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Formation of Ordered Self-Assembled Monolayers by Adsorption of Octylthiocyanates on Au(111)

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Self-assembled monolayers (SAMs) were formed by the spontaneous adsorption of octylthiocyanate (OTC) on Au(111) using both solution and ambient-pressure vapor deposition methods at room temperature and 50 °C. The surface structures and adsorption characteristics of the OTC SAMs on Au(111) were characterized by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The STM observation showed that OTC SAMs formed in solution at room temperature have unique surface structures including the formation of ordered and disordered domains, vacancy islands, and structural defects. Moreover, we revealed for the first time that the adsorption of OTC on Au(111) in solution at 50 °C led to the formation of SAMs containing small ordered domains, whereas the SAMs formed by vapor deposition at 50 °C had long-range ordered domains, which can be described as ($\sqrt{3} \times 2\sqrt{19}$)R5° structures. XPS measurements of the peaks in the S 2p and N 1s regions for the OTC SAMs showed that vapor deposition is the more effective method as compared to solution deposition for obtaining high-quality SAMs by adsorption of OTC on gold. The results obtained will be very useful in understanding the SAM formation of organic thiocyanates on gold surfaces.

Introduction

Self-assembled monolayers (SAMs) formed by organic thiols on gold have been extensively studied due to a fundamental interest in their surface science and their many potential applications in corrosion inhibition, biosensors, nanopatterning, and molecular electronics.^{1–18} Alkanethiols are known to be the best precursors for obtaining well-ordered SAMs with a high structural reproducibility and chemical stability. The surface properties for the fabrication of more complicated molecular

systems can be easily tuned by introducing a variety of organic functional groups at the termini of alkanethiols.^{19–32} As a result, alkanethiol SAMs on metal surfaces have been frequently used for various practical applications. However, one of the drawbacks encountered during the formation of organosulfur SAMs is that the thiol group can be oxidized to disulfides and/or other oxidized compounds during SAM formation in solution.^{33–35} To overcome this problem, SAMs prepared using organic thiosulfates having a high chemical oxidation stability were fabricated and characterized by various surface sensitive techniques. It has been revealed that, even though organic thiosulfate on metal surfaces forms chemisorbed SAMs as in the case of thiols, the adsorption kinetics and structural properties of the SAMs are largely different

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from those of the corresponding thiols.^{35,36} In particular, it is expected that thiosulfate SAMs have a relatively lower surface coverage and many defects as compared to thiol SAMs. Acetyl-protected organic thiols have become good precursors against oxidation and have demonstrated the ability to form SAMs on gold surfaces via an acid- or base-catalyzed deprotection process.^{37,38} However, the addition of extraneous reagents for deprotection and the labile deprotected group affect SAM formation, resulting in unexpected SAM properties.

Recently, as an alternative precursor, Ciszek et al. demonstrated that aromatic and alkylthiocyanates form chemisorbed SAMs via Au–S bond formation, as in the case of SAMs prepared by thiols.^{39,40} They suggested that the cyano group could be removed from the surface in the form of $[\text{Au}(\text{CN})_2]^-$ groups through “a surface-mediated reduction of the thiocyanate”. These results were supported by X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), ellipsometry, and contact angle (CA) measurements. The film thickness and CA values showed a small difference between two SAMs formed by organic thiocyanates and thiols having an identical molecular backbone, suggesting structural differences of the SAMs. However, thus far, there has been no report describing molecular-scale features of organic thiocyanate SAMs on Au(111).

The main purpose of this work was to provide molecular-scale information about the surface structure of organic thiocyanate SAMs. It is very interesting and meaningful to compare the structure of thiocyanate SAMs with that of thiol SAMs on Au(111), which will give us a better understanding of the self-assembly phenomena of organic molecules depending on the sulfur headgroup attached to different chemical environment groups, R–S–H or R–S–CN. In this work, the structural and binding characteristics of octylthiocyanate (OTC) SAMs on Au(111) prepared by solution and vapor deposition methods were examined by scanning tunneling microscopy (STM) and XPS. We report the first STM results showing molecular-scale structures of ordered OTC SAMs and provide meaningful information about the selection of a deposition method for the fabrication of organic thiocyanate SAMs with a high degree of structural order.

Experimental Procedures

OTC was synthesized according to a method described previously¹ and was confirmed by ^1H -NMR. The Au(111) substrates were prepared by the vacuum deposition of gold onto freshly cleaved mica sheets prebaked at 300 °C with a base pressure of $\sim 10^{-7}$ to 10^{-8} Torr. After deposition, the substrates were annealed at 330 °C in the same vacuum chamber for 2 h. STM imaging showed that the Au(111) substrates contain a herringbone surface reconstruction structure on atomically flat large gold terraces, implying a clean Au(111) surface.

OTC SAMs were prepared by solution and ambient-pressure vapor deposition to understand OTC SAM formation in terms of the deposition method used. To compare SAM formation of octanethiol (OT) and OTC containing the same alkyl chain length, both SAMs were prepared by immersing the gold substrates in a 1 mM ethanol solution at room temperature or 50 °C for 1 day (solution deposition). OTC SAMs were also prepared by ambient-pressure vapor deposition. The gold substrates were placed in a 3 mL V-vial containing 3 μL of OTC neat liquid, and then the V-vial was tightly sealed with Parafilm after capping. The vial was kept at 50 °C in a drying oven

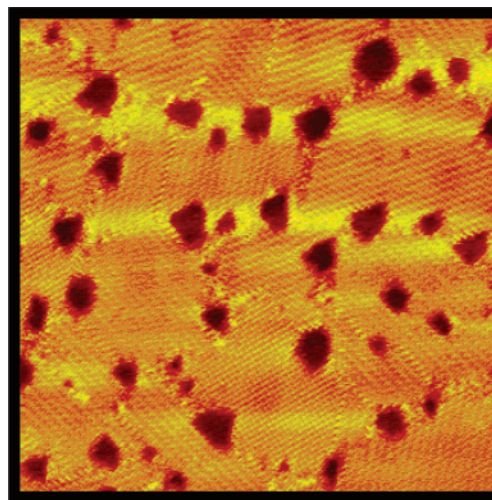


Figure 1. Typical STM image showing well-ordered domains of OT SAMs on Au(111) prepared by solution deposition at room temperature for 1 day (75 nm \times 75 nm).

for 24 h. After the SAM samples were taken from the vials, they were immediately rinsed with pure ethanol to remove weakly adsorbed molecules from the surface.

STM measurements were performed using a NanoScope E (Veeco) and a commercially available Pt/Ir tip (80:20). All STM images were obtained in the constant current mode in air at room temperature using a bias voltage (V_b) ranging from 300 to 500 mV and a tunneling current (I_t) ranging from 0.30 to 0.60 nA between the tip and the sample for the imaging conditions. All STM images were treated with a plane subtraction using the “flatten command” in the NanoScope software. We note that these imaging conditions do not affect SAM structures by the STM tip because we could not find the formation of any structural defects or structural transitions during STM imaging. The lattice constants of the ordered phase for OTC SAMs were obtained by using an average value of intermolecular distances extracted from different areas with the same structure. XPS measurements were performed with a Theta Probe (Thermo Fisher Scientific Inc.). The emitted electrons were collected at angles from 23 to 83° with a multichannel plate. The spectra were calibrated with the $\text{Au}4f_{7/2}$ peak at 84.0 eV. The energy positions of the observed peaks were determined using a curve-fitting analysis.

Results and Discussion

The STM image in Figure 1 shows the surface structure of OT SAMs on Au(111) formed after immersion of the Au(111) substrates in a 1 mM ethanol solution at room temperature for 24 h. The OT SAMs shown in Figure 1 have typical surface characteristics, such as well-ordered domains with a $c(4 \times 2)$ superlattice, domain boundaries, and vacancy islands (VIs, dark holes) that can be observed from SAMs of various alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$, generally, $n \geq 6$).^{3,4} On the basis of high-resolution STM observation for alkanethiol SAMs on Au(111), it was observed that the depth of VIs was 0.25 nm, consistent with the Au(111) monatomic step height, reflecting that the VIs are defects in the gold layer beneath the SAMs, which caused subsequent height differences in the SAM surface formed over gold.^{3,4,41,42}

The STM images in Figure 2 show the surface structure of OTC SAMs on Au(111) after immersion of the gold substrates in a 1 mM ethanol solution at room temperature for 1 day. As compared to the surface characteristics of the OT SAMs on Au(111) shown in Figure 1, the OTC SAMs showed markedly different surface characteristics, even though both SAMs were

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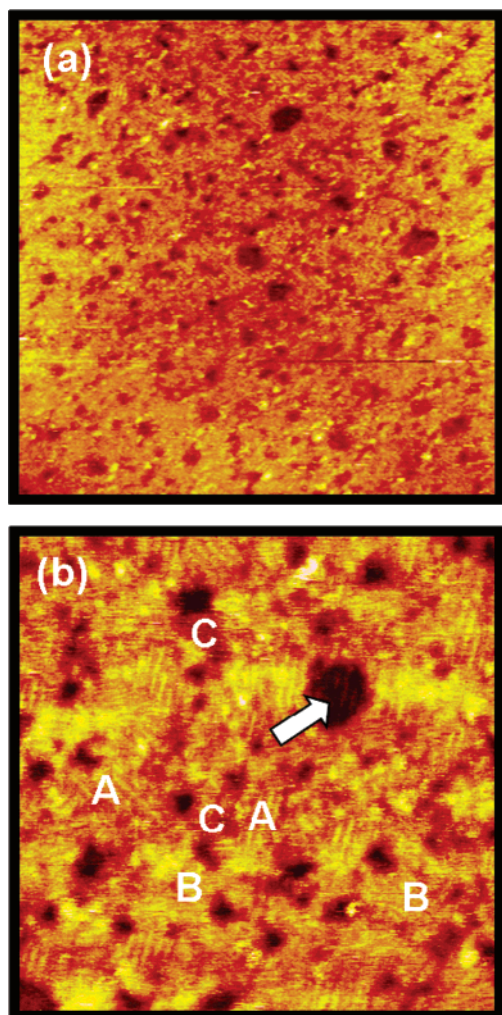


Figure 2. STM images showing partial ordered domains, disordered phases, and small bright spots of OTC SAMs on Au(111) prepared by solution deposition at room temperature for 1 day. Scan sizes were (a) 150 nm \times 150 nm and (b) 65 nm \times 65 nm.

prepared using the same experimental conditions. The STM image with a large scan size (150 nm \times 150 nm) in Figure 2a shows a unique surface structure of the OTC SAMs. A magnified STM image (65 nm \times 65 nm) shown in Figure 2b clearly reveals that the intrinsic surface structures of the OTC SAMs consist of small ordered domains (A), disordered phases (B), partially adsorbed phases (C), many small bright spots, and dark holes (VIs) with an irregular shape and size that have not been observed in conventional alkanethiol SAMs.^{3,4,41,42} It was found that the adsorption of OTC molecules on Au(111) at room temperature led to the formation of SAMs with small ordered domains (region A), which differ from OT SAMs with large well-ordered domains containing a hexagonal packed ($\sqrt{3} \times \sqrt{3}$)30° or $c(4 \times 2)$ superlattice.^{3,4} The STM image of region A in Figure 2b for OTC SAMs on Au(111) shows an ordered row structure. Structural details for the ordered domains of OTC SAMs will be discussed later (see Figure 5). The ordered rows were also observed inside the VIs, as indicated by the arrow in Figure 2. On the other hand, the disordered phases (B) were also observed in the OTC SAMs, suggesting that OTC would not form fully ordered SAMs over the entire gold surface. We hypothesize that the phase (C) with an intermediate brightness between the ordered phases and the VIs in STM imaging contains a few adsorbed molecules (very low surface coverage) because similar phases were observed around the domain boundaries and VIs after desorption of

molecules from the surface.⁴² On the other hand, the origin of the small bright spots in the OTC SAMs on the Au(111) surface is not clear at present. The depths of the dark holes were measured to be about 2.4–2.7 Å, which are nearly the same values as the monatomic step height of gold and can be assigned as vacancy islands (VIs) appearing in the formation process of chemisorbed SAMs.

Ciszeck et al. proposed that the dissociative adsorption of organic thiocyanate on gold gives rise to the adsorption of the cyano group and the organic thiolates via Au–S bond formation. Subsequently, the cyano group can be removed from the surface in the form of $[\text{Au}(\text{CN})_2]^-$ species during the self-assembly process, resulting in the formation of fully covered thiolate SAMs. This self-assembly mechanism of organic thiocyanates on gold was strongly supported by XPS measurements.^{39,40} In light of this suggested mechanism, we expect that the adsorption of cyano groups on gold during the initial stage of SAM growth could prevent a fast diffusion of thiolate molecules on gold surfaces, which is a strong driving force for the formation of two-dimensional (2-D), well-ordered SAMs with large domains, as described in an earlier paper.⁴³ As a result, OTC molecules can form partially ordered SAMs with small domains and molecular aggregations (small bright spots) that can appear during the self-assembly of molecules.⁴⁴ On the other hand, a portion of the small bright spots also may be related to the $\text{Au}(\text{CN})$ intermediate species adsorbed on the gold surface because we detected the peak in the N 1s region corresponding to the $\text{Au}(\text{CN})$ species at 399.5 eV (see Figure 7).⁴⁰ In addition, the adsorption of the cyano group during the initial SAM growth is probably a reason for the formation of VIs having irregular sizes and shapes (see Figure 2).

It was reported that the surface structures of alkanethiol SAMs on Au(111) were strongly influenced by the temperature of the thiol solution and that alkanethiol SAMs containing large ordered domains and a few VIs on gold can be obtained at a high solution temperature.⁴⁵ To examine the effect of solution temperature on SAM formation, we examined the surface structure of OTC SAMs on Au(111) formed after immersion of gold substrates in a 1 mM ethanol solution at 50 °C for 1 day (Figure 3). It was found that the structural ordering of OTC SAMs on Au(111) was greatly enhanced and that the number of VIs was remarkably reduced, as shown in Figure 3a. The disordered phases (B phase) observed in the OTC SAM samples prepared in the room temperature solution (Figure 2) were nearly eliminated from the OTC SAM samples prepared in the solution at 50 °C (Figure 3). From this result, we found that the surface structures of OTC SAMs on Au(111) were markedly influenced by the solution temperature. It also has been reported that an elevated solution temperature can enhance the structural order and domain sizes of alkanethiol SAMs.^{19,20} Figure 3b clearly shows the formation of ordered SAMs with three domain orientations (indicated by A on the image) and partially adsorbed phases (C). The domain sizes observed ranged from a few nanometers to 15 nm, which is still small as compared to other SAM systems, even if the OTC SAMs were formed at high solution temperatures.

Recently, Deering et al. found that alkanethiols on Au(111) would form 2-D ordered SAMs with large domains when using an ambient-pressure vapor deposition method at 70 °C.²⁷ The obtained SAM structures were quite similar to those acquired after annealing pre-covered alkanethiol SAMs at an elevated temperature^{3,4} or after solution deposition at 78 °C.⁴⁵ On the

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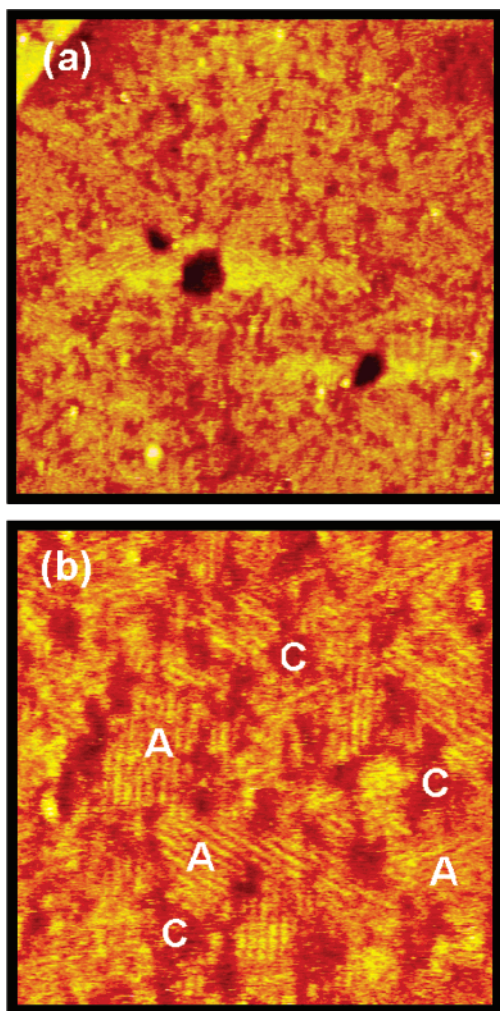


Figure 3. STM images showing three domain orientations of ordered phases (A) and partially adsorbed phases (C) of OTC SAMs on Au(111) prepared by solution deposition at 50 °C for 1 day. Scan sizes were (a) 150 nm \times 150 nm and (b) 65 nm \times 65 nm.

other hand, it has been demonstrated that the properties of the solvent used for SAM formation affect the size of the 2-D ordered domains and the number and distribution of VIs, suggesting that the interactions between solvent and molecule are one major factor for determining 2-D SAM structures.⁴⁶ The ambient-pressure vapor deposition method at a high temperature is another way to obtain OTC SAMs with a higher degree of structural order, by excluding the interactions between solvent and molecule (dipole–dipole interactions). The STM images in Figure 4 show the surface structure of the OTC SAMs on Au(111) prepared by ambient-pressure vapor deposition at 50 °C. Interestingly, the obtained surface structures of the OTC SAMs are markedly different from those of the OTC SAMs prepared by solution deposition at 50 °C. Large ordered domains with a single domain orientation (A) were usually observed, as shown in Figure 4a. The size of the partially adsorbed domains (C) also significantly increased, and the fraction of the area of this phase to the total surface area was measured to be approximately 25–30%. From these results, we assumed that the solvent molecules interacting with CN groups adsorbed on the Au(111) surface after the dissociative adsorption of C8S–CN hinder the surface diffusion of alkanethiolates during the initial SAM growth stage, resulting in the formation of small ordered domains in solution. On the other hand, the removal mechanism of the cyano groups in vapor

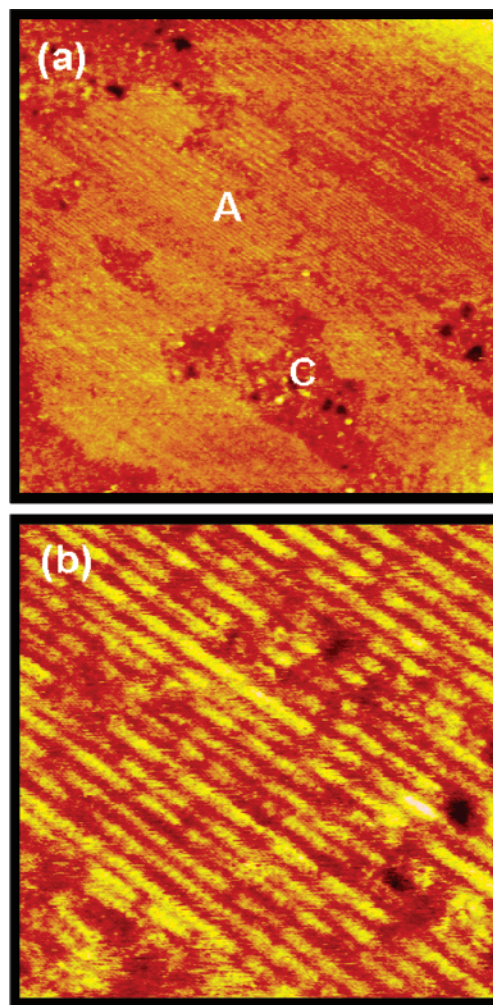


Figure 4. STM images showing long-range ordered domains of OTC SAMs on Au(111) prepared by ambient-pressure vapor deposition at 50 °C for 1 day. Scan sizes were (a) 150 nm \times 150 nm and (b) 30 nm \times 30 nm.

deposition may be different from that in solution deposition. Although the cyano groups can be easily removed from the surface as the form of $[\text{Au}(\text{CN})_2]^-$ in solution,^{39,40} this ionic molecule seems to be difficult to remove from the surface in vapor because it is formally a salt and not expected to have an appreciable vapor pressure. Therefore, the cyano groups during vapor deposition may be removed from the surface as the form of other chemical species instead of $[\text{Au}(\text{CN})_2]^-$. At the present stage, however, we do not understand as to why or how the cyano groups leave the surface during vapor deposition. Our STM and XPS data have a limit to reveal an exact self-assembly mechanism for the formation of OTC SAMs from vapor deposition. Hence, we need more extensive studies by means of other various surface sensitive techniques to elucidate it.

Figure 4b shows the magnified molecular row structure of the OTC SAMs from the A phase. In this work, we clearly demonstrated that the choice of deposition method is very important for controlling the 2-D structure of the OTC SAMs, although the surface structures of alkanethiol SAMs are not very dependent on the deposition method.⁴⁷

The high-resolution STM image in Figure 5a shows the paired ordered rows of the OTC SAMs revealed by enlarging the image of Figure 4b. A 2-D filtered image inserted on the STM image

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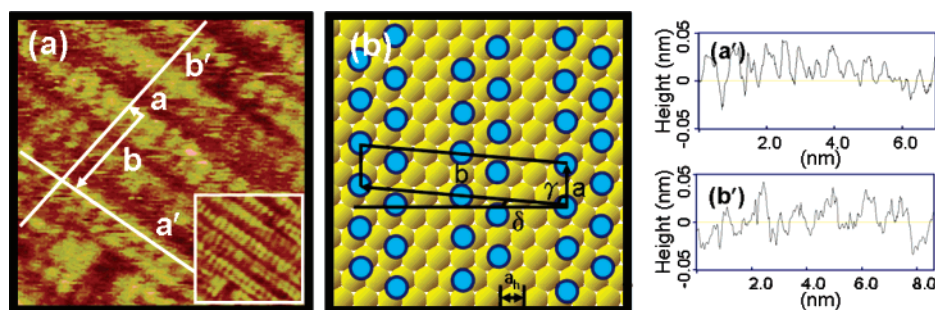


Figure 5. (a) High-resolution STM image showing the paired molecular rows of OTC SAMs on Au(111) formed by ambient-pressure vapor deposition at 50 °C for 1 day. The inset is a 2-D filtered image (7 nm \times 7 nm) that shows a high degree of structural order. (b) Schematic structural model of the proposed structure for OTC SAMs. The lattice constants extracted from the STM image are $a = 5.0 \text{ \AA} = \sqrt{3}a_h$, $b = 12.6 \text{ \AA} = 2\sqrt{19}a_h$, $\delta = 5^\circ$, and $\gamma = 85^\circ$, where $a_h = 2.89 \text{ \AA}$, corresponding to the atomic distance of the Au(111) lattice. (a' and b') Height profiles along the lines a' and b' on the image show the periodicities of the adsorbed molecules in the OTC SAMs.

clearly shows a high degree of structural order of the OTC SAMs with the paired molecular rows. Figures 5a' and b', taken along lines a' and b', corresponding to the oblique unit cell in Figure 5a, show the periodicities of the OTC molecules in the SAMs. The lattice constants extracted from the STM image are $a = 5.0 \text{ \AA} = \sqrt{3}a_h$, $b = 15.2 \text{ \AA} = 2\sqrt{19}a_h$, $\delta = 5^\circ$, and $\gamma = 85^\circ$, where $a_h = 2.89 \text{ \AA}$ corresponding to the atomic distance of the Au(111) lattice.

Although STM images can mainly give us information about 2-D structural features of SAMs rather than the location of binding sites of sulfur atoms, we proposed a schematic structural model (Figure 5b) based on the distances between molecules in 2-D molecular arrangements of OTC SAMs on Au(111). This model can be successfully reproduced only when all sulfur atoms in OTC SAMs occupy bridge sites of the Au(111) lattice. On the other hand, some differences in imaging would be expected for inequivalent molecules in the unit cell, which may be due to a difference in molecular orientation. However, such a reason for OTC SAMs is still very unclear at this moment and under consideration. The observed structure is assigned as a $(\sqrt{3} \times 2\sqrt{19})R5^\circ$ structure containing two molecules in the unit cell, which is comparable to the hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ or $c(4 \times 2)$ structure for OT SAMs. Although the previous XPS characterization suggested that alkylthiocyanates would generate thiolate SAMs with $(\sqrt{3} \times \sqrt{3})R30^\circ$ packing arrangements on gold,⁴⁰ the molecular-scale STM study revealed that OTC SAMs have a completely different molecular packing structure than OT SAMs. The average areal density for the OTC SAMs was calculated to be $30 \text{ \AA}^2/\text{molecule}$, which is different from that for the OT SAMs at $21.6 \text{ \AA}^2/\text{molecule}$. In addition, the schematic structural model in Figure 5b clearly shows that OTC SAMs have a missing-row structure. However, differently from the formation of closely packed SAMs by OT, we can not explain clearly why OTC molecules would prefer to form the missing-row phases. We only assume that the formation of low-density OTC SAMs may be due to the lower adsorption activity of sulfur atoms by the cyano groups with an electron withdrawing property and/or the hindering of 2-D molecular self-assembly by the cyano groups.

To understand the interactions between the sulfur atoms in OTC and the gold surface depending on the deposition methods, we examined XPS spectra in the S 2p region of the OTC SAMs on Au(111) prepared by solution deposition (Figure 6a) and ambient-vapor deposition (Figure 6b) at 50 °C for 1 day. The S 2p peaks generally appeared as a doublet corresponding to $2p_{3/2}$ and $2p_{1/2}$ peaks with an intensity ratio of 2:1 by spin-orbital splitting.^{48–50} Both OTC SAMs have three S $2p_{3/2}$ peaks at 161.4,

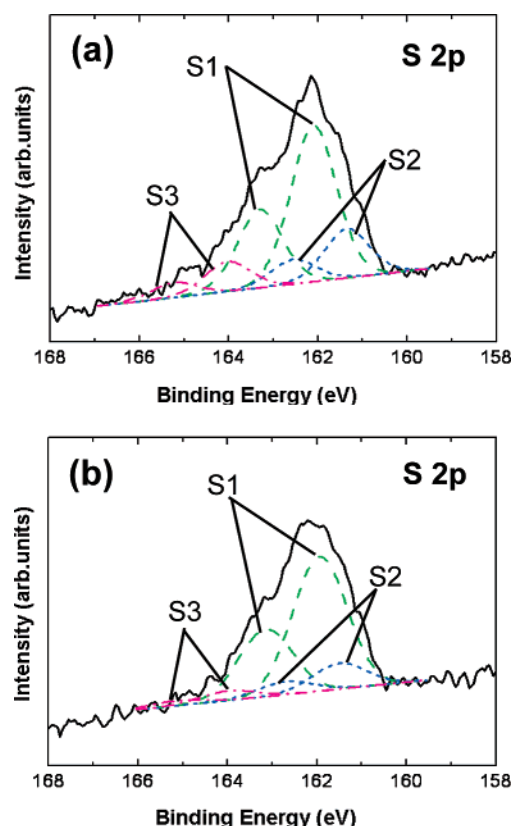


Figure 6. XPS spectra in the S 2p region of OTC SAMs on Au(111) prepared by (a) solution deposition and (b) ambient-pressure vapor deposition at 50 °C for 1 day.

162.0, and 164.0 eV, which are often observed in alkanethiol SAMs^{48–50} or other organosulfur SAMs.^{51,52} The S1 and S2 peaks at 162.0 and 161.4 eV can be assigned to the bound sulfurs, whereas the S3 peak can be assigned to the unbound sulfurs. The strong bound sulfur peak (S1) and unbound sulfur peak (S3) are usually observed from well-ordered alkanethiol SAMs. However, although the bound sulfur peak (S2) with a relatively weak intensity was often found in alkanethiol SAM systems with a low surface coverage or other complicated SAM systems with a lower structural order, the origin is still under discussion.^{50–53}

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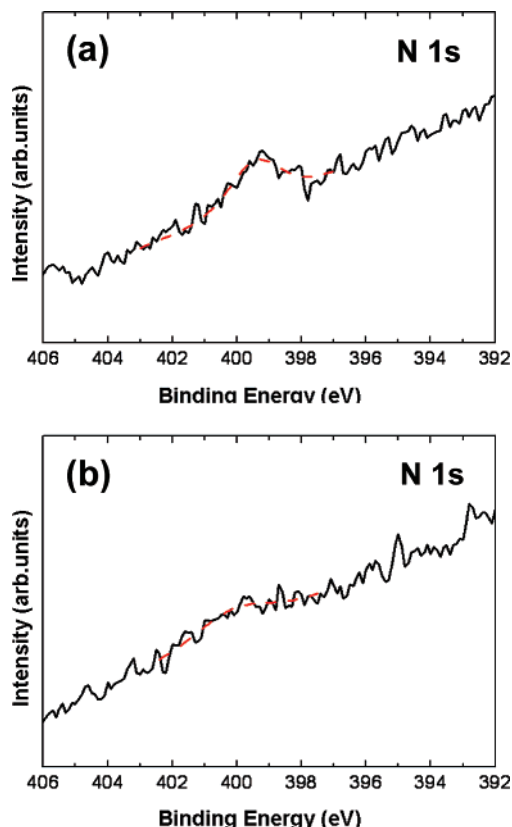


Figure 7. XPS spectra in the N 1s region of OTC SAMs on Au(111) prepared by (a) solution deposition and (b) ambient-pressure vapor deposition at 50 °C for 1 day.

From the XPS measurements, it is clear that OTC SAMs on Au(111) would form via the formation of S–Au chemical bonds after the cleavage of the C8S–CN bonds. We found that the relative peak intensities of the bound sulfurs (S1 and S2) against the unbound sulfurs (S3) for OTC SAM samples formed in solution and vapor phase deposition were measured to be 6.85 and 16.87, respectively. In addition, the relative peak intensities of the main bound sulfurs (S1) related to 2-D molecular ordering against the unbound sulfurs (S3) for these SAM samples were measured to be 5.22 and 14.16, respectively. The relative peak intensities of the bound sulfurs against the unbound sulfurs for OTC SAMs obtained by vapor deposition are markedly larger than those obtained by solution deposition. This result strongly implies that OTC SAMs with a higher degree of structural order can be obtained by vapor deposition, which is in good agreement with our STM results. On the other hand, the relative intensities of carbon C 1s against Au 4f [C 1s/Au 4f] and sulfur S 2p against Au 4f [S 2p/Au 4f] for OTC SAM samples formed in solution were estimated to be 0.059 and 0.0093, respectively. In the case of OTC SAMs formed in vapor, these values were estimated to be 0.049 and 0.0073, respectively. From this result, it is suggested that the adsorption amount of OTC molecules increased when the solution deposition method was used for SAM fabrication.

Figure 7 shows XPS spectra in the N 1s region of the OTC SAMs on Au(111) prepared by solution deposition (Figure 7a) and ambient-pressure vapor deposition (Figure 7b) at 50 °C for

1 day. The N 1s peak with a relatively strong intensity was observed at 399.5 eV from the OTC SAM sample formed in the solution phase, whereas the intensity of the N 1s peak observed from the OTC SAM sample formed in the vapor phase was minimal. We note here that the N 1s peaks are not noise because the experimental conditions for obtaining the N 1s peaks were the same as those obtaining the S 2p peaks (the number of scans is 120 times and each scan time is 50 ms). The bad S/N ratio of the N 1s peaks results from the lower concentration of the nitrogen as compared to the sulfur. It was suggested that the N 1s peak at 399.5 eV originated from the Au(CN) intermediate species adsorbed on the surface during the etching of the metal surface by the cyano group.^{39,40} From this result, we can expect that there still exists a small amount of intermediate species on the surface prepared by solution deposition. On the other hand, we could not find any adsorption peaks for the cyano group at 397.9 eV for either of the OTC SAMs. Therefore, we mention clearly that the cyano groups generated during the self-assembled process of OTC on Au(111) seem to be missing. By comparing the intensity of the N 1s peak obtained from both SAMs, we have concluded that, as compared to solution deposition, the vapor deposition method was more effective for obtaining high-quality SAMs by the adsorption of organic thiocyanates.

Conclusion

STM observation showed that SAMs formed by the spontaneous adsorption of OTC on Au(111) in solution at room temperature have unique surface structures consisting of small ordered domains, disordered phases, partially adsorbed phases, multiple small bright spots, and VIs with irregular shapes and sizes that were not observed in alkanethiol SAMs. Although it was suggested that organic thiocyanates would form similar thiolate SAMs, as in the case of organic thiols, molecular-scale STM studies revealed that the structures of the OTC SAMs were markedly different from those of the OT SAMs. The unique structures of the OTC SAMs can be ascribed to the adsorption of cyano groups generated by the bond cleavage of C8S–CN during the initial SAM growth. Moreover, we revealed that the adsorption of OTC on Au(111) in solution at 50 °C led to the formation of SAMs containing small ordered domains, whereas OTC SAMs formed in vapor at 50 °C had long-range ordered domains with paired molecular rows, which can be described as a $(\sqrt{3} \times 2\sqrt{19})R5^\circ$ structure. The XPS measurements revealed that OTC SAMs on Au(111) formed via the formation of S–Au chemical bonds after the cleavage of the C8S–CN bond. STM and XPS results clearly demonstrated that the vapor deposition method was more effective than solution deposition for obtaining a high-quality SAM by adsorption of OTC thiocyanates on gold.

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