

## EXAFS and XANES Spectroscopical Analysis of Bacterial Biosorption of Heavy Metals

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Many bacteria or fungi have a cell wall or envelope that is capable of passively adsorbing high levels of dissolved metals usually via a charge-mediated attraction. The cell surface of many microorganisms, including cyanobacteria, consists of biopolymer such as polysaccharides, proteins, and lipids, which act as a basic binding site of heavy metals. The functional groups within the cell wall provide the amide, amine, hydroxyl, carboxylic, imidazole, sulfate, sulfhydryl, phosphate, and thiol groups that can bind metals.

The valency and fine structure of Hg atom adsorbed or accumulated in fungal or bacterial biomass have not been well studied. The XANES and EXAFS offer the basic knowledge of understanding the oxidation states and fine structures of Cd atom in biomass toward a further study on the biosorption and bioaccumulation mechanism of heavy metals.

The EXAFS and XANES spectra were collected at the Spring-8 beamline SP12B1 of the JASRI. The electron storage ring was operated with an energy of 8.0 GeV and a current of 100-200 mA. Data were collected in fluorescence or transmission mode with a Lytle ionization detector for the Cd (26711 eV) K-edge experiments at room temperature. The EXAFS data will be analyzed by using the UWXAFS 3.0 program and FEFF 8.0 codes.

The cell surface of genetically-engineered *Escherichia coli* bacteria might consist of biopolymer such as polysaccharides, proteins, and lipids, which act as a basic binding site of Cd ions. The functional groups within the cell wall of genetically-engineered *Escherichia coli* bacteria provided the sulfate ( $\text{SO}_4^{2-}$ ), thiol (mercaptan) or sulfhydryl (mercapto, R-SH) groups that can bind Cd ions. Especially, thiol or sulfate functional groups are stronger sites bound with Cd ions and may form Cd-SH or CdSO<sub>4</sub> complex. The S and Cd EXAFS

spectra indicating the Cd-S species with bond distances of  $1.98 \approx$  and  $2.05 \approx$ , respectively were found in Figures 1(a) and 1(b). Coordination numbers (CN) of the Cd-S species from Cd and S EXAFS spectra were 2.3 and 2.5, respectively. The uptake of Cd ions can take place by entrapment in the cellular structure and subsequent sorption onto the binding sites present in the cellular structure of genetically-engineered *Escherichia coli* bacteria.

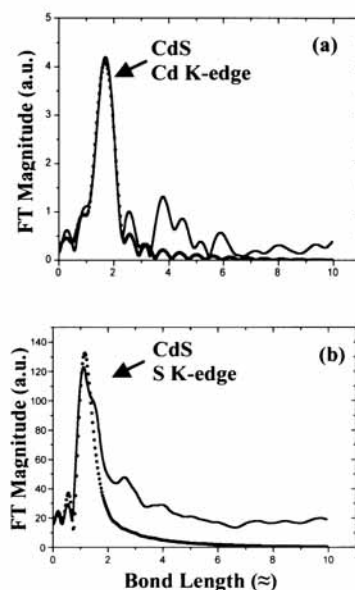


Figure 1 FT of (a) S (CdS) and (b) Cd (CdS) K-edge EXAFS oscillation  $k^{-1}$  (k) of the Cd-absorbed genetically-engineered *Escherichia coli* bacterial biosorbents.

## In-situ X-ray Absorption Spectroscopy Studies the Formation mechanism of XC-72 Carbon Supported Silver Nanoparticles in Microemulsion System

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For the nanoparticle designs and for the process scaling up, the formation mechanism of nanoparticles is very important to provide the detailed information of the cluster growth. In order to understand the formation mechanism of metallic cluster in microemulsion system, in-situ XAS is a powerful technique to provide the variation of the electronic structure for the selected absorber and the local environment around the selected absorber. In this study, the microemulsion solution composes  $\text{AgNO}_3$  as a salt dissolved into distilled water, heptane as an oil phase and AOT as a surfactant. The hydrazine microemulsion solution was used as a reducing agent. The results from in-situ XAS measurement are shown in the following.

Figure 1 shows the successive variation of XANES of Ag K edge for Ag microemulsion solution at different hydrazine dosages. The edge energy position shifts to higher energy and the intensity of the white line decreases as an increase of hydrazine dosages, indicating that  $\text{Ag}^+$  was reduced to form  $\text{Ag}^0$  cluster. The FT spectra of Ag L<sub>III</sub>-edge for Ag microemulsion solution were shown in figure 2 at different dosages of hydrazine. The peak intensity of FT spectra for Ag-Ag contribution increases gradually and that for Ag-O contribution disappears as the dosages of hydrazine increases, which is consistent with the result of XANES spectra. The further EXAFS analysis will be carried out to provide deep insight into the formation mechanism of Ag/XC-72 metallic

nanoparticles in microemulsion.

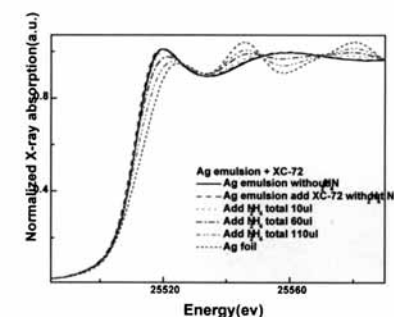


Figure 1 XANES spectra of Ag K edge for  $\text{AgNO}_3$ /AOT/heptane/XC-72 microemulsion system at different dosages hydrazine.

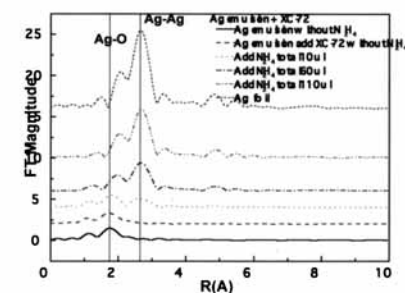


Figure 2  $k^3$ -weighted FT spectra of Ag K edge for  $\text{AgNO}_3$ /AOT/heptane/XC72 microemulsion system at the different dosages hydrazine.