Self-Assembled Monolayers

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Kinetically Stable, Flat-Lying Thiolate Monolayers[**]

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Although self-assembled monolayers (SAMs) were introduced over 20 years ago,[1,2] the attention they receive is still increasing. This is in part because these ultrathin organic adlayers are making their way into a variety of technical applications.[3,4] Of the numerous approaches for the fabrication of SAMs, the one based on the chemisorption of organothiols onto Au surfaces has become the most widely used. During the formation process, the S–H bond is cleaved to yield the binding species, thiolate. The SAMs obtained in this way usually consist of molecules standing upright or slightly tilted with respect to the surface normal. This phase is considered to be the most favored thermodynamically.[1,2]

Herein we report an unexpected effect on the structure of the resulting SAMs when the thiol group is modified. We demonstrate this novel strategy to manipulate the structure of SAMs for the case of thioacetates, in which the H atom in the SH unit is replaced by an acetyl group.

Although organothioacetates are frequently used,[5–12] their adsorption behavior on gold surfaces remains unclear. An early paper[13] reported that organothiolate adlayers formed from thioacetates have a similar structure and quality to those obtained from the respective thiols (possibly through hydrolysis or solvolysis in solution). A more recent study,[14] however, reported that it is not possible to grow well-defined SAMs of a benzylic dithioacetate.

As thioacetates are often used for the preparation of organic monolayers on metals,[5–12] we carried out a detailed multitechnique study on the formation of SAMs on Au substrates. As a model substance we chose dodecyl thioacetate ($CH_3(CH_2)_{11}SCOCH_3$; $C_{12}SAc$), as the monolayers of its corresponding thiol have been thoroughly characterized.[15–18] To rule out any effects of small amounts of free thiols, we carried out several consecutive fractional distillations to prepare a highly pure thioacetate, as in the past trace amounts of thiols in the starting materials have led to false conclusions about the monolayer-forming properties of dialkylsulfides.[19–21]

SAMs prepared from $C_{12}SAc$ and, for comparison, from dodecanethiol ($C_{12}SH$) were investigated by infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, optical ellipsometry, contact-angle measurements, and scanning tunneling microscopy (STM; see the Supporting Information).

Whereas ellipsometry suggests the formation of incomplete SAMs from $C_{12}SAc$ with a thickness of 30 % relative to those of the $C_{12}SH$ reference system (6 vs. 18 Å), the water contact angle of 65° for the $C_{12}SAc$ SAMs implies the presence of an organic surface with exposed methylene groups (as opposed to high-density dodecanethiolate SAMs with a contact angle of around 110°, characteristic for the presence of methyl groups[22]). This result could indicate either strong disorder or flat-lying molecules. More definitive clues can be found in the XPS and NEXAFS data, in which a shift of the C 1s core levels and the resonances of unoccupied orbitals, respectively, indicates the presence of *n*-alkyl chains adsorbed flat on a metal surface.[23,24] The IR spectra also reveal significant differences relative to those obtained for dense thiolate SAMs, which also indicate the presence of a saturated hydrocarbon chain with its C–C–C backbone orientated parallel to the substrate (Figure 1). Note that the

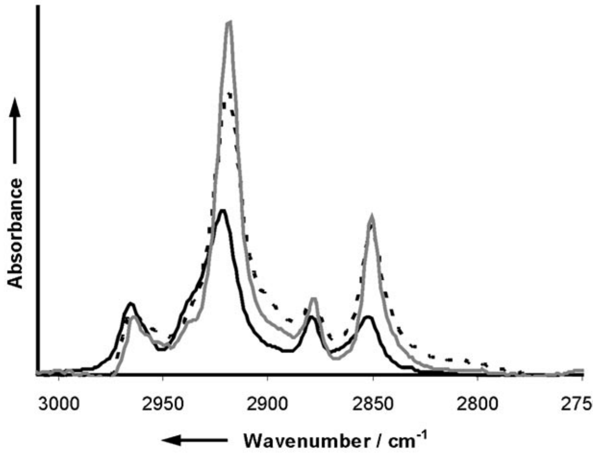

Figure 1. C–H vibrational region of the IRRA spectra of the monolayers formed from $C_{12}SAc$ (solid black line) and $C_{12}SH$ (solid gray line), as well as that of the $C_{12}SAc$-derived monolayer after re-immersion into $C_{12}SH$ solution (dashed line). The significantly lower intensity of the signals in the $C_{12}SAc$-derived monolayer hints at a much lower coverage, whereas re-immersion of this layer forms monolayers similar to those obtained directly from $C_{12}SH$.

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usual selection rules do not apply for the case of an intimate contact of the alkyl chains with the metal surface.[25,26]

As alkanethiolate-based SAMs in which the alkyl chains are orientated parallel to the substrate have only been observed previously as intermediates,[27,28] additional experiments were carried out by using high-resolution scanning tunneling microscopy (STM). The STM data reproduced in Figure 2 clearly demonstrate the presence of a striped phase, which is a typical signature of low-density, intermediate SAM phases.[26,29–34]

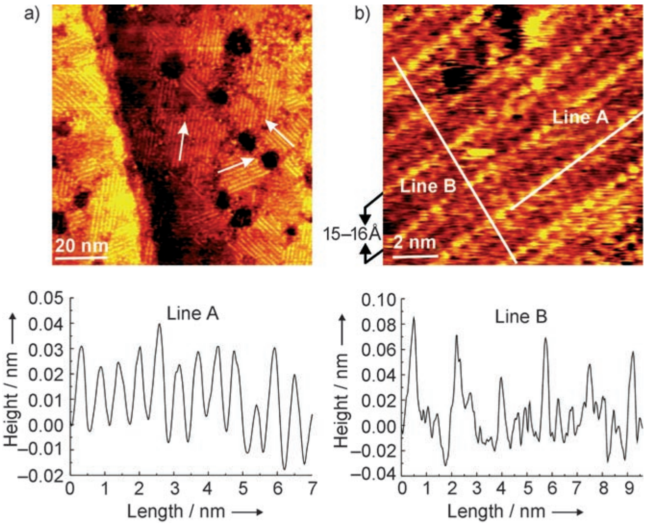

Figure 2. STM data of the monolayer formed from $C_{12}SAc$. The survey indicates a number of rotational domains with the typical depressions in the gold surface (a). At higher magnification, single molecules become visible (b). The line scans (bottom) allow determination of the $(p\times 2\sqrt{3})$ structure.

The STM data reveal a rectangular unit cell with a length of the long sides equal to about 15–16 Å and that of the shorter side amounting to 5 Å. In accord with earlier analysis of such intermediate phases,[31–33] we propose a rectangular $(p\times 2\sqrt{3})$ structure containing two molecules per unit cell. It should be mentioned that in the case of an orientation of the molecules parallel to the longer vector (and thus perpendicular to the rows of neighboring sulfur atoms) the value of p should be 6, which would result in a calculated unit-cell length of 17.3 Å.

Although a number of different flat-lying phases have already been reported,[26–33] this particular phase has, to the best of our knowledge, not been observed before. All previously known striped phases show either a head-to-head arrangement with a stripe width significantly larger than the alkanethiolate length (up to twice) or an alternating (intercalating) ordering with a pairing of the sulfur atoms in the form of double rows, thus resulting in a typical elongated "plaid" pattern.[32] In contrast to these previously reported structures, the pattern observed in this case is clearly striped with single sulfur rows separated by the length of a molecule.

A closer inspection of the STM data reveals that smaller islands with a more densely packed phase exist in between the areas of the flat-lying phase. The STM micrographs of this phase are assigned to the high-density $(2\sqrt{3}\times 3)$ structure (also known as $c(4\times 2)$) commonly found for the upright phase in alkanethiolate-based SAMs.[16,18] This upright-standing phase was never found to cover more than 40 % of the gold surface, even after prolonged exposure times (five days) to the $C_{12}SAc$ solution.

The fact that the $(2\sqrt{3}\times 3)$ islands (which appear higher in the STM micrographs) are always localized at the domain boundaries of the striped phase (Figure 3) or near surface defects (in particular step edges) suggests that the transformation of the striped phase containing flat-lying molecules into the dense, upright $(2\sqrt{3}\times 3)$ phase is significantly hindered. As the latter phase should be thermodynamically more stable, we conclude that there must be a kinetic limitation that hinders the formation of adsorbed thiolates from the thioacetate.

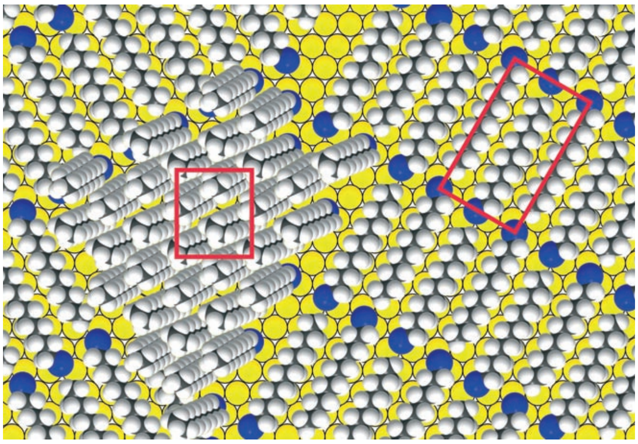

Figure 3. Model of the surface layer formed upon adsorption of $C_{12}SAc$ (top view). The surface is dominated by the flat-lying phase with the molecules lying next to each other with alternating orientation. At domain boundaries or defects the $(2\sqrt{3}\times 3)$ structure with upright molecules can be formed because of the accessibility of the gold surface for further $C_{12}SAc$ molecules.

This behavior can be rationalized as follows: For the transformation of $C_{12}SAc$ into the binding thiolate some reagent must be present, as these molecules are chemically stable in ethanol. In our case, this reagent is the gold surface, which facilitates the cleavage by formation of the stable Au–S bond (the leaving acetyl group probably reacts with the ethanol). As soon as the gold surface is covered by the low-density monolayer, the contact between the gold surface and the $C_{12}SAc$ molecules is hindered, thus suppressing the quick formation of the denser phase. Only at the domain boundaries or structural defects is the gold substrate sufficiently exposed to permit the further generation of thiolate molecules, eventually leading to the formation of the upright phase in these places.

An important test experiment for this hypothesis is the immersion of the $C_{12}SAc$ SAMs that exhibit the striped phase into a solution of $C_{12}SH$. All the experimental techniques employed in this study reveal that the SAMs formed by this two-step process are very similar to the SAMs formed from

$C_{12}SH$ in a one-step process (see, for example, the solid gray line in Figure 1).

In conclusion, we have demonstrated that—in contrast to previously reported results—high-purity thioacetates do not form self-assembled monolayers with the same $(2\sqrt{3}\times 3)$ structure that is obtained from the corresponding thiols. Instead, the thioacetates form a highly ordered striped phase with flat-lying molecules antiparallel to each other, a structure that has not yet been reported. The introduction of a leaving group at the sulfur atom thus results in the formation of a different, kinetically stable (!) SAM structure, even though the resulting species bound to the Au substrate is the same as in the case of the monolayers derived from the respective thiol. These leaving-group effects on the structure and quality of organothiolate SAMs provide a new possibility to control the properties of this versatile class of materials.

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