ENHANCING THE DEGREE OF PHASE SEPARATION IN BINARY SELF-ASSEMBLED MONOLAYERS COMPOSED OF 10-AMINO-1-UNDECANETHIOL AND 6-CARBOXY-1-MERCAPTANETHIOL ON Au (111) BY USING FLUOREN-9-YLMETHYL N-(11-MERCAPTOUNDECYL)CARBAMATE

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Abstract

The degree of phase separation of binary Self-Assembled Monolayers (SAMs) composed of 10-amino-1-undecanethiol (AUT) and 6-carboxy-1-mercaptanethiol (MHA) on Au (111) prepared by two methods has been compared. The first preparation method used direct-coadsorption of AUT and MHA from the bulk solution to give the binary SAMs of (d-AUT-MHA). The second method utilized fluoren-9-ylmetyl-N(11-mecaptoundecyl)carbamate (FAUT) to form the initial phase separated binary SAMs of FAUT-MHA having higher degree of phase separation than SAMs of d-AUT-MHA. Fmoc residues removal from SAMs of FAUT-MHA resulted in the final binary SAMs of AUT-MHA.The results obtained in the study of the SAMs by cyclic voltammetry and scanning tunneling microscopy provided clear evidences for the enhancement of phase separation in the final binary SAMs of AUT-MHA.

Keywords. Binary self-assembled monolayers, phase separation,Fmoc.

1. INTRODUCTION

The mix of two alkanethiols for preparing phase-separated binary SAMsis very useful for tailoring the surface properties of various metals. For instant, binary SAMs composed of oppositely charged domains of alkanethiol with nano scale in two-dimensional on the surface of Au(111) serves as a good material for immobilizing different types of proteins/enzymes used for applications in biology and biochemistry [1,2]. The phase separation of binary alkanethiolate SAMs forms nanometer scale domains whose terminal and chain length can be controlled, giving more capabilities for applications. Numerous techniques have been studied to achive the phase separation on noble metal surface, such as nanografting [3], lithographic technique [4, 5], electrostatic self assembly [6], or synthesis fromself organisation in air-water interface [7]. Another simple technique can also provide a separation in a mixing solution of two or more components due to the magnitude of intermolecular interactions between neighboring molecules [8]. Thus, phase separated binary SAMs can be formed by spontaneous adsorption of two alkanethiols having different chain lengths [9], or similar chain lengths [10,11].In the case of spontaneous adsorption of two thiols that forms a homogenous state, artificial phase-separated binary SAMs can be prepared by selective replacement method based on an electrochemical desorption technique [12,13]. This technique has been applied to the scanning tunneling microscopy (STM) tip -induced lithography [14].

In the present paper, we introduce a new method to enhance the degree of phase separation in binary SAMs composed of two oppositely charged domains on Au(111): AUT and MHA. In the new method, we utilized the removable 9-fluorenmethoxy-carbonyl (Fmoc) residue to increase intermolecular interactionsin the initial binary SAMs of FAUT-MHA in comparison with SAMs of d-AUT-MHA due to stronger Van de Waals interactions. We expected this increase can give clearer phase separation in the initial binary SAM of FAUT-MHA, and the degree of phase separation in the final binary SAMs of AUT-MHA is not influenced by Fmoc residue removal.

2. EXPERIMENTAL

2.1. Chemicals and Materials

Fluoren-9-ylmethyl-N(11-mecaptoundecyl) carbamate, 6-carboxy-1-mercaptanethiol (Dojindo), and 11-amino-1-undecanethiol hydrochloride (Dojindo) were used without further purification. All other chemicals were of reagent grade and used without purification.

2.2. Preparation of Au(111) substrates

Au(111) substrates were prepared by vapor deposition of gold on a mica plate. 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 8h in ambient atmosphere immediately before use.

2.3. Preparation of binary SAMs

Binary SAMs of FAUT-MHA (SAM 1) and d-AUT-MHA (SAM 2) were prepared by immersing Au (111) substrates for 24 h in an ethanolic solution of FAUT and MHA for SAM 1 and of AUT and MHA for SAM 2, respectively, where the total thiols concentration was kept at 1 mM.

The composition of SAMs was controlled by the molar ratio of MHA $\mathcal{X}_{MHA}^{sol}$. Here, $\mathcal{X}_{MHA}^{sol}$ is defined as:

$$\mathcal{X}_{MHA}^{sol} = C_{MHA}^{sol} / C_{total}$$

Where C_i^{sol} is the molar concentration of i (i: FAUT, AUT and MHA).

For SAM 1: $C_{total} = (C_{FAUT}^{sol} + C_{MHA}^{sol})$

For SAM 2: $C_{total} = (C_{AUT}^{sol} + C_{MHA}^{sol})$

2.4. Preparation of the final phase-separated binary SAMs of AUT-MHA from SAMs of FAUT-MHA

The Fmoc residue of FAUT was removed from SAM 1 by immersing SAM 1 into a solution of N,N-dimethylformamide containing 20 % piperidine (PP/DMF) for 12 min. Figure 1 illustrated the two methods for preparation of binary SAMs of AUT-MHA. The SAM was then rinsed with ethanol and dried in air.

2.5. Instruments and measurements

For cyclic voltammetry (CV), a thiol adsorbed gold substrate was mounted at the bottom of a cone-shape cell by using an elastic O-ring. The electrode was 0.126 cm^2 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 a scan rate of 20 mV/s at 25±2 °C.
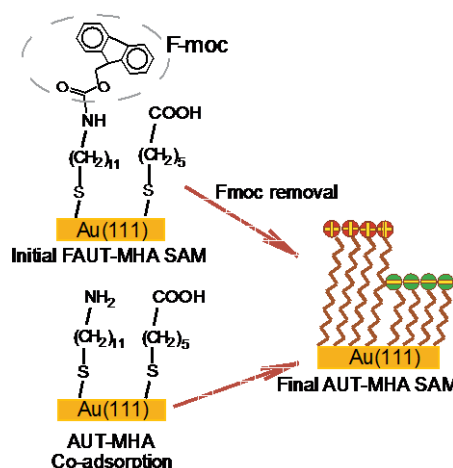

Fig. 1: Schematic illustration of two methods for preparation of phase separated binary SAMs of AUT-MHA

Scanning tunneling microscope (STM) images were obtained with a NanoScope III (Digital Instruments). Tips were prepared by electrochemical etching of Pt$_{80}$Ir$_{20}$ wires and coated by Apiezo Wax. In-situ STM measurements were carried out in 100 mM NaClO$_4$ solution, in constant-current mode. All experiments were performed at ambient temperature.

3. RESULTS AND DISCUSSION

In order to compare the phase separation between the binary SAMs of FAUT-MHA and d-AUT-MHA, CV was used to investigate their reductive desorption in KOH solution [15]. Fig. 2 displays CV for the reductive desorption of SAM 1 and SAM 2. Single peaks in curves a, c correspond to the reductive desorption of single component SAMs of FAUT and MHA, respectively. The difference in peak potentials reflects the difference in Giff energy of alkanethiolate adsorbed on the Au(111) surface [16]. FAUT and MHA were coadsorbed on the Au(111) surface to form the initial binary SAMs of FAUT-MHA. CV for the reductive desorption of this binary SAM is shown in curve b. The peak at more positive potential corresponds to the desorption of MHA domains, while the peak at more negative potential is attributed to the desorption of FAUT domains [17]. Two separated peaks can be observed with peak separation being about 150 mV. This indicates that FAUT and MHA form separated domains on the Au(111) surface [17].
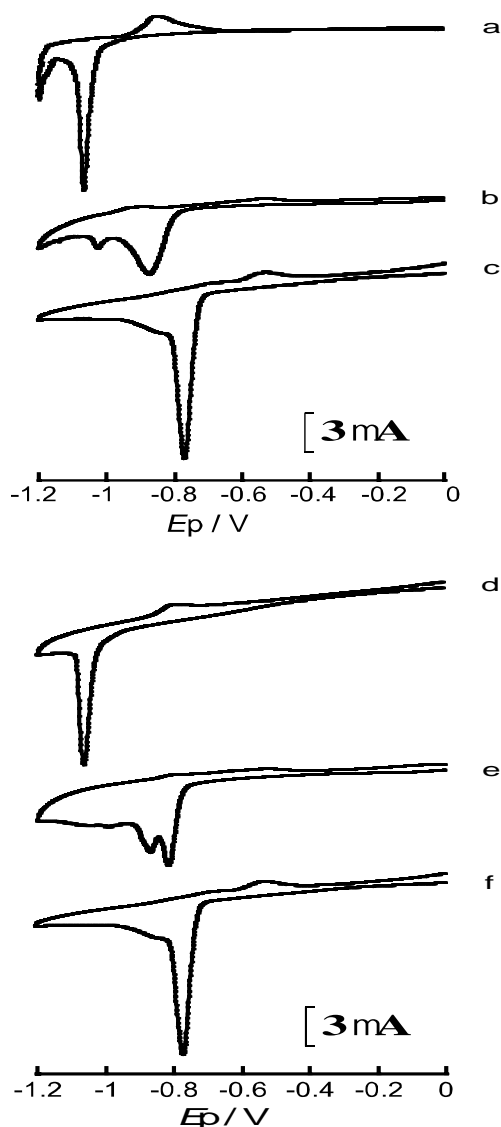
the mutual solubility of adsorbed alkanethiolates on the surface [18].

Fig. 2: CV for the reductive desorption of SAMs: (a) FAUT, (b) the initial binary SAMs of FAUT-MHA, (c,f) MHA, (d) AUT, (e) d-AUT-MHA

Similarly, curves d÷f show desorption peaks of single component SAMs of AUT, binary SAM of d-AUT-MHA, and single component SAM of MHA, respectively. The peak separation in curves b, e is compared for showing the difference in the degree of phase separation. Obviously, this comparison reveals that the phase separation in the initial binary SAMs of FAUT-MHA is greater than that in SAMs of d-AUT-MHA due to the greater value of peak separation. This means that FAUT domains and MHA domains are more separated from each other in comparison with domains of AUT and MHA. The other clear evidence is the more positive shift of the desorption peak of AUT domains in comparison with that of FAUT domains. The peak shift reflects
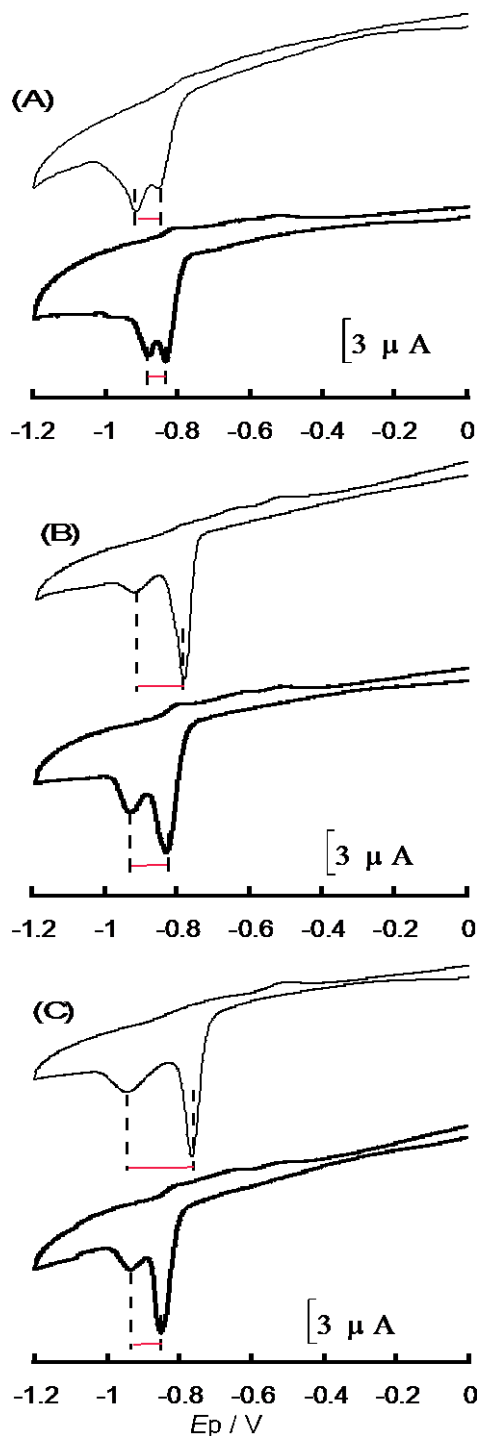

Fig. 3: CV for the reductive desorption of final binary SAMs of AUT-MHA (thin curves) and d-AUT-MHA (thick curves) at various concentrations: (A) 1 mM, (B) 100 μM, (C) 10 μM

Thus, the results obtained clearly reflect the lower mutual solubility in the initial binary SAMs of FAUT-MHA in comparison with binary SAMs of d-AUT-MHA. This can be interpreted by prevention

of FAUT domains on the Au(111) surface to the adsorption of MHA molecules from the bulk solution into this phase due to their hydrophobicity [13]. The enhancement of the degree of phase separation in the final SAMs of AUT-MHA obtained by Fmoc residue removal can be further seen clearly when lowering concentrations of thiols in ethanolic solutions as shown in Fig.3. In this figure, typical CVs for the reductive desorption of the final binary SAMs of AUT-MHA prepared from the initial binary SAMs of FAUT-MHA by removing Fmoc residue and d-AUT-MHA at various concentrations are shown. This comparison clearly indicates that the lower the concentration, the more increase in the peak separation between two reductive desorption peaks. This suggests an enhancement of the degree of phase separation of binary SAMs of AUT-MHA and d-AUT-MHA. Comparison of peak separation in curves in (A)÷(C) reveals the higher degree of phase separation in SAMs of AUT-MHA compared with that of SAMs of d-AUT-MHA. Interestingly, some behaviors of the phase separation have been observed when lowering the concentrations as shown in Fig. 4. First, the lower the concentration, the lower the value of $\mathcal{X}_{MHA}^{sol}$ at which the phase separation can be taken placed in the final binary SAMs of AUT-MHA. Second, the lower the concentration, the wider the range of $\mathcal{X}_{MHA}^{sol}$ in which the phase separation can be taken placed. It is noticed that SAMs of AUT-MHA were prepared from the binary SAMs of FAUT-MHA which consists of hydrophobic (FAUT) and hydrophilic (MHA) components, and there is a difference in the alkyl chains length between these hydrophobic components having longer chain length are preferred to adsorb on the surface due to their stronger surface activity than hydrophilic component having shorter chain length [13]. Thus, one possible explanation for both behaviors is that at lower concentration the surface activity of FAUT is decreased, reducing competition between FAUT and MHA molecules from solution bulk for adsorption.
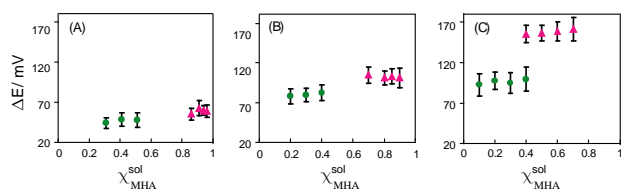

Fig. 4: Variation of peak separation by concentration of the final SAMs of AUT-MHA (▲) and SAMs of d-AUT-MHA (●) at 1mM (A), 100 μM (B) and 10 μM (C)

The enhancement of degree of phase separation can also be clearly observed in in-situ STM images as shown in Fig. 5. Comparison between images (a) and (b) indicates that the area of brighter spots increases with lowering $\mathcal{X}_{MHA}^{sol}$, suggesting that the brighter areas correspond to the AUT domains, while the darker areas are MHA domain. In addition, some black points can be seen. They are pits on the surface formed during immersing Au(111) substrates in ethanolic solution [19].
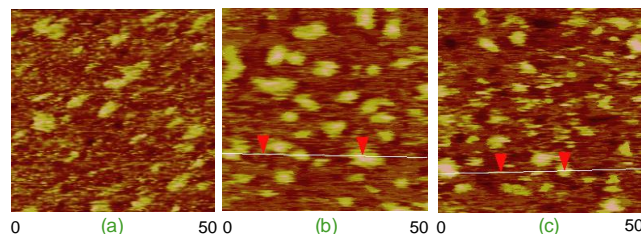

Fig. 5: In-situ STM images of 50 nm x 50 nm of the final SAMs of AUT-MHA at $\mathcal{X}_{MHA}^{sol} = 0.95$ (a), $\mathcal{X}_{MHA}^{sol} = 0.87$ (b); and d-AUT-MHASAM at $\mathcal{X}_{MHA}^{sol} = 0.65$(c)

The images clearly show that the brighter areas in the final binary SAMs of AUT-MHA (a,b) are larger than the AUT domains in SAMs of d-AUT-MHA (c), and that many small brighter spots existed in image (C). These are again evidences for the enhancement of the phase separation in the final SAMs of FAUT-MHA.

4. CONCLUSION

Evidences for the enhancement of the degree of phase separation between AUT and MHA domains prepared by the new method in comparison with that prepared by direct coadsorption of AUT and MHA components are clearly shown. The results obtained suggest that Vander Waals interactions between lateral Fmoc groups in binary SAMs of FAUT-MHA play the key role in intermolecular interaction for enhancing the phase separation of the final binary SAMs of AUT-MHA.

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