Hard X-ray absorption spectroscopy of a gold complex included by cyclodextrin

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Introduction

Gold recovery using the inclusion of cyclodextrins (CDs) has been proposed as an environmentally friendly method [1]. This method is as simple as mixing $KAuBr_4$ and CD in a 1:2 ratio; α-CD forms gold-containing nanowires that precipitate immediately, whereas β- and γ-CD do not. Crystallographic analysis suggests that the different binding positions of K to CD determine whether nanowire formation occurs or not. To investigate the difference in the binding of K to each CD in aqueous solution, X-ray absorption spectroscopy of the K1s absorption edge was performed at the beamline BL-11 of HiSOR.

Experiment

A mixture of $KAuBr_4$ aq. (20 mM) and CD aq. (40 mM) was prepared and the measurements were carried out on drop-dried films. 20 μl of the solution was dropped onto a potassium-free quartz glass and vacuum dried. This process was repeated five times to obtain a K-containing thin film with sufficient concentration to be used for fluorescence measurement. A special holder was used for the measurement as a solution and the concentration of $KAuBr_4$ aq. was 50 mM. The sample was placed in the He chamber, and synchrotron radiation was incident at an angle of 45° to the normal of the sample. The incident light intensity for normalization was measured by filling the ion chamber with He-N_2 mixed gas.

Results and Discussion

First, solid samples of KCl and KBr were measured for energy calibration (Figure 1). The obtained spectrum of KCl is good agreement with the previous study [2] and the energy axis was calibrated at the Pre-edge peak 3610.2 eV and Post-edge peak 3614.2 eV. Figure 2 shows the spectra of $KAuBr_4$ in film and liquid and a 1:2 mixture of $KAuBr_4$ and α-CD in the film. In the drop-dried film of $KAuBr_4$ aq., K^+ and $AuBr_4^-$ are considered to be ionically bonded and not expected to form molecular orbitals by coordination bonds. Therefore, the K^+ 1s→4p transition appears strongly at 3611.5 eV. On the other hand, the spectrum of $KAuBr_4$@α-CD is similar to that of liquid $KAuBr_4$ due to the coordination of some H_2O to K^+. In Figure 3, the spectra of drop-dried films when various CDs are mixed with $KAuBr_4$ solution. Comparing each spectrum, there is a difference especially in the intensity around 3610 eV. The spectra were fit and separated by the components for each peak and the difference in the peak intensities is discussed in point of the binding of K to each CDs.

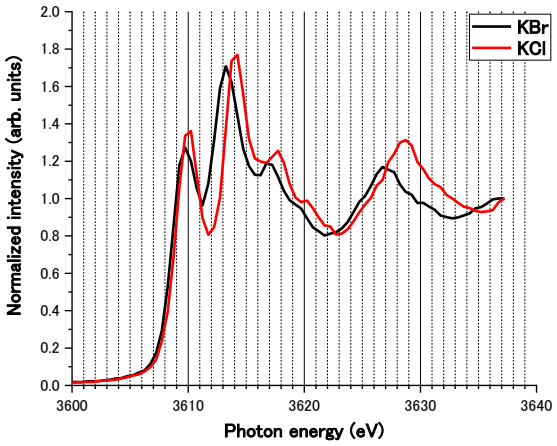

Figure 1 XAS spectra of KCl and KBr at the K1s edge.

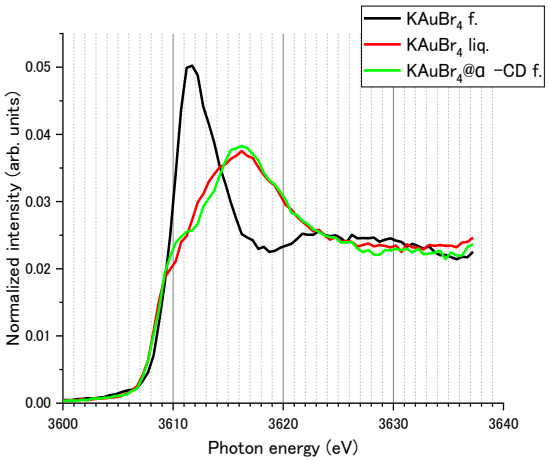

Figure 2 XAS spectra of $KAuBr_4$ (film), $KAuBr_4$ (liquid), and $KAuBr_4$@α-CD (film) at the K1s edge.

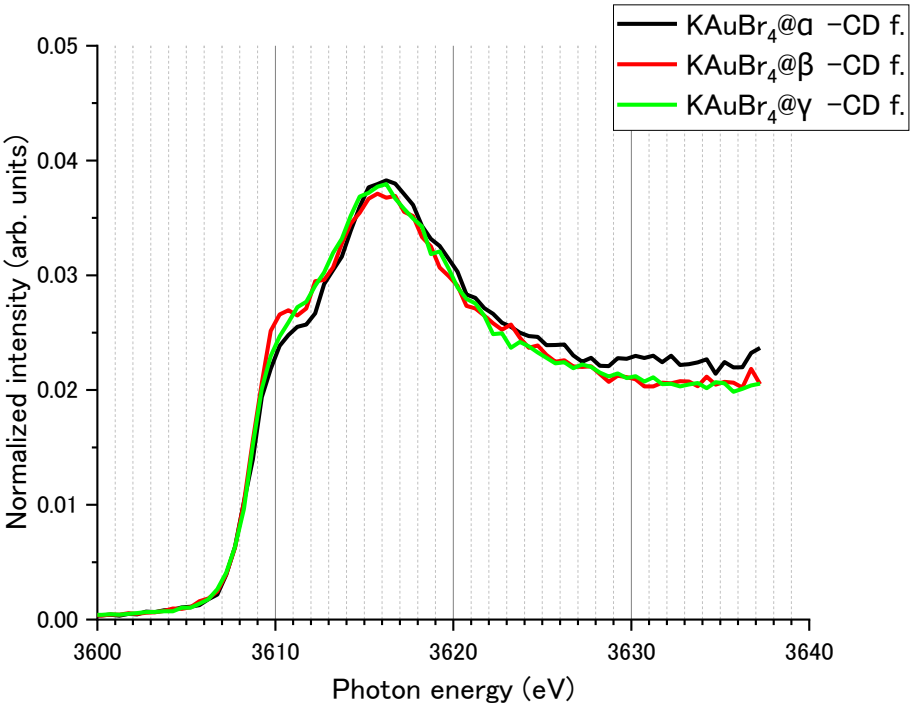

Figure 3 XAS spectra of $KAuBr_4$@α-CD, @β-CD, and @γ-CD (film) at the K1s edge.

REFERENCES

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