

An Adsorption Process Study on the Self-Assembled Monolayer Formation of Octadecanethiol Chemisorbed on Gold Surface

Dong Ho Kim, Jaegun Noh,[†] Masahiko Hara,[†] and Haiwon Lee*

Dept. of Chemistry, Hanyang University, Seoul 133-791, Korea

[†]*Frontier Research System, The Institute of Physical and Chemical Research (RIKEN),*

Hirosawa, Wako, Saitama 351-0198, Japan

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The self-assembled formation of octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$) on a gold substrate was studied using a quartz crystal microbalance (QCM) and a scanning tunneling microscope (STM). From the QCM measurements at various concentrations of octadecanethiol solutions in hexane and alcohol, the adsorption process of octadecanethiol onto Au was confirmed to consist of two steps as follows: (i) fast but disordered adsorption and (ii) a thermodynamically controlled rearrangement for uniform packing of octadecanethiol. Also, it was revealed that the adsorption rate became faster in ethanol than in hexane since less solubility of octadecanethiol in ethanol could help the formation of the monolayers. At 5×10^{-7} M solution, the monolayer formation was monitored by STM. The morphology of monolayer region was initially circular (diameter size: 7.26 ± 2.1 nm) and gradually changed to a stripe type after several minutes. At higher concentration, the self-assembled monolayer was formed immediately after the solution was introduced to a substrate.

Keywords : Self-assembly, Alkanethiol, STM, QCM.

Introduction

The molecular self-assembly of long chain alkanethiols on Au has drawn considerable attention during the past decade, since self-assembled monolayers (SAMs), unlike Langmuir-Blodgett (LB) films, have strong adhesion to a substrate, high degree of thermal and chemical stabilities, and mechanical strength. These properties, along with the relative easiness in the preparation, result in many potential applications to nanotechnology. Also, a wide range of synthetic possibilities to enhance these properties allows us to use SAMs as a basic component in a molecular engineering approach. Many recent works on the alkanethiol monolayer adsorbed on the gold surface have been focused on the structure and properties of these organic films adsorbed on gold. X-ray diffraction and STM measurements revealed that this system forms a specific monolayer structure on Au(111) surfaces,¹⁻⁵ with an IR measurement showing that all-trans aliphatic chains of the alkanethiolate are oriented at $\sim 30^\circ$ with respect to the normal of the gold surface.⁶ These monolayers are densely packed, with ~ 5 Å of an interchain spacing confirmed by He diffraction and STM measurements.^{1,7} However, there have been relatively a few studies about the formation mechanism of the monolayers.

Bain and coworkers observed two stages in the adsorption process of alkanethiols onto metal surfaces using ellipsometry and contact angle measurements.⁸ In this study, other methods, *i.e.* QCM and scanning tunneling microscopy (STM), are going to be employed to verify the adsorption process of octadecanethiol. A QCM comprises a thin piezoelectric quartz crystal sandwiched between two gold electrodes. When the electric field is applied to the crystal through the two electrodes, the shear vibration of the crystal is induced that pro-

vide an alternating electric field which induces shear vibration of the quartz crystal at its resonance frequency. A QCM is a well-established tool in mass-sensitive detection based on an oscillating quartz crystal. Even though the QCM is not very selective, it responds quantitatively to any interfacial mass change and provides information that would be difficult to obtain with other methods. When a monolayer or thin film on a QCM electrode exhibits a rigid-layer behavior, the QCM provides the absolute information on the mass change at the solid-liquid interface. The recent advances in QCM instrumentation make it easy to apply this technique to liquid systems. In addition to its advanced strength, the applications of QCM have been widened due to a low cost of the device and its submonolayer sensitivity. For example, it is widely employed as a sensor such as for gas sensing, immunoassay, surface analysis, electrochemical analysis, and detection of trace ions.

In this study we report the trends revealed in the adsorption process of octadecanethiol monolayers with different solvents and concentrations using an *in-situ* QCM method. The frequency shifts during adsorption follow a simple exponential relaxation. A QCM with a resonance frequency of ~ 10 MHz is sensitive to mass changes as small as several nanograms. Even though the frequency change of coupled mechanical and electrical oscillation depends on several factors, interfacial mass changes are mainly related to the frequency change. This relation is formulated in Sauerbrey equation as follows⁹:

$$\Delta f = k \Delta m \quad (1)$$

where Δf is a measured frequency shift, k is a constant, and Δm is the mass change. In our experiment, 1 Hz frequency change from the fundamental frequency of the QCM is equal

to 1 ng mass loading on Au plate. In this work we will identify the two-step formation of octadecanethiol onto Au and investigate the consistency of the previous studies on wetting thickness with our results.

Early STM studies revealed that alkanethiol monolayers on Au(111) exhibit a distribution of pitlike defects, which do not exist on the bare Au surfaces.¹⁰⁻¹² This observation caused some interests in physical and electrochemical blocking abilities of alkanethiol monolayers which may be applied to biosensing or corrosion control. We carried out a STM investigation on the self-assembly process of octadecanethiol onto Au(111) in air condition by controlling the surface coverage as changing dipping times. STM allowed to visualize the monolayer formation and to characterize its structure and orientation.

Experimental Section

A QCM measurement. Commercially available 10 MHz AT-cut quartz crystals were used for all experiments. Both sides of a quartz crystal were coated with a 100 Å Cr layer beneath a 1000 Å layer of Au. The quartz crystals were installed in a teflon holder so that only one electrode with an area of 0.2 cm² was exposed to a deposition solution. The oscillating frequency was measured with HP 53131A Universal Counter (Hewlett Packard, Santa Clara, CA, USA) and the data was accumulated to an IBM compatible personal computer for the data treatment. 6 seconds of a gate time and 5V of output voltage were used in the frequency measurements. The crystals were cleaned in a piranha solution (30% H₂O₂ : 98% H₂SO₄, 1 : 3 by volume) at room temperature for 10-15 seconds and rinsed thoroughly by deionized water. After cleaning, the crystal was mounted in a cell and a small amount of pure solvent was introduced into the cell. The output frequency for the crystal in a pure solvent was recorded for 1-2 hrs in order to establish a stable baseline.

STM measurements. All experiments were performed in air with a Nanoscope III (Digital Instruments, Santa Barbara, CA, USA) and a mechanically cut tips (Pt/Ir (80 : 20)) (Digital Instruments). All the images were acquired using a constant current mode or a constant height mode. Au substrates were prepared by the vacuum evaporation of gold onto freshly cleaved mica plates prebaked to 300 °C for 2 hrs under 10⁻⁷~10⁻⁸ torr. After deposition, a substrate was annealed at 460 °C in a furnace for 4 hrs to obtain a large flat single crystal surface. SAMs were prepared by dipping the gold substrates into 0.5 μM octadecanethiol solution in ethanol during an appropriate time period.

Results and Discussion

In this study, we determine the amounts and the rate of mass change of the alkanethiol adsorbed on gold from the octadecanethiol solution. This kinetic response, arising from a system that is initially far from equilibrium, provides fundamental information at the initial stage in the self-assembly

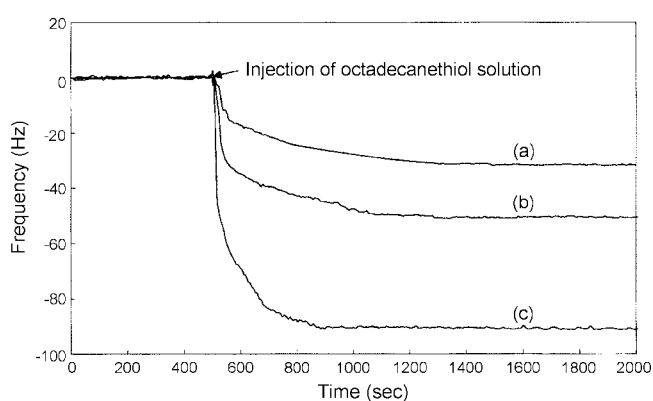


Figure 1. Frequency changes of QCM with adsorption of octadecanethiol on the gold surface in various concentrations of octadecanethiol: (a) 0.1, (b) 1, (c) 10 mM.

process of octadecanethiol monolayers. Hexane and ethanol were selected as a solvent for octadecanethiol in order to investigate the rate of solubility in the adsorption process.

Figure 1 shows the frequency change during the adsorption process at various concentrations of octadecanethiol in hexane. The frequency shifts measured by the QCM method were 32 Hz in 0.1 mM, 51 Hz in 1 mM, and 91 Hz in 10 mM of the solution. As shown in Figure 1, the adsorption rate of octadecanethiol on gold surface increases as the concentration of octadecanethiol solution increases. In 0.1 mM octadecanethiol solution, it took approximately 800 seconds for the monolayer to be completely formed over the surface, while 560 seconds in 1 mM solution and 120 seconds in 10 mM solution in hexane. These observations indicate the correlation of the formation rate with the concentration of the solution. In higher concentrated solution, the two-step mechanism was preferred and the formation rate became faster. The adsorption rate of alkanethiol onto clean gold depended on the thiol concentration, temperature, and solvent. Initially, most of the monolayer was formed within a few minutes and the frequency shifts are close to their limiting values as shown in Figures 1 and 2. Because of the fast diffusion rate of thiol molecules, octadecanethiol molecules can reach at the electrode surface immediately after an injection of octadecanethiol solution and can react with the gold atoms on the surface. It leads thiols to monolayer formation easily even though the orientation is not well-ordered and the thiol molecules can not be formed over the whole surface. During the second stage, the disordered and defected layer is oriented gradually and uniformly and consolidated due to the van der Waals attraction between the two neighboring alkyl chains in the thiol molecules. These findings are supported by the second harmonic generation spectroscopy,¹³ X-ray photoelectron spectroscopy,^{14,15} near-edge X-ray absorption fine structure spectroscopy,¹⁶ scanning tunneling microscopy (STM),¹⁷⁻²⁰ and QCM.

The adsorption trends at 0.1 and 1 mM octadecanethiol in ethanol were presented as Curves a and b in Figure 2, respectively. The frequency shift obtained from Curve a is 49 Hz at 170 seconds after the injection which is equivalent

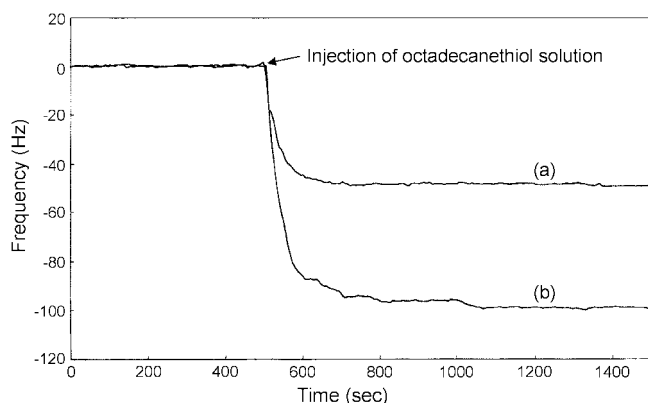


Figure 2. The adsorption trends of octadecanethiol in ethanol solution. The concentrations of octadecanethiol are (a) 0.1, (b) 1 mM.

to 49 ng mass loading on Au plate. The Curve b shows the QCM frequency shift for the adsorption of 1 mM which indicates the more than one monolayer formation. The maximum frequency shift is 99 Hz, which is 34% higher value than the calculated value of monolayer formation using surface coverage of 3.3 mg/m^2 for octadecanethiol on Au.²¹ Since the formation of the second layer result from the van der Waals interaction with the first layer on the substrate, the second layer can neither be formed uniformly nor be stabilized. Accordingly, the shear wave propagates differently and gives rise to variations in the Df for each layer. This deviation in the QCM measurements can be explained by the formation of multilayer.^{22,23} A positive deviation in frequency shift from the calculated value could be understood as follows. Since it is not understood how the roughness of the first layer affect the formation of the second layer on the first, the roughness of a gold electrode can be overestimated in the calculation. Due to the increase of surface roughness, we expected a little higher frequency change than that of theoretical value. There may be also excess physisorbed molecules on the top of the monolayer because of the difficulty in removing physisorbed molecules. Simple washing or sonicating the electrode is impossible during the *in-situ* frequency measurement. In addition, one possible model of formation of partial octadecanethiol multilayers on gold surface proposed by Y. T. Kim *et al.* is via the formation of disulfides.²⁴ Thiols are oxidized to disulfides in the presence of oxygen and the solubility of disulfides in ethanol is much less than that of thiols.²⁵⁻²⁶ If a solution of octadecanethiol in ethanol is exposed to oxygen and oxidized to disulfide, the oxidized disulfide can be precipitated onto the monolayer. Hence, the deposition of disulfide may be enhanced by the interaction between a terminal methyl group of octadecanethiol. There is also a report about the multilayer formation of alkanethiols on gold by gas phase adsorption.²²

Rowe *et al.*²⁷ reported the incremental change per methylene unit in the characteristic free energy and it was founded to be -19 kJ/mol for adsorption from ethanol and -0.8 kJ/mol from 1-hexanol. From another report on solvent effects,⁸ we could find out that a self-assembly adsorption process of

Table 1. The frequency shift of self-assembled octadecanethiol deposited on gold

Solvent	Concentration (mM)	Δf (Hz)	Δt (sec)
hexane	0.01	32	800
	0.1	51	560
	1	91	120
ethanol	0.01	49	170
	0.1	99	65

hexadecanethiol in ethanol is greater than in hexadecane. In the monolayer formation using 0.1 mM octadecanethiol, a QCM frequency change in the monolayer formation using hexane as a solvent was only 65% of Δf measured in the monolayer formation using ethanol. In case of 1 mM octadecanethiol solution, the frequency change of octadecanethiol in ethanol after full adsorption is about two times higher than in hexane. In our experiments, octadecanethiol solution in ethanol shows a faster adsorption rate than in hexane as shown in Table 1. This solvent effect can be explained in terms of the different solvation energies of the two solvents, which can moderate the dispersive forces in the monolayer. Hexane is a better solvent than ethanol for alkanethiols. The high solubility of octadecanethiol in hexane delays the monolayer formation. The poorer solvents for the alkanethiol produce better SAMs. This effect was also observed in the other system. Schneider and Buttry *et al.* could alter the adsorption kinetics of an alkanethiol using selection of a specific electrolyte solvent.²⁸ This work showed the adsorption kinetics strongly depended on the property of solvent.

STM images in Figures 3-5 show the surface morphologies of octadecanethiol SAMs on Au(111) depending on a deposition time.²⁹⁻³² At very low surface coverage, the thiols

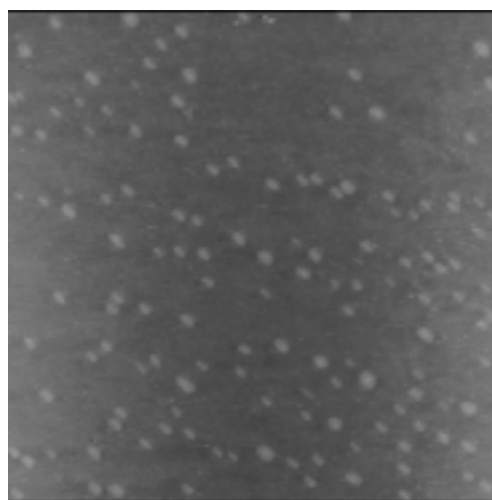


Figure 3. Constant current STM image obtained after 1 min of deposition in $0.5 \mu\text{M}$ ethanol solutions of octadecanethiol on Au(111). The STM image shows an ordered nucleation of these molecules on Au during the initial SAM growth stage. The scan size was $200 \text{ nm} \times 200 \text{ nm}$, and imaging conditions were 500 mV and 0.42 nA in the constant current mode.

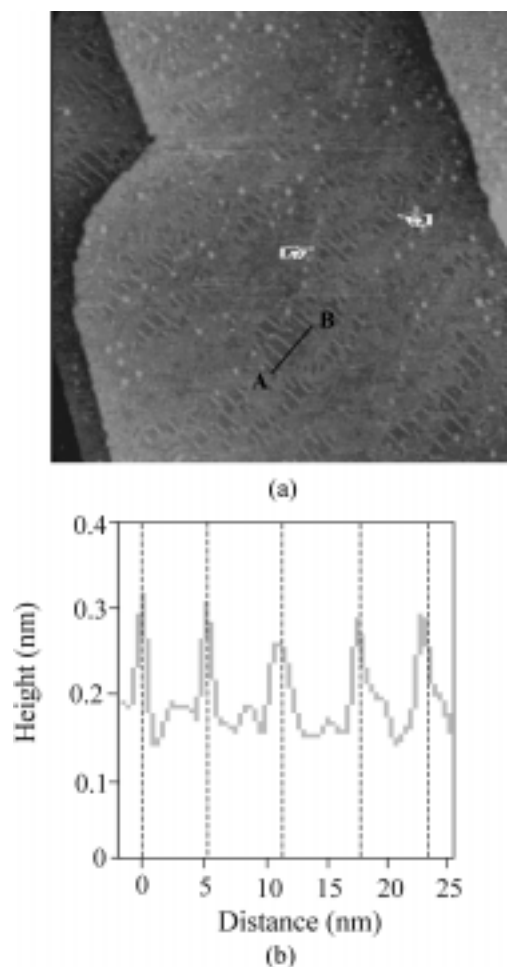


Figure 4. Constant current STM image obtained after 5 min of deposition in $0.5 \mu\text{M}$ ethanol solutions of octadecanethiol on Au(111). (a) The STM image shows the striped-phase and the distance between two bright lines is 5.6 nm. The scan size was $200 \text{ nm} \times 200 \text{ nm}$, and imaging conditions were 500 mV and 0.3 nA in the constant current mode. (b) "Height" profile along the line trace AB. The dotted lines mark a pot of each peak.

can be regarded as a lattice-gas phase that is characterized by a low area density of rapidly diffused surface-confined thiols. When this lattice-gas reaches a critical surface coverage, stable alkanethiol islands starts to be nucleated. After dipping a gold substrate in $0.5 \mu\text{M}$ octadecanethiol solution for 1 min, the monolayer formation process is revealed as follows: individual molecules on the surface can be bound initially at periodic herringbone dislocations, which are induced to relieve the surface strain, and grown up as an island type *via* further aggregation. The STM image in Figure 4(a) shows the reconstruction of octadecanethiol SAMs on Au(111) surface after 5 min. This image contains two kinds of stripe structures whose interfacing distances are different from each other. In Figure 4(a), the wide stripe was dominantly observed and the narrower stripe was rarely observed. Bright rows correspond to the sulfur atoms. The wide stripe are aligned with an inter-row spacing of $56 \pm 0.4 \text{ \AA}$, which show good agreement with twice of the molecular length of $\text{CH}_3\text{-(CH}_2\text{)}_{17}\text{SH}$. The cross-sectional profile along the rows is

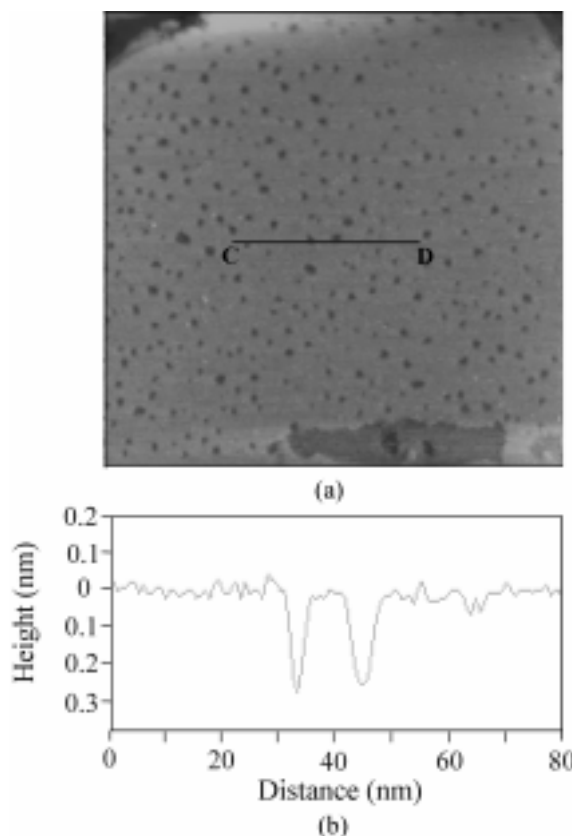


Figure 5. Constant current STM image obtained after 1 h of deposition in $0.5 \mu\text{M}$ ethanol solutions of octadecanethiol on Au(111). (a) Au vacancy islands nucleate after 1 h deposition. The scan size was $200 \text{ nm} \times 200 \text{ nm}$, and imaging conditions were 500 mV and 0.4 nA in the constant current mode. (b) Sectional view along lines C and D in Figure 5a shows a 0.25 nm depth of vacancy island features.

shown in Figure 4(b). The narrow stripe structure (pointing fingers) has a $32 \pm 1.1 \text{ \AA}$ corrugation period perpendicular to the stripe. This value is little larger than 28 \AA , the theoretical molecular length. The paired structure was reproducibly observed in different experiments, so it is not the artifact due to a tip. This observation showed that octadecanethiol is preferentially head-to-head configuration, *i.e.*, thiol-to-thiol, but occasionally is oriented as head-to-tail. Accordingly, the striped phases of octadecanethiol consists of the thiol molecules lying horizontally to the gold surface. The hydrocarbon backbones are fully extended and in all-trans conformation. This structure cannot be expected if the chemisorption was formed since chemisorbed thiol molecules was assembled vertically to a gold substrate.³³ Thus, the molecules in this striped phase should be physisorbed. This striped phase is the first condensed phase that nucleates on Au(111) during deposition of octadecanethiol and has been observed in prior diffraction studies.^{34,35} After surface reaches saturation coverage of the striped phase of octadecanethiol, the striped phase is shifted to a standing-up phase until the surface reaches saturation. The holes shown in Figure 5(a) have been seen in many other STM studies on SAMs.^{9,36-39} While some studies proposed that the pit-like defects resulted

from the missing or loosely-packed alkanethiols,^{10,11} other groups suggested that they were an electronic artifact of the STM contrast mechanism.^{40,41} However, the Au vacancy model was later confirmed by a number of STM studies. Formation of these Au vacancy islands is explained by the fact that the Au atoms are ejected from the surface by the herringbone structure compression. The depth of the depression is found to be about 0.25 nm (Figure 5b) and is independent of the chain length of the adsorbed molecules. This depth equals the height of step edges in the thiol-modified gold surface and consistent with the Au(111) single-atom step height on the bare gold samples. It suggests that the pits were originated from defects in the Au layer than defects in the alkanethiol layer. Therefore, not only Au but also thiol molecules are removed simultaneously. Our STM data shows a good agreement with the QCM measurements which propose the two steps in the adsorption process.

Conclusions

The two-step mechanism proposed for the adsorption process of octadecanethiol monolayer on Au has been clearly confirmed by QCM measurements in this work. Also the effect of solvent was revealed using hexane and ethanol. The low solubility of octadecanethiol in ethanol was preferred to form the SAMs. The self-assembled process of octadecanethiol monolayer is initiated by a low-density striped phase through a complex, intermediate stage and finally reached to the standing-up phase. The STM images of octadecanethiol self-assembled monolayers in Figure 4(a) show rows of bright regions and suggest that the molecules lie horizontally to the surface and are arranged to stripes. Also, we showed the formation of vacancy island defects in octadecanethiol monolayers assembled on gold surface. The vacancy islands were formed by adsorbate-induced shrinkage of the surface lattice. This excess density should create in-plane compressive stress that could result in ejection of the excess Au atoms.

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