

Development of S *K*-edge NEXAFS spectroscopy using soft x-ray in the atmosphere and solution conditions

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Introduction

The interface between metal and organic molecule plays the central role in developing new bio-related devices as has been extensively studied. For example, metal-molecular interface between gold and sulphur (S-Au) atoms has received considerable attention over the years because of its strong chemical bond; thus, we pay attention to this strong bond in the present work.

NEXAFS spectroscopy using vacuum ultraviolet and soft x-ray is a powerful tool to reveal the electronic structures for bio-molecules such as DNA and Proteins because the *K* shells of the atoms of bio-molecules exist in this energy region (from 100eV to 3000eV). However, the problem lies in the fact that most of soft x-ray spectroscopy usually work under vacuum condition. For the development of bio-molecular devices, it is significant to reveal the molecular dynamics under atmospheric environments. Accordingly, we have recently developed the instrumental system that allows us to measure wet samples under atmospheric conditions using fluorescence yield method.

In the present report, we describe the results for the measurement of the S *K*-edge NEXAFS spectroscopy for L-cysteine [HSCH₂CH (NH₂) COOH] molecule of adsorbed state and in aqueous solution.

Experimental

All systems were developed at the BL 27A soft X-ray station. The chemical bonding states in atmosphere and aqueous solutions were evaluated by the S *K*-edge NEXAFS spectroscopy using fluorescence yield mode. We note in the total yield mode that it is not very easy to separate sulfur characteristic fluorescence from high background signals coming from the substrate Au 3*d* absorption. In order to reduce the background, we used a new x-ray detector which combined ZnS:Ag scintillator and a photomultiplier tube (PMT). The samples investigated were L-cysteine adsorbed on gold substrate in atmosphere and L-cysteine dissolved in aqueous solutions.

Result and Discussion

Figure 1 show the S *K*-edge NEXAFS spectra for (a) L-cysteine adsorbed on gold substrate in atmosphere and (b) aqueous solutions including L-cysteine molecule. The spectra were taken with low incident angle ($\theta=3^\circ$).

In figure (a), we confirmed that the lower energy peak (marked A) is close to that for multilayer L-cysteine,

while the higher one (marked B) is most likely for molecules strongly interacted with the substrate. Thus, we here tentatively consider that the both peaks originate from resonant excitation from S 1*s* to valence unoccupied σ^* orbitals that are localized at the S-C bond[1]; hereinafter, this resonance is referred to as S 1*s* $\rightarrow \sigma^*(S-C)$.

In figure (b), we show the S *K*-edge NEXAFS spectra for L-cysteine molecule in aqueous solution in two different pH environments (pH=4.01 and pH=9.18). Careful inspection indicates that the intensity ratio between the pre-edge structures of A and B are different for the two pHs. This is most probably ascribed to the changing of ionic structure of L-cysteine molecule depending on pH condition, as estimated in zwitter ion nature of amino acid.

In summary, we succeeded in measuring the S *K*-edge NEXAFS for L-cysteine adsorbed on gold substrate in atmosphere and L-cysteine aqueous solutions using fluorescence yield. Furthermore, this system makes it possible to directly observe the molecular dynamics in aqueous environments, which may contribute to create new road for the development of bio-molecular devices.

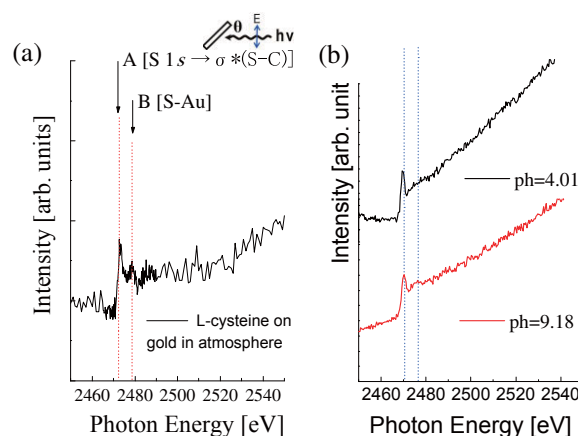


Fig. 1 (a) S *K*-edge NEXAFS spectra in atmosphere condition and (b) S *K*-edge NEXAFS spectra in aqueous solution in pH=4.01 and pH=9.18

References

[1] R.Chauvistre, J.Hormes, E.Hartmann, N.Etzenbach, R.Hosch, J.Hahn, Chem. Phys. 223, 93(1997) 2.

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