

Paper

Spectroscopic Study on the Adsorption Reaction of L-Cysteine on Cu nanoparticle/Ag under *in vivo* condition

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We have studied the adsorption reaction of L-Cysteine on Cu nanoparticle by S K-edge NEXAFS measurement. The Cu nanoparticle used for the adsorption reaction is fabricated by the gas evaporation method. The results of the NEXAFS measurement are given as follows. The electron transfer between Cu nanoparticle and substrate changes the chemical state of Cu nanoparticle. The behavior of adsorbed L-Cysteine is influenced by the electron transfer between Cu nanoparticle and substrate. This result suggests the possibility that the catalytic activity of nanoparticle can be controlled by the electron transfer between nanoparticle and substrate.

1. Introduction

Decay of protein is caused by decay of tissue. These decays are accompanied with pathogenesis of cancer or ulcer. We speculate that the production of the thiol molecule deriving from sulfur containing amino acid in our body is caused by the decay of protein. Detecting of this thiol molecule has a possibility to enable using for the screening test of cancer or ulcer. If the nanoparticle with a large specific surface area is used for the detection, the number of adsorbed molecule per unit area of sample is increased. In the measurement of the Near Edge X-ray absorption Fine Structure (NEXAFS), the increase of the amount of adsorbed molecule in the measurement area of sample facilitates the detection of the adsorbed molecule. As a result, the nanoparticle has the advantage of facilitating the detection of adsorbed molecule. However, there is various sulfur containing molecule in our body[1]. To discriminate between thiol molecule and other sulfur containing molecules, it is important to find the material with surface, which has an advantage of adsorbing thiol molecule without dissociation.

If the thiol molecule dissociates after the adsorption, it is difficult to determine whether the adsorbed molecule is thiol molecule or other sulfur containing molecules. In our previous study, the L-Cysteine, which is the thiol molecule in our body, adsorbed on Cu single crystal surface

without dissociation[2]. Assuming from that results the L-Cysteine adsorbs on Cu nanoparticle without dissociation. For this assumption, Cu nanoparticle is usable for the detection of thiol molecule. Thus, revealing the adsorption reaction mechanism is important. We focus on the adsorption reaction of L-Cysteine on Cu nanoparticle in this study.

We have not studied the adsorption reaction of L-Cysteine on Ag, however, we have used Ag polycrystalline sheet to support Cu nanoparticle. In our previous study, dimethyl sulfide (DMS), which is sulfur containing molecule, adsorbed on Ag polycrystalline sheet without dissociation[3]. Therefore, we speculate that L-Cysteine also does not dissociate on Ag substrate surface.

In the case of Cu nanoparticle on Ag substrate, we think that the adsorption reaction of L-Cysteine on Cu nanoparticle is influenced by interaction between Cu nanoparticle and Ag substrate. T. Toda *et al.* have reported about the catalytic performance of phosphoric acid fuel cells[4]. The catalytic performance of Pt alloy is higher than that of pure Pt. The catalytic reaction of Pt is influenced by the interaction, which is caused by alloying the metal of catalyst. If the metal nanoparticle has a contact with the metal substrate surface, it is thought that the surface atoms of the substrate influence the chemical adsorption reaction of L-Cysteine on Cu nanoparticle surface. In the case of metal

nanoparticle on the metal substrate, it has the possibility that an electron transfer occurs at the interface between Cu nanoparticle and Ag substrate.

The purpose of this study is to reveal the influence of interaction between Cu nanoparticle and Ag substrate by the measurement of S-K edge NEXAFS under water environment to simulate *in vivo* condition.

2. Experimental

Cu nanoparticle was fabricated by the gas evaporation method using Cu (4N4) sheet as an evaporation source. The gas evaporation method provides the Cu nanoparticle, which has clean surface[5]. The Cu nanoparticle was deposited on the Ag and Ni polycrystalline sheets. The Ni polycrystalline sheet was heated at 873 K in air to make a layer of insulating oxide. It is thought that the oxide layer inhibits an electron donation from Cu nanoparticle to Ni substrate. Therefore, it is speculated that the adsorption reaction of L-Cysteine on Cu nanoparticle is not influenced by interaction between Cu nanoparticle and substrate. Fabricated samples are showed in the table 1. These samples were set in L-Cysteine aqueous solution of 20 ml (0.25 mol/l) at room temperature for 12 hours. We rinsed off the physisorbed molecules on samples by distilled water before the NEXAFS measurement. To simulate *in vivo*, these samples were packed by use of the polyethylene ($[-CH_2-CH_2-]_n$) film with distilled water to keep water environment. The X-ray attenuation by the polyethylene film and water is negligibly small because of the thickness of the film and water is very thin. It is necessary to use the soft X-ray to measurement of S K-edge (around 2470 eV) NEXAFS. An intensity of soft X-ray is attenuated by air. However, the measurement under atmospheric condition of He gas (He-path) enables the using soft X-ray. The measurement of S K-edge NEXAFS under water environment was carried out by the yielding fluorescence X-ray at the BL-3 with He-path on Hiroshima Synchrotron Radiation Center (HSRC)[6].

Table 1. Fabricated samples.

Sample	Substrate	Cu nanoparticle
1	Ag	Deposited
2	Ni	Deposited
3	Ag	Not deposited
4	Ni	Not deposited

3. Results and discussion

AFM measurement

Diameter of Cu nanoparticle was measured by AFM. The AFM observation was carried out by tapping mode. We used the measured height value of Cu nanoparticle to evaluate the diameter of nanoparticle. Figures 1 and 2 show the measured AFM image and distribution of Cu nanoparticle on Si wafer. The diameter of Cu nanoparticle was estimated to be 6.4 ± 1.6 nm.

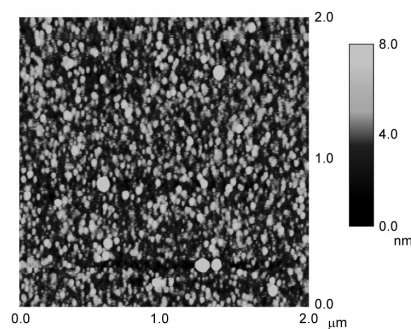


Figure 1. AFM image of Cu nanoparticle on Si wafer.

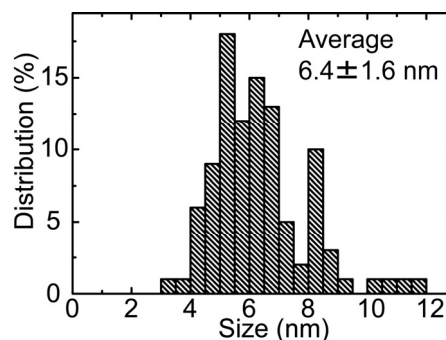


Figure 2. Distribution of Cu nanoparticle diameter.

NEXAFS measurement

Table 2 shows the height of the edge jump of S K-edge NEXAFS spectra for samples 1 - 4. Edge jump is defined as the difference in fluorescence yield intensity at the pre-edge (2465.0 eV) and post-edge (2487.5 eV) photon energies of the NEXAFS spectra. Height value of the edge jump is related to the amount of S atom. Because of the L-Cysteine molecule contains S atom, the height value of the edge jump is proportional to the amount of adsorbed L-Cysteine molecule. D. Tomihara *et al.* have reported that the Cu(100) surface has the adsorption sites of L-Cysteine[2]. We expect the amount of adsorbed L-Cysteine on sample with Cu nanoparticle is larger than that of sample without Cu nanoparticle.

As shown in table 2, the height value of edge jump for sample 1 is larger than that for sample 2. The amount of adsorbed L-Cysteine and/or

L-Cysteine thiolate on sample 1 is larger than that of sample 2. Thus, it is thought that the amount of adsorbed L-Cysteine has been increased by the presence of Cu nanoparticle. There is the Cu nanoparticle on sample 3. The amount of adsorbed L-Cysteine on sample 3 should be larger than that of sample 4. Although enlarged view of the spectra for samples 3 and 4 is not shown here, there is little difference of amount of adsorbed L-Cysteine between samples 3 and 4. Therefore, the chemical state of substrate is important for the adsorption reaction of L-Cysteine as well as Cu nanoparticle.

To reveal the influence of interaction between Cu nanoparticle and substrate on adsorption reaction of L-Cysteine on Cu nanoparticle surface, we compare the spectrum for sample 1 (Cu nanoparticle/Ag) with that for sample 3 (Cu nanoparticle/heated Ni). There is a significant difference in the height value of the edge jump between samples 1 and 3. As described in experimental section, the heated Ni polycrystalline sheet at 873 K in air has an oxide layer on the surface. Because of this oxide layer is chemically stable, it is thought that an electron donation from Cu nanoparticle to Ni substrate is prevented by the oxide layer. In the case of sample 3, the adsorption reaction of L-Cysteine on Cu nanoparticle is influenced by only the interaction between L-Cysteine and Cu nanoparticle. On the other hand, in the case of sample 1, there is not oxide layer on the Ag substrate surface. It is thought that there is the electron donation from Cu nanoparticle to Ag substrate. Therefore, we think that the adsorption reaction of L-Cysteine on Cu nanoparticle surface is influenced by the electron donation from Cu nanoparticle to substrate.

Figure 3 shows the S K-edge NEXAFS spectra for samples from 1 to 4, L-Cysteine powder[7] and atomic S on Rh(100)[8]. To compare the chemical state of adsorbed L-Cysteine, all spectra for samples are normalized by the edge jump. As shown in Figure 3, a peak at around 2473.0 eV is assigned to the L-Cysteine. A peak at around 2470.0 eV is assigned to the atomic S, which is the element of dissociated L-Cysteine.

In comparison with the spectra for samples 1 and 2, the shapes of the spectra are similar. However, the peak intensity at around 2470.0 eV of spectrum for sample 2 is larger than that of sample 1. The sample 2 has the larger amount of the atomic S, which is originated from L-Cysteine, than the sample 1. On the other hand, the peak intensity at around 2470.0 eV of spectra for samples 3 and 4 are larger than that of samples 1

and 2. Hence, the amount of the dissociated adsorbates on samples 3 and 4 are larger than that of the samples 1 and 2. There is little difference of the amount of adsorbed L-Cysteine between samples 3 and 4. In comparison with the spectra for samples 1 and 3, the amount of adsorbed L-Cysteine on sample 1 is three orders as large as that on sample 3. In addition, there is also the difference of the chemical state of adsorbed L-Cysteine. The amount of dissociated element of the adsorbed L-Cysteine on sample 3 is larger than that on sample 1. Despite the samples 1 and 3 have Cu nanoparticle, the adsorption behaviors of L-Cysteine are different. This result indicates that the difference of adsorption reaction does not depend on the presence of Cu nanoparticle. The difference between samples 1 and 3 is the substrate metal. Therefore, we have focused on the interface between Cu nanoparticle and substrate metal.

In the case of sample 3, there is not the electron transfer between substrate surface and Cu nanoparticle because of the layer of insulating oxide. Yagi *et al.* have reported about the adsorption behavior of $(\text{CH}_3)_2\text{S}$ molecule on $c(10 \times 2)\text{Ag}/\text{Cu}(100)$ surface in the previous study[9]. They showed the occurrence of the electron transfer from Cu(100) surface to the over layer Ag atoms. It is thought that there is the electron transfer from Cu nanoparticle to Ag substrate as well as $c(10 \times 2)\text{Ag}/\text{Cu}(100)$ surface. Thus, we speculate that the Ag substrate has squeezed the electron from Cu nanoparticle at the interface between Cu nanoparticle and Ag substrate. Generally, the back donation of electron to antibonding orbital of adsorbed molecule causes the molecular dissociation. In the case of this study, if there is the back donation of electron from Cu nanoparticle to the antibonding orbital of adsorbed L-Cysteine, the dissociation of adsorbed L-Cysteine is caused. When the L-Cysteine adsorbs on the Cu atoms that is squeezed the electron by Ag substrate, it is thought that the back donation does not occur. We have speculated that the L-Cysteine adsorbs on Ag substrate surface and interface between Cu nanoparticle and Ag substrate. Judging from this discussion, adsorbed L-Cysteine on the interface is difficult to dissociate into atomic S. On the other hand, as shown in table 2, the amount of adsorbed L-Cysteine on sample 1 is larger than that of sample 2. The amount of adsorbed L-Cysteine on the interface is larger than that on Ag substrate surface for sample 1. The amount of the adsorbed L-Cysteine is increased by the presence of the

interface. As a result, the chemical state and the amount of adsorbed L-Cysteine are influenced by the interface, which has the electron transfer. Therefore, the interface is important for the adsorption reaction of L-Cysteine.

Table 2. Height of the edge jump of NEXAFS spectra for samples 1 - 4.

Sample	Height of the edge jump
1	0.29
2	1.02×10^{-2}
3	2.90×10^{-3}
4	3.80×10^{-3}

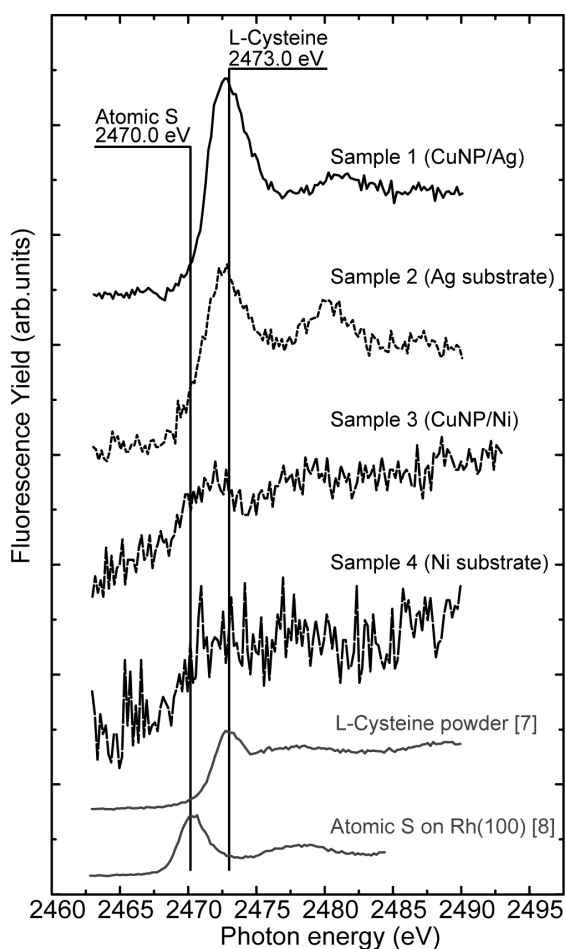


Figure 3. S K-edge NEXAFS spectra for samples from 1 to 4, L-Cysteine powder, atomic S on Rh(100). Spectra of samples are normalized to the height value of the edge jump.

4. Conclusion

We have studied the adsorption reaction of L-Cysteine on Cu nanoparticle by S K-edge NEXAFS under water environment. Fabricated Cu nanoparticle has high dispersion. The diameter of the Cu nanoparticle is estimated to be 6.4 ± 1.6 nm. There is the interaction between Cu nanoparticle and substrate. The Ag substrate

squeezes the electron from Cu atoms at the interface between Cu nanoparticle and Ag substrate. The adsorbed L-Cysteine does not dissociate into the atomic S on the interface. The amount of the adsorbed L-Cysteine is increased by the presence of the interface. The behavior of the adsorption reaction of L-Cysteine is influenced by the interface, which has the electron transfer. This study has revealed that the interface between Cu nanoparticle and Ag substrate is important for the L-Cysteine adsorption on the Cu nanoparticle.

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