Highly Ordered Coronene Adlayer on Au(111) Surface Formed in Benzene Solution: In situ Scanning Tunneling Microscopy Study

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The technique of in situ scanning tunneling microscopy (STM) revealed that a highly ordered adlayer of coronene molecules was formed on an Au(111) surface by first immersing the substrate in benzene containing dissolved coronene and then transferring it into an aqueous solution of $HClO_4$.

In interfacial electrochemistry, scanning tunneling microscopy (STM) has been widely accepted as a powerful tool for understanding the structure of adsorbed layers of molecules at electrolyte-electrode interfaces.[1,2] High-resolution STM has made it possible to directly determine packing arrangements and even internal structures of organic molecules adsorbed at electrode-electrolyte interfaces. We have previously reported adlayer structures of benzene, naphthalene and anthracene on well-defined Pt(111),[3] Rh(111),[3,4] and Cu(111)[5] electrode surfaces using aqueous solutions of these molecules.

However, it has been difficult to investigate adlayer structures of larger aromatic molecules such as perylene, and coronene because of their low solubility in aqueous electrolytes. Nevertheless, we have been interested in extending our investigation of adlayer structures of aromatic compounds to include such large molecules. For the present study, we selected coronene, which is a hydrophobic planer molecule composed of six symmetrically arranged benzene rings, especially because it has already been studied on highly ordered pyrolytic graphite (HOPG), MoS_2 and metal surfaces in ultrahigh vacuum (UHV) by using low-energy electron diffraction (LEED),[6] near-edge X-ray absorption fine structure (NEXAFS),[7] STM,[7,8] and scanning tunneling spectroscopy (STS).[9] Ordered organic layers are usually prepared by the molecular beam epitaxy (MBE) technique in UHV environment.[6–9]

In this paper, we propose a new approach for the preparation of a highly ordered coronene adlayer on Au(111) surface by immersing it into coronene-benzene solution, and report the results of our successful in situ STM imaging of the adlayer structure of coronene directly attached to a well-defined Au(111)-(1 × 1) electrode surface in 0.1 M $HClO_4$. The packing arrangement of coronene on Au(111) electrode was accurately determined by high-resolution STM.

Au(111) single-crystal electrodes were prepared by the Clavilier method.[10] Coronene adlayer was formed on an Au(111) electrode by immersion into a *ca.* 10 μM coronene solution in benzene for 10–20 s, after the electrode was flame-annealed in a hydrogen flame and quenched into ultrapure water saturated with hydrogen.[10] The coronene-adsorbed Au(111) was rinsed by pure benzene, ultrasonicated in ultrapure water for 20 s to remove excess benzene, and then transferred into an electrochemical cell for STM measurements. The solution was prepared with $HClO_4$ (Cica-Merck) and ultrapure water (Milli-Q SP-TOC; $\geq 18.2\,M\Omega\,cm^{-1}$). Coronene and benzene were obtained respectively from Aldrich (sublimed, 99%) and Kanto Chemical Co. (Spectroscopy Grade) and used without further purification. Electrochemical STM measurements were performed by using a Nanoscope E with a tungsten tip etched in 1 M KOH. To minimize residual faradic currents, the tips were coated with nail polish. STM images were recorded in the constant-current mode. All potential values are referred to the reversible hydrogen electrode (RHE).

Figure 1 shows typical STM images of a coronene adlayer acquired at 0.75 V (near the OCP) on Au(111) in 0.1 M $HClO_4$. In the image acquired for the relatively large area of $50 \times 50\,nm^2$, each coronene molecule can be clearly recognized as shown in Figure 1a. A highly ordered molecular array was observed consistently over the wide terraces with almost no pits. The molecular rows consist of bright spots and cross each other at an angle of either 60° or 120° within an experimental error of ±2°. To obtain structural details of the coronene adlayer, molecular resolution STM images were also acquired at 0.75 V. A typical high-resolution STM image is shown in Figure 1b. Each molecule of coronene is clearly seen as a hexagon consisting of small spots. A cross-sectional profile along the arrow sign in Figure 1b is shown in Figure 1c. From this profile, the length of a side of one bright hexagon was found to be *ca.* 0.95 nm, which is in good agreement with the molecular diameter. The average corrugation height was found to be *ca.* 0.1 nm, which is comparable to that of benzene, naphthalene and anthracene, supporting that coronene molecules adsorbed on Au(111) surface lie flat on the Au surface. Therefore, each bright hexagon is attributed to one coronene molecule with a flat-lying orientation on the Au(111) surface. The intermolecular spacing along the $\langle 110 \rangle$ direction was estimated to be 1.17 ± 0.03 nm, which corresponds to 4 times the Au lattice constant (4×0.289 nm). A precise comparison between this image and that of the underlying Au(111)-(1 × 1) lattice revealed that the molecular rows are in parallel with the atomic directions of Au(111). From the result described above, the adlattice of coronene on Au(111)-(1 × 1) can be defined as a (4 × 4) structure with a surface coverage of 0.0625, as shown by the adlattice superimposed in Figure 1b. Identical (4 × 4) structures were consistently observed in the potential range between 1.0 and 0.1 V. It is noted that the CV profile of an Au(111) electrode which had been immersed in pure benzene containing no coronene was essentially the same as that observed with a clean Au(111) electrode, indicating that benzene does not adsorb on Au(111) surface. In this study, the (4 × 4) symmetry was also confirmed by ex situ LEED measurement in UHV. Details will be described in a separate paper.[11] Very recently, the LEED study on the adlayer structures of coronene formed on Au(111) using MBE in UHV was reported by Seidel et al.[12] The close-packed (4 × 4) adlayer of coronene was formed on Au(111) not only in solution but also

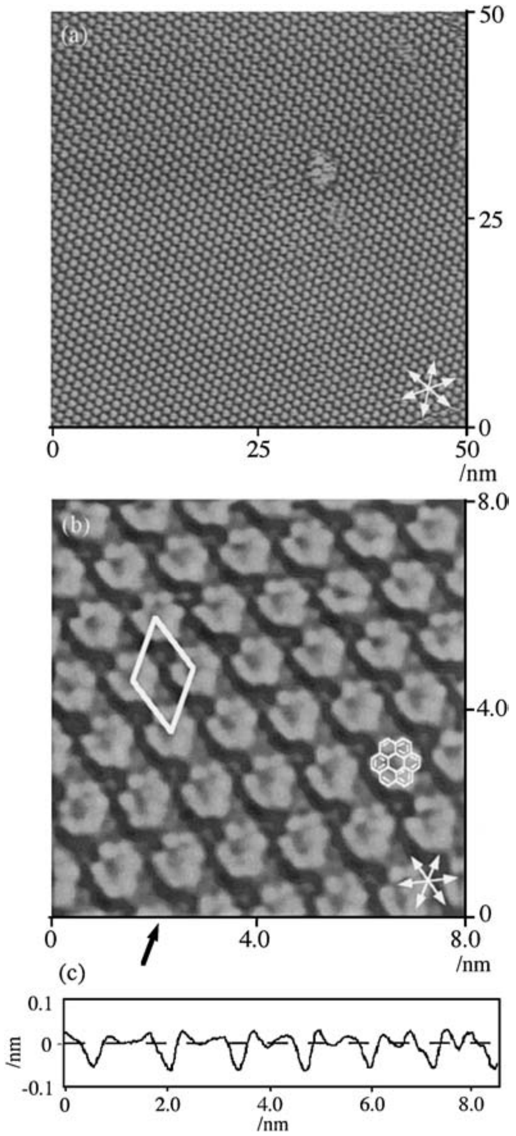

Figure 1. (a) large-scale ($50 \times 50\,\mathrm{nm}^2$) and (b) high-resolution ($8 \times 8\,\mathrm{nm}^2$) STM images of coronene adlayer on Au(111) surface in 0.1 M $HClO_4$ acquired at 0.75 V vs RHE. Potential of the tip and tunneling current were 0.35 V and (a) 7.0 nA and (b) 28.6 nA, respectively. Three set of arrows indicate the close-packed direction of Au(111) substrate. The cross-sectional profile in (c) depicts the corrugation along the arrow in (b).

in UHV. A model of coronene adlayer on Au(111) surface is presented in Figure 2. Although an experimental proof has not been presented in this study, the center of coronene is assumed to be located on a three-fold hollow site of Au(111)-(1×1) as a preliminary model.

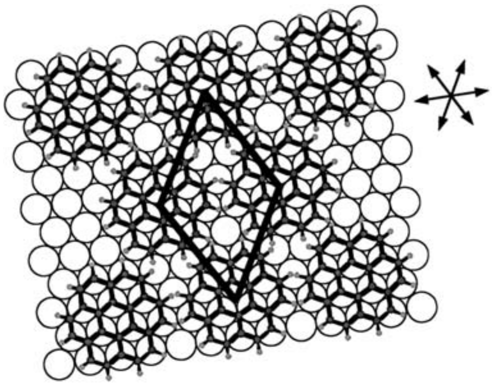

Figure 2. Proposed model of coronene-adsorbed on Au(111) surface with a (4×4) unit cell.

In summary, we succeeded for the first time in preparing a highly ordered coronene thin film using the coronene-benzene solution and in resolving the packing arrangement and the internal structure of each coronene molecule adsorbed on Au(111) electrode in $HClO_4$ at room temperature by high-resolution STM. Coronene formed a highly ordered adlayer on Au(111) surface. The high-resolution STM image revealed a commensurate (4×4) symmetry with a flat-lying orientation at 0.75 V vs RHE. The method described above is expected to be extendable to the investigation of many other water-insoluble organic molecules.

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