

Formation and Structure of Self-Assembled Monolayers of Octylthioacetates on Au(111) in Catalytic Tetrabutylammonium Cyanide Solution

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The formation and structure of self-assembled monolayers (SAMs) by the adsorption of acetyl-protected octylthioacetate (OTA) on Au(111) in a catalytic tetrabutylammonium cyanide (TBACN) solution were examined by means of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). Molecular-scale STM imaging revealed that OTA molecules on Au(111) in a pure solvent form disordered SAMs, whereas they form well-ordered SAMs showing a $c(4 \times 2)$ structure in a catalytic TBACN solution. XPS and CV measurements also revealed that OTA SAMs on Au(111) formed in a TBACN solution have a stronger chemisorbed peak in the S 2p region at 162 eV and a higher blocking effect compared to OTA SAMs formed in a pure solvent. In this study, we clearly demonstrate that TBACN can be used as an effective deprotecting reagent for obtaining well-ordered SAMs of thioacetyl-protected molecules on gold.

Key Words: Octylthioacetate, Tetrabutylammonium cyanide, Self-assembled monolayers, Scanning tunneling microscopy, X-ray photoelectron spectroscopy

Introduction

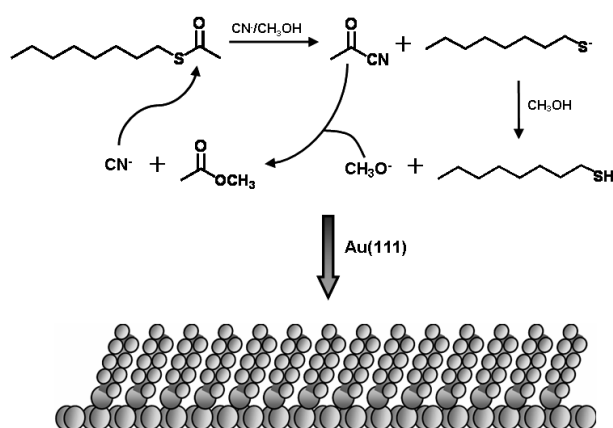
Organic self-assembled monolayers (SAMs) on metals have attracted considerable attention as a result of their interesting properties and technical applications in corrosion inhibition, chemical sensors, biosensors, nanopatterning, and molecular electronic devices.¹⁻⁸ Notably, alkanethiols on gold surfaces can form chemisorbed SAMs with a high degree of structural order, which can be described as a hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° structure or a $c(4 \times 2)$ superlattice.^{1,9-13} Due to their reliable structural order and high stability, they are often used as a molecular template for the construction of functional nanostructures. However, the thiol group is sensitive to oxidation and can form disulfides or other oxidized products in a solution containing a trace amount of oxygen.^{14,15} The undesirable oxidation of thiols prevents the formation of a homogeneous interface structure in SAMs. To overcome this problem, thioacetyl-protected organic molecules with a high chemical stability in air or solution have been used as alternative precursors for SAM formation.¹⁶⁻²⁴ However, these SAMs formed in a solution without a catalyst at room temperature were composed mainly of disordered or partially ordered phases with small domains.¹⁶⁻²¹ It was also observed that the surface structures and structural order were markedly influenced by experimental conditions such as incubation time,¹⁷ solution temperature,^{19,21} and solvent.²⁰ To enhance the structural order of these SAMs, a transformation from thioacetate to free thiol via the deprotection of thioacetate in solution is required. Thus far, strong acid or base conditions have frequently been used for deprotection. For instance, SAMs of thioacetyl-protected conjugated molecules on gold for electronic device applications were fabricated in strong acid- or base-catalyzed solutions.^{14,16,22,23} However, these harsh deprotection conditions result in the formation of SAMs with structural damage or unexpected structural transformation

of the organic target molecules.^{14,15,22} Therefore, it is essential to develop a effective and mild method for deprotection of thioacetyl-protected molecules in organic solvents. Recently, it was demonstrated that tetrabutylammonium cyanide salt (TBACN) can function as a good deprotection reagent against a variety of organic thioacetates with a relatively high deprotection yield.¹⁵ However, for practical use of this deprotection method for SAM fabrication, the formation and surface structure of SAMs prepared by thioacetyl-protected molecules should be understood from the molecular-scale point of view.

In this study, to elucidate the effect of TBACN on the SAM formation of thioacetyl-terminated molecules on Au(111), we examined SAM samples formed in a 1 mM methanol solution of octylthioacetate (OTA) containing a catalytic TBACN solution using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). The effect of TBACN was evaluated by comparing the surface structures of OTA SAMs and well-known octanethiol (OT) SAMs on Au(111).

Experimental Section

OTA was synthesized by refluxing potassium thioacetate with 1-bromooctane at room temperature (RT) for 3 h in ethanol. The product was purified by column chromatography using a mixture of hexane and ether (100:1 v/v) as an eluent, and confirmed by ¹H-NMR analysis. The Au(111) substrates were prepared by the thermal evaporation of gold onto freshly cleaved mica sheets pre-heated at 300 °C with a base pressure of 10⁻⁷-10⁻⁸ Torr. OTA SAMs were formed by dipping the Au(111) substrates in a 1 mM methanol solution of OTA or in a 1 mM OTA methanol solution containing a catalytic amount (0.5 mol equivalent per thioacetate) of TBACN at RT for 24 h. Note that prior to the immersion of the Au(111) substrates into



Scheme 1. Catalytic deprotection of thioacetyl groups and the formation of OTA SAMs on Au(111) in a catalytic TBACN solution.

the catalytic TBACN solution, the deprotection of the thioacetyl group of OTA molecules was performed in the catalytic TBACN solution at 50 °C for 3 h. Scheme 1 shows the deprotection pathway of thioacetyl groups¹⁵ and the formation of OTA SAMs on Au(111) in the TBACN solution. The deprotection of acetyl group in OTA can be easily accomplished by attacking cyanide ion (CN⁻) provided by TBACN, resulting in the formation of a free thiol. Then by dipping the Au(111) substrates in this solution, OTA SAMs on Au(111) can be formed *via* chemical reaction between the sulfur headgroup and gold surface, as shown in Scheme 1. The obtained SAM samples were rinsed thoroughly with pure methanol to remove weakly adsorbed molecules prior to surface analysis.

STM measurements were carried out with a NanoScope E (Veeco, Santa Barbara, CA) and a commercially available Pt/Ir (80:20) tip. All STM images were obtained in air using a constant current mode at room temperature. Image conditions were the bias voltages ranging from 250 to 650 mV and the tunneling currents ranging from 300 to 600 pA between the tip and the sample. 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 multi-channel plate. The spectra were calibrated with the Au 4f_{7/2} peak at 84.0 eV. The energy positions of the observed peaks were determined using a curve-fitting analysis. Electrochemical measurements were carried out with the BAS-100 employing a three electrode cell. The SAM covered-gold electrode was used as the working electrode, and a platinum wire and Ag/AgCl (KCl sat.) were used as the counter and reference electrodes, respectively. CV measurements were performed in a 1 mM K₄[Fe(CN)₆] solution containing 1 M KCl as the supporting electrolyte.

Results and Discussion

The STM images in Figure 1 show the typical surface structures of OTA SAMs on Au(111) formed after immersion of the Au(111) substrates in a pure solvent at RT for 24 h. Although several ordered domains with a very small domain size were observed, as indicated by the arrows in Figure 1a, OTA SAMs were mainly composed of disordered phases and

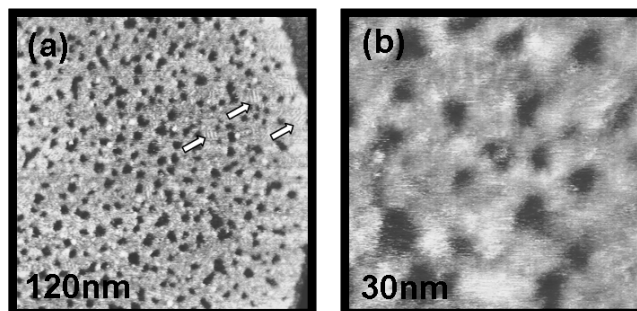


Figure 1. STM images of OTA SAMs on Au(111) formed after the immersion of the Au(111) substrates in a pure solvent at RT for 24 h. Scan sizes were (a) 120 nm × 120 nm and (b) 30 nm × 30 nm.

a number of vacancy islands (VIs). Contrary to the formation of well-ordered OT SAMs on Au(111),^{9,10} we found that thioacetyl-protected OTA molecules on Au(111) do not form well-ordered SAMs, as shown in Figure 1b. The remarkable difference in the structural order of SAMs formed by OTA and OT molecules with an identical alkyl chain length is due to the lower chemical activity of the sulfur headgroup attached to OTA compared to that attached to OT. This is because the electron-withdrawing acetyl group binds directly to the sulfur headgroup of OTA. In addition, the VIs in Figure 1b were not clearly visualized by STM imaging, suggesting that OTA SAMs did not form two-dimensional crystallized phases that have often been observed in close-packed ordered SAMs.¹² Based on this STM result, thioacetyl-terminated OTA molecules do not form well-ordered SAMs in a pure solvent. It has also been shown that thioacetyl-terminated tolane molecules do not form ordered SAMs in a pure solvent without any catalytic solution.¹⁷⁻²¹ Therefore, we suggest that deprotection of the thioacetyl group is needed to improve the structural order of OTA SAMs on Au(111).

STM images in Figure 2 show the surface structures of OTA SAMs on Au(111) after the immersion of the Au(111) substrates in a catalytic TBACN at RT for 24 h. The 120 nm × 120 nm STM image in Figure 2a presents the formation of large ordered phases with a domain size of approximately 100 nm, which is exceptionally larger than that of OT SAMs which ranges from 20 to 50 nm.^{12,13,24,25} Molecularly resolved STM images in Figures 2b and c clearly show that OTA SAMs have a hexagonal packing arrangement, which can be described as a well-known c(4 × 2) structure (see the unit cell in Figure 2c) which is usually observed in alkanethiol SAMs.^{12,13,24,25} By comparing the STM results of Figures 1 and 2, it is clear that thioacetyl-terminated OTA molecules on Au(111) can form SAMs with a high degree of structural order in TBACN solution, suggesting that TBACN is effective at *in situ* deprotection of thioacetyl groups to produce free thiols. We also found that the distribution and shape of VIs for OTA SAMs are quite different from alkanethiol SAMs with a relatively uniform distribution and size of VIs. This result implies that TBACN can also affect the formation of VIs. However, we do not fully understand the formation mechanism of such unusual VIs in a catalytic TBACN solution at present.

To determine the effect of catalytic TBACN on the adsorption conditions of OTA SAMs on Au(111), we examined the

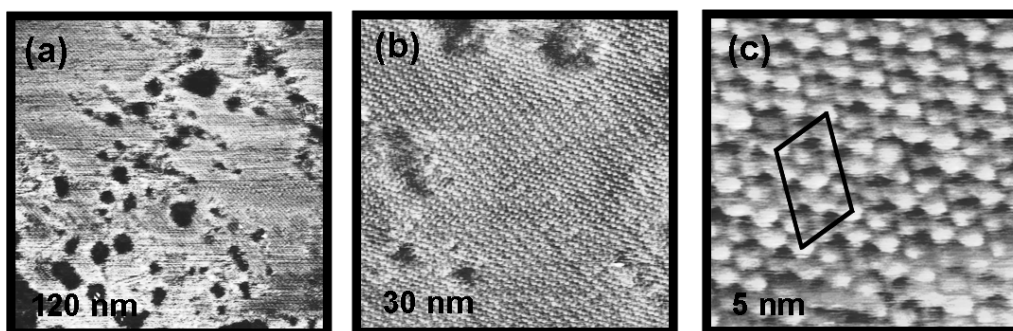


Figure 2. STM images of OTA SAMs on Au(111) formed after the immersion of the Au(111) substrates in a catalytic TBACN at RT for 24 h. Scan sizes were (a) 120 nm \times 120 nm, (b) 30 nm \times 30 nm, and (c) 5 nm \times 5 nm.

XPS spectra in the S 2p region of OTA SAMs on Au(111) formed in a pure solvent and a catalytic TBACN solution (Figure 3). Note that the S 2p spectra were observed as two components of S 2p_{3/2} and S 2p_{1/2} peaks with an intensity ratio of 2:1 resulting from spin-orbit splitting effects.^{26,27} Figure 3 shows a large difference in the S 2p XPS spectra from both OTA SAMs on Au(111). Three S 2p_{3/2} peaks from OTA SAMs formed in a pure solvent were observed at 161.3 (S2 peak), 162 (S1 peak), and 163.4 eV (S3 peak), as shown in Figure 3a, whereas two S 2p_{3/2} peaks from OTA SAMs formed in a catalytic TBACN solution were observed at 162 (S1 peak) and 163.4 eV (S3 peak), as shown in Figure 3b. The S1 and S2 peaks are assigned as bound sulfur (chemisorbed sulfur) and

the S3 peak is assigned to the unbound sulfur (physisorbed sulfur) based on observations of various organosulfur SAMs.^{7,8,17,26,27} The presence of intense bound sulfur peaks for OTA SAMs on Au(111) is good evidence for the formation of chemisorbed SAMs *via* the deprotection of thioacetyl groups in a pure solvent or a TBACN solution. In contrast, an S2 bound peak with a relatively strong intensity at 161.3 eV was observed in OTA SAMs prepared in a pure solvent, whereas this peak was not observed in OTA SAMs prepared in a catalytic TBACN solution. The S2 peak has been observed in SAM samples with low surface coverage or a disordered phase.²⁶ Consistent with the previous XPS results, we found that OTA SAMs with disordered phases, as shown in Figure 1, have the additional bound peak of S2 (Figure 3a).²⁶ This differently-bound sulfur may have resulted from a change in the adsorption geometry of molecules. Moreover, the XPS peak features of OTA SAMs formed in a catalytic TBACN solution are nearly the same as those observed in alkanethiol SAMs containing well-ordered domains, and our STM result agrees with this XPS finding. Our STM and XPS results clearly demonstrate that TBACN can be used as an effective catalytic reagent for the formation of well-ordered SAMs on gold surfaces by thioacetyl-protected molecules.

Figure 4 shows cyclic voltammograms of (a) a bare Au(111) electrode, (b) a Au(111) electrode modified by OTA

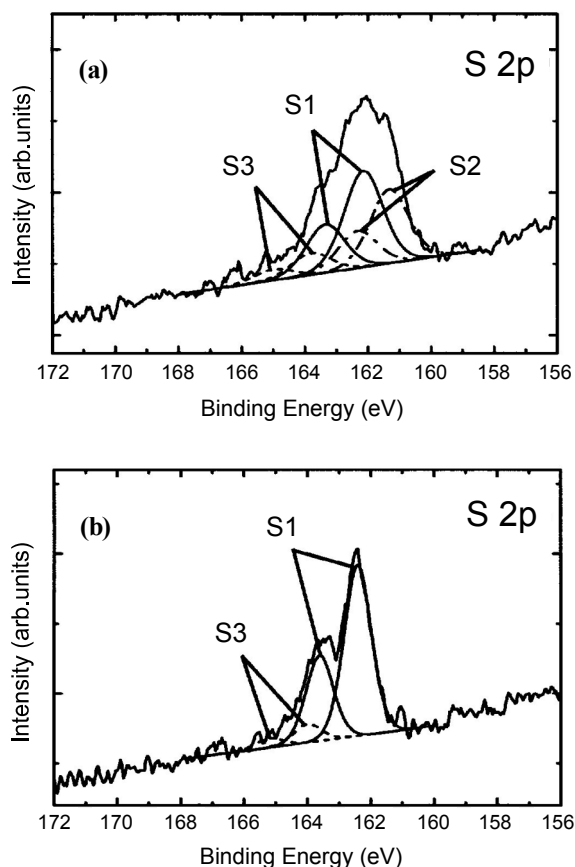


Figure 3. XPS spectra in the S 2p region of OTA SAMs on Au(111) formed in (a) a pure solvent and (b) a catalytic TBACN solution.

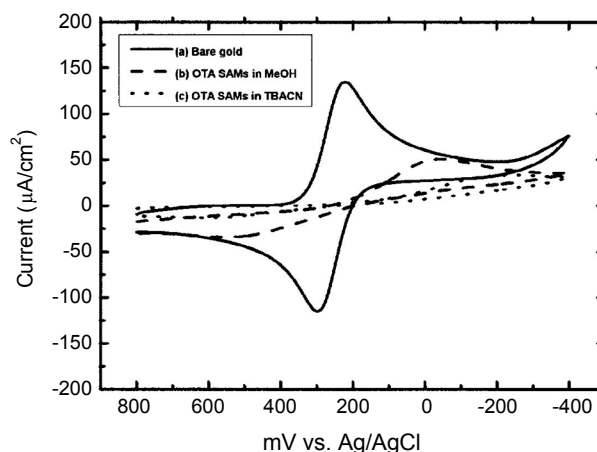


Figure 4. Cyclic voltammograms of (a) a bare Au(111) electrode, (b) a Au(111) electrode covered with OTA SAMs formed in a pure solvent, and (c) a Au(111) electrode covered with OTA SAMs formed in a catalytic TBACN solution.

SAMs formed in a pure solvent, and (c) a Au(111) electrode modified by OTA SAMs in a catalytic TBACN solution containing 1 mM $K_4[Fe(CN)_6]$ and 1 mM KNO_3 . The peak currents (I_p) for each electrode were measured as (a) 160.48, (b) 50.08, and (c) $10.3 \mu A/cm^2$, respectively. We found that the Au(111) electrodes modified with OTA SAMs have lower peak currents compared to the bare gold electrode, implying the formation of OTA SAMs. Particularly, the Au(111) electrode covered with OTA SAMs formed in a TBACN solution showed a higher blocking effect for the electrochemical reaction than that covered with OTA SAMs formed in a pure solvent, which indicates that OTA SAMs with a high degree of structural order can form in the catalytic TBACN solution. This result is also in good accord with the STM results.

Conclusions

The catalytic effect of TBACN on the SAM formation of thioacetyl-protected OTA molecules on Au(111) was investigated by STM, XPS, and CV. A high-resolution STM study demonstrated that although OTA molecules in a pure solvent do not form ordered SAMs, they can form the highly ordered SAMs with a $c(4 \times 2)$ structure in a catalytic TBACN solution. The OTA SAM samples showed the same spectral features in the S 2p region as those observed in well-ordered alkanethiol SAMs, suggesting that OTA molecules form chemisorbed SAMs via effective deprotection of the thioacetyl-protected group in the catalytic TBACN solution. In addition, CV measurements revealed that OTA SAMs on Au(111) formed in a catalytic TBACN solution showed a higher blocking effect compared to OTA SAMs formed in a pure solvent. In this study, we clearly demonstrated that TBACN is an effective catalytic reagent for the formation of thioacetyl-terminated organic SAMs with a high degree of structural order on gold.

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References

1. Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.
2. Krämer, S.; Fuierer, R. R.; Gorman, C. B. *Chem. Rev.* **2003**, *103*, 4367.
3. Schreiber, F. *J. Phys.: Condens. Matter* **2004**, *16*, R881.
4. Yokota, Y.; Fukui, K.-i.; Enoki, T.; Hara, M. *J. Am. Chem. Soc.* **2007**, *129*, 6571.
5. Crook, R. M.; Ricco, A. J. *Acc. Chem. Res.* **1998**, *31*, 219.
6. Flood, A. H.; Stoddart, J. F.; Steuerman, D. W.; Heath, J. R. *Science* **2004**, *306*, 2055.
7. Choi, Y.; Jeong, Y.; Chung, H.; Ito, E.; Hara, M.; Noh, J. *Langmuir* **2008**, *24*, 91.
8. Noh, J.; Jeong, Y.; Ito, E.; Hara, M. *J. Phys. Chem. C* **2007**, *111*, 2691.
9. Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117.
10. Kwon, S.; Choi, J.; Lee, H.; Noh, J. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2008**, *313-314*, 324.
11. Noh, J.; Kato, H. S.; Kawai, M.; Hara, M. *J. Phys. Chem. B* **2006**, *110*, 2793.
12. Noh, J.; Hara, M. *Langmuir* **2001**, *17*, 7280.
13. Noh, J.; Hara, M. *Langmuir* **2002**, *18*, 1953.
14. Cai, L.; Yao, Y.; Yang, J.; Price, D. W.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 2905.
15. Holmes, B. T.; Snow, A. W. *Tetrahedron* **2005**, *61*, 12339.
16. Tour, J. M.; Jones II, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
17. Jeong, Y.; Lee, C.; Ito, E.; Hara, M.; Noh, J. *Jpn. J. Appl. Phys.* **2006**, *45*, 5906.
18. Jeong, Y.; Han, J. W.; Kim, N.; Lee, Y.; Lee, C.; Hara, M.; Noh, J. *Bull. Korean Chem. Soc.* **2007**, *28*, 2445.
19. Jeong, Y.; Kwon, S.; Kang, Y.; Lee, C.; Ito, E.; Hara, M.; Noh, J. *Ultramicroscopy* **2007**, *107*, 1000.
20. Jeong, Y.; Chung, H.; Noh, J. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2008**, *313-314*, 608.
21. Jeong, Y.; Han, J. W.; Lee, C.; Noh, J. *Bull. Korean Chem. Soc.* **2008**, *29*, 1105.
22. Stapleton, J. J.; Harder, P.; Daniel, T. A.; Reinard, M. D.; Yao, Y.; Price, D. W.; Tour, J. M.; Allara, D. L. *Langmuir* **2003**, *19*, 8245.
23. Chen, L.; Yang, J.; Yao, Y.; Price, D. W. Jr.; Dirk, S. M.; Tour, J. M. *Langmuir* **2004**, *20*, 1335.
24. Poirier, G. E.; Tarlov, M. *J. Langmuir* **1994**, *10*, 2853.
25. Delamarhe, E.; Michel, B.; Gerber, C.; Anselmetti, D.; Güntherodt, H.-J.; Wolf, H.; Ringsdorf, H. *Langmuir* **1994**, *10*, 2869.
26. Ishida, T.; Hara, H.; Kojima, I.; Tsuneda, S.; Nishida, N.; Sasabe, H.; Knoll, W. *Langmuir* **1998**, *14*, 2092.
27. Castner, D. G.; Hinds, K.; Grainger, D. W. *Langmuir* **1996**, *12*, 5038.