Observation of Highly Ordered 3 × 4 Phase of Ethanethiol Self-Assembled Monolayer on Au(111)

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A novel observation of a highly ordered self-assembled monolayer of ethanethiol (a very short-chain alkanethiol) on Au(111) is reported. A good structural perfection of the monolayer allowed a surprisingly high-resolution STM imaging clearly uncovering the unique 3 × 4 unit cell and the detailed atomic arrangement therein. Along with the infrared reflection absorption spectrum of the monolayer the results indicate that the interchain interactions involving such short alkyl chains can still play a dominant role in controlling the overall monolayer structure.

The self-assembled monolayers (SAMs) of alkanethiols [$CH_3(CH_2)_{n-1}SH$; hearafter referred to as C_n] on Au(111), as simple and well-structured model systems of organically modified solid surfaces, have attracted considerable attention over the years.[1,2] The structure and the extent of order in C_n SAMs on gold depend on two main factors, i.e., the interaction between the gold surface and the thiol head groups, and the dispersion forces between the alkyl chains. The latter forces in turn depends on the alkyl chain length, and it has been suggested that below ~C_8 the interchain interaction becomes so weak as to cause substantial loss of order and packing density.[3–5] The so-called $p\times\sqrt{3}$ pin stripe structure is what was most frequently observed in STM studies of such short-chain (e.g., C_4) SAMs.[6–9] The weak interchain interactions and the resulting loss of order have also been addressed in connection to the frequent difficulty to achieve good resolution for STM imaging of short-chain SAMs.[7,8]

In marked contrast to these earlier observations, we have recently found that even in the shortest chain-length regime of C_2–C_4 the corresponding SAMs deposited on high-quality Au(111), sputter-grown on mica,[10,11] may invariably develop so highly ordered monolayer structures that atomic or molecular resolution can easily be achieved with in-air STM imaging. The good quality of our Au(111) film as the substrate for alkanethiol SAMs was confirmed earlier by a detailed study of the formation of octanethiol (C_8) SAMs from a dilute ethanolic solution (e.g., 0.01 mM).[12] In this paper we focus on the far shorter-chain C_2 SAM on Au(111) and illuminate its unique 3 × 4 structure observed for the first time in our recent STM work.

Ethanethiol was obtained from Wako Pure Chemical Industry, Ltd., and used without further purification typically in the form of 0.1 mM solution in ethanol solvent. There the Au(111) films were bathed for desired periods at room temperature, rinsed by running ethanol, and then blown dry by nitrogen. The kinetics of C_2 chemisorption on Au(111) was studied by XPS analysis with an ESCA-750 spectrometer (Shimadzu Corp.), with the S_{2p}/Au_{4f} intensity ratio as a convenient measure of the overall thiol coverage. We thus found that the saturation coverage of C_2 occurred well within a minute at the thiol concentration in solution 0.1 mM or above.

The in-air STM imaging was done by using a Nanoscope I microscope (Digital Instruments Inc.) with a mechanically cut Pt/Ir tip under the constant current mode. The sample bias and the tunneling current were typically –400 mV and 0.1 nA, respectively, corresponding to the junction impedance of 4 GΩ. Figure 1 shows a typical series of STM images taken in the saturation coverage regime, along with a model lattice of circles that fully accounts for the observed atomic arrangement. The ~150 nm-wide image (Figure 1A) demonstrates a remarkably low density of vacancy islands (pit-like features) as compared to what have commonly been observed for longer-chain SAMs on Au(111).[2] This observation, though beyond the scope of this paper, may suggest that the alkyl chain length likewise plays some critical role in the formation of the vacancy islands. The higher-resolution images (Figures 1B and 1C) not only uncover the unique packing arrangement of the C_2 SAM but also testify to a high degree of its structural perfection. Major defects seen in these images are the rotational or twin-like boundaries that are indicated by the parallel dotted-line arrows drawn in Figure 1B.

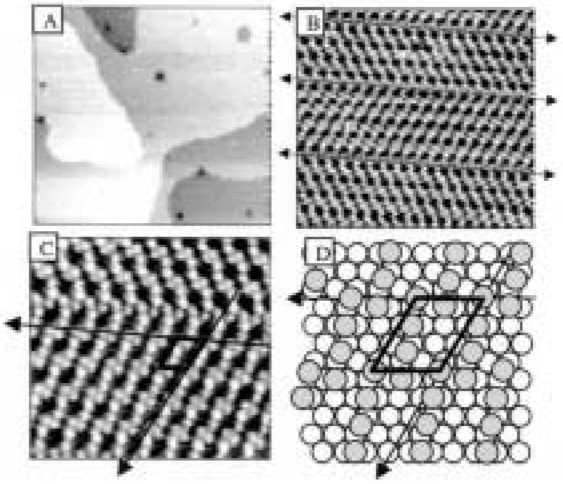

Figure 1. A series of STM images taken with varied scan windows (A: 153 ×142 nm^2 ; B: 15.3 × 14.2 nm^2; C: 8.2 × 7.6 nm^2) for C_2 SAM deposited on Au(111), and its structural model (D) with white and gray circles representing Au and S atoms, respectively. The dotted-line arrows drawn across image B show twin-like boundaries characteristic of C_2 SAM. The oblique 3 × 4 unit cell superimposed on image C and on the model lattice has its two axes lying in the nearest neighbor directions of the Au(111) lattice.

Figure 1C, where all the individual thiols (it is most probably the S atoms that make up the high-resolution image here) are distinctly resolved, is fully compatible with the model given in Figure 1D. The oblique unit cell, superimposed on this highest-resolution image and on the model lattice, has dimensions of a = 8.7 Å and b = 11.6 Å (3 and 4 times the Au lattice constant), thus representing a 3 × 4 superlattice structure. At each lattice point there are four S atoms arranged in a row with ~3.8 Å regular spacing, which can be successfully reproduced in the model only by arranging all the S atoms on the bridge sites (not on the hollow sites) of the Au(111) lattice. Note in addition that the occupation of four thiols per unit cell of the above dimensions (87 Å^2) gives the overall packing density identical with that (4.6×10^{14} cm^{-2}) of the familiar $\sqrt{3} \times \sqrt{3}$ structure.

It should be noted that the arrangement of S atoms suggested in Figure 1 has a considerably low symmetry and never ensures identical nearest-neighbor environments for every S atom. This is difficult to rationalize just on the basis of the substrate–thiol interaction,[13] so that the interchain interactions involving the C_2 alkyl chains, however weak they are, must have something to do with this unique packing arrangement. The infrared reflection absorption spectroscopy (IR-RAS) analysis of the C_2 SAM provides most useful information in this regard. A typical spectrum for the C–H stretch region taken by using a FTS-30 FTIR spectrometer (Bio-Rad Laboratories Inc.) with a *p*-polarized light is shown in Figure 2. The predominant feature is a sharp peak at 2917 cm^{-1}, due to the antisymmetric C–H stretch of the methylene group [ν_a (CH_2)]. It is remarkable that the C_2 SAM has only one CH_2 group per molecule, and yet such a distinguishable $\nu_a(CH_2)$ mode shows up in the IR-RAS spectrum at the position identical to that (2918 cm^{-1}) for solid crystalline phase of long-chain alkanethiols (n > 15).[3] For this to be realized under the IR-RAS selection rule the C_2 alkyl chains need to unanimously adopt the conformation as shown in the inset of Figure 2, with the plane defined by the C–C–S bonds nearly parallel to the substrate.[14]

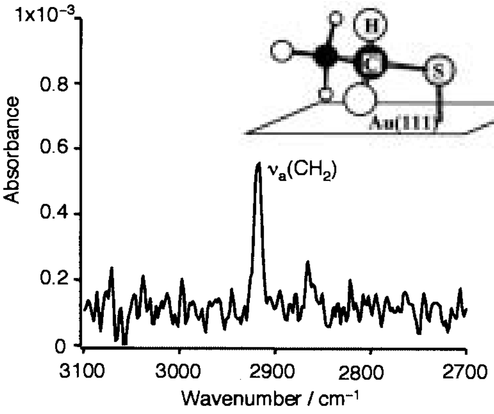

Figure 2. IR-RAS spectrum in the C—H stretch region taken for C_2 SAM on Au(111). The inset shows molecular conformation of C_2 framework compatible with the spectrum predominated by a sharp peak due to the antisymmetric stretch of CH_2 group.

On the basis of the above molecular geometry, a reasonable (but yet hypothetical) picture of the entire packing arrangement can in fact be drawn as shown in Figure 3 as a top-view diagram. The point is that in this manner the interactions between the C_2 alkyl chains would be maximized and that this alkyl-chain packing constraint explains why the thiol head groups adopt the so unique 3×4 structure as shown in Figure 1.

In summary, we have observed for the first time a novel 3×4 phase of highly ordered C_2 SAM on Au(111), providing the opportunity of an extremely high resolution STM imaging in air. Despite the very short alkyl chains of the C_2 SAM, our observation indicates that the interchain interactions still play a dominant role to determine the molecular packing arrangement.

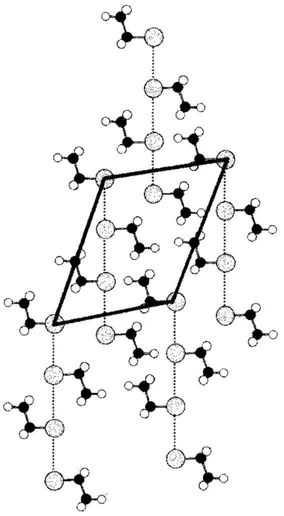

Figure 3. A top-view model of molecular packing of C_2 SAM on Au(111) based on the STM image and IR-RAS spectrum. Large gray circles represent S atoms arranged according to Figure 2, and small black and white circles show C and H atoms of C_2 alkyl chains, respectively.

A detailed analysis and comparison of the SAM structures in the C_2–C_4 range will further add to the knowledge of the interchain interactions involving such short alkyl chains.

References and Notes

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9 Similar stripe structure have also been observed in low-coverage SAMs of longer alkanethiols, and they could form as an intermediate phase before evolution of the dense $\sqrt{3} \times \sqrt{3}$ phase. See R. Yamada and K. Uosaki, *Langmuir*, **14**, 855 (1998) and references therein.

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13 Though only at considerably low (110 K) temperature, Kondoh and Nozoye found a similar 3×4 unit cell for a methylthiolate monolayer on Au(111), and suggested a dominant role of Au–S interactions therein (H. Kondoh and H. Nozoye, *J. Phys. Chem. B.*, **103**, 2585. (1999)). However, neither this interpretation nor the proposed clustering of sulfur atoms (into tetramers at each corner of the unit cell) is comparable to the points made in our present paper.

14 This geometry may cause some interaction between the CH bonds of the methylene group and the metal surface, thereby affecting the frequency of the CH stretching vibration more or less. The measured frequency (2917 cm^{-1}), however, is still well within the range that can definitely be assigned to the normal $\nu_a(CH_2)$ mode. A strong interaction with metal in the case of flat-on *n*-alkanes causing a serious shift of this peak to 2908 cm^{-1} is discussed in: M. Yamamoto, Y. Sakurai, Y. Hosoi, H. Ishii, K. Kajikawa, Y. Ouchi, and K. Seki, *J. Phys. Chem. B.*, **104**, 7370 (2000).