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S. H. Song [a], K. M. Park [a], S. M. Chang [a], C. Nakamura [b], J. Miyake [b] & W. S. Kim [c]

[a] Dept. of Chem. Eng., Dong-A Univ. Pusan, 604-714 Korea

[b] NAIR, 1-1-4, Higashi, Tsukuba 305-8562, Japan

[c] Dept. of Chem. Eng., Kyunghee Univ., Yongin, Kyongkee-do 449-701, Korea

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S. H. Song, K. M. Park, and S. M. Chang
Dept. of Chem. Eng., Dong-A Univ. Pusan, 604-714 Korea

C. Nakamura and J. Miyake
NAIR, 1-1-4, Higashi, Tsukuba 305-8562, Japan

W. S. Kim
Dept. of Chem. Eng., Kyunghee Univ., Yongin, Kyongkee-do 449-701, Korea

Oligopeptides such as PSP1 (Tyr-Ala-Gly-Tyr-Cys) and PSP2 (His-Ala-Ser-Tyr-Ser-Cys), which interact strongly with a typical cationic porphyrin derivative, are synthesized. The structure and morphology of PSP1 and PSP2 monolayers self-assembled on Au surface have been investigated by using X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM). XPS of the monolayers provides evidence that the primary adsorbate species are bonded to Au through the sulfur atom comprised in the species. It is revealed from XPS spectroscopy and AFM images that PSP2 is self-assembled better on Au surface than PSP1. This experimental result is well consistent with the prediction based on steric energies of Au-Peptide bond.

Keywords: AFM image; oligopeptide; porphyrin; self-assembly; steric energies; XPS spectroscopy

1. INTRODUCTION

Self-Assembled monolayers (SAMs) have gained much attention of recent researches due to their potential applications in many fields such as biosensors, corrosion inhibition, wetting control, and biomolecular and electronic devices [1]. The SAMs are also interested as fundamental model systems of various interfaces such as electrode/electrolyte interfaces and cell membranes [2]. An approach comprising electrode modification with

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functionalized alkanes, resulting in well-defined two-dimensional self-assembled monolayers (SAMs), has provided model systems for understanding fundamental physical, chemical, and biological interfacial processes [3–4].

To construct a designed SAM, it is essential to understand the fine structure and growth process of the SAM. The structure of the SAM has been studied by using various techniques including diffraction methods, scanning tunneling microscopy (STM), atomic force microscopy (AFM) and XPS spectroscopy. Recently, it is found that STM measurement with high gap impedance provides real images of individual alkanethiol molecules on metal substrates [5]. The well known ordered structure of $\sqrt{3} \times \sqrt{3}$ means that one thiol molecular is bond in the center of three Au atoms at the Au(111) surface [6].

Owing to redox potentials and photo-reactive pigments, the porphyrin derivatives are highly potential for wide applications, including catalytic, magnetic, sensing, and biological areas. As such, since the porphyrin rings in the myoglobin and cytochrome c are stabilized by docking into a hydrophobic pocket of proteins, which is often formed by aromatic residues [7], the interaction between the porphyrin and proteins (peptide domains) is counted as one of the key reactions in biochemical application. Thereby, it is important for the application of porphyrin to investigate the characteristics of SAM of peptide by exploiting the interaction between porphyrin and oligopeptide [8]. However, the characteristics of SAM of peptide constructed by binding of cystein on Au(111) at sub-monolayer coverages, remain much unrevealed.

In the present study, therefore, a comprehensive investigation of SAMs is carried out with the simplest peptides of thiol, and cystein adsorbed from the liquid phases to form the monolayer on Au(111) via Au–S bond. The primary attention of the present work is to focus toward the surface spectroscopic characterization of PSP1 and PSP2 peptides chemisorbed from the liquid phase on Au(111), with a point of view to elucidate the adsorption mechanism, adsorbate bonding, and molecular orientation.

2. EXPERIMENTAL

Peptide synthesis is performed by using an Fmoc solid phase strategy with a PepPlus 9050 synthesizer (PerSeptive) [9]. The crude peptide is purified by using a reversed phase HPLC system with a LibraKit RPC18 column (Shimadzu). The SAM is exploited to examine the existence of Au(111) terraces on the gold surface. Gold sample, Au(111), are prepared by sputtering and annealing onto freshly cleaved mica. Self-assembled monolayers are produced by incubating the gold substrates for 12 hours in a solution containing 0.5 mM of the peptides dissolved in trifluorethanol

and 10 mM MOPS buffer. Under these conditions the peptides adopt the α-helix secondary structure [8].

XPS spectroscopy is used to confirm the formation of Au-S bonds as well as unbound sulfur. The thickness of the SAM is measured by using intermittent contact mode AFM images and also calculated on the basis of the XPS spectroscopic results.

3. RESULTS AND DISCUSSION

In order to investigate the binding strength between Au and atoms comprised in PSP1 and PSP2, an Al *K*-α induced XPS spectrum for PSP1 and PSP2 monolayers, which are self-assembled on Au(111), with a wide range of energy spectrum are measured and fitted by using Gaussian/Lorentzial line shape. The binding energy spectrum of peptide atoms of oxygen(ls), nitrogen(ls), carbon(ls) and sulfur(2p) are found in range of 150–600 eV and that of gold (4f) is at around 100 eV. As the formation of SAMs of PSP1 and PSP2 on Au(111) is originated from the interaction between sulfur atom of peptides and Au, the binding energies of sulfur(2p) and gold(4f) core levels are important. By analyzing the sulfur and gold core levels, it is allowed estimated that the fraction of binding and unbinding thiol group and the thickness of SAM formed on the Au surface are estimated.

In Figure 1, an Al *K*-α induced XPS spectrums of the sulfur (2p) core level are displayed. The energy peaks of sulfur atom of peptides (PSP1 and PSP2) self-assembled on Au(111) appears in energy band between 161 and 165 eV. While the three energy peaks in XPS spectrum on SAM of PSP1 are induced by adsorption of peptides on Au(111), the four peaks in the spectrum are monitored with SAM of PSP2. Among those in the spectrum, the peak at 165 eV is originated from SH of unbinding peptides of PSP1 and PSP2 and the rest of peaks are due to the SH of binding peptides. Thereby, these experimental results implicitly indicates that the SAMs of PSP1 and PSP2 on Au(111) are not formed only by chemical binding but also physical adsorption of sulfur on Au atoms. Via integration of the energy peaks, in addition, it could be estimated that three molecules of PSP2 are combined with Au for formation of SAM, whereas two molecules of PSP1 are adsorbed on Au.

In the XPS spectrum of PSP1 and PSP2 SAM on Au(111), the energy peaks appearing between 168 and 170 eV is found to arise from adsorption of sulfur(2p) atom involved in MOPS (SO_3) buffer solution. In this range of binding energy, two energy peaks are generally induced due to the electron motions in sulfur ($2p_{1/2}$ and $2p_{3/2}$). In Figure 1, the peak A at 169.5 eV is originated from sulfur($2p_{1/2}$) and the peak B at 168.2 eV is from sulfur ($2p_{3/2}$). High intensity of energy peaks for the sulfur of MOPS implies that

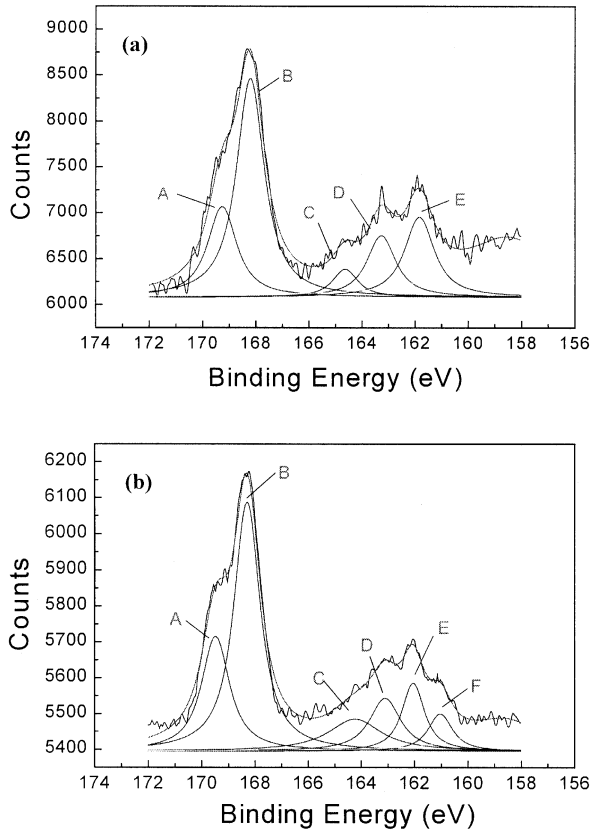

FIGURE 1 XPS spectra of sulphur (2p) core level of (a) PSP1 and (b) PSP2.

more sulfur atoms of MOPS are adsorbed on Au(111) than ones of peptides. Based on the integration of peaks, it could be estimated that 12 sulfur atoms of MOPS (SO_3) are adsorbed on Au.

By attenuation of the Au($4f_{7/2}$) signal of XPS upon SAM, the estimation of thickness of the peptide overlayer on Au is allowed. Based on a method of the inelastic mean free path (IMFP) of the Au($4f_{7/2}$) photoelectron, while the thin layer of PSP1 below 2 nm is formed on Au(111), the overlayer of PSP2 self-assembled on Au(111) is about 2–3 nm. These estimations of the overlayer thickness are good in agreement with the calculated values via Chem Office software (version 5.0, Cambridge Soft Co., U.S.A.).

The formation of SAMs of PSP1 and PSP2 on Au(111) is examined by the AFM images, as shown in Figure 2. From these images, it could be found that more dense overlayer on Au(111) is formed by PSP2 than PSP1, which means that PSP2 binding with Au is preferred to PSP1. This observation by

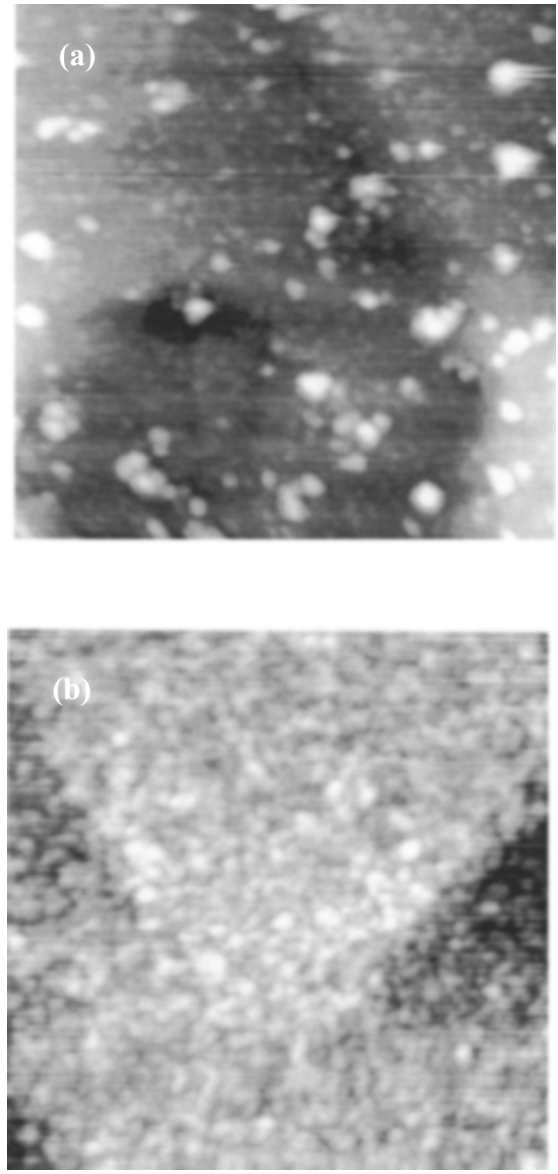

FIGURE 2 AFM images of SAM of (a) PSP1 and (b) PSP2 on Au (111).

AFM is consistent with that of XPS spectrum of sulfur(2p) core levels. In addition, it is also confirmed that the SAM thickness of PSP1 and PSP2 on Au estimated by XPS spectrum is well matched with one measured by AFM.

The steric energies of Au-peptide when one thiol group is bound with three Au-atoms, are 331.643 kcal/mol of PSP1, 75.043 kcal/mol of PSP2. Au-PSP2 is more stable than Au-PSP1 and PSP2 is well bound on Au(111) than PSP1.

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