

Metal-molecular interface of L-cysteine on gold surface

Mitsunori HONDA*, Yuji BABA, Norie HIRAO and Tetsuhiro SEKIGUCHI
JAEA, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

Introduction

Metal-molecular interface as bond state information is indispensable to control molecular devices and sensors using bio-molecules. For instance, thiol (R-SH) is well known as forming a strong chemical bond with Au surface through interaction of SH group and Au atoms [1, 2]. But little is known about the behaviour of interface states between Au and sulfur atoms. Thus the investigation of the metal-molecular interface is essential for understanding the mechanism of chemical bond formations in order to design molecular devices. In this report, we describe XPS and NEXAFS studies of L-cysteine adsorbed on Au surface, which show that Au-S interface forms specific chemical bond.

Experimental

All experiments were carried out at the BL-27A soft X-ray station. We concentrated on amino acids, i.e., L-cysteine [$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$] as sulfur-containing molecules, because SH exists at the end of the carbon chains. The chemical bonding states at the metal-molecular interface were measured by near edge X-ray adsorption fine structure (NEXAFS) at the S K-edge, and S 1s X-ray photoelectron spectroscopy (XPS). The molecules were evaporated using Knudsen-cell. Two kinds of films were prepared, i.e., monolayer and multilayer of L-cysteine on gold surfaces.

Result and Discussion

S K-edge NEXAFS spectra for multi-layered and mono-layered L-cysteine are shown in Fig.1. In multi-layered sample, a sharp peak is observed at 2475.0 eV (marked A). It was reported that this peak originates from resonant excitation from S 1s to valence unoccupied σ^* orbitals that are localized at the S-C bond [3]. (Hereinafter we call this peak as S 1s $\rightarrow \sigma^*(\text{S-C})$). On the other hand, in mono-layered sample, 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 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.

Figure 2 shows the S 1s XPS spectra for L-cysteine on gold surface. The spectra (a) and (b) represent multi-

layered and mono-layered samples, respectively. For multi-layered sample, only one main peak (marked A) is observed at 2472.2 eV. It is presumed that this peak corresponds to the S 1s from sulfur atoms in molecular L-cysteine. For mono-layered sample, on the other hand, two peaks are observed. The position of the lower-energy peak (marked A) is close to that for the multi-layered sample. It is deduced that the higher-energy peak at 2480.4 eV (marked B) originates from the formation of chemical bond between sulfur and gold atoms. Interestingly, newly one peak is appeared at only mono-layered coverage of L-cysteine in the S 1s XPS spectrum. This newly one peak (marked B) in fig. 2 (b) indicated that S 1s core level shifts to deep side.

On the basis of these results, it is elucidated that the electrons are donated from the sulfur atom to the gold substrate, and the sulfur atoms are positively charged. We conclude that the strong Au-S bonds that are recently used for the immobilization of molecules are due to the observed specific Au-S bond.

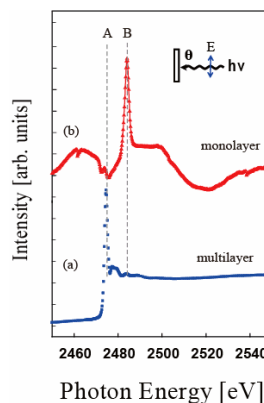


Fig. 1 S K-edge NEXAFS spectra for L-cysteine on the gold surface taken by total electron yield. The spectra (a) and (b) represent multi-layered and mono-layered sample, respectively.

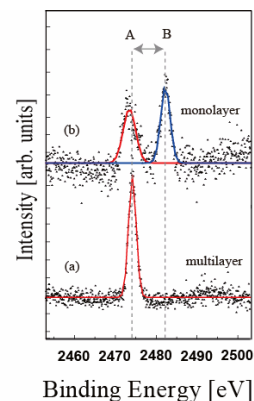


Fig. 2 S 1s XPS spectra for L-cysteine on the gold surface which was taken at $h\nu = 3000$ eV. The spectra (a) and (b) represent multi-layered and mono-layered sample, respectively.

References

- [1] M. R. Albert, *The Surface Scientist's Guide to Organometallic Chemistry* (American Chemical Society, Washington, DC, 1987).
 - [2] A. Ulman, *An Introduction to Ultrathin Organic Films* (Academic Press, San Diego, 1991).
 - [3] R. Chauvistre *et al.*, Chem. Phys. **223**, 293 (1997).
- *honda.mitsunori@jaea.go.jp