Self-Assembled Monolayers

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Onset of Crystalline Order in 1-Nonanethiol Monolayers Deposited from Solution**

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A plethora of applications of thiol self-assembled monolayers (SAMs) have been developed during the last two decades.[1] A unique combination of factors, such as ease of preparation,

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mechanical robustness, transferability, and a broad choice of commercially available metallic substrates and thiols, has prompted their use in a variety of scientific areas such as molecular electronics,[2] corrosion protection,[3] nanolithography,[4] electrochemical sensing,[5] and cellular adhesion.[6] Moreover, there seems to be a wide acceptance that these systems exhibit a high degree of structural order, particularly in the prototypical case of alkanethiol ($HS-(CH_2)_n-CH_3$) SAMs deposited on Au(111). This assumption is well supported from X-ray and helium diffraction,[7] IR,[8] and STM[9] studies carried out under either ultrahigh vacuum (UHV) or ambient conditions, but it turns out to be more controversial when the organic monolayer is in contact with a liquid phase. A number of in situ STM and AFM studies of alkanethiol monolayers[10] (with $2 \leq n \leq 17$) have visualized ordered domains in the presence of a variety of solvents, which include water, ethanol, 2-butanol, and heptane. In all cases, these domains reproduce the $(\sqrt{3}\times\sqrt{3})$R30° overlayer structure that is observed in the absence of solvent, and some of them display also the characteristic c(4×2) superlattice (Figure 1).[10d–f] However, in situ vibrational spectra of these monolayers indicate the presence of some conformational disorder near the alkyl chain terminus.[11] There is also a conspicuous lack of reported diffraction results that support the persistence of crystalline order when the monolayer is in contact with a liquid phase.[12] Herein, we report the time evolution of the diffraction peaks associated with the appearance of the $(\sqrt{3}\times\sqrt{3})$R30° structure in a 1-nonanethiol SAM deposited on Au(111) from an ethanolic thiol solution. The presence of a liquid phase is shown to disrupt the monolayer structure, and crystallographic order is seen to develop only when the contacting solution is removed.

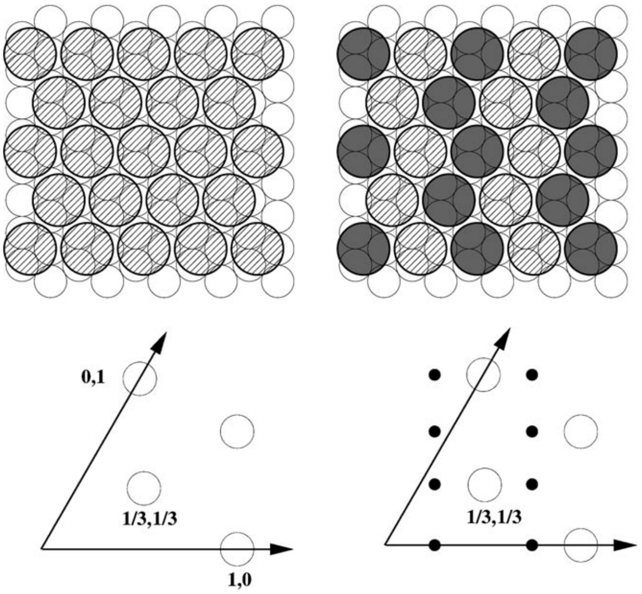

Figure 1. Real-space (top) and reciprocal-space (bottom) representations of the $(\sqrt{3}\times\sqrt{3})$R30° structure (left) and of its c(4×2) superlattice (right), which describe a typical packing of alkanethiol SAMs deposited on Au(111). Small and large circles in the real-space representations correspond to gold atoms and alkanethiol chains, respectively.

1-Nonanethiol monolayers were deposited on Au(111) by thiol adsorption from an ethanolic solution. No diffraction peaks were observed at the 1/3,1/3,1 reciprocal-space position during the deposition (≈2 h) and rinsing (≈10 min) stages. When ethanol was replaced by a continuous flow of helium (≈30 mL min^{-1}), a diffraction peak, characteristic of the $(\sqrt{3}\times\sqrt{3})$R30° overlayer structure, developed over a long time period (≈10 h; see Figure 2a and solid triangles in Figure 3 for the time evolution of the Bragg peak). It should be noted that no diffraction peak was detected if the sample was kept in contact with the solution for up to 20 h. It was verified that the

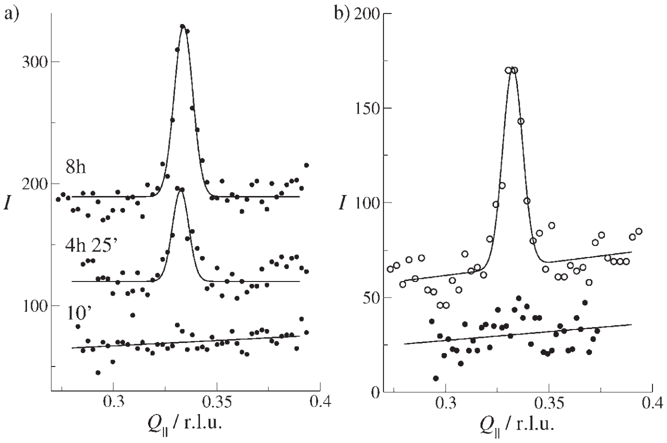

Figure 2. Time evolution of intensity of the 1/3,1/3,1 Bragg peak as a function of the in-plane momentum transfer (r.l.u. = reciprocal lattice units) a) after replacing ethanol by a continuous flow of helium, and b) after the previously ordered 1-nonanethiol monolayer (○) is put into contact with liquid ethanol for 30 min (●). Plots have been shifted vertically for clarity. The time elapsed since the liquid phase was removed from the thin-layer cell is indicated on each plot.

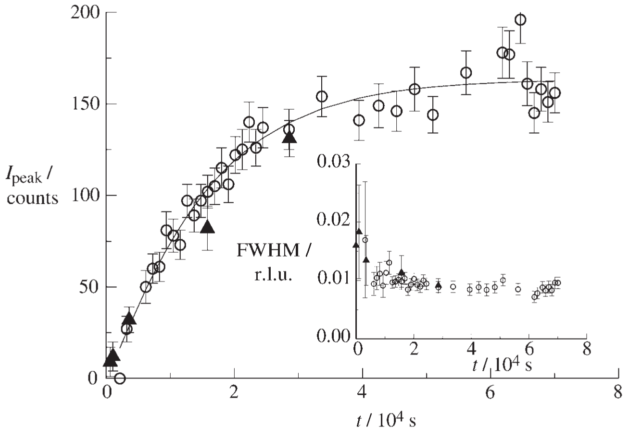

Figure 3. Background-subtracted peak intensity of the 1/3,1/3,1 in-plane Bragg peak as a function of the time elapsed since the solution was removed. Triangles (▲) are data obtained just after monolayer formation, and circles (○) were recorded after the already-ordered monolayer was put into contact with ethanol for 30 min (some of these peaks are shown in Figure 2). The solid line is the best fit of Equation (1) to the data. The inset shows the corresponding FWHM values of the peak.

background signal in both Au(111) crystal truncation rods (CTRs) and thiol structure rods remained constant during the measurements, thereby ruling out the possibility that the development of the diffraction peak could be due to a decrease in the solvent background.

To assess whether the observed ordering process was initiated after removal of the liquid phase, rather than after completion of a full monolayer coverage in the presence of ethanol, the already ordered monolayer was subjected to a wetting/drying cycle by successive injection of ethanol and helium. As shown in Figure 2b, contact with the liquid phase destroys completely the crystalline order in the SAM, whereas the previous ordering sequence is regained upon flushing again the cell with helium (see circles in Figure 3). The good agreement between the two sets of data in Figure 3 indicates the absence of significant X-ray induced damage in the monolayer, which is likely to be precluded by the continuous flow of helium over the sample.[13]

After the kinetic runs were completed, the final thiol structure was inspected by recording a complete set of in-plane and out-of-plane X-ray scans (see Experimental Section). The intensity ratios of the measured Bragg rods are identical to those reported by Fenter et al. for decanethiol SAMs,[14] which indicates that the 1-nonanethiol monolayers presented herein also display the c(4×2) superstructure.

The time evolution of the ordering process illustrated in Figure 3 can be reproduced by Equation (1),[15] in which θ is

$$\theta(t) = \frac{I(t)}{I_{t\to\infty}} = 1-\exp(-k\,t^{n}) \qquad (1)$$

the surface coverage of ordered domains, I is the intensity of the diffraction peak, and k and n are kinetic parameters whose physical meaning is analysed below. The best fit to the data in Figure 3 is obtained for $k = 2.2\times10^{-5}\,\mathrm{s}^{-1}$ and $n = 1.1$. According to the Kolmogorov–Avrami theory,[15] n is related to the effective dimensionality of the growing domains. A value of n close to 1 may arise in either a) a constant rate of nucleation, combined with ordered domains of homogeneous size whose number increases with time, or b) an instantaneous (delta-shaped) nucleation rate, combined with a domain growth along one dimension only.[15] It is possible to discriminate between these two alternatives by considering the time evolution of the full width at half maximum (FWHM) values of the diffraction peaks, which are a measure of the average domain size ($l = 2\pi/\mathrm{FWHM}$).[16] As shown in the inset of Figure 3, peak widths remain constant during the ordering process, thus providing a time-independent average mosaic size of 50 nm. This behavior is consistent with our first hypothesis only, and it provides a straightforward visualization of the ordering process as a sequence of sudden crystallization events that affect individual domains independently. The invariance of the average domain size with respect to repetitive wetting/drying cycles suggests that domain boundaries remain undisturbed by exposing the monolayer to a liquid phase and that their pattern is determined after completion of a full monolayer adsorption from solution. The kinetic parameter k defines the time scale of monolayer crystallization. Additional experiments carried out in a controlled atmosphere chamber indicate that full removal of the solvent molecules from the monolayer appears to be a rate-limiting prerequisite for the onset of the ordering process. The presence of a limited number of intercalated solvent molecules in the disordered monolayer is supported by the electrochemical quartz balance and ellipsometric measurements reported by Blanchard and Karpovich.[17]

Our results provide for the first time evidence of the dynamic structure of alkanethiol SAMs in contact with a liquid phase. The observation of crystalline order found with X-ray diffraction after hours without solvent is coherent with other SAMs X-ray diffraction experiments developed under UHV.[14] We have verified that the obtained crystalline order for the thiol SAMs in such conditions extends in both in-plane and out-of-plane directions. Though the X-ray diffraction is more sensitive to atoms with a higher atomic number (Z), the fact that 1-nonanethiol monolayers contain nine carbon atoms per sulphur atom means the overall scattering power of the monolayer is governed by the carbon moiety. The structural study of the data obtained from the ordered SAM shows that the rod intensity value measured at the surface for the normal momentum transfer $L = 1$ is mainly governed by the total chain structure factor.[14] Thus, the observed ordering process can be unambiguously associated with a rearrangement of the whole alkyl chains. Furthermore, in situ IR experiments have also provided evidence of solvent-induced disorder in these monolayers, although it was apparently confined to the outermost methyl groups.[11] Our results show that in the presence of a liquid phase, even if the thiol heads can be periodically arranged on the gold substrate, the alkyl chains, which contribute most of the monolayer scattering power at the recorded L position, do not display long-range order, particularly along the surface normal where the scanning probe techniques are silent.

We have shown in this work how reversible switching between crystalline order and disorder in a 1-nonanethiol monolayer can be accomplished by alternately exposing the monolayer to ethanol or to a helium stream. Analysis of the time-dependent X-ray measurements has provided a detailed description of the surface crystallization process.

Experimental Section

Ethanol and 1-nonanethiol were obtained from Aldrich and used without further purification. Au(111) single crystals were purchased from MaTeck (Germany), as 10 mm diameter disks. They were first anodically electropolished and then annealed in a hydrogen flame. The electropolishing/annealing cycle was repeated until a sharp diffraction pattern, characteristic of a clean flat gold surface, was obtained. The Au(111) single crystals were then mounted in a thin-layer flow cell with a polyethylene window. The gold surface was flushed with a deoxygenated solution of 1-nonanethiol (10 mM) in ethanol for 2 h. Electrochemical desorption experiments confirmed that a fully grown thiol monolayer is produced under these conditions.[18] After completion of the adsorption stage, samples were washed with pure ethanol and kept under a helium stream during the measurements. Diffraction experiments were performed at the W1.1 beamline of the HASYLAB synchrotron at DESY with a wavelength of 0.1397 nm. The angle of incidence of the X-ray beam was fixed at 2°. Two sets of data were collected to characterize the 1-nonanethiol SAM structure: 1) in-plane data having an L index (i.e., the ordinal Miller index of the surface-normal momentum transfer in reciprocal lattice units, r.l.u.) close to 1, which was shown in preliminary experiments to be very sensitive to the arrangement of the carbon atoms in the monolayer. L is related to the perpendicular momentum transfer ($Q_\perp$ with $Q_\perp = L \times c^*$, where L is the ordinal Miller index of the perpendicular momentum transfer and $c^* = 2\pi/c = 0.8891\ \text{Å}^{-1}$ is the inverse lattice parameter of the Au(111) substrate); 2) out-of-plane data corresponding to different rods. The sample holder was in thermal contact with an electrical resistance to control its temperature at $30 \pm 2\,^\circ\text{C}$.

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