Metal-molecular interface of sulfur-containing amino acid and thiophene on gold surface

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Abstract. Chemical-bonding states of metal-molecular interface have been investigated for L-cysteine and thiophene on gold by x-ray photoelectron spectroscopy (XPS) and near edge x-ray adsorption fine structure (NEXAFS). A remarkable difference in Au-S bonding states was found between L-cysteine and thiophene. For mono-layered L-cysteine on gold, the binding energy of S 1s in XPS and the resonance energy at the S K-edge in NEXAFS are higher by 8-9 eV than those for multi-layered film (molecular L-cysteine). In contrast, the S K-edge resonance energy for mono-layered thiophene on gold was 2475.0 eV, which is the same as that for molecular L-cysteine. In S 1s XPS for mono-layered thiophene, two peaks were observed. The higher binding-energy and more intense peak at 2473.4 eV are identified as gold sulfide. The binding energy of smaller peak, whose intensity is less than 1/3 of the higher binding energy peak, is 2472.2 eV, which is the same as that for molecular thiophene. These observations indicate that Au-S interface behavior shows characteristic chemical bond only for the Au-S interface of L-cysteine monolayer on gold substrate.

1. Introduction
Metal-molecular interface as bond state information is indispensable to control molecular devices and sensors using bio-molecules. Recently a formation of strong chemical bond between sulfur and gold was found and it has been used for the immobilization of sulfur-terminated organic molecules on gold substrate as an anchor [1—3]. For instance, thiols(R-SH) on gold surface are the prototypical self-assembled monolayers (SAMs) system in which Au-S covalent bonding anchors the molecules to the surface. As to the bio-molecules, proteins or artificial peptides have been shown to bind to gold surfaces through sulfur atoms [4, 5]. L-cysteine containing a sulfur atom in the molecule itself is a unique amino acid forming a chemical bond with gold surface through interaction of SH group with Au atoms [6, 7]. It has been reported that L-cysteine molecule dimerizes with L-cysteine pairs on Au (110) surface [8]. However, it is not fully understood as to why L-cysteine forms strong chemical bond with gold. So it is essential to clarify chemical bonding states between sulfur-containing molecules and gold. Core-level spectroscopies such as XPS and NEXAFS are effective methods to research metal-molecular interfaces. NEXAFS is a suitable method for the study of chemical state of Au-S bond, since it provides information about the electronic structures of both core levels and valence unoccupied states that are localized at the sulfur atom. Especially, NEXAFS at the S K-edge has advantages over that at the S L-edge because the core-to-valence resonance peak directly probes the valence unoccupied 3p* states due to the dipole selection rule [9—12].
In this study, we report the Au-S interface bond state between L-cysteine and gold surface using S K-edge NEXAFS and S 1s XPS analyses. For comparison, thiophene molecule, sulfur containing hetero-cyclic molecules, was also investigated as a molecule without-SH bond. Only for interface between L-cysteine and gold, we found a specific Au-S bond that has never been observed in metal sulfides nor the other sulfur compounds. The origin of the specific chemical bond is discussed on the basis of the differences in XPS and NEXAFS between L-cysteine and thiophene.

2. Experimental

All experiments were carried out at the BL 27A soft X-ray station in the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Japan. The double crystals of InSb (111) were used as a monochromator. The energy resolution of the monochromator was 1.1 eV at 2.5 keV (sulfur K-edge). This beam line has the end station consisting of two ultra high vacuum systems (UHV system), i.e., main analyzing chamber and sample preparation chamber. The base pressure of both chambers was in the order of 1.0 × 10⁻⁷ Pa. The main analyzing chamber consisted of a hemispherical electron energy analyzer (VSW Co. Class-100) for XPS measurements, manipulator and gas-dosing system. Preparation chamber was equipped with Knudsen-cell (K-cell) evaporator, quartz crystal thickness monitor and sample transfer system. The NEXAFS spectra were measured by a total electron yield (TEY) obtained by the sample drain current. The incident angle of the X-ray beam was 90° from the surface. The photon energy was calibrated by using Au 4f½/2 peak (E_b=84.0 eV) in the XPS spectra. L-cysteine was purchased from TOKYO KASEI KOGYO Co., Ltd (purity: 99.9 %). The thin films were grown by vacuum deposition method using K-cell evaporator. We prepared two kinds of films. One is multi-layer and the other is mono-layer. The thickness of the films was determined by the XPS measurements. In the XPS spectra for L-cysteine, the intensities of the C 1s, N 1s, O 1s and S 1s peaks normalized by the photoionization cross sections of the respective orbitals were in good agreement with the atomic composition of L-cysteine. This confirming that no contamination such as hydrocarbon or water existed and the molecules were not decomposed during the evaporation. Thiophene molecules were degassed by several freeze-pump-thaw cycles, and dosed onto the clean surface of gold at room temperature. For the preparation of multi-layered thiophene, the gold substrate was cooled at 77 K.

3. Result and discussion

S K-edge NEXAFS spectra for multi-layered and mono-layered L-cysteine are shown in Figure 1. In multi-layered sample, a sharp peak is observed at 2475.0 eV (marked A). It was reported that this peak originates from the resonant excitation from S 1s to valence unoccupied σ* orbitals that are localized at the S-C bond [13]. (hereinafter we call this peak as S 1s → σ*(S-C). For mono-layered sample, on the other hand, a sharp peak is located at 2484.0 eV (marked B), which is higher by 9.0 eV than that for multi-layered L-cysteine. For multi-layered sample, it is considered that the NEXAFS spectrum at the S K-edge represents the molecular L-cysteine, because most of the sulfur atoms do not interact with gold even if the sulfur atoms in L-cysteine at the top surface layer chemically interact with gold. The high energy peak observed in the NEXAFS spectrum for mono-layered sample (peak B) suggests that strong chemical bonds are formed between sulfur atoms and gold. For XPS, we have observed that the S 1s peak for multi-layered L-cysteine is located at 2472.2 eV [14]. For mono-layered sample, on the other hand, another peak was observed at 2480.4 eV originating from the formation of chemical bond between sulfur and gold atoms, so the energy shift of the S 1s between mono and multi-layered L-cysteine was 8.2 eV [14].

In order to confirm whether the unique chemical shift observed in mono-layered L-cysteine on gold is specific only to S-Au bond or not, we have investigated the XPS and NEXAFS spectra for
Figure 1. S K-edge NEXAFS spectra for L-cysteine taken by total electron yield. The spectra (a) and (b) represent multi-layered and mono-layered samples, respectively.

Figure 2. Molecular structures of L-cysteine (a) and thiophene (b).

the thiophene molecules. The molecular structure of thiophene is shown in fig. 2. Thiophene is aromatic ring molecule and sulfur atom is coordinated to two carbon atoms without SH bond. In figure 3, spectra (a) and (b) show the S K-edge NEXAFS spectra for mono-layered thiophene and mono-layered L-cysteine film, respectively. A sharp peak is observed at 2475.0 eV (marked A) for thiophene film while scarcely any peak is observed around 2480.0 eV where a strong peak is observed for mono-layered L-cysteine. This means that there is no specific chemical bond in mono-layered thiophene film on gold. The S 1s XPS spectra for the L-cysteine and thiophene on gold are shown in Figure 4. In mono-layered L-cysteine, the higher binding-energy and more intense peak (marked B) was already explained as Au-S specific bond. On the other hand, the binding energy for mono-layered thiophene appears at 2473.4 eV, but no peak is observed around 2480 eV. The energy shift of the S 1s between multi-layered and mono-layered thiophene is 1.2 eV. The energy difference between mono- and multi-layered films for thiophene is fairly small compared with those for L-cysteine. This means that there is no specific chemical bond in the case of mono-layered thiophene on gold substrate. These results lead to important conclusion that the observed specific chemical state representing large chemical shift is inherent to Au-S interface for mono-layered L-cysteine.

On the basis of these results, we confirmed unique result that the binding energy of the S 1s in XPS and resonance energy at S K-edge in NEXAFS are large for mono-layered L-cysteine on gold in comparison with those for mono-layered thiophene. As to the XPS results for Au-S interfaces, Petoral Jr. et al. reported that the S 2p binding energy for thiol molecule on gold surface is lower by 2.0 eV than that for molecular thiol, and they ascribed this energy shift to strong molecule-surface interaction [15]. Similar results were reported by the other groups [16–18]. However, the binding-energy shift of our result for mono-layered L-cysteine is opposite to those reported in previous papers. In addition, the value of energy shift (8.2 eV) is fairly larger than those shown in these reports. In the case of general metal sulfide, it is known that the charge transfer occurs from metal to sulfur, so the formal charge state of the sulfur atom is nearly $S^{2-}$. Considering the opposite direction of the present chemical shift, it is presumed that the charge transfer provides from sulfur to gold for mono-layered L-cysteine. The S 1s XPS results for sodium thiosulfate (Na$_2$S$_2$O$_3$), where the formal charge states of central and terminal sulfur atoms are $S^{6+}$ and $S^{2-}$, respectively, reveal that the chemical shift between $S^{6+}$ and $S^{2-}$ is 7.5 eV [19]. Thus it is elucidated that the formal charge state of sulfur atom in mono-layered
L-cysteine is close to $S^{6+}$.

In conclusion, we found a specific Au-S bond formation only in mono-layered L-cysteine on gold, where the formal charge state of sulfur is nearly $S^{6+}$, in contrast to normal metal sulfides. Such highly positive charge state in sulfur was not observed for thiophene film. Also, the $S^{6+}$ states were not observed for mono-layered L-cysteine on the other substrates such as copper and indium tin oxides [14]. Although both thiol and cysteine have SH bond, the essential difference in the molecular structures between thiol and cysteine is that cysteine has functional groups such as carboxyl and amino groups. Considering electron-withdrawing character of amino group, we anticipated that functional groups of amino acids participate in strong bond formation about Au-S interface. In these circumstances, we conclude that the observed unique chemical shift interpreted by the electron donation from sulfur to gold is inherent to sulfur-containing amino acids. This specific bond gives important information to know the influence from adsorption of bio-molecules in construction of the new bio-molecule devices.

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