A New Superlattice of Cyclohexanethiol Self-assembled Monolayers on Au(111) Formed at a Low Solution Temperature

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High-resolution scanning tunneling microscopy (STM) imaging revealed that cyclohexanethiols (CHTs) on Au(111) form high-density self-assembled monolayers (SAMs) with a $(5 \times 2\sqrt{3})R35^\circ$ superlattice at a low solution temperature of −20 °C. This packing structure is comparable to a $(5 \times 2\sqrt{10})R48^\circ$ superlattice formed at room temperature. From this result, it was found that the two-dimensional structure of CHT SAMs on Au(111) was strongly influenced by the solution temperature, unlike alkanethiol SAMs.

Alkanethiol self-assembled monolayers (SAMs) on gold have been extensively studied as a typical model system for understanding molecular self-assembly phenomena and as a good molecular template for technological applications in biosensing, nanopatterning, corrosion inhibition, and molecular electronic devices.[1–6] It has been generally considered that the two-dimensional (2D) structures of SAMs are determined by both the chemical interactions between the sulfur head groups and gold and lateral interactions between the tail groups. Quite recently, new types of SAMs by formed from thiols containing spherical hydrocarbon cage tail groups were fabricated and characterized, and molecular-scale STM observations showed the unique 2D molecular arrangements due to the bulky tail groups.[7–9] In addition, the adsorption of cyclohexanethiols (CHTs) with a flexible 6-membered aliphatic ring on the Au(111) results in the formation of well-ordered SAMs.[10] The observed oblique unit cell containing two different molecular features can be described as a $(5 \times 2\sqrt{10})R48^\circ$ superlattice. It was expected that this unique structure originated from two geometrical isomers, the equatorial and axial chair isomers, in CHT SAMs. On the other hand, the development of methodology to control the surface structure of SAMs is one of the very important fundamental and practical issues for the design of devices and sensors. It has been found that the properties of the solvent are among the important factors for controlling surface structures of the SAMs.[11,12] Yamada et al. also found that solution temperature in the formation of alkanethiol SAMs on Au(111) significantly affects the size of ordered domains and the number and size of vacancy islands.[13]

In this study, we examined the molecular-scale structures of CHT SAMs on Au(111) formed at a low solution temperature of −20 °C by STM, and it was found that the adsorption behaviors of CHT molecules with a flexible ring during SAM formation were markedly different from those of alkanethiols. In addition, we report a new phase of CHT SAMs, which is assigned as a $(5 \times 2\sqrt{3})R35^\circ$ superlattice.

Cyclohexanethiol ($C_6H_{11}SH$, CHT) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification. The Au(111) substrates on mica were prepared by vacuum deposition as described previously.[3] To investigate the structures of CHT SAMs formed at low temperature, CHT SAMs were formed by immersing the Au(111) substrate into a 1 mM ethanol solution of CHT at −20 °C (in a freezer) for 1 h. After the SAM samples were removed from the solutions, they were rinsed with pure ethanol to remove physisorbed molecules from the gold surface. STM measurements were carried out with a NanoScope E (Veeco, Santa Barbara, CA) and a commercially available Pt/Ir tip. All STM images were obtained in air using constant current mode at room temperature. The bias voltage and tunneling current were typically 500 mV and 300 pA, respectively.

STM images in Figure 1 show the formation of well-ordered CHT SAMs on Au(111) from a 1 mM ethanol solution at −20 °C. We found that structural behaviors of CHTs on Au(111) are markedly different from those of decanethiols (DTs) formed at a temperature of −20 °C.[13] Although decanethiol SAMs formed at −20 °C were composed of very small nucleation-like ordered domains with a size of a few nanometers and many small uncountable VIs, CHT SAMs have relatively larger domains ranging from 30 to 120 nm and a small number of vacancy islands (VIs). Figure 1a shows one-directional-ordered domains (A) and disordered phases (B). Interestingly, most vacancy islands were connected by disordered phases. This suggested that the disordered phases were formed as a result of a structural collapse of the 2D-ordered phases derived from the lateral diffusion of Au atom occurring in the process of the Ostwald ripening of the VIs.[2] After the formation of local disordered phases, it seemed that it was difficult for the CHT molecules to form ordered phases because of the high flexibility of the molecular backbone of CHT. From this study, we determined that although the 2D-ordered structures of DT SAMs were not influenced by the Ostwald ripening process of VIs, those of CHT SAMs were significantly influenced by such processes.

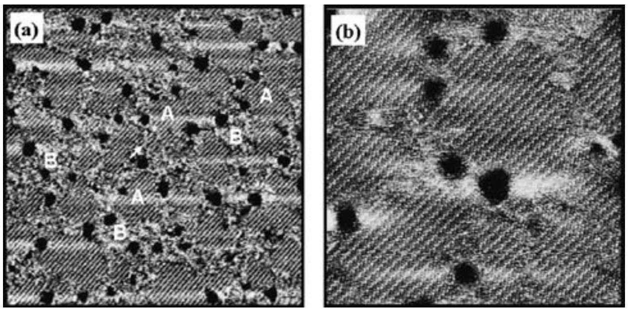

Figure 1. STM images showing well-ordered phases of CHT SAMs on Au(111) formed at a solution temperature of −20 °C. Scan sizes were (a) 120 nm × 120 nm and (b) 50 nm × 50 nm, respectively.

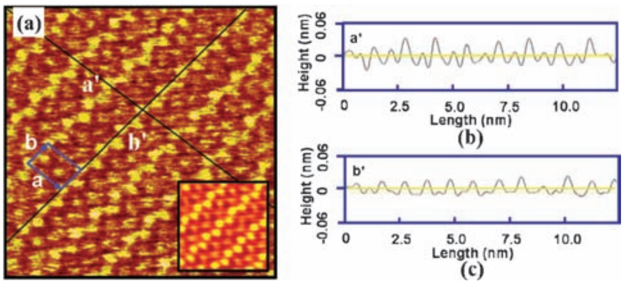

Figure 2. (A) Molecularly resolved STM image of CHT SAMs on Au(111). Scan size was 5 nm × 5 nm. The STM image reveals the zigzag bright and dark rows. Height profiles along lines a′ and b′ on the image show the periodicities of the adsorbed molecules in packing arrangements of CHT SAMs. The inset is a 2D filtered STM image (5 nm × 5 nm) that shows a high-degree of structural order.

This result can be ascribed to both the weak van der Waals interactions between cyclic rings and the conformational dynamics of CHT rings. In contrast to the poor structural ordering of DT SAMs formed at −20 °C, CHT SAMs have high structural ordering with large ordered domains, as shown in Figure 1b. Such a remarkable difference in structural ordering between CHT and DT SAMs can be attributed to a difference in the diffusion rate of molecules at the initial SAM growth stage. It was reported that the diffusion rate of alkanethiols with short alkyl chains on a gold surface is much faster than that of alkanethiols with longer alkyl chains, which mainly results from weaker van der Waals interactions between the shorter alkyl chains.[14] Therefore, we assume that the diffusion rate of CHT molecules on Au(111) is faster than that of alkanethiols. As a result, CHT molecules can form 2D well-ordered SAMs, even at a solution temperature of −20 °C.

The molecularly resolved STM image in Figure 2 clearly shows a new molecular packing arrangement of well-ordered CHT SAMs on Au(111) formed at −20 °C. In particular, a 2D filtered STM image inserted on the STM image shows a high degree of structural order in the CHT SAMs with the zigzag bright and dark molecular rows. The cross-sectional profiles in Figures 2b and 2c taken along lines a′ and b′, corresponding to the oblique unit cell in the Figure 2a, show the superperiodicities of the CHT molecules in the SAMs. The lattice constants of the oblique unit cell extracted from the high-resolution image are: $a = 14.42 \pm 0.1\,\text{Å} = 5a_\mathrm{h}$, $b = 10.01 \pm 0.1\,\text{Å} = 2\sqrt{3}a_\mathrm{h}$, $\delta = 35^\circ$ and $\gamma = 81^\circ$ (see Figure 3a). The zigzag molecular rows have a repeating unit of 5.83 and 6.15 Å intermolecular distances.

On the basis of the high-resolution STM images, we propose a schematic structural model (Figure 3a) and a space-fill drawing model (Figure 3b) for molecular packing arrangements of CHT SAMs on Au(111). The observed new structure can be assigned as a $(5 \times 2\sqrt{3})\mathrm{R}35^\circ$ superlattice, which is completely different from the $(5 \times 2\sqrt{10})\mathrm{R}48^\circ$ superlattice formed at room temperature. From the model of Figure 3a, it was found that all sulfur atoms in the CHT SAMs preferentially occupied bridge sites of the Au(111) lattice. The average areal density for the CHT SAMs with a unit cell of a $(5 \times 2\sqrt{3})\mathrm{R}35^\circ$ superlattice was calculated to be 36.09 Å^2/molecule, whereas that for CHT SAMs with the unit cell of $(5 \times 2\sqrt{10})\mathrm{R}48^\circ$ superlattice was calculated to be 87.8 Å^2/molecule. From this result, we elucidated that the molecular density of the CHT SAMs formed at −20 °C was 2.4 times higher than that of CHT SAMs formed at room temperature. We assumed that the formation of such high-density SAMs at low temperature is due to a decrease in the conformational dynamics of flexible ring in CHT molecules adsorbed on Au(111) surface. The unit cell of the CHT SAMs contains two different molecular spots in imaging contrast. As suggested in the previous study,[10,15] the bright molecular spots in STM image of Figure 2a correspond to CHT molecules with the equatorial conformers and the dark ones correspond to these with the axial conformer because the equatorial conformer is more protruded than the axial conformers. As a result, the equatorial conformer had brighter imaging contrast compared to the axial conformer.

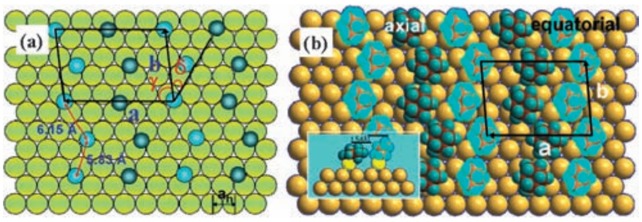

Figure 3. (a) Structural model and (b) space-fill drawing model of the proposed structure for CHT SAMs on Au(111). The lattice constants extracted from the STM image are: $a = 14.42\,\text{Å} = 5a_\mathrm{h}$, $b = 10.01\,\text{Å} = 2\sqrt{3}a_\mathrm{h}$, $\delta = 35^\circ$ and $\gamma = 81^\circ$ where $a_\mathrm{h} = 2.88\,\text{Å}$ and represents the atomic distance of the Au(111) lattice. The inset in Figure 3b shows a side view of axial and equatorial isomers in CHT SAMs.

In summary, we have observed for the first time a $(5 \times 2\sqrt{3})\mathrm{R}35^\circ$ superlattice of the high-density ordered CHT SAMs on Au(111) formed at −20 °C. The new structure is comparable to the $(5 \times 2\sqrt{10})\mathrm{R}48^\circ$ superlattice of CHT SAMs formed at room temperature. Based on this result, we have clearly determined that the solution temperature plays a key role in determining the 2D packing arrangements of CHT SAMs on Au(111).

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