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Nano-scale characterization of binary self-assembled monolayers under an ambient condition with STM and TERS†

Noriko N. Horimoto,‡ Shigeru Tomizawa, Yasuhiko Fujita, Shinji Kajimoto and Hiroshi Fukumura*

Gold surfaces were modified by benzyl-mercaptan (BM) and then partly replaced with benzenethiol (BT), which formed binary self-assembled monolayers (SAM). Initially BT randomly replaced BM in the monolayer, but at long exchange times >15 nm radius domains were observed with specific relative composition of BT and BM.

Surface properties strongly depend on molecules adsorbed on surfaces. Hence the formation of self-assembled monolayers (SAMs) by using a variety of functional molecules is useful for controlling surface characteristics such as wettability, friction, adhesion, and so on. This method would be even promising for the fabrication of chemical and biological sensors. Bain and Whitesides have shown for the first time that the mixing ratio of binary SAMs on gold changes the surface hydrophilicity.[1] They have reached the conclusion that two components do not form phase-segregated macroscopic islands, rather dispersed on a molecular scale.

Nanostructures of binary-SAMs can be studied by scanning tunneling microscopy (STM) if the STM images of the two components differ in shape significantly.[2,3] For many combination of molecules used in binary-SAMs, however, it is difficult to characterize nanostructures by STM alone. In this case, STM and electrochemical methods (voltammetry) are combined to obtain the average fraction change of the two molecular components on the surface.[4] Recently, surface enhanced Raman spectroscopy (SERS) has been applied in addition to STM and voltammetry.[5]

Surface properties in ambient environments differ from those under low temperature vacuum conditions. This is because molecules at surfaces are more mobile and flexible at room temperature, interacting with surrounding gaseous compounds and water molecules, which would give a significant influence on surfaces. Very recently it has been reported that the nature of GFP protein adsorbed on gold surfaces is also affected by the surface hydrophilicity and hydrophobicity.[6] It is crucial therefore to examine *in situ* surface properties in ambient environments. The use of STM tip-enhanced Raman-spectroscopy (STM-TERS) enables us to obtain topographic and spectroscopic information of surfaces at a high spatial resolution in real space.

In this report, we have studied the nanostructure of BT/BM binary SAMs formed by an exchange reaction by using STM-TERS. We found out that upon exchange of a BM-SAM with BT, initially the replacement occurred randomly, and eventually the dispersion of the ratio of BM and BT upon various positions became evident.

The instrument used in this work is described in our previous work.[7] Briefly, an STM system (NT-MDT, NTEGRA) was combined with a homemade Raman system (an Andor Tech. DU420 CCD camera with a Solar TII MS-35011 spectrometer), where a linearly polarized He–Ne laser (632.8 nm) light illuminated a sample surface from the top through a long working distance objective lens (Mitutoyo N.A. 0.7). A gold tip was held at an angle of about 45 degrees with respect to the sample. Gold tips were fabricated by electrochemical etching of a gold wire (Nilaco, 0.25 mm diameter).[8] Au(111) substrates for binary SAMs were first soaked in a 10 mM ethanol solution of BM for 24 h. Subsequently, the substrate was immersed in a 10 mM BT solution for a given period of time. After each immersion to a solution of thiol, the substrate was rinsed with ethanol and dried with N_2 gas. Vibrational frequencies of adsorbed molecules were calculated with Gaussian 03 (B3LYP functionals with LANL2DZ basis sets for Au and 6-311+g** basis sets for other atoms).[9]

Upon STM observation of BM-SAMs on Au(111), pits of subnanometer depth appeared along with the steps of Au(111), as is reported in previous studies.[10] Similar images were observed at a BT/BM-binary SAM exchanged with BT (Fig. 1). After 20 h immersion to BT solution, the surface looked very different from the original. This suggests that the thiol exchange reaction affected surface morphology of Au(111), while the surface remained almost unchanged up to 1 h.

TERS spectra of one-component SAMs on Au(111) taken at different points on the surface are shown in Fig. 2. Definitely,

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Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki Aoba, Sendai 980-8578, Japan. E-mail: fukumura@m.tohoku.ac.jp; Fax: +81 22 795 6570; Tel: +81 22 795 6567

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‡ Present address: Center for Emergent Matter Science, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. E-mail: horimotoatpc@gmail.com; Fax: +81 48 462 1554; Tel: +81 48 462 1111 ext. 6318.

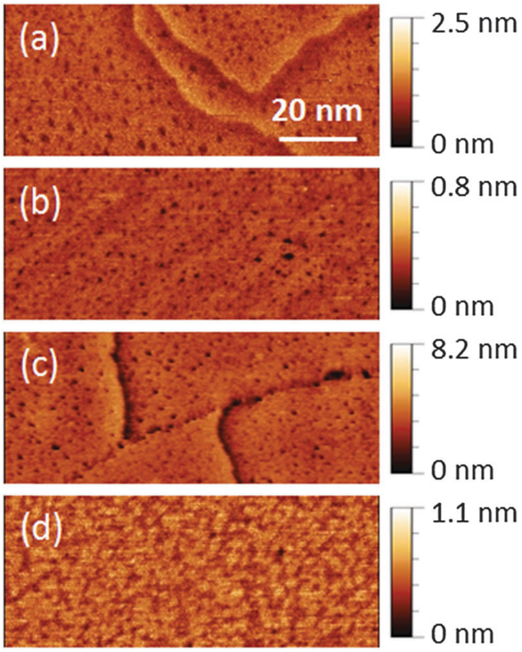

Fig. 1 SAM surfaces on Au(111) observed with STM: (a) the original BM; (b) 1 h immersion in BT solution.; (c) 5 h immersion in BT solution.; (d) 20 h immersion in BT solution.

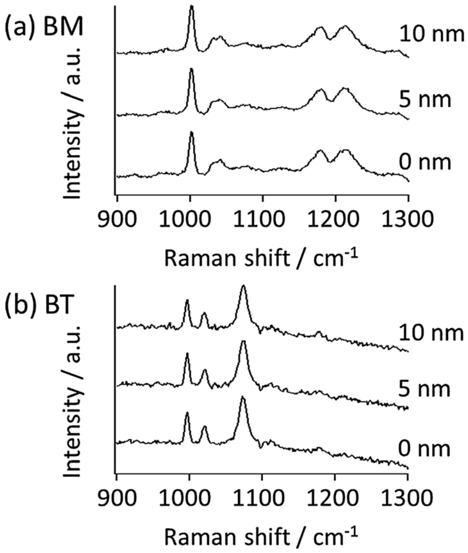

Fig. 2 TERS spectra of singly adsorbed molecules on Au(111) surfaces: (a) BM; (b) BT. Each spectrum is the average of 5 time measurements on a horizontal point indicated at the right side.

no peaks were observed without the tip. This indicates that Raman signals were obtained only with the aid of the strong field enhancement by the tip, *i.e.* only molecules in the close vicinity of the tip were observed. It should be noted that spectral shapes and intensities did not fluctuate so much as far as one-component systems were measured in our setup (Fig. 2).

In the BM-SAM spectra, three Raman peaks appearing at 997, 1179, 1205 cm^{-1} present the spectral features of BM, which are assigned to ring breathing, C_{CH_2}–C_{phenyl} stretch + C–H in-plane bending, C_{CH_2}–H out-of-plane bending, respectively. In the BT spectra of BT-SAM, Raman peaks at 995, 1018, 1069 cm^{-1} are attributed to ring out-of-plane deformation + C–H out-of-plane bending, ring in-plane deformation + C–C symmetric stretching, C–C symmetric stretching + C–S stretching, respectively. The two bending peaks at around 1200 cm^{-1} for BM and the strong single peak for BT at around 1070 cm^{-1} were clearly shifted to low frequencies compared with non-reacted solids nor liquids, indicating that both BM and BT were chemisorbed at Au(111) surfaces (Supplement 1, ESI†).

A series of spectra of a BM surface after 1 h exchange time with BT is shown in Fig. 3(a). The 1069 cm^{-1} peak due to BT was clearly observed, while the two peaks due to BM at around 1200 cm^{-1} became ambiguous. This indicates that desorption of BM and adsorption of BT occurred on the Au(111) surface.

For the 60 min exchanged sample, the characteristic twin peaks at around 1200 cm^{-1} originated from BM fluctuating from place to place, while TERS spectra taken on a 30 min exchanged sample showed more prominent twin peaks. Since absolute spectral intensities of TERS generally varied with many factors like optics, tip and sample conditions including enhancement factors,[7] we further analyzed binary SAM samples by taking spatial and temporal average values. We believe that the reliability of our instrument is high enough when ratios of peaks are compared, although spectral intensities often decayed probably due to changes in optical setups and tip conditions in addition to damage to samples caused by probe light irradiation (Supplement 2, ESI†).

In order to understand the nanoscale distribution of BT and BM in BT/BM-binary-SAMs in detail, we collected TERS spectra at different positions on a single sample surface; five TERS spectra were measured at each position spaced by 5 nm or 10 nm, and the spectral data were averaged over each position. Then intensity ratios between specific TERS peaks (*e.g.* I_{1174} *vs.* I_{1209} for BM-SAM, I_{999} *vs.* I_{1072} for BT-SAM, $I_{1174} + I_{1209}$ *vs.* I_{1072} for BT/BM-binary-SAM) were calculated (Supplement 3, ESI†). For one-component-SAMs, TERS ratios between two peaks varied only slightly between positions. The variation between each position was within ±20% of the average value. This indicates that the ratio within BT signals or BM signals is almost the same independent of positions. The fact that BT-SAM has a larger variation than BM-SAM may reflect the orientation disorder of the BT-SAM.[11] For a binary-SAM, which was originally a BM chemisorbed Au(111) surface and then immersed in BT solution for 30 min, the TERS intensity ratio $(I_{1174} + I_{1209})/I_{1072}$ stayed nearly constant as one-component SAMs. A BT/BM binary SAM made with 60 min immersion in BT solution, however, showed marked deviation in its spectral ratio reaching ±50% of the average value within a 100 nm scan range.

TERS enhancement radius, *i.e.* the radius where Raman signals from molecules only inside it are observed, can be calculated using an equation reported previously.[12] Since tip radii were 20–50 nm in our experiments and tip-sample distances for general STM measurements fall in 1–2 nm, the TERS enhancement radii are estimated to be 6–15 nm in this study. Accordingly, the ratio between BT and BM is considered to differ from place to place within 15 nm radii in the 60 min exchanged binary-SAM, whereas phase segregation of BT if any would not extend more than a radius of 15 nm in the 30 min exchanged binary SAM.

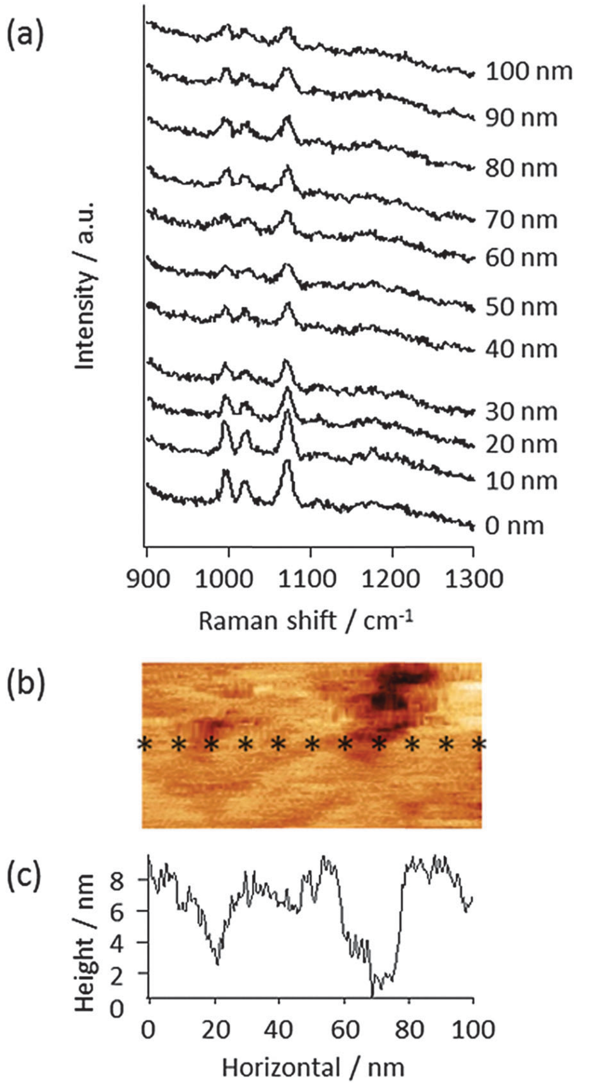

Fig. 3 (a) TERS spectra of two component (BT/BM) SAM on a Au(111) surface. The immersion time in BT solution was 1 h. Each spectrum is the average of 5 time measurements on a horizontal point indicated at the right side of the spectrum. The STM morphology and the height profile of the measured surface are, respectively, shown in (b) and (c).

The formation of BT/BM binary SAMs in this experiment has clearly shown that chemisorbed BM molecules can be exchanged with BT in methanol. Such an exchange reaction can occur through slow desorption of disulfide and fast adsorption of thiol in the case of gold surfaces as the desorption time scale is similar to the exchange one.[13] The exchange reaction yield reaches a plateau that is much smaller than 100% after 50 h, which is attributed to stronger binding of thiols at defect sites, restraining the exchange reaction. This means that the initial process would be desorption of BM from weaker binding sites on gold surfaces, and then BT would be chemisorbed at the vacancy. It is therefore easy to imagine that areas where BT molecules occupy at the surface would not be big as 15 nm, being rather mixed with BM molecules at the initial stage of the exchange reaction, as we have observed at the 30 min immersion surface.

We have found that the distribution of BT after 60 min immersion was inhomogeneous. This implies three possibilities: (1) strong binding sites to BM may inhibit the exchange reaction and as a result BT just looks aggregated at weak binding sites; (2) there are cooperative processes to induce exchange reactions at the neighbour of BT; (3) BT molecules laterally diffuse on the surface and form BT-rich domains. The case (2) may be supported by the result of first principles total energy calculations for BT SAMs on Au(111).[14] The van der Waals interaction between BT molecules in SAMs is estimated to be 9.65 kJ mol^{-1} which is 4 times larger than thermal energy at room temperature. Au–S bond energies of alkanethiols are experimentally obtained to be 126 kJ mol^{-1} irrespective of alkyl chain lengths.[15] Inter-molecular interactions, therefore, may play an important role in forming BT rich regions in SAMs rather than a bond energy difference between BT and BM molecules. The case (3) may be supported with MD simulations showing that the lifetimes of Au–S bonds for BT and BM are estimated to be 551 ps and 219 ps, respectively.[16] Adsorbed molecules with gold adatoms may move at gold surfaces in solution at room temperature.[17,18]

In conclusion, binary-SAMs formed by the exchange reaction were studied by STM-TERS. Upon replacement of BM-SAM with BT, exchange occurred randomly for the first 30 minutes, and after that, at the exchange time of 60 minutes, the dispersion of the ratio of BM and BT upon various positions became prominent.

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