Scanning tunneling microscopy on the formation of lipoamide-cyclodextrin monolayer on Au(111)

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β-cyclodextrin molecules modified with lipoamide residue (LP-β-CyD) were self-assembled on an Au(111) surface in ethanol solution, and the growth process was studied by scanning tunneling microscopy. At the initial stage, adsorption sites were not only random, but also partially linear ordering, which suggests the existence of some influence by the herringbone structure of the Au(111) surface. According to the macroscopic analysis, the subsequent growth process was explained by the Elovich model, which is based on the repulsive interaction between adsorbed molecules. However, when the immersion time increased, island structures began forming. This result suggests the interaction between LP-β-CyD molecules as attractive, which in fact is more probable in consideration of the possibility of the hydrophobic and the hydrogen bonding interactions between CyD molecules. Finally, formation of a single LP-β-CyD layer was clearly confirmed. © *2000 American Institute of Physics.* [S0003-6951(00)01405-4]

In order to design and develop multifunctional molecular devices, the formation of thin/monolayer films using the self-assembling technique has been the main focus of many researchers.[1–20] Among them, the formation of cyclodextrin (CyD) derivative monolayers is attracting considerable attention because of their high potential for applications such as in novel molecular recognition sensors. CyDs are donut-shaped cyclic oligosaccharides consisting of several glucopyranose units [Fig. 1(a)], and are able to form host–guest complexes by including various molecules (guest molecules) in their cavities.[6] In addition, the inclusion process can be controlled by chemical modification of CyDs with additional residues. For example, when an azobenzene molecule, which shows a cis-trans transformation by photostimulation, is attached to the top of the CyD cavity,[7] the inclusion process becomes controllable by photoswitching. Therefore, if the formation of the CyD monolayer is achieved, a multifunctional molecular device can be realized.

Recently, Rojas *et al.* showed the high potential of CyD molecules as a molecular receptor by cyclic voltammetry for thiolated CyDs self-assembled on Au.[8] Since thiolated CyDs are adsorbed onto the Au surface as a result of the chemical bonding between S atoms in the molecules and the Au surface, they are considered to be located on the Au surface

with their cavity axis aligned perpendicular to the surface. The conformation was confirmed by the analysis of the fourier transform infrared-reflection absorption spectroscopy.[9] When a Au electrode was covered by only pentanethiol molecules, no redox signal of the electroactive marker, ferrocene
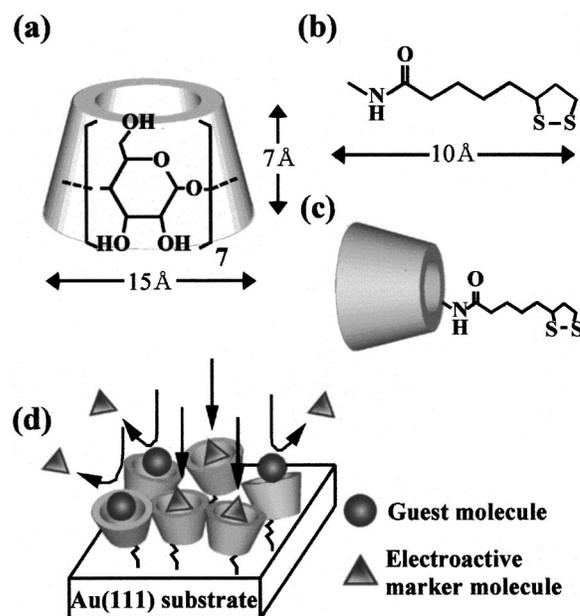

FIG. 1. Schematic structures of (a) β-CyD, (b) LP, (c) β-CyD modified with LP, and (d) molecular recognition by LP-β-CyD monolayer.

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molecules, was observed because the pentanethiol molecules prevented the electroactive marker from reaching the Au surface. However, when the Au electrode was covered by both pentanethiol and thiolated β-CyD molecules, the reversible redox current could be measured. Furthermore, using CyDs modified by lipoamide residue, Suzuki *et al.* demonstrated that the signal of the redox current by the ferrocene carboxylic acid changed with the concentration and a species of the guest molecules in the solution.[10–12] Namely, inclusion of the guest molecules prevented the electroactive marker from reaching the Au surface through the cavity [Fig. 1(d)]. These results led to the suggestion that CyD monolayers were formed, and the existence of guest molecules could be identified due to the reduction in the current. However, from the analysis of a similar system by plasmon and surface polariton spectroscopy,[13] a quasidoublelayer structural model was proposed to explain the observed change in the dielectric constant.[14] Furthermore, the formation process of the molecular layer was explained by the Elovich mechanism which includes a repulsive interaction between molecules. Since, CyDs contain many hydroxyl groups [Fig. 1(a)], attractive interaction between CyDs due to the hydrogen bonds is considered to be more probable.[3–5] Hydrophobic interaction is supposed to work as attractive, too. As has been described, despite the important characteristics of the CyD/Au system, some contradictions exist among the obtained results. Therefore, in order to utilize the high potentiality of this system, it is extremely important to clarify this point. As is well known, since macroscopic measurements give information averaged over the surface, the results sometimes differ from the microscopic structure. For example, regarding the growth process of the self-assembled alkanethiols on Au(111), macroscopic analyses such as contact angle measurement and ellipsometry predicted it to be according to the Langmuir model, i.e., initial random and homogeneous adsorption.[15] In addition, the molecular arrangement determined by He atom diffraction and other method was a $\sqrt{3} \times \sqrt{3}$ structure.[16] However, the microscopic analysis using scanning tunneling microscopy (STM) and atomic force microscopy revealed that a nucleation and domain growth mode existed in the process, and coexistence of the closed packed $c(4 \times 2)$ and $n \times \sqrt{3}$ (n: integer) structures was confirmed at the initial stage.[17,18] Furthermore, formation of numerous pit-like defects was observed during the growth process.

In consideration of these facts, in order to utilize the high potentiality of the CyDs that has been demonstrated by Rojas *et al.*, structural analysis of CyD/Au(111) from a microscopic viewpoint is urgently required. Therefore, we performed the first microscopic analysis of this system using STM. As considered, the obtained results were completely different from those predicted by the macroscopic analyses.

Figure 1 shows the schematic structures of (a) β-CyD (consisting of seven glucopyranose units), (b) lipoamide residue (LP), and (c) thiolated β-CyD derivative used in this study. As shown in Fig. 1(c), CyDs were modified with a lipoamide residue chemically added onto the primary hydroxyl side (LP-β-CyD).[11] The molecules were grown on the Au substrates by immersing the substrates into the 0.01 mM ethanol solution with LP-β-CyD molecules at room temperature. The Au(111) substrates were prepared by the vapor
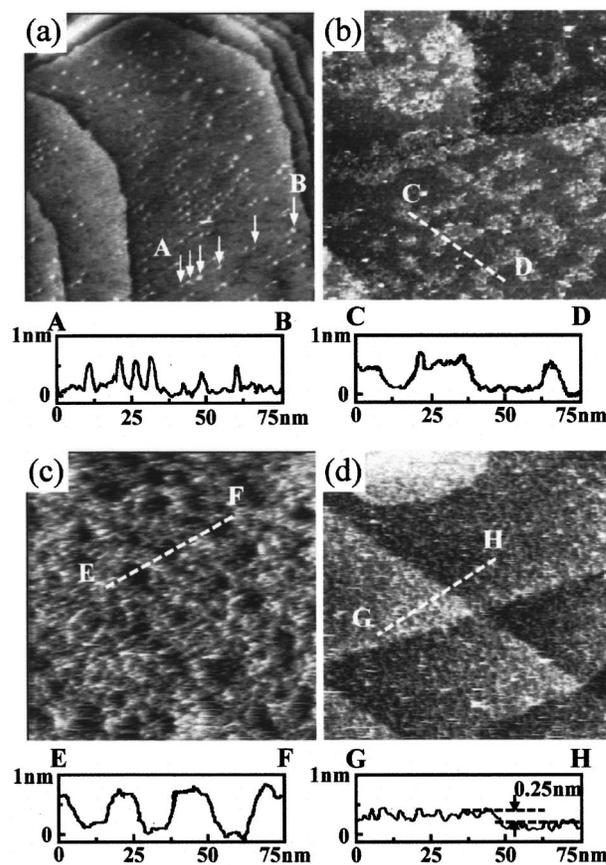

FIG. 2. STM images of LP-β-CyD on Au(111) (150 nm $\times$ 150 nm) formed by different immersion times, (a) 3 s ($Vs = 1.0$ V, $It = 0.2$ nA), (b) 6 s ($Vs = 2.0$ V, $It = 0.3$ nA), (c) 60 s ($Vs = 1.0$ V, $It = 0.2$ nA), and (d) 10 min ($Vs = 2.0$ V, $It = 0.2$ nA), respectively.

deposition of about 75-nm-thick gold films onto freshly cleaved mica sheets. During Au deposition, 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. Brief flame annealing was performed before each experiment. The Au(111)-22 $\times \sqrt{3}$ herringbone structure was clearly observed on these surfaces by STM.

In order to analyze the molecular structure and the growth mechanism, the LP-β-CyD/Au samples with different molecular densities were prepared by changing the immersion time from 3 s to 12 h. They were repeatedly rinsed with ethanol solution and dried with nitrogen gas flow. According to previous studies,[14] physisorbed molecules can be clearly removed by the rinsing process, and only chemisorbed molecules remain on the surface. All STM observations were performed in constant current mode in air at room temperature using Pt/Ir tips.

Figure 2 shows STM images of the LP-β-CyD molecules adsorbed on Au(111) for different immersion times; (a) 3, (b) 6, (c) 60 s, and (d) 10 min. Cross sections along A–B, C–D, E–F, and G–H in STM images are also shown. The amount of adsorbed LP-β-CyD molecules increased with the immersion time, as predicted. However, the detailed adsorption process, as observed by STM, was completely different from that predicted from the macroscopic analyses.

First, at the initial stage, a few LP-β-CyD molecules adsorbed on the Au(111) surface. These adsorption sites

Appl. Phys. Lett., Vol. 76, No. 5, 31 January 2000

Yasuda *et al.* 645

were not only random, but looked in part linearly ordered, as shown in Fig. 2(a). According to the recent STM study of the self-assembled 4-mercaptopyridine molecules similarly formed on the Au(111) surface, a similar molecular nucleation along the ordered lines was observed.[19] Similarly ordered nucleation was also observed for a Ni atom on the Au(111) formed by vapor deposition.[20] These results indicate that the herringbone reconstructed structure of the Au(111) surface strongly influences the molecular adsorption at the initial stage. In consideration of these facts, the adsorption site of the LP-β-CyD molecules may be related to the herringbone structure as in the other cases. Since the herringbone structure is relaxed rapidly by the molecular adsorption, further study is necessary to clarify its effect on the growth mode in the very early stage.

Next, we analyze the growth process in further detail. According to the macroscopic measurements,[14] the growth process of CyD derivatives is considered to be governed by the Elovich growth model;

$$d\Theta/dt \sim (1-\Theta)\exp(-\alpha\Theta/RT)$$

where, Θ, α, and R represent surface coverage, activation energy, and gas constant, respectively. The rate equation is based on the repulsive interaction between molecules as is represented by the Θ-dependent exponential factor. Increase in the number of unoriented molecules on the surface is an example for the suppression. However, as is shown in Fig. 2(b), islands of LP-β-CyD molecules are formed on Au(111). Since island formation is caused by the attractive interaction between molecules, the observed structure can not be explained by the Elovich or the simple Langmuir ($\alpha \to 0$) model. In fact, in consideration of the fact that CyDs contain many hydroxyl groups [Fig. 1(a)], attractive interaction between LP-β-CyDs due to the hydrogen bonds is more probable. This difference may be due to the uncertainty of the macroscopic analysis. In fact, there exist large error bars in the data on which the Elovich model was based.[14] Therefore, ruling out the island growth mode from the data only appears to be difficult.

As shown in the cross sections, the height of the molecules in Figs. 2(a)–2(c) is ~0.6 nm, and is in good agreement with the size of a single CyD. Since STM measurements were performed in air, CyD molecules were directly on the substrate. When the molecular density is saturated [Fig. 2(d)], molecules are almost uniformly adsorbed, and triangularly shaped terraces are observed on Au(111), which reflects the surface structure of the Au(111) substrate. And the height difference between two neighboring terraces is 0.25 nm, which is close to the value of an Au(111) step height. Therefore, contrary to the quasidoublelayer structure predicted on the basis of the macroscopic analysis, a monolayer structure is formed on the surface.

As has been discussed, the structure and growth process

of the self-assembled LP-β-CyD on Au(111) were studied using STM. The obtained results were different from those predicted by the macroscopic analysis. At the initial stage, LP-β-CyD molecules, as being partially influenced by the herringbone structure, adsorbed on the Au surface. Since island formation was observed in the intermediate stage, interaction between the LP-β-CyD molecules must be attractive, which differs from the previous predictions of the Elovich model. Finally, distinct monolayer structural formation of LP-β-CyD molecules was observed on the surface. Since the other works were performed using Au substrates without confirming their surface structures, atomic scale structure of the Au surface may play an important role in the observed formation process. In any case, since LP-β-CyD molecules form a monolayer on Au, application of the LP-β-CyD/Au system for the fabrication of multifunctional molecular devices has become more probable.

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