Time-Dependent Organization and Wettability of Decanethiol Self-Assembled Monolayer on Au(111) Investigated with STM

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A detailed study on the time-dependent organization of a decanethiol self-assembled monolayer (SAM) at a designed solution concentration onto a Au(111) surface has been performed with scanning tunneling microscopy (STM). The SAMs were prepared by immersing Au(111) into an ethanol solution containing 1 μM decanethiol with different immersion times. STM images revealed the formation process and adlayer structure of the SAMs. It was found that the molecules self-organized into adlayers from random separation to a well-defined structure. From 10 s, small domains with ordered molecular organization appeared, although random molecules could be observed on Au(111) at the very initial stage. At 30 s, the SAM consisted of uniform short stripes. Each stripe consisted of sets of decanethiol mainly containing eight molecules. With the immersion time increasing, the length of the stripes increased. At 5 min, the alkyl chains overlapped each other between the adjacent stripes, indicating the start of a stacked process. After immersing Au(111) in decanethiol solution for 3 days, a densely packed adlayer with a $(\sqrt{3} \times \sqrt{3})R30°$ structure was observed. The formation process and structure of decanethiol SAMs are well related to sample preparation conditions. The wettability of the decanethiolate SAM-modified Au(111) surface was also investigated.

Introduction

Dependent on intermolecular and molecule−surface interactions, the molecules adsorbed on solid surfaces will self-organize into various structures and form self-assembled monolayers (SAMs). Among these SAMs, alkanethiol SAMs on gold surfaces is one of the most classical and intensively investigated systems because of their representative properties—ease of preparation and long-term stability.[1−8] The study on alkanethiol SAMs has been an important issue not only in fundamental research but also in industrial applications such as wetting,[9] corrosion,[10] adhesion,[11] and chemical and biological sensors.[12,13] On the other hand, self-assembling has become one of the powerful and well-established techniques in the "bottom-up" strategy of nanotechnology. The self-organized molecular structure or self-assembled monolayer with precise control of structure and special function could provide promising functional materials for construction of nanodevices that could not be prepared by microfabrication. After continuous effort, abundant information on alkanethiol SAMs has been collected. Recently, Love et al. reviewed the advances over the past 5 years from 1999 to 2004 on the SAMs formed with alkanethiols and their derivatives onto gold, silver, copper, palladium, mercury, and other alloys.[14] They summarized the results from more than 770 papers and took alkanethiol SAMs as a form of nanotechnology, showing the importance of thiolate-related SAMs. As a result of the studies, it is known that the formation of an alkanethiol SAM will undergo several stages from initial random to final densely packed orderings on a solid surface, although the corresponding relationship between structure and sample preparation conditions is still an important topic in SAM study.

Various techniques have been employed to investigate the structure and formation of alkanethiol SAMs. Some of these techniques are contact angle measurement and ellipsometry,[2] quartz crystal microbalance,[15,16] infrared reflection absorption spectroscopy,[17] X-ray photoelectron spectroscopy,[18] thermal desorption spectroscopy,[19] second harmonic generation,[20] and scanning probe microscopy (SPM), especially STM and atomic force microscopy (AFM). For acquiring atomic or molecular resolution on a solid surface, STM has been proven to be a powerful and useful tool in monitoring the adlayer formation.[21] Poirier and Pylant investigated the processing of alkanethiols onto Au(111) by controlling the surface coverage using a gas-phase deposition in ultrahigh vacuum (UHV) condition.[22] A stripe structure at low coverage and a well-known densely packed upright phase at saturation coverage were observed by STM, respectively. Tamada et al. found the domain formation of alkanethiol molecules on Au(111) at the initial stage of the self-assembly process by AFM.[23] The Uosaki group reported at least three steps in the self-assembly process of alkanethiol molecules on Au(111) by electrochemical STM.[24] At the very initial stage, adsorbed molecules did not arrange in an ordered structure, then led to the initial ordered structures such as stripe structures, finally arranged in a $(\sqrt{3} \times \sqrt{3})R30°$ structure. Poirier et al. found six phases of decanethiol molecules on Au-(111) including two metastable and four stable phases,[25] although Toerker et al. reported three other different phases on decanethiol monolayers.[26] Kolb et al. carried out a systemic study on alkanethiol adsorption on gold single-crystal surfaces in aqueous electrolyte solution.[27] They reported the effect of alkanethiol molecules on cyclic voltammograms and surface structures and revealed the potential-dependent structures. The studies reported demonstrate the structural complexity with SAMs.

The alkanethiol SAMs can be fabricated in UHV, electrolyte solution, and ambient conditions, although the structures formed in different environments may be different. Among these conditions, forming an alkanethiol SAM in an ambient environ-

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ment is facile and much easier than in UHV. Various alkanethiols can be simply dissolved in solvent. By immersing the solid substrate into the solutions, SAM will be formed without the use of special equipment. Therefore, understanding the adsorption and formation process of the alkanethiol SAM prepared in mild conditions such as room temperature and ambient environment will bring convenience in nanodevice fabrication and surface modification. Owing to the complexity of structure formation with preparation conditions, it still remains the significant challenge in the study of alkanethiol SAMs.[28,29] For example, to obtain a reproducible, stable, and structurally defined SAM, it is necessary to understand the effect of the solution concentration, immersion time, and substrate lattice on the SAM. If the structure of a SAM can be predicted from experiment condition, it will be very useful in nanotechnology.

In this paper we will give a relationship between adlayer structure and formation condition; we will also reveal the formation process of decanethiol SAMs. By immersing an Au-(111) single crystal into an ethanol solution containing 1 μM decanethiol, the time-dependent organization of decanethiol molecules was monitored by STM. The formation process is clearly revealed by higher resolution STM images. It is found that decanethiol molecules spontaneously adsorb on the Au-(111) surface and form an ordered adlayer through four steps: (1) random separation in lower surface coverage, (2) stripe structure, (3) stacking process, and (4) densely packed adlayer. The first step is very fast. After less than 10 s, small domains appear on the Au(111) surface with an ordered structure. At 30 s, a short-stripe structure is observed. Each stripe consists mainly of regular eight decanethiol molecules. With the immersion time increasing, the length of the stripes increases. Meanwhile, the alkyl chains of the neighboring decanethiol molecules start to stack with each other. Finally, a densely packed ($\sqrt{3} \times \sqrt{3}$) R30° structure is observed. On the basis of the STM observation, the structures of SAMs at different stages can be predictable. The Au(111) surface modified with a decanethiolate SAM shows the change in its wettability. The present work reveals the time-dependent organization of decanethiol SAM and is a good supplement for the thiolate SAM study.

Experimental Section

1-Decanethiol (HS(CH$_2$)$_9$CH$_3$) from Fluka was used without further purification. The solution containing decanethiol molecules (ca. 1 μM) was prepared with ethanol (Acros Organics, USA). A 0.1 M HClO$_4$ solution was used as electrolyte solution and prepared by diluting ultrapure HClO$_4$ (Cica-Merck, Kanto Chemicals) with Milli-Q water.

A well-defined Au(111) electrode was prepared by crystallization of a molten ball formed at the end of a Au wire (99.999%) in a hydrogen–oxygen flame.[30] One of the Au(111) facets on the gold bead for cyclic voltammogram (CV) measurements was mechanically cut, polished with successively finer grades of Al$_2$O$_3$, and annealed at 900 °C for 24 h to remove defects on the surface. Before each measurement, the Au(111) electrode was annealed in a hydrogen–oxygen flame and quenched in ultrapure water saturated with hydrogen. The molecular adlayers were prepared by immersing the single-crystal Au bead into the ethanol solution containing 1 μM decanethiol. After different immersing times, the Au bead was rinsed with ethanol solution to remove the remnant sample molecules and then was used for STM, CVs, and contact angle measurements. Because it takes time to obtain the first image after the sample is removed from solution containing thiol molecules, we use the immersion time to compare all adlayers.
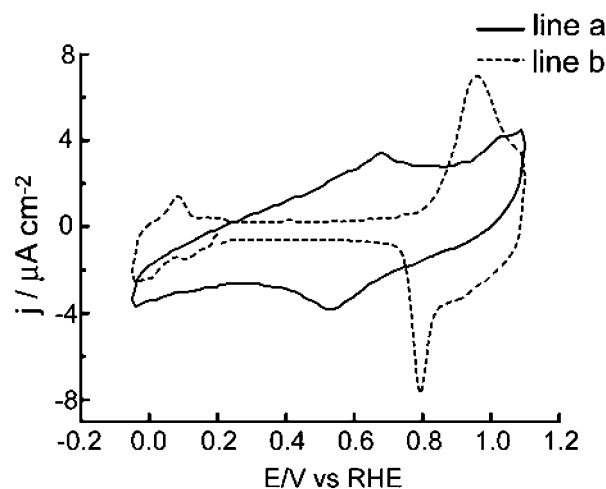
Figure 1. Cyclic voltammograms of Au(111) in 0.1 M HClO$_4$ in the absence and presence of a decanethiolate adlayer. The scan rate was 50 mV/s.

Setting up the sample for the STM cell requires almost the same amount of time.

Cyclic voltammogram experiments were carried out with an EG&G PAR (Princeton Applied Research) Basic Electrochemical System. Before measurement, the solution was degassed with nitrogen. A homemade standard electrochemical cell with a reversible hydrogen electrode (RHE) in 0.1 M HClO$_4$ and a Pt counter electrode was used for electrochemical measurement. All potentials are reported with respect to the RHE.

A Nanoscope E scanning tunneling microscope (Digital Instruments, CA) was used for in situ STM observation. The tunneling tips used were prepared by electrochemical etching of a tungsten wire (0.25 mm in diameter) in 0.6 M KOH, subsequently coated with clear nail polish to minimize faradaic currents.

To prevent the sample contamination from the atmosphere, STM observation of prepared SAMs was performed in solution, which is a well-used method in SAM study.[31] Electrode potentials for STM observation in all experiments were fixed at 0.55 V positioning at the double layer region where no redox reaction takes place. All STM images shown here were acquired in the constant-current mode, and they were flattened raw data without any processing such as low-pass or high-pass.

Contact angle measurements were performed by a sessile drop method on a Dataphysics OCAzo contact angle system at ambient and room temperature. The volume of the water droplet used for the measurements was 2.0 μL. All reported contact angles are the average of five measurements taken at different locations of the Au(111) substrate.

Results and Discussion

Cyclic Voltammogram. A cyclic voltammogram was employed to confirm the adsorption and surface redox reaction of a decanethiol SAM on Au(111). Figure 1 shows CVs of a well-defined Au(111) electrode in 0.1 M HClO$_4$ in the absence and presence of decanethiol molecules, respectively. Herein, "presence" means that the Au(111) electrode was immersed into a solution containing decanethiol molecules for 30 s and a decanethiol SAM formed on the substrate surface. The CVs of Au(111) with decanethiol adlayers formed at different immersing times were also investigated. Here, we show Figure 1 as an example.

The CVs were recorded at a scan rate of 50 mV s^{-1}. The first scan was started at 0.5 V in the cathodic direction. The
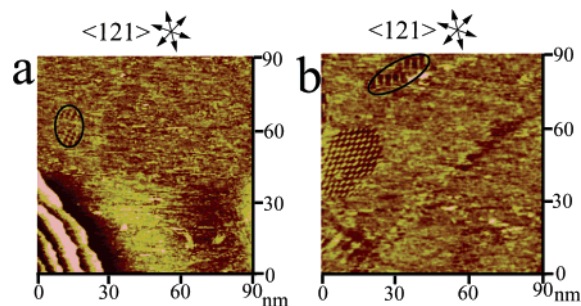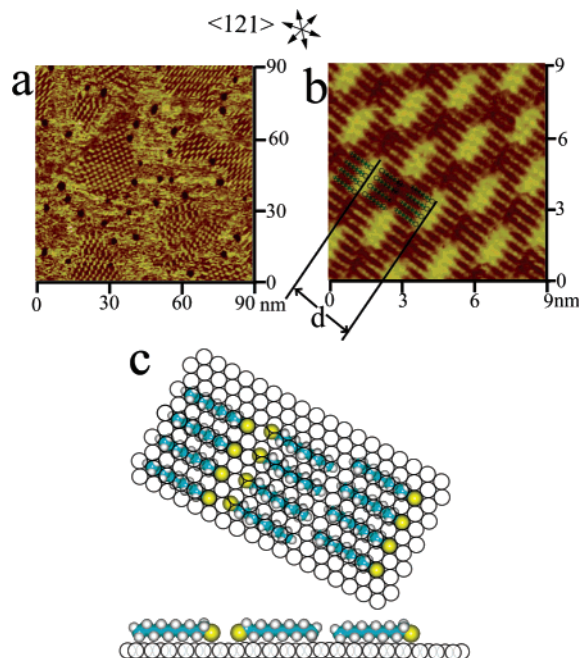
Figure 2. Large-scale STM images of decanethiol molecules adsorbed on Au(111) for 5 s (a) and 10 s (b). The imaging conditions are for (a) $E = 550$ mV, $I_{tip} = 1.1$ nA; and for (b) $E = 550$ mV, $I_{tip} = 1.2$ nA.

CV of the bare Au(111) electrode (line a) scanned in the double-layer potential region from 0 to 1.1 V shows a pair of reconstruction peaks, indicating that the well-defined Au(111) electrode is free from contamination.[32] After examination of the bare Au(111) electrode, the electrochemical behavior of Au-(111) modified with a decanethiol SAM is investigated. The potentials applied onto the Au(111) electrode were gradually scanned from the double layer region to negative hydrogen adsorption and the positive oxidation region, respectively. It can be seen that the shape of the CV (line b) of a decanethiol-covered Au(111) electrode is totally different from that of a bare Au(111) electrode. A sharp pair of anodic−cathodic peaks at 0.96 and 0.8 V appear while the reconstruction peaks disappear. The result indicates that decanethiol molecules have adsorbed on the Au(111) electrode. To explain the signification of the sharp pair of peaks, an STM experiment was carried out. The decanethiol molecules could be observed in the potential region from 0.30 to 0.75 V. But in potentials more than 0.8 V, the molecules begin to desorb from the Au(111) electrode. Therefore, the sharp pair of anodic−cathodic peaks in CV may be due to the oxidative desorption. On the other hand, in the negative potential region, the reductive desorption peaks, two small cathodic peaks at 0.1 and 0.01 V, respectively, can also be observed. A detailed study on the origin of these peaks is now in progress.

From the electrochemical results, it is learned that from 0.30 to 0.75 V the decanethiol SAM adsorbs on the Au(111) electrode without electrochemical reaction. Therefore, the structure of the SAM formed in the immersion process will be preserved at this potential region such as 0.55 V for the decanethiol SAM.

STM Measurements. A series of surface structures of Au-(111) with decanethiol molecules adsorbed at different immersion times are directly observed by STM. We can monitor the formation process of the SAMs. As the immersion time increases from 5 s to 10 min, the decanethiol molecules adsorb on the Au(111) surface and self-organize into stripe structures with different lengths. When the immersion time increases to 3 days, a densely packed phase appears. STM imaging revealed the time-dependent organization process.

Initial Stages at 5 and 10 s. To demonstrate the time-dependent organization, we carried out a series of experiments at different immersion times. Figure 2a is a large-scale STM image obtained from the immersion of the Au(111) crystal in the solution for 5 s. From this image it is seen that the surface is covered by random molecules and molecular clusters. In the area indicated by a circle, a molecular resolution STM image can be achieved. However, the clusters are unstable and will disappear in the next scanning of the image. The results indicate that in the very initial stage of the SAM formation the molecules randomly adsorb and separate on the Au(111) surface.


Figure 3. (a) Large-scale and (b) higher-resolution STM images of decanethiol molecules adsorbed on Au(111) for 30 s. The imaging conditions are $E = 550$ mV, $I_{tip} = 1.0$ nA. (c) Proposed structural model for the ordered adlayer of decanethiol molecules adsorbed on Au(111). The stripes are mainly composed of eight molecules.

When the immersion time was increased to 10 s, a typical STM image of the SAM is shown in Figure 2b. It can be found that there are two domains of different size as circled in the image. The molecules in the domains self-organize into stripe structure. The stripe structure is stable in the scanning area. The length of each stripe in the large domain is almost identical. The results indicate the start of a defined SAM formation. After immersion for 10 s, the surface coverage of molecules increases. Therefore, the mobility of surface molecules is limited, which results in the formation of a stable SAM locally.

A Short Stripe Organization Mainly by Eight Molecules at 30 s. Figure 3a is a large-scale STM image showing a decanethiolate adlayer on the Au(111) surface. The SAM was formed after immersing the gold crystal into the ethanol solution containing 1 μM decanethiol molecules for 30 s. It can be seen from this image that the Au(111) surface is modified with decanethiol molecules separated in several discontinuous domains. In this immersion stage, part of the decanethiol molecules have not organized into a defined adlayer. Therefore, almost half the area in the frame is covered by random molecules. The pits in the image are the common feature of thiol adsorption on the gold surface.

Details of the molecular organization in the domains are revealed by a higher-resolution STM image. Figure 3b is an expanded STM image of Figure 3a. It is clear that the domain consisting of uniform molecular clusters in a stripe configuration is similar to the morphology of alkanethiolate adlayers on the Au surface. The stripe rows are parallel to the $\langle 121 \rangle$ direction of the Au(111) lattice. The length of every short stripe is measured to be 1.44 nm. The stripes are composed of individual decanethiol molecules. A careful observation found that each decanethiol molecule could be seen as a straight line with a big bright spot and five small bright spots. From the chemical structure of the molecule and results in the literature,[33] the big bright spots can be attributed to the sulfur atom and the small bright spots correspond to the positions where hydrogen atoms locate with carbon atoms in alkyl chains. The length of an
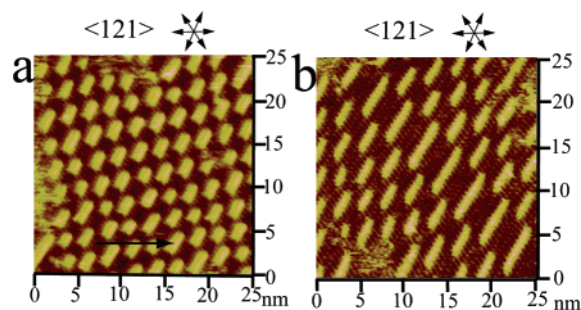
Figure 4. Large-scale STM image of decanethiol molecules adsorbed on Au(111) for (a) 1 min, and for (b) 2 min. The imaging conditions are for (a) $E = 550$ mV, $I_{tip} = 1.3$ nA; and for (b) $E = 550$ mV, $I_{tip} = 1.3$ nA.

individual molecule is measured to be 1.10 nm, consistent with the size in its chemical structure of a decanethiol molecule. It is well-known that the skeleton of an alkyl chain can take parallel and vertical orientations with the substrate when an alkanethiol molecule adsorbs on a solid surface.[34,35] In this image, five bright dots are observed in an alkyl chain. The alkyl skeleton contains 10 carbons in a decanethiol molecule. If the alkyl chain is parallel to the Au(111) surface, we can see 10 bright spots with a zigzag arrangement. However, the information from the STM image suggests that the decanethiol molecule adsorbs with the plane of the alkyl skeleton vertical to the underlying Au(111) surface in the present experiment.

From the higher-resolution STM image, it is seen that the S atoms of the decanethiol molecules take a head-to-head configuration in a stripe. The intermolecular distance in the $\langle 121 \rangle$ direction is measured to be 0.48 nm. A disulfide structure was reported in the literature, in which the sulfur atoms in the neighboring molecules form a dimeric structure.[36] However, in the present adlayer, the S—S distance is larger than that in a disulfide. The sulfur atoms in different molecular rows form a zigzag arrangement. The distance d between the neighboring stripes indicated in Figure 3b is measured to be about 3.28 ± 0.2 nm (ca. $11.5a$, $a = 0.288$ nm, the diameter of a gold atom). Intriguingly, we found that each stripe is composed mainly of eight sample molecules. We observed more than 10 domains. Most of the stripes in these domains consist of eight molecules with the same arrangement as that in Figure 3b. The molecular model for this feature is drawn in Figure 3c.

On the basis of the STM observation, a structural model for the decanethiolate SAM on the Au(111) surface in Figure 3b is temporarily proposed in Figure 3c. The skeletons of alkyl chains align along the $\langle 110 \rangle$ direction with vertical orientation on the underlying Au(111) lattice resulting in only five bright spots, as observed in the STM top view. The distance between the neighboring stripes is 3.28 nm. By carefully measuring and analyzing the distance and arrangement ordering between sulfur atoms in the two different molecular rows in a stripe, the sulfur atoms are put at different top and 3-fold positions in the model. The model is consistent with the STM results in Figure 3b and similar to the model proposed by Leo et al.,[33] although they did not confirm the detail information of the orientation of the alkyl skeleton.

Compared with the images in Figures 2 and 3, the scanning sizes of 90 nm × 90 nm in these images are the same. But the molecular domains increase with ordered stripes. The molecular organization seems to be through a process from the initial nuclear formation such as the unstable cluster and stable cluster in Figure 2a to the gradual growth of molecular stripes.

Stripe Length Increases with Immersion Time. Figure 4, parts a and b, shows typical STM images of decanethiol SAM on
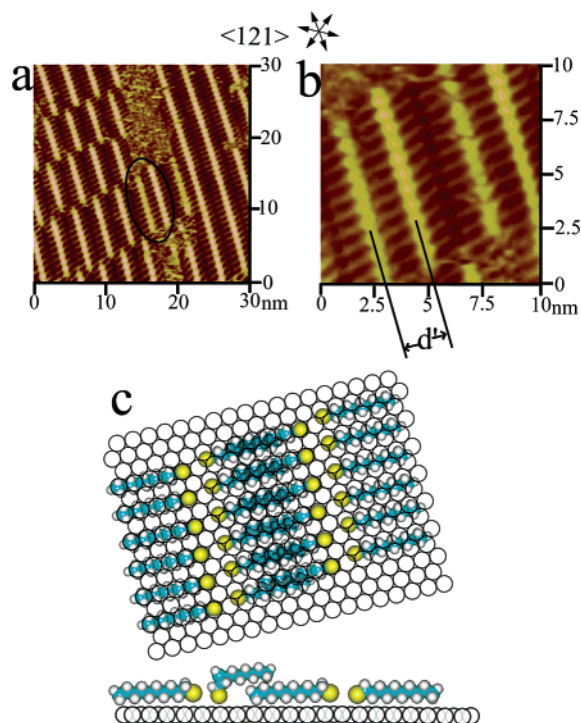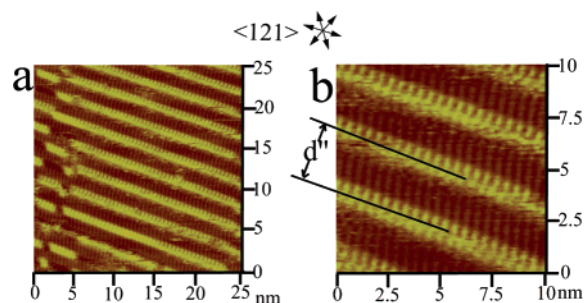

Figure 5. (a) Large-scale and (b) higher-resolution STM images of decanethiol molecules adsorbed on Au(111) for 5 min. The imaging conditions are $E = 550$ mV, $I_{tip} = 1.1$ nA. (c) Proposed structural model for the ordered adlayer of decanethiol molecules adsorbed on Au(111). The stacking structure appears.

the Au(111) surface when immersion times are 1 and 2 min, respectively. It can be seen from the images that the decanethiol SAM is composed of stripes. Although the stripes still align with the $\langle 121 \rangle$ direction of the underlying Au(111) lattice and the molecular organization remains unchanged, the length of the stripes increases. In fact, in Figure 3a, we could also see longer stripes than those consisting of eight molecules occasionally. However, the adlayers in Figure 4 are composed mainly of longer stripes. In Figure 4a, the length of some stripes, such as that indicated by an arrow is 2.47 ± 0.2 nm, and some stripes may contain more than eight sample molecules in a stripe. In Figure 4b, the length of the longest stripe reaches to about 6 nm, containing more than 20 sample molecules. With the increase of immersion time, the surface coverage of decanethiol molecules will increase. On the other hand, the molecules have more time to organize on the solid surface. Therefore, the molecules will self-organize into a more dense organization. From the observed results, it appears that the short stripes could incorporate each other and combine into long stripes during the SAM formation. The origin and driving force of the gradual growth are attributed to the self-organization of the molecules. The final structure induced is the equilibrium state of the organization under a definite coverage.

Stacking Structure at 5 min. By increasing immersion time to 5 min, the molecular stripes become longer. Figure 5a is a typical STM image acquired on a SAM prepared at this immersion time. On the right part of the image, it is seen that the stripes extend the whole frame. The stripe length is measured to be more than 30 nm. On the left side, the length of most stripes reaches at least 7 nm.

Although the molecular organization in a stripe is almost the same as that in Figure 4, it is found that a stacking structure appears in this immersion time. The stacking feature can be seen in the part circled in Figure 5a. It is clear that the distance between the two stripes in the circle is shorter than the stripe
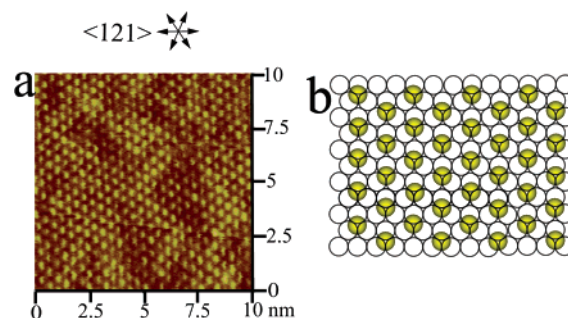
Figure 6. (a) Large-scale and (b) higher-resolution STM images of decanethiol molecules adsorbed on Au(111) for 10 min. The imaging conditions are $E = 550$ mV, $I_{tip} = 1.2$ nA. The stacking structure can be seen in most of the image.

Figure 7. (a) Higher-resolution STM image of decanethiol molecules adsorbed on Au(111) for 3 days. The imaging conditions are $E = 550$ mV, $I_{tip} = 1.0$ nA. (b) Proposed structural model for the ordered adlayer of decanethiol molecules adsorbed on Au(111).

distance in the other part of the image. Figure 5b is a higher-resolution STM image of the circled part in Figure 5a. The orientation of the stripe is still along ⟨121⟩. The stripe distance d' from the bright band, which is the position of sulfur atoms, is measured to be 2.19 ± 0.2 nm, which is shorter than the distance d in Figure 3b. From the STM image and measured distance, it is concluded that a new organization of the decanethiol molecules is formed. The organization originates from the stacking process of alkyl chains in alkanethiol molecules as reported in the literature.[26] The alkyl chains in the neighboring stripes are now overlapping each other, resulting in the stacking structure. The results clearly demonstrate the starting of a stacking process in the present experiment condition. A potential structural model for the stacking structure is proposed in Figure 5c. The alkyl chains in one molecular row of a stripe bend and overlap onto the molecules in another molecular row. The model is consistent with the STM observation and with that described in refs 25 and 26. The special organization induces a shorter stripe distance and a stacking structure. In this configuration, the decanethiol molecules are packed densely in a high surface coverage.

The stacking process proceeds with an increase of immersion time. Figure 6a is a STM image recorded on the decanethiolate adlayer when the Au(111) electrode was immersed in decanethiol molecules for 10 min. The stacking structure can be seen in most of this image. The molecular stripes are extending over the atomically flat Au(111) surface in a length more than several tens of nanometers. Figure 6b is a higher-resolution STM image showing the details of the molecular organization. The alkyl chains and bright bands in the stripes are clearly revealed in the image. The interstripe periodicity d'' is decreased to about 2.2 ± 0.2 nm (ca. $7.5a$), indicating a close-packed organization of decanethiol molecules with increasing immersion time.

A structure similar to that in Figure 6 was consistently found on the decanethiolate adlayer, even when the immersion time was increased to 30 min. The length of stripes became longer, and the stacking structure could be seen in a scanning area of 100 nm × 100 nm. However, when the sample was immersed into the solution containing decanethiol molecules for 3 days, a new structure was found. Figure 7a is a typical STM image recorded on a SAM at this experiment condition. The structure can be proposed as a well-known ($\sqrt{3} \times \sqrt{3}$)-R30° symmetry which is consistent with the results reported in the literature.[37,38] Figure 7b is a structural model for this molecular organization, which is an acknowledged one.[39] The sulfur atoms in decanethiol molecules are located in 3-fold positions of the underlying Au-(111) lattice.

The time-dependent experiments reveal the formation process of decanethiol molecules on the Au(111) surface. During this process, different structures such as eight molecular groups and
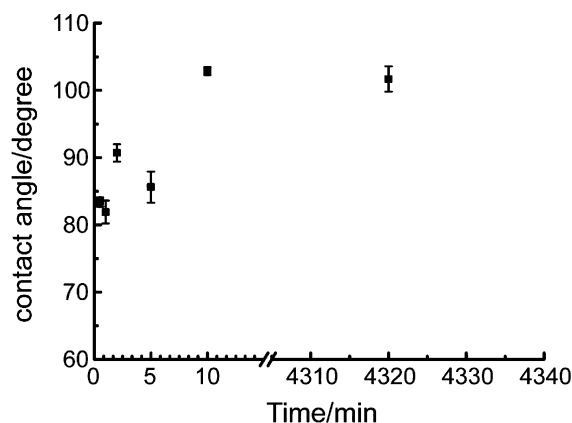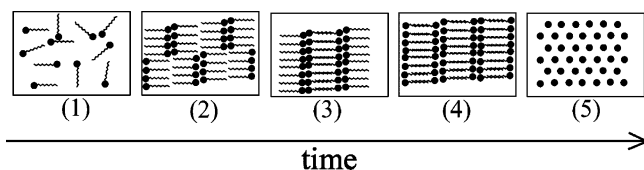

Figure 8. Water contact angle measurement of decanethiolate SAM-modified Au(111) at different immersion times.

stripes could arise due to the variation of the surface coverage and ordering time. The eight molecular group is believed to be one of the intermediate structures. Through a continuous transformation and reorganization, alkanethiol molecules finally form a close-packed adlayer on the Au(111) surface as described in Figure 7 after immersion for 3 days. As mentioned in the Introduction section, the alkanethiolate SAM-modified surface usually shows special surface properties such as wettability. From a random separated adlayer to a close-packed adlayer, the surface wettability was measured to investigate the relationship between the evaluative structure and function.

Contact Angle Measurement. A contact angle measurement was employed to investigate the decanethiol SAM-modified Au-(111) surface. The results of water contact angles measured from the decanethiolate SAM-modified Au(111) are shown in Figure 8. With the increasing of immersion time from 30 s to 5 min, there is no obvious fluctuation of the contact angle. However, the contact angle was changed to $102.9 \pm 0.6°$ when the immersion time is 10 min. With the growth of the decanethiolate adlayer, the surface coverage of the molecules will increase from a loose adlayer to a dense one. The adlayer will form on the surface. The modified Au(111) surface will be prevented by hydrophobic alkyl chains and methyl groups from water adsorption. Therefore, the hydrophobic ability is enhanced. The measurement is consistent with the results reported previously in the literature, [4,40] showing the change of surface property with surface structure.

Conclusion

In summary, we have investigated the process of formation of the decanethiolate self-assembled adlayer on the Au(111) electrode at different immersion times by CV, ECSTM, and

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Figure 9. Schematic diagram of the time-dependent organization: (1) random molecules, (2) small molecular stripes, (3) beginning of stacking organization, (4) stacking organization, (5) final dense structure.

contact angle measurement. The molecular organization was monitored by in situ STM. The systematic study gives a clear image on how the SAMs form and reveals the time-dependent dynamic process on the thiolate/Au interface. The SAM originated from random molecules at the very initial stage, then showed nucleation with small molecular clusters, stable short stripes, stacking organization, and final dense structure. The molecules show a high mobility and active reorganization on the Au(111) surface during the adlayer formation. The schematic diagram in Figure 9 could illustrate the whole time-dependent organization. The results provide the detailed information of alkanethiolate SAM formation on Au(111). We believe the study is a good supplement for investigating the formation process of a thiolate SAM on a solid surface. The time-dependent and predictable structure should be useful in nanotechnology.

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