Nanostructures of Short-Chain Alkanethiol Monolayers on Au(111) : Molecular Arrangements at Phase Boundaries

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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. Self-assembled monolayers of short-chain alkanethiols terminated with functional groups, such as a carboxylic acid, 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 [1-4]. We used in situ electrochemical scanning tunneling microscopy (EC-STM) to study the interfacial nanostructures of self-assembled monolayers of 3-mercaptopropionic acid ($HSCH_2CH_2COOH$: MPA) on Au(111) in solution, and describe here the detailed molecular arrangements at phase boundaries of the ordered MPA domains.

An Au(111) single crystal electrodes was used in this study and the monolayers were prepared by immersing a clean Au(111) electrode into a freshly prepared modifying solution containing 50 μ M MPA. In situ STM imaging of the monolayers was carried out in perchloric acid solution. The electrode potential was controlled with respect to the reversible hydrogen electrode (RHE).

MPA molecules formed a molecularly ordered monolayer with a (3×3) structure on Au(111) [5]. We frequently found interesting phase boundaries between two ordered MPA domains, where the ordered molecular rows parallel to the direction of Au(111) atomic rows were mismatched. Figure 1(a) shows a high-resolution STM image for one of the phase boundaries between the ordered MPA domains on Au(111) in 0.05 M $HClO_4$. The ordered molecular rows aligned to the direction of Au(111) atomic rows were composed of clusters of 6-7 spots, in which three neighboring MPA molecules in triangular positions stand slightly close due to intermolecular hydrogen bonding. The average value of intermolecular distances was 0.453 nm. At an interface of the two nearly perfect (3×3) domains, the molecular rows were displaced as indicated by an arrow, and the mismatch deviation was found to be ca. 0.25 nm.

Figure 1(b) shows a model structure of the phase boundary shown in Fig. 1(a). The molecular arrangement resembles that of the $(\sqrt{3} \times \sqrt{3})R30°$ structure, but three adjacent MPA molecules in triangular position are slightly gathered to form each MPA cluster in this model. The clusters are arranged linearly and repeatedly along the direction of Au(111) atomic rows to construct the (3×3) structure. The rhombic (3×3) unit cell with a triangular cluster of three MPA molecules was superimposed in Figs. 1(a) and (b). At the domain boundary, two (3×3) domains are shifted by one-third of the (3×3) unit cell and a single molecular row of MPA as indicated by an arrow is inserted between the two domains. The inserted MPA molecules at the domain boundary were shown as shaded balls in the model. In addition, other phase boundaries with different molecular arrangements were observed in the MPA monolayers, and will be also discussed.

References

[1] T. Sawaguchi, F. Mizutani, I. Taniguchi, *Langmuir*, **14**, 3565 (1998);
[2] T. Sawaguchi, F. Mizutani, S. Yoshimoto, I. Taniguchi, *Electrochim. Acta*, **45**, 2861 (2000).
[3] T. Sawaguchi, Y. Sato, F. Mizutani, *Electrochemistry*, **67**, 1178 (1999); **69**, 962 (2001).
[4] T. Sawaguchi, Y. Sato, F. Mizutani, *J. Electroanal. Chem.*, **496**, 50 (2001) .
[5] T. Sawaguchi, Y. Sato, F. Mizutani, *J. Electroanal. Chem.*, **507**, 256 (2001); *Phys. Chem. Chem. Phys.*, **3**, 3399 (2001).

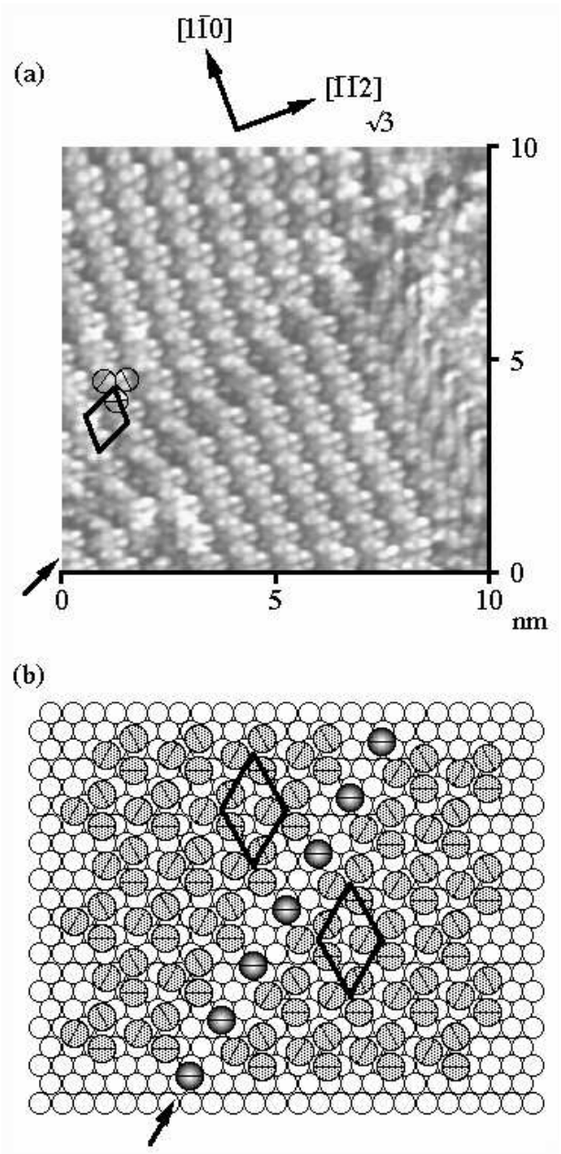

Figure 1 (a) A high-resolution STM image of the self-assembled monolayer of MPA on Au(111) in 0.05 M $HClO_4$. (b) Real space model for the structure of the MPA monolayer on Au(111). Open circles and shaded circles with an inner line correspond to Au atoms and MPA molecules, respectively. Shaded balls indicate MPA molecules at the domain boundary. The superimposed rhombus in the image and model indicates the (3×3) unit cell. An arrow shows the phase boundary between two ordered MPA domains.