchers to monitor *in situ* the self-assembly of thiols on gold were Fruböse and Doblhofer [6]. They could not find any significant potential dependence of the kinetics of ODT (octadecylthiol) self-assembly on gold. In contrast, our own experiments show that there is a significant potential dependence for the self-assembly of thiols on gold, but that indeed it is less pronounced for the longer thiols, e.g. ODT, than for the shorter ones, e.g. decanethiol (DT).

This is shown in Figs. 2 and 3: the normalized capacity curves $\Delta C/\Delta C_{max}$ for adsorption from 2×10^{-5} M thiol solution are shown for a series of potentials between -900 mV and $+900$ mV. The normalization $\Delta C/\Delta C_{max}$ has been performed to facilitate comparison of the capacity curves for different potentials: $\Delta C(t)$ is the change of capacity after adsorption time t at a given electrode potential, and ΔC_{max} is the maximum change of capacity due to self-organization of a full, highly ordered thiol film at the same potential.

In Fig. 3, the capacity curves for $E = -400$ mV are representative for an intermediate potential range (curve B) which ranges from $E = -400$ mV to $E = +200$ mV and where there is only a slight potential dependency. For more anodic potentials (curve C) the kinetics of thiol self-assembly decrease significantly with increasingly more anodic potentials. But this effect is much
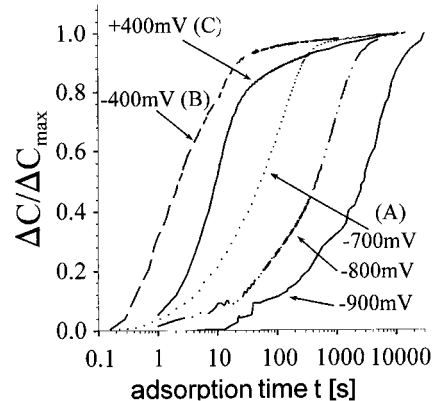
Fig. 3 Normalized capacity change vs adsorption time for adsorption of DT from 2×10^{-5} M, nitrogen-purged ethanolic solution
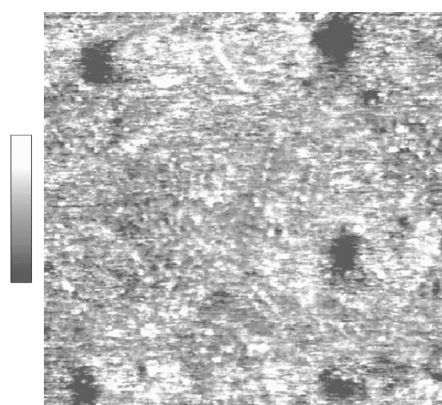
more drastic for cathodic potentials (curve A): the process of ODT self-assembly at $E = -900$ mV is more than two orders of magnitude slower than that at $E = -400$ mV, while for DT the adsorption is more than three orders of magnitude slower.

The focus of this paper will be on the intermediate potential and the cathodic potential ranges: on the intermediate potential range because it includes the open circuit potential (OCP) of gold in ethanol (varying between -300 and $+100$ mV, depending on contamination and residual amounts of oxygen in the nitrogen purged ethanol solution) and the point of zero charge (PZC), about -220 mV and on the cathodic potential range because this latter is the potential range which is of importance for the system thiol/iron.

Interestingly, the decline in the velocity of thiol self-organization for cathodic potentials is not uniform for all adsorption times: it is less pronounced at shorter than at longer adsorption times. For DT, the capacity change at 2 s is $\Delta C/\Delta C_{max} \approx 0.47$ for $E = -400$ mV; the same value is reached for $E = -900$ s at about 2000 s. At 0.3 s it is $\Delta C/\Delta C_{max} \approx 0.06$, which is reached for $E = -900$ mV after 40 s.

Concerning STM, the films that are prepared within the intermediate potential range are comparable to those known from the literature, which have been prepared without potential control [7–10], i. e. under varying OCP conditions. STM imaging at different intermediate stages of the film growth shows that the film growth can be separated in three stages:

1. Fast adsorption of thiols and formation of a disordered film (Fig. 4); at -400 mV the thiol density reaches 80–90% of the thiol density in the $\sqrt{3} \times \sqrt{3}$-structure within the first 5 s.

2. Formation of domains of highly ordered thiol molecules ($\sqrt{3} \times \sqrt{3}$-structure) and subsequent domain growth (ca. 10–1000 s).

3. Healing of defects after the domains have grown together.

A typical example for stage two is shown in Fig. 5: a 120×120 nm^2 scan image of a decanethiol film adsorbed for 20 s at -400 mV. Two monatomic terraces of the Au(111) surface can be seen. The domains appear in the STM image as elevated areas on the terraces, of lateral dimensions of 5–20 nm. The thiols in the domains are in the highly ordered $\sqrt{3} \times \sqrt{3}$-structure. The area between the domains is covered by the afore-mentioned disordered thiol film, where the thiol density is 80–90% of the density in the highly ordered structure. Also visible are the characteristic holes known from the literature (see [7–10] and references therein). These were never observed in the domains but only in the disordered thiol film between them. The coverage of the surface by domains increases steadily during the first 120 s, where about 85% of the surface area are covered by domains,
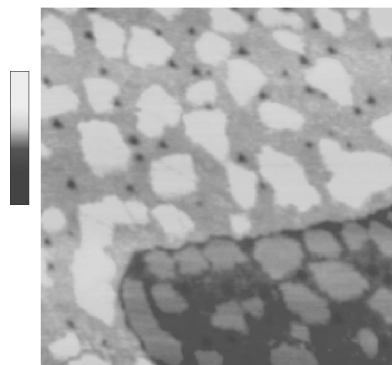
$xy = 120 \times 120$ nm^2, $\Delta z = 1$ nm

Fig. 5 Decanethiol film adsorbed at -400 mV, after 20 s. Approximately 40% of the surface is covered with highly-oriented domains of the $c(4 \times 2)$-structure

$xy = 20 \times 20$ nm^2, $\Delta z = 0.2$ nm

Fig. 4 Decanethiol film adsorbed at -400 mV, after 10 s. The surface is covered by scattered circular dots which show a short-range order. Since on images of thiol films obtained after longer exposure times these circular dots are identified with individual thiol molecules, the film obviously consists of not-highly-ordered thiol molecules of an already high density
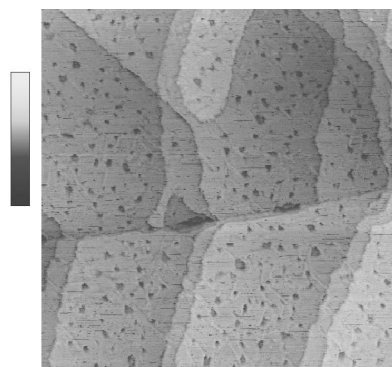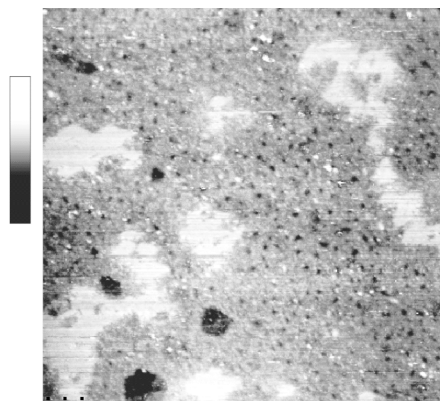

$xy = 120 \times 120$ nm^2, $\Delta z = 5$ nm

**Fig. 6** Decanethiol film adsorbed at -400 mV. Final structure after 2 h

$xy = 200 \times 200$ nm^2, $\Delta z = 1$ nm

Fig. 7 After 10 min of adsorption time the surface is partly covered by fuzzy domains

but the final structure as seen with STM seems to be reached only after 1–2 h (Fig. 6).

At cathodic potentials, the thiol self-organization takes place at a rather decreased velocity. Figure 7 shows a 200×200 nm^2 scan image of a thiol film adsorbed for 10 min at −800 mV from nitrogen-purged solution: at −800 mV the amount of adsorbed thiol is lower for 10 min of adsorption time than at −400 mV for 20 s. Most of the surface is covered by disordered film where the thiol density is thought to be very low, since no molecular resolution has been achieved in areas of disordered film on samples that have been adsorbed at cathodic potentials.

While the domain boundaries are fairly smooth and the domains are roughly circular at −400 mV, at −800 mV the domains are fuzzy, and in a close-up view
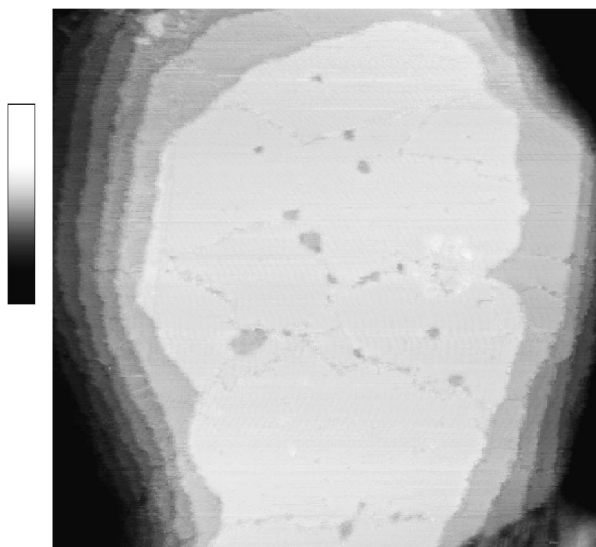
$xy = 200 \times 200$ nm^2, $\Delta z = 1$ nm

Fig. 8 Final structure: domain size up to 50 nm by 100 nm

it can be seen that most of them consist of very small nano-domains interconnected by thin stripes of two or three molecular thiol rows [11].

During the subsequent 2 h or 4 h of adsorption time the number of nano-domains in these agglomerations increases, and the area covered by a single agglomeration can have lateral dimensions of 30–100 nm or even in some cases up to 200 nm. In the final film, this leads to domains of the same size (Fig. 8).

Discussion

Adsorption

The results presented above show that the electrode potential has a significant influence on the velocity of the thiol self-organization and on the domain shape at intermediate stages during the thiol self-organization, especially at cathodic potentials.

The question is how to explain these effects. The fact that the influence of potential is less significant at shorter adsorption times than at longer adsorption times can be explained by a two-step process for the adsorption:

– The first step of the thiol adsorption is kinetically determined by the physisorption, i. e. displacement of the ethanol molecules by the thiol molecules. The dependence of the physisorption energy on the electrode potential is predominantly determined by the dependence of the respective dipole energies on the electrode potential [12]. The physisorption should be the fastest at the point of zero charge (PZC) (here ca. −220 mV), and indeed film formation is fastest at −200 mV. The electrosorption valencies for physisorbing organic molecules on metal surfaces are usually in the range of $\gamma \approx 0.02–0.08$ [13], which equals a dependence of the respective dipole energies of the order of several kJ/molV (multiplication by F). This first step can be written as

$$RSH + Au\text{-}EtOH \rightarrow RSH\text{-}Au + EtOH$$
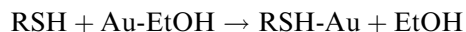
– The second step is characterized by the strong decline in the velocity of adsorption at cathodic potentials, and only here can the distinction between first and second step be really made. It could be explained by an oxidative step, for which ΔG should decrease by

Table 1 Domain and pit area as a function of time. The first 120 s are the most important ones for the thiol self-organization at −400 mV in 2×10^{-5} M ethanolic thiol solution

Adsorption time	Domain area	Pit area
10 s	10–15%	(?)
20 s	ca. 40%	2–3%
40 s	ca. 60%	4–5%
60 s	ca. 70%	5–7%
120 s	ca. 85%	5–8%
2 h	ca. 100%	7–10%

several tens of kJ/molV when going to more cathodic potentials. At positive potentials this step would be much faster than the physisorption step, so that the latter is always rate-determining at positive potentials. Since it is known from XPS investigations that the thiol sulfur is not oxidized when chemisorbing on the gold surface, the assumption in the literature is that gold thiolates are formed [14–18], i.e. that the gold atoms participating in the thiol adsorption are oxidized. So most likely the rate determining step is

$$RSH\text{-}Au \rightarrow RS\text{-}Au + H^+ + e^-$$

So far nothing is known about the follow-up reactions, i.e. what happens to the proton and the electron. But it is obvious that both must leave the interface quickly, because otherwise, at cathodic potentials, the reverse reaction would take place immediately and no film could be formed at cathodic potentials. Actually, it is remarkable that even though the film formation is slowed down immensely, a full film is still formed. Usually the surface coverage is a stronger function of concentration and potential [19]. This is in accordance with the fact that thiol chemisorption is considered to be irreversible.

In the studies by Porter et al. [20] in alkaline solutions it could be shown that desorption occurs (at very cathodic potentials) in the form of thiolates just before the onset of hydrogen evolution. In acidic solutions, no desorption can be observed before the onset of hydrogen evolution.

Domain growth

The domain growth at potentials between −400 mV and +200 mV can be explained by a simple nucleation and growth process. The fuzzy domain shape for intermediate stages of self-organization at cathodic potentials is more difficult to explain. Now at cathodic potentials, the dipole energy of thiols adsorbed in an upright position is less favorable than that of flat adsorbed thiols. So the assumption can be made that the thiol molecules adsorb flat onto the surface at cathodic potentials. The alkane chains of the thiols in the flat positions are expected to have only a weak interaction with the alkane chains of thiols which are tilted 30° to the surface normal. It is more likely that the thiol molecules are erected by van der Waals interaction with other flat adsorbed thiol molecules: the van der Waals interaction is increased by assuming the upright position.

This theory is supported by the fact that the dependence of the thiol adsorption on the electrode potential is less significant for longer thiols. While the dipole energy of a thiol molecule in the upright position increases with increasingly cathodic electrode potentials and does not depend very much on chain length[1], the van der Waals interaction depends strongly on chain length, more strongly supporting the erection of the thiol molecules the longer the chain length.

The chain-chain interaction of the flat adsorbed thiols will be greatest in small units or micelles. This results in the development of small nano-domains of upright thiol molecules from such micelles of adsorbed ones, which then grow together in agglomerations that look like domains with fuzzy domain shapes. In contrast to the intermediate potentials (Fig. 4), at cathodic potentials no molecular resolution can be achieved for the early stages of adsorption. This is a sign of a very low thiol density on the surface, which is also supported by XPS investigations. This has to be expected, since the physisorption becomes less favorable at cathodic potentials and the balance between physisorption and desorption keeps the density down, which can only be increased by chemisorption of thiols. So the kinetics of the domain growth at cathodic potentials will be determined by the chemisorption process. The chemisorption at cathodic potentials is easier for thiols with longer alkane chains, because an increasing fraction of the potential difference drop between metal surface and solution occurs over the alkane-chain, reducing the difference in potential between metal and sulfur head.

Conclusion

It has been demonstrated that the electrode potential affects the kinetics and mechanisms of thiol self-organization on Au(111).

At cathodic potentials the thiol molecules adsorb flat onto the metal surface, and only in a second step do they assume an upright position. This has been concluded from a comparison of the shape of the domains at intermediate steps of film formation for different potentials. It explains the problems that are encountered when trying to prepare thiol monolayer films on cathodically polarized iron surfaces. Since iron is far more reactive than gold, the flat adsorption of the thiols leads to thiol cracking and subsequently to unstable thiol monolayers. Only multilayer formation may lead to electrochemical stable films, but the mechanical stability of those multilayers is not sufficient for technical applications: only stable monolayer films of suitably functionalized thiols would make good adhesion promotion, not multilayers bound by comparatively weak van der Waals forces to the layers supporting them.

If thiols are to be used as adhesion promoters on reactive metals, new ways of film preparation or new kinds of thiols will have to be tried. For example, it would be interesting to find out if thiol film self-organization might be possible in the range of active-metal dissolution, i. e. at more cathodic potentials than those considered possible right now, or if thiols with other dipole moments might be promising.

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[1] Since the dipole moment does not vary very much for thiols with more than six carbon atoms, the dipole energy does not vary very much either

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