

# Surface wettability and spectroscopic studies on miscibility and ion adsorption of binary biomimetic self-assembled monolayers on gold surfaces

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**Abstract**—Binary self-assembled monolayers (SAMs) have been much studied due to their high applicable potential as a model of biomimetic surfaces. However, the research about miscibility of binary SAMs has not much been investigated yet. In this work, we focused on analyzing the binary SAMs composed of mercaptohexadecanoic acid (MHA)-hexadecanethiol (HDT) on gold surfaces with Cassie equation, Israelachvili equation, and FTIR spectroscopy to confirm that the binary SAMs are well mixed. As a result, MHA-HDT binary SAMs are considered miscible because the result obtained from FTIR spectra is in good agreement with that calculated by Israelachvili equation for the case that two different molecules are well mixed on the surface. Also, the adsorption of cadmium ions on binary SAMs was confirmed by the appearance of carboxylate stretching bands.

Key words: Self-assembled Monolayers, Binary Miscibility, FTIR Spectroscopy, Surface Wettability

## INTRODUCTION

Surface reactivity is known to be highly sensitive to the details of structural and compositional distribution of reactive materials as well as impurities [1-3]. Controlling nano-scale surface properties, including the abundance and the spatial distribution of functional group sites, will give a chance to develop biocompatible biomaterials, biosensors, protein adsorption, and molecular electronics [4,5]. Generally in materials aspects, investigation of chemical properties at the heterogeneous surfaces is more relevant to catalytic systems than that at the homogeneous ones [6,7].

Mixing phenomena at air/water interfaces have been much studied about patch or domain formation when two kinds of materials are mixed because the degree of domain formation is a key factor to control the mechanism for membrane receptor and enzyme activity such as protein patching for cell-cell recognition, ligand binding, transport, catalysis, and transmembrane signaling [8-10]. Meanwhile, fabrication of mixed self-assembled monolayers (SAMs) is another method for making a multicomponent system on a solid substrate. Recently, mixed SAMs have been attracting attention due to their high applicable potential as a model of biomimetic surfaces [11-13].

To investigate lateral steric effects, Lahiri et al. [14] studied the binding of carbonic anhydrase to mixed SAMs composed of benzenesulfonamide as a binding ligand and ethylene glycol groups as a surface matrix. However, they did not demonstrate whether the mixed monolayers are well-mixed or not. Riepel et al. [15] controlled the mixing conditions that lead to optimum binding capacity of streptavidin. Mixed SAMs prepared from loading solutions containing 75-95% of the biotinylated alkanethiol resulted in high

immobilization level of functional streptavidin. Although an addition of inert to original pure surface plays an important role to change the properties of the surface reactivity, the mechanism has not been found because it is very difficult to make a mixed template and analyze up to the molecular level [16,17]. Therefore, many researchers have tried to describe the mixed surface by using molecular simulations [18-20].

In this work, we analyzed the binary SAMs composed of MHA-HDT on gold surfaces with surface wettability (Cassie equation and Israelachvili equation) and FTIR spectroscopic studies. External-reflection (ER) FTIR spectroscopy was used to calculate the composition of monolayer on the mixed SAMs composed of MHA-HDT molecules. Also, the adsorption of cadmium ions to mixed SAMs was confirmed by the appearance of carboxylate stretching bands.

## EXPERIMENTAL SECTION

### 1. Materials

16-Mercaptohexadecanoic acid (MHA;  $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ ; 90%), 1-hexadecanethiol (HDT;  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ ; 92%), and cadmium chloride ( $\text{CdCl}_2$ ; 99.9%) were obtained from Aldrich and used without further purification. Ethanol used as a solvent was purchased from Fluka (99.8%) and filtered with 0.20  $\mu\text{m}$  (Millipore; millex-FG). Water used in experiments was first distilled and then purified with a Millipore-Q purifying system. The resistivity of final deionized water (DI) was 18.2  $\text{M}\Omega\cdot\text{cm}$ .

### 2. Preparation of SAMs

A thermal evaporator operation at  $\sim 10^{-6}$  torr was used to deposit  $\sim 500$  Å of titanium and  $\sim 100$  Å of gold (99.99%) onto silicon wafers (LG siltion; (111) plane). The wafers were stored at room temperature and cut into smaller size (20 mm $\times$ 20 mm) before use. Evaporated gold substrates (Au/Ti/Si) can be cleaned by a brief (5 min) exposure to  $\text{H}_2\text{SO}_4/\text{KCr}_2\text{O}_7$  solution (10 : 1 v/v) and washed with DI water for enough time. Binary solutions (MHA and HDT) for self-assembly are prepared in concentration of 1 mM with varying

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