Monolayer formation of 6-deoxy-6-thiol-β-cyclodextrin on a Au(111) surface studied by scanning tunneling microscopy

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Mono(6-deoxy-6-thiol) β-cyclodextrins (β-CyD–SH) were grown on a Au(111) surface in ethanol solution, and monolayer formation process of which was studied by scanning tunneling microscopy for the first time. At the initial stage, β-CyD–SH molecules were adsorbed on the Au(111) surface not only randomly, but also partially in a linear ordering. In the following stage, islands were formed and resulted in a uniform monolayer. The observed mechanism is completely different from the model predicted on the basis of the macroscopic result, the Langmuir model. An attractive interaction exists between β-CyD–SHs, contrary to the prediction by the model. The observed growth processes are quite similar to what was previously observed for lipoamide–β-cyclodextrin (LP–β-CyD). However, in the case of β-CyD–SH, the islands did not grow in size as compared to the case of LP–β-CyD, and the number of the islands increased to form a uniform monolayer. This characteristic indicates that the interaction strength ratio of CyD–Au to CyD–CyD is larger for β-CyD–SH than that for LP–β-CyD. © *2001 American Vacuum Society.*

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I. INTRODUCTION

Cyclodextrins (CyDs) have a donut-shaped structure consisting of several glucopyranose units as shown in Fig. 1(a), and are able to include various guest molecules in their cavities.[1] Due to this characteristic, they play important roles in the field of catalysts, artificial enzymes, and biosensor devices, such as drug deliverers and material removers with high selectivity. Since structures of CyDs are very simple, they are also important as the models for the analysis of the functions of more complicated molecules.

On the other hand, self-assembled monolayers (SAMs) of organic molecules have been studied extensively in developing the interfacial systems that provide various functional properties on solid surfaces.[2] From a practical point of view for the industrial applications, formation of SAMs on the Au surface by using the molecular chains such as thiols has been most attractive. This technique easily provides stable and highly packed monolayers of functional molecules by simple treatments such as immersion or vapor deposition processes. With this advantage, high potential is expected to realize new molecular devices by fabricating the micromorphology of materials; microcontact printing,[3] lithography with ultraviolet light, and so on. Therefore, in order to use the high potentiality of CyD materials, it is important to establish this technique for the case of CyDs.

Recently, Rojas *et al.* confirmed, by using the electrochemical method, that SAMs of the thiolated CyD derivatives work as molecular receptors to achieve molecular recognition sensors.[4] Thiolated CyD derivatives are adsorbed onto the Au surface by the chemical bonding between sulfur atoms in the molecular chains of thiols and the Au surface, resulting in the CyDs having their cavity axis aligned perpendicular to the Au surface. The conformation of CyD/Au gives functions as a recognition sensor, since CyDs can selectively include molecules into their cavities.

In our recent work, we performed the first microscopic analysis on the structure and formation process of lipoamide–β-cyclodextrin (LP–β-CyD) on the Au(111) surface by using scanning tunneling microscopy (STM), and confirmed that LP–β-CyD molecules uniformly formed a monolayer on the Au substrate.[5] However, in the case of thiolated CyDs modified with long molecular chains, such as LP–β-CyD, the flexibility of the long molecular chain induces unstable CyD motions, resulting in the lower efficiency of the function. Therefore, in order to utilize the high

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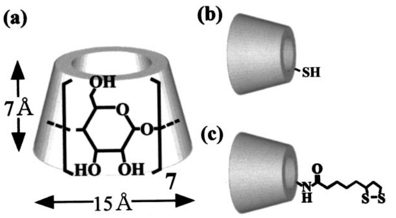

FIG. 1. Schematics of: (a) β-cyclodextrin (CyD), (b) β-CyD–SH, and (c) LP–β-CyD.

potentiality of the material further, it is necessary to clarify the possibility of stabilizing the Au/CyD system using thiolated CyD derivatives with shorter molecular chains. Among such derivatives, since mono(6-deoxy-6-thiol) β-CyD (β-CyD–SH) has only one thiol group on the primary hydroxyl side, the CyD/Au system using β-CyD–SH is expected to be one of the most favorable candidates to realize a stable structure to have a high efficient molecular recognition system.

In consideration of the facts described above, we performed STM analysis on the monolayer formation process of β-CyD–SH molecules on the Au(111) surface. The results obtained were compared with those obtained for the case of LP–β-CyD, which has a longer molecular chain.

II. EXPERIMENT

Figure 1 shows the schematic structures of: (a) β-CyD (consisting of seven glucopyranose units) and (b) mono(6-deoxy-6-thiol) β-cyclodextrin (β-CyD–SH) used in this study. In order to compare the characteristic of β-CyD–SH with the case of CyD modified with longer molecular chains, CyD modified with a lipoamide residue [Fig. 1(c)] was also prepared, and STM observation was performed again.

These molecules were grown on Au substrates at room temperature by immersing the substrates into the 0.01 mM ethanol solution containing the molecules. Au(111) substrates were prepared by the vapor deposition of about 75-nm-thick gold films onto freshly cleaved mica sheets. During Au deposition, the temperature of the mica substrates was kept at 450 °C. The deposition rate was 0.3–1.0 Å/s and vacuum pressure was 1.0×10^{-7} Torr. Following the deposition, they were annealed at 550 °C for 2 h. Each substrate was briefly flamed using a H_2 torch before each experiment. The Au(111)-$22\times\sqrt{3}$ herringbone structure was clearly observed by STM. In order to analyze the molecular structure and the growth mechanism, the β-CyD–SH/Au samples with different molecular densities were prepared by changing the immersion time from 3 s to 6 h. The samples were repeatedly rinsed with ethanol solution and dried with nitrogen gas flow. According to the previous studies, physisorbed molecules can be clearly removed by the rinsing process, and only chemisorbed molecules remain on the surface.[6] All STM observations were performed in constant current mode in air at room temperature using a Pt/Ir tip.

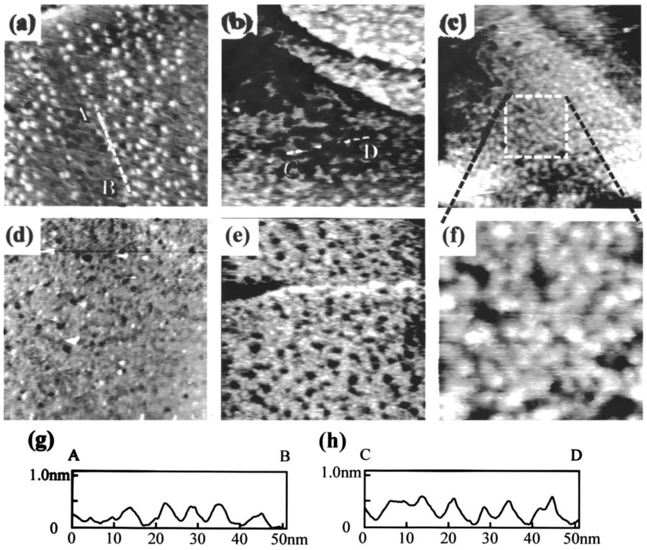

FIG. 2. STM images of β-CyD–SH on Au(111) formed by different immersion times (100 nm×100 nm, $V_s=0.5$ V, $I_t=0.3$ nA): (a) 3 s, (b) 6 s, (c) 60 s, (d) 10 min and (e) 1 h, respectively, (f) magnification of (c). (g) and (h) cross sections along A–B in (a) and C–D in (b), respectively.

III. RESULTS

Figure 2 shows STM images of β-CyD–SH molecules adsorbed on the Au surface for different immersion times of (a) 3 s, (b) 6 s, (c) 60 s, (d) 10 min, and (e) 1 h, respectively. For comparison, results obtained for LP–β-CyD are shown in Figs. 3(a) 1 s, 3(b) 6 s, 3(c) 60 s, 3(d) 10 min, 3(e) 1 h, and 3(f) 3h.

At the initial stage, β-CyD–SH molecules adsorbed on the Au surface not only randomly, but also in partially linear ordering, as shown Fig. 2(a). Similar structure was observed at the initial adsorption stage of LP–β-CyD on the Au sur-

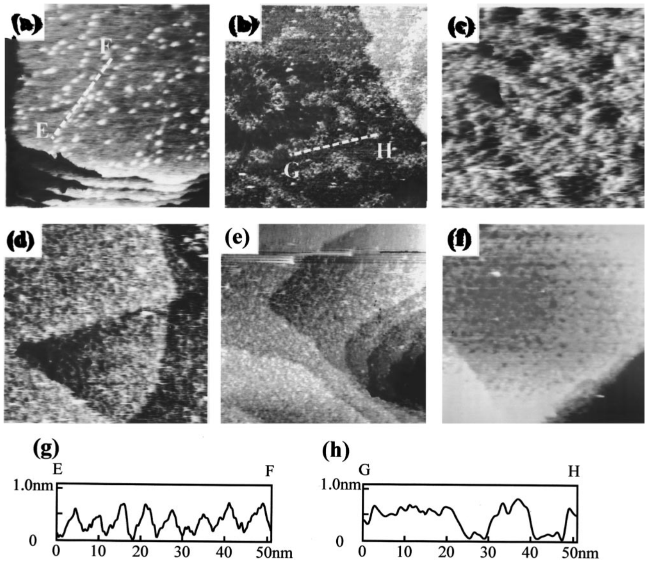

FIG. 3. STM images of LP–β-CyD on Au(111) formed by different immersion times (100 nm×100 nm, $V_s=0.5$ V, $I_t=0.3$ nA): (a) 3 s, (b) 6 s, (c) 60 s, (d) 10 min, (e) 1 h, and (f) 6 h, respectively. (g) and (h) show the cross sections along A–B in (a) and C–D in (b), respectively.

face. These results indicate that the herringbone reconstructed structure of the Au(111) surface must have an influence on the molecular adsorption at the initial stage.

As shown in the cross sections in Figs. 2 and 3, the apparent height of β-CyD–SH and LP–β-CyD molecules was about 0.4 and 0.6 nm, respectively. The difference in the height was confirmed by measuring the height of the single Au atomic steps, 0.25 nm. The height difference may be related to the difference of the molecules used for the modification. For example, it may be due to the fact that the LP–β-CyD molecule has a stable lipoamide residue. However, further analysis including theoretical calculation is needed to understand the details.

In the following stage, many island structures were observed as shown in Fig. 2(b). As the immersion times were increased, the Au surface was fully covered with β-CyD–SH [Fig. 2(c)], and β-CyD–SH molecules were adsorbed densely as expected.

The observed initial growth processes of β-CyD–SH are almost the same as that of the LP–β-CyD case shown in Fig. 3. However, details were different. Island size of LP–β-CyD grew with the immersion time until the formation of a monolayer. On the other hand, in the case of β-CyD–SH, the islands did not grow in size, and the number of islands increased to form a monolayer [Fig. 2(c)]. Growth speed and time to complete the monolayer formation were shorter for the case of β-CyD–SH. With further increase of the immersion time after monolayer formation, many etch pit-like defects appeared for both cases [Figs. 2(d)–2(e) and 3(f)].

IV. DISCUSSION

As shown Figs. 2(c) and 2(f), β-CyD–SH molecules adsorbed on the Au surface and formed a monolayer structure with high density as expected. According to the macroscopic analysis, the growth process of the β-CyD–SH molecule was explained by the Langmuir mechanism, which is the growth model without any interaction between molecules.[6] However, in the observed growth process of β-CyD–SH, many island structures were observed [Fig. 2(b)] as well as the case of LP–β-CyD molecules [Fig. 3(b)]. Since island formation is induced by the attractive interaction between molecules, the observed process cannot be explained by the Langmuir model. In consideration of the fact that CyDs contain many hydroxyl groups [Fig. 1(a)], attractive interaction between CyD molecules is expected to occur due to the hydrogen bonding as observed experimentally.

The wrong prediction on the basis of the previous works is thought to be due to the uncertainty of the macroscopic analysis. Since macroscopic analyses only give information averaged over the surface, accurate analysis of the microscopic structure is difficult. Our observation of the β-CyD–SH growth mode strongly indicates the importance of the microscopic analysis as previously pointed out through the STM experiment on LP–β-CyD.

In the case of LP–β-CyDs, as the immersion time increased, the island size of LP–β-CyD grew until the completion of the monolayer formation. On the other hand, in the case of β-CyD–SH, the island did not grow in size, but the number of island increased to form a monolayer. Figure 4 shows the histogram of the observed island sizes of β-CyD–SH (gray bar) and LP–β-CyD (white bar) molecules, respectively. The data were extracted from the STM images obtained for 6 s immersion time [Figs. 2(b) and 3(b)], respectively. The island size and dispersion are smaller for the case of β-CyD–SHs. In the case of β-CyD–SH, the observed island size was saturated through the growth (average diameter was about 6.6×6.6 nm^2), and monolayer was formed by the increase in the number of islands.

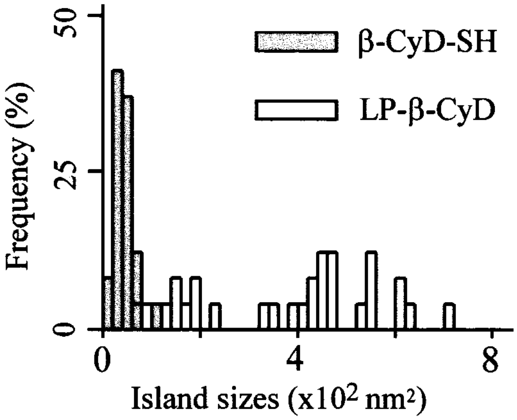

FIG. 4. Histogram of observed island size of β-CyD–SH and LP–β-CyD, respectively. The sampling of dates performed the results of STM images for 6 s immersion times.

Generally, the diffusion length of molecules on the Au surface is a crucial factor to govern the island size, and is determined by the relation of the intermolecular interaction between CyD molecules and the chemical reaction process between Au and S atoms in molecular chains. In consideration of the observed smaller island size for β-CyD–SH, it is concluded that the strength ratio of interactions, CyD–Au to CyD–CyD, is larger for β-CyD–SH than that for LP–β-CyD.

Etch pit-like defects in the alkanethiol monolayer are considered to be formed by the release of Au atoms due to S–Au interaction.[7] Since the time to form the monolayer and the appearance of the etch pit-like defect were faster for the case of β-CyD–SH, β-CyD–SH molecules are more strongly adsorbed on the Au surface compared to LP–β-CyD.

V. CONCLUSION

The structure and growth process of β-CyD–SH molecules adsorbed from ethanol onto the Au(111) surface were studied microscopically using STM for the first time. The results obtained were completely different from those predicted on the basis of the macroscopic analyses. The observed interaction between β-CyD–SH molecules was attractive, which differs from the previous predictions of the Langmuir model of no interaction between the molecules. From our STM analysis, structure and growth of the CyD adlayer depend on the kind of CyD derivatives, suggesting the existence of controllability of the functional molecular structures on the Au surface by changing the immersion time and the kind of molecular chains.

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