

In Situ STM Investigation of Self-Assembled Monolayers of Short-Chain Alkanethiols Terminated with Functional Groups on Au(111)

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Formation of organic monolayers on metal surfaces in solution has attracted wide attention in the fields of fundamental surface science and interfacial electrochemistry [1]. Self-assembled monolayers of alkanethiols on gold have been intensively studied with great interest and it is well known that they are closely packed through the thiolate-gold bond formation and hydrophobic interaction between alkyl chains [2,3]. On the other hand, alkanethiols terminated with functional groups, such as a carboxylic acid and an amine, are much more important for many applications. Because of specific functions of the terminal groups, they have been used to control surface properties and immobilize foreign molecules on the monolayer [4,5]. In this study, in situ scanning tunneling microscopy (STM) was employed to investigate self-assembled monolayers of short-chain alkanethiols terminated with carboxylic acid and amine, i.e., 3-mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{COOH}$: MPA) and 2-aminoethanethiol ($\text{HSCH}_2\text{CH}_2\text{NH}_2$: AET), on Au(111) in solution.

Au(111) single crystal electrodes were prepared by the crystallization at the end of Au wires in a hydrogen-oxygen flame and final treatment of the Au(111) followed the well-known annealing-and-quenching method. The monolayers were prepared by immersing a clean Au(111) electrode into a freshly prepared modifying solution containing 50 μM thiol. In situ STM imaging of the monolayers was carried out in perchloric acid solution with a Nanoscope E, and an electrochemically etched tungsten or Pt/Ir(80:20) tip was used with coating of transparent nail polish to minimize the faradaic current. The electrode potentials were referred to the reversible hydrogen electrode (RHE).

Figure 1 shows a high-resolution STM image for MPA monolayers on Au(111) in 0.05 M HClO_4 . It was clearly observed that the MPA monolayer exhibited a molecularly ordered structure, which showed a distinctive pattern consisting of plenty of bright spots. The preferential direction through the brightest spots were exactly parallel to a $[110]$ direction, i.e. the close-packed direction of the Au(111) substrate. A periodic distance between the brightest spots was found to be 0.890 nm, which corresponds to 3 times the Au(111) lattice constant (0.2885 nm). The STM image indicates that the MPA monolayer can be explained by a (3×3) structure [6,7], and the rhombic (3×3) unit cell was overlaid in the Fig. 1. It is also seen that 6 – 7 spots were gathered near the corner of the (3×3) unit cell, where the distance between the nearest spots was measured to be 0.275 nm and the next neighbor distance of the spots was 0.452 nm. In consideration of the molecular size of MPA, it is expected that three MPA molecules were located in the vicinity of the corner of (3×3) unit cell, and each MPA molecule appeared as two spots which presumably originate from oxygen atoms of the carboxylic group of MPA molecules. The intermolecular distance of 0.452 nm for the MPA monolayer was slightly smaller than that of 0.5 nm for long-chain alkanethiol monolayers. It is suggested that intermolecular interaction

exists in the MPA monolayer, which is thought to be hydrogen bonding among the terminal carboxylic acid groups of neighboring MPA molecules. The in situ STM imaging revealed the existence of intermolecular hydrogen bonding in the MPA monolayer.

The AET monolayers exhibited a patched surface feature with ordered and fuzzy portions. In the molecularly ordered portion, the AET monolayer with a rectangular $(p \times \sqrt{3})$ structure was observed, showing a striped pattern with molecular rows extending toward a $[121]$, the so-called $\sqrt{3}$ direction, and a periodic distance of 0.5 nm. Although details of the fuzzy portions are not clear yet, it is thought that the AET monolayer would be distorted by hydration of terminal amine groups. These results indicate the complexity of the episurface of the MPA and AET monolayers due to the intermolecular hydrogen bonding at the terminal functional groups.

References

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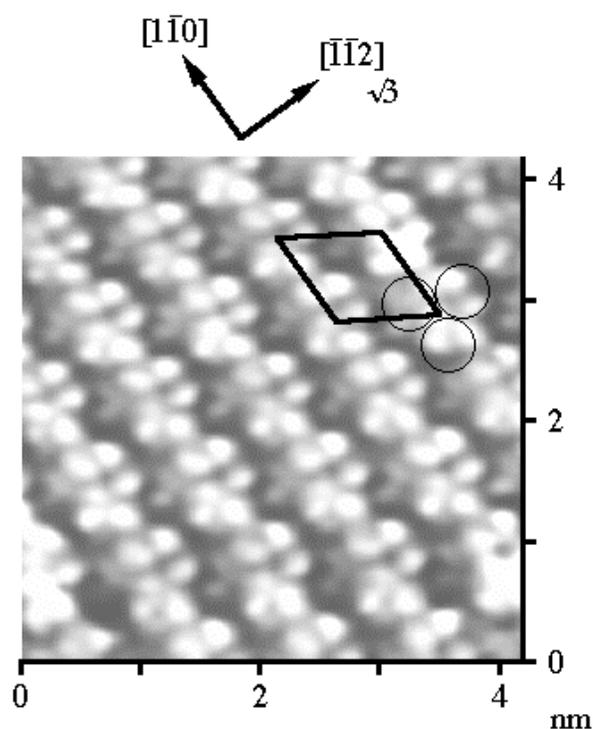


Figure 1 A high-resolution STM image of self-assembled monolayers of MPA on Au(111) in 0.05 M HClO_4 . The potentials of the sample and tip were 0.75 and 0.26 V vs. RHE, respectively. The tunneling current was 4 nA. The rhombic (3×3) unit cell was overlaid in the image.

