

ARTIFICIALLY PHASE SEPARATED TERNARY SELF-ASSEMBLED MONOLAYERS COMPOSED OF 11-AMINOUNDECANETHIOL, 1-DODECANETHIOL AND 10-CARBOXY-1-DECANETHIOL ON Au(111) PREPARED BY ELECTROCHEMICALLY SELECTIVE REPLACEMENT TECHNIQUE

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Received 25 September 2014; Accepted for Publication 20 April 2015

Abstract

The template ternary self-assembled monolayer composed of 11-amino-1-undecanethiol (AUT), 1-dodecanthiol (DDeT) and 2-hydroxyethanethiol (MEL) prepared by coadsorption method forms two types of domain in nano meter scale on Au(111): one mainly composed of AUT and DDeT, the other mainly composed of MEL. After replacing MEL with 10-carboxy-1-decanethiol (CDT) by use of electrochemically selective replacement technique, the final ternary SAMs of AUT-DDeT-CDT composed of AUT-DDeT domains and CDT domains having similar alkyl chain length have been obtained. Results also indicate that the presence of adsorbed DDeT molecules enhances the phase separation between AUT-DDeT and CDT domains. This can be explained by the increase in the surface activities of hydrophobic DDeT in the AUT-DDeT domains of the final ternary SAMs.

Keywords. Ternary self-assembled monolayers, artificially phase separated SAMs.

1. INTRODUCTION

Self-assembled monolayers (SAMs) of organosulphur compounds on metals surfaces comprise a wide field of potential applications due to their versatility in modifying surfaces in a controllable manner. Two-component monolayers comprise various advantage over a one-component monolayers, that is these monolayers enable us to tailor the properties of the mixed SAMs to specific requirements, for instant, for controlling the coverage [1], conformation [2] or electron transfer of redox-proteins [3, 4]. The combination of various functional groups, for example, allows the control of the degree and distribution of hydrophilicity or hydrophobicity as well as charged terminal functional groups on the monolayer surface [5, 6].

One of intensive studies of SAMs composed of multi-component is mixing state of adsorbed molecules during assembly to form mixed SAMs. In the previous study, the mixing state and behaviors of binary SAMs composed of two ionizable components: CDT and AUT formed by coadsorption from solution have been investigated. It was found that this type of binary SAMs forms a mixing state in molecular level [6]. This behavior of the binary

SAMs was interpreted by the inter-molecular interactions between adjacent molecules adsorbed on the surface [6]. Therefore, it is essential to preparing a type of SAMs composed of CDT domains and AUT domains having nano scale because this type of SAMs is very promising for immobilizing multiple proteins used for preparing biosensors, as well as for studying electron transfer from redox proteins immobilized on the SAMs surface to the electrode through long alkyl chains.

In the present study, SAMs composed of three components having two types of separated domains: one mainly composed of CDT and the other mainly composed of AUT prepared by electrochemically selective replacement technique to form the artificially phase separation. The third component is used for tailoring the surface properties of AUT domains. This can be a model for using multi-component to modify the surface properties of alkanethiolate SAMs.

2. EXPERIMENTAL

2.1. Materials

10-carboxy-1-decanethiol (Dojindo), 11-amino-1-

undecanethiol hydrochloride (Dojindo), 2-hydroxyethanethiol (Tokyo Kasei Kogyo) and 1-dodecanthiol (Wako) were used without further purification. All other chemicals were of reagent grade and used without purification.

2.2. Au(111) samples preparation

The mica was baked at 580 °C prior to the vapor deposition and maintained at 580 °C during the deposition of Au (99.99 %). The Au substrates were then annealed at 530 °C for 8 h in ambient atmosphere immediately before use.

2.3. The template ternary SAMs preparation

The template ternary SAMs of AUT-DDeT-MEL were prepared by immersing Au (111) substrates for 24 h in the ethanolic solution consisting of AUT, DDeT and MEL, where the total thiol concentration was kept in 1 mM. The composition of the template SAMs was controlled by keeping the molar ratio of AUT and DDeT at 1:1, varying the molar ratio of MEL, X_{MEL}^{sol} . Here, X_{MEL}^{sol} was defined by $X_{MEL}^{sol} = C_{MEL}^{sol} / C_{total}$, and $C_{total} = (C_{MEL}^{sol} + C_{AUT}^{sol} + C_{DDeT}^{sol})$, where C_i^{sol} is molar concentration of i (i : AUT, DDeT and MEL).

2.4. The final ternary SAMs preparation

MEL domains were removed from the surface of template ternary SAMs of AUT-DDeT-MEL by applying a potential of -0.65 V for 20 minutes in a 0.5 mM KOH solution. After removal of MEL, the substrates were rinsed with ethanol and dried in air. The substrates were then immersed in 1 mM solution of CDT for 15 – 20 min to form the final ternary SAMs of AUT-DDeT-CDT.

2.5 Methods and measurements

For cyclic voltammetry (CV), a thiol adsorbed gold substrate was amounted at the bottom of a cone-shape cell by using an elastic O-ring. The electrode was 0.126 cm² estimated from the diameter of the O-ring. Electrolyte solution 0.5 M KOH was deaerated with Ar for 20 min. The potential was referred to an Ag|AgCl|sat'd KCl electrode. All measurements were performed with scan rate: 20 mV/s, at 25±2 °C.

In X-ray Photoelectron Spectroscopy (XPS) measurements, the SAMs employed in the XPS

studies were thiol adsorbed gold substrate with approximately 0.3 cm². The X-ray source was monochromated KMg α .

Scanning tunneling microscope (STM) images were carried out with a NanoScope III (Digital Instruments). Tips were prepared by electrochemical etching Pt₈₀Ir₂₀ wires and coated by Apiezo Wax. In-situ STM measurements were carried out in 100 mM NaClO₄ solution, in constant-current mode. All experiments were performed at ambient temperature.

3. RESULTS AND DISCUSSION

The formation of the template phase separated ternary SAMs of AUT-DDeT-MEL was investigated by CV technique. Fig. 1A shows the reductive desorption voltammograms of the templates SAMs prepared at various values of X_{MEL}^{sol} . The voltammograms clearly show two separated reductive desorption peaks, suggesting the phase separation of two types of adsorbed thiolate domain [7]. The peaks at more positive potential decrease with decreasing X_{MEL}^{sol} , while the peaks at more negative potential increase. This suggests that the peak at more positive potential corresponds to the reductive desorption of domains mainly composed of MEL molecules, while the peak at more negative potential corresponds to the reductive desorption of domains mainly composed of both alkanethiolate AUT and DDeT (AUT-DDeT).

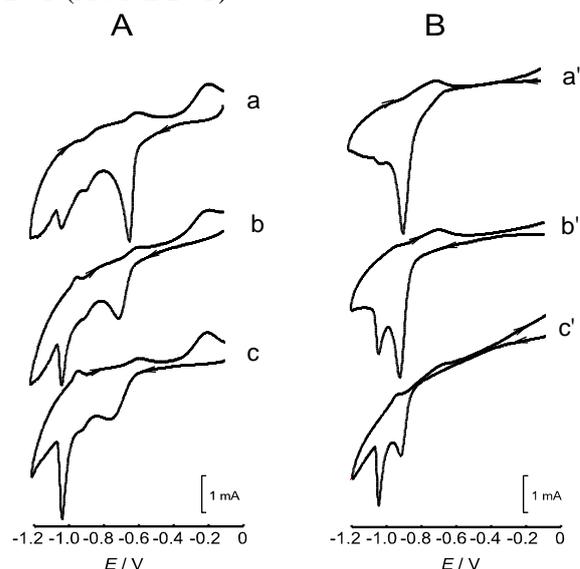


Fig. 1: Cyclic voltammograms for the reductive desorption of SAMs. (A) the template ternary SAMs of AUT-DDeT-MEL prepared at X_{MEL}^{sol} (a) 0.7; (b) 0.65; (c) 0.6. (B) The final ternary SAMs of AUT-DDeT-MEL: (a'÷c') prepared from (a÷c) in (A), respectively

Binary SAMs composed of shorter alkyl chain length (n) hydrophilic component and longer n hydrophobic components were studied [8]. It was found that hydrophobic components are more surface active than hydrophilic ones. This is attributed to the reason for the surface composition between MEL and AUT-DDeT adsorbed on the surface of Au(111) = 0.5 (which is roughly estimated from the ratio of two reductive desorption peak areas of MEL and AUT-DDeT) when $\chi_{MEL}^{sol} > 0.6$.

In the present study, the presence of AUT in AUT-DDeT domains has been examined by use of XPS. Signals attributed to the deprotonated and protonated amino-terminated group at 398.5 eV and 401 eV, respectively can be observed (data not shown). The presence of DDeT alkanethiolates in AUT-DDeT domains can be recognized by following aspects. First, the reductive desorption peak of AUT-DDeT domains in the template ternary SAMs was about 40 mV more negative than that of single AUT domains of the binary SAMs of AUT-MEL, which was investigated in previous work [9]. Second, the value of full width at half maximum (*FWHM*) of the reductive desorption peak of the template AUT-DDeT domains was about 28 mV, which is significantly smaller than that of the reductive desorption peaks of single AUT domains [9]. The last, it is different from the template binary SAMs of AUT-MEL, the phase separation of the template ternary SAMs of AUT-DDeT-MEL can be taken place in the range of χ_{MEL}^{sol} from 0.6 ÷ 0.8. This range is greater than that to form phase separation of binary SAMs of AUT-MEL [9]. These evidences also suggest that the presence of DDeT enhances the stability of AUT-DDeT domains. This may be reasonably interpreted in terms of the stronger surface activity of the hydrophobic alkanethiolate than hydrophilic AUT at the ω position [8].

In the previous study, the reductive desorption peak of single SAM of MEL was found at -0.62V [9]. Hence, in the present work, by applying a potential of -0.65 V to remove completely MEL domains of the template ternary SAMs of AUT-DDeT-MEL from the Au(111) surface, CV was used to examine and showed the disappearance of the reductive desorption peak of MEL. The final ternary SAMs of AUT-DDeT-CDT was obtained by refilling CDT from the bathing ethanolic solution. Fig. 1 B shows the voltammograms for the reductive desorption of the final ternary SAMs at various values of χ_{MEL}^{sol} . In this figure, two separated peaks

can be observed clearly, reflecting the phase separation in the final ternary SAMs [7]. In these voltammograms, the peak at -0.93 V is attributed to the reductive desorption of CDT domains due to the decrease in the height of this peak with lowering χ_{MEL}^{sol} . Similarly, the peak at -1.05 V corresponds to the reductive desorption of AUT-DDeT domains. The peak separation, ΔE , of two separated peaks in these voltammograms was about 120 mV. That clearly shows the high degree of phase separation between AUT-DDeT domains and CDT domains in the final ternary SAMs of AUT-DDeT-CDT. Interestingly, with the presence of DDeT molecules, ΔE in CV for the ternary SAM of AUT-DDeT-CDT was greater than that of binary SAMs of AUT-CDT prepared from the template ternary SAM AUT-MEL [10]. The presence of DDeT molecules may thus increase the stability of AUT-DDeT domains due to the increase in the hydrophobicity of this domain. After replacing MEL with CDT, voltammograms show that the shift of the reductive desorption peaks of CDT domains with varying the χ_{MEL}^{sol} was very small, it is very close to the peak potential for the reductive desorption of the single component SAM of CDT. This suggests that CDT domains in the final SAMs of AUT-DDeT-CDT are nearly pure [11].

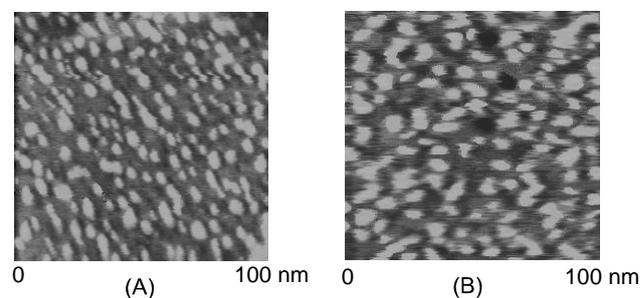


Fig. 2: In-situ STM images of (A) the template ternary SAMs of AUT-DDeT-MEL prepared at $\chi_{MEL}^{sol} = 0.6$; (B) the final ternary SAM of AUT-DDeT-CDT prepared from the template ternary SAM in (A)

The phase separation of the template ternary SAMs of AUT-DDeT-MEL and the final ternary SAMs of AUT-DDeT-CDT can be imaged by STM measurements. Fig 2 shows a typical in-situ SAM images of the template ternary SAMs prepared at $\chi_{MEL}^{sol} = 0.6$ and the final ternary SAMs, in which the phase separation can be clearly seen by brighter spots and darker areas. In these images, brighter spots correspond to AUT-DDeT domains, and darker areas are attributed to the CDT domains [12].

The size and the shape of the brighter spots in two images are similar with each other, suggesting that AUT-DDeT domains in the template ternary SAMs are not effected by electrochemically selective replacement technique.

4. CONCLUSIONS

The phase separation of the ternary SAMs of adsorbed alkanethiolates having similar alkyl chain length formed by electrochemically selective replacement technique has been investigated. The final ternary SAMs have two clearly separated domains, one mainly composed of negatively charged CDT and the other mainly composed of positively charged AUT tailored with DDeT molecules. The presence of DDeT molecules plays the role in not only tailoring the AUT domain but also in increasing the phase separation between two types of domains. This artificially phase separated ternary SAM can be a model of SAMs composed of multi-components that forms separated domains, and can be useful for immobilizing multiple macro molecules used for producing bio-sensors.

Acknowledgement. *The author would like to express his special thanks to Prof. Takashi Kakiuchi for his kindly support and valuable discussions.*

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