Formation of Molecularly Ordered Domain of 1-Decanethiol in the Mixed Self-Assembled Monolayer with Bis(4-pyridyl)disulfide - A Scanning Tunneling Microscopy Observation

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Scanning tunneling microscopy (STM) of self-assembled monolayers (SAMs) on Au(111) prepared from mixtures of bis(4-pyridyl) disulfide and 1-decanethiol revealed that patched domains of each organosulfur compound were formed.

Research on the self-assembly of organosulfur compounds on gold surfaces has been carried out extensively. The self-assembled monolayers (SAMs) of organosulfur compounds are often used to introduce specific functionalities such as redox properties to electrode surfaces.[1-5] One of the most important applications of SAMs is as a promoter for the direct electron transfer between electrodes and redox proteins such as cytochrome *c*.[6-11] The use of a pyridine-terminated thiol as the promoter for electrochemistry of cytochrome *c* was reported by Taniguchi et al.,[6] Haladjian et al.[7] and Hill and his colleagues[8,9] To clarify the relationship between the properties of the monolayer and the ability for promoting the electrochemistry of cytochrome *c*, we investigated the electrochemical response of cytochrome *c* at the gold electrodes modified with mixed SAMs consisting of promoter molecules, such as bis(4-pyridyl) disulfide and mercaptopropionic acid, and barrier molecules, i.e., n-alkanethiols, of various molar ratios.[12,13] We suggested that domain formation of the promoter and barrier molecules plays a very important role in determining the electrochemical response of cytochrome *c*. In order to discuss the effect of domain formation more quantitatively, we determined the real composition and the degree of mixing of the mixed SAMs by electrochemical and electrochemical quartz crystal microbalance measurements during the reductive desorption of the SAMs.[13,14]

The study on mixed SAMs is important not only for the understanding of electrochemistry of cytochrome *c* on the electrode modified with the mixed SAMs but also for the design and the construction of SAMs of various functionalities with micro-/nano- domains of multicomponents which can be formed by controlling the phase separation characteristics. The real compositions of mixed SAMs have been determined by using results of contact angle,[15-18] ellipsometric thickness,[15-18] infrared spectroscopy (IR),[16] mass spectrometry[17] and X-ray photoelectron spectroscopy (XPS).[15,17,18] Although scanning tunneling microscopy (STM) measurements with high gap impedance have been proven to provide the real-space structural information of SAMs with atomic resolution,[19,20] this method has not yet been applied to mixed SAM systems. Overney et al. observed the phase separation in the mixed Langmuir -Blodgett (LB) films of perhydro arachidic acid ($C_{19}H_{39}COOH$) and fluorinated carboxylic acid ($C_9F_{19}C_2H_4OC_2H_4COOH$) monolayer by lateral force microscope but with much lower resolution.[21]

In this paper, we carried out structural studies on SAMs prepared from ethanol solution containing bis(4-pyridyl) disulfide and 1-decanethiol ($C_{10}SH$) by means of STM. The effects of molar ratio in the modifying solution on the composition, domain size and order of the SAMs were investigated. We observed molecularly resolved $\sqrt{3}$ x $\sqrt{3}$ structure on the some portion of $C_{10}SH$ domains in the mixed SAMs for the first time.

Gold substrates were prepared by vacuum evaporation of gold onto glass surfaces whose temperature was kept at 300 °C during the evaporation. The substrate was flame-annealed and Au(111) terraces were observed on the resulting gold surface on the STM image. The substrate was modified by dip-treatment in ethanol solutions containing bis(4-pyridyl) disulfide (Aldrich) and/or $C_{10}SH$ (Tokyo Kasei) for 1 h at room temperature.[2,3] The total concentration of modifying molecules was 1 mM.[2,4] After the modification, the gold substrate was thoroughly washed by ethanol and dried under N_2 atmosphere. Nanoscope E+ (Digital Instruments) and PicoSPM (Molecular Imaging) were used as the controller and microscope of the STM, respectively. STM measurements were carried out in air under a bias of 700 mV and a tunneling current of 30 pA.

Figure 1 (a)-(d) shows STM images of SAMs prepared from pure $C_{10}SH$ (a, b) and bis(4-pyridyl) disulfide (c, d) solutions. The STM image of $C_{10}SH$ SAM (Figure 1 (a)) is essentially the same as those reported previously.[22] Domains of over several hundreds nm^2 with clear domain boundaries were observed in the STM image of $C_{10}SH$ SAM (Figure 1 (a)). The height difference between the central portion and the upper-right corner was ca. 0.3 nm, i.e., monoatomic step height of gold. It is clear many domains exist on one gold terrace. Various types of defects were observed at domain boundaries. Dark spots of various diameters observed at domain boundaries may be etch-pits as the depth of these spots was ca. 0.3 nm, i.e., monoatomic height of gold.[19] Figure 1(b) is a typical high resolution image of these domains. The molecularly resolved $\sqrt{3}$ x $\sqrt{3}$ structure is known to be a typical structure of alkanethiol monolayers.[19,20,23-26]

Quite different STM images were obtained for pyridyl thiolate

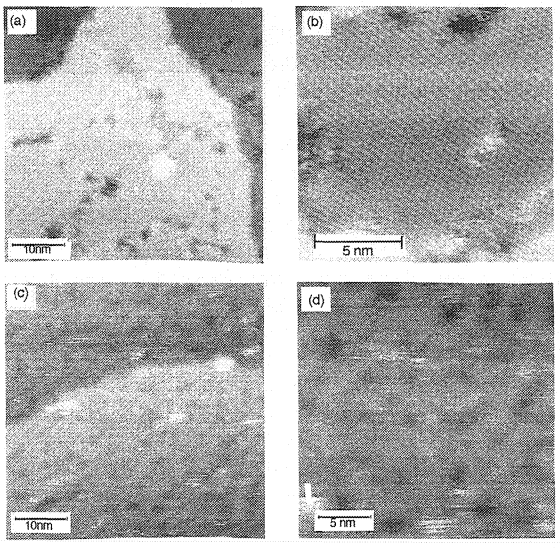

Figure 1. STM images of gold surfaces modified by dip-treatment (1 h) in ethanol solution containing $C_{10}SH$ (a, b) and bis(4-pyridyl) disulfide (c, d) (concentration : 1 mM) . The imaging sizes are: 50 nm x 50 nm (a, c), 25 nm x 25 nm (b) and 15 nm x 15 nm (d).

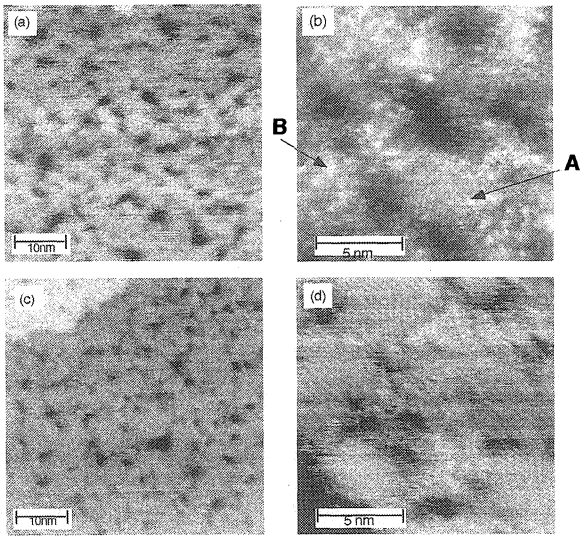

Figure 2. STM images of gold surfaces modified by dip-treatment (1 h) in ethanol solution containing bis(4-pyridyl) disulfide and $C_{10}SH$ with the mole ratio of 9.5 : 0.5 (a, b) and 9 : 1 (c, d). Total concentration of thiol is 1 mM (bis(4-pyridyl) disulfide was assumed to correspond to two pyridylthiol molecules when it was adsorbed). The imaging sizes are: 50 nm x 50 nm (a, c) and 15 nm x 15 nm (b, d). See details in the text.

monolayer (Figure 1(c) and (d)). Low resolution image (Figure 1(c)) shows no rigid structures but many defects. No clear molecular image was observed even in the high resolution image (Figure 1(d)). It must be noted here that this does not mean the molecularly ordered structure was not formed. Since the observation was carried out in air, there is a possibility that adsorption of water molecules on the hydrophilic pyridyl moieties prevents the observation of the molecularly resolved image.

Figure 2 shows STM images of gold substrates modified by dip-treatment in solutions containing bis(4-pyridyl) disulfide and $C_{10}SH$ with mole ratios of 9.5:0.5 (a, b) and 9:1(c, d). Low resolution image of the former (Figure 2(a)) shows some domain structures with many defects. Domain sizes were much smaller than those of $C_{10}SH$ SAM (Figure 1(a)). High resolution image (Figure 2(b)) shows that some portions have the molecularly resolved $\sqrt{3}$ x $\sqrt{3}$ structure indicated by "A". These portions should be the domains of $C_{10}SH$ SAM. This is the first time that a molecularly resolved structure was observed at mixed SAM. Many spots of ~ 0.5 nm were also observed in this image indicated by "B". These spots may correspond to each pyridyl thiolate molecule as the size of these spots agrees with that of the molecule. Spots of similar size were observed at the SAM of piperidine on Au(111).[27] The reason why pyridyl thiolate molecule can be imaged in the mixed SAM and not in the pure pyridyl thiolate SAM is not clear at the present stage. The portions where these spots were observed were sometimes higher than the domains of $C_{10}SH$ SAM. This may be due to the aggregation of pyridyl thiolate molecules. Although it is rather difficult to determine the areas occupied by the $C_{10}SH$ SAM and the pyridyl thiolate SAM, it is certain that the area occupied by the $C_{10}SH$ domains was much higher than that expected from the composition of the modifying solution, 5%. This is in good agreement with previously reported results in which real composition of the SAM was determined by electrochemical reduction of thiols.[13, 14]

When the content of $C_{10}SH$ in the modifying solution was increased to 10%, the domain structure of $C_{10}SH$ molecules became clearer (Figure 2(c)) and the areas with bright spots which corresponded to pyridyl thiolate molecules decreased (Figure 2(d)). Furthermore, the areas of highly ordered domains of the $\sqrt{3}$ x $\sqrt{3}$ structure increased quite significantly (Figure 2(d)). The size of the domains was still smaller than that of the SAM prepared from pure $C_{10}SH$ solution. These results indicate that the $C_{10}SH$ SAM and the pyridyl thiolate SAM formed separate domains and the size of the highly ordered $C_{10}SH$ SAM domains increased with the increase of the content of $C_{10}SH$ in the modifying solution.

The observation of the molecularly resolved $C_{10}SH$ domains in the mixed SAMs supports our previous proposal that alkanethiol of long hydrocarbon chain and bis(4-pyridyl) disulfide do not absorb uniformly but form patched domains of certain size because of attractive hydrophobic interaction between alkyl chains of alkanethiols so that reversible electron transfer between cytochrome *c* and gold can take place at the domains of pyridyl thiolate exchange.[12] The fact that neither an ordered structure nor clear domains of pyridyl thiolate was observed both at pure bis(4-pyridyl) disulfide SAM and the mixed SAM modified gold suggests that interaction between pyridyl thiolate molecules are weaker than that between alkane thiols. Thus, the phase separation and domain formation are primarily due to the strong attractive hydrophobic interaction between alkyl chains of alkanethiols. STM investigation of a wide variety of mixed SAMs should provide very important fundamental information on the formation and properties of SAMs.

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