Ultrafast XAFS Studies on the Photoabsorption Processes

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Abstract: We have investigated photoabsorption processes of oxides using pulse x-rays emitted from X-ray free electron laser (XFEL) "SACLA". The target was photocatalysts such as WO_3 and $BiVO_4$ which were excited with 400 nm pulse lasers. Its photoabsorption and decay processes were monitored by XFEL pulses using a pump-probe method We could follow the process with 500 fs time resolution. We could determine the electronic state and structure changes in the photoabsorption process in the talk and discuss the future directions.

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Keywords: Pump-probe, XAFS, XFEL.

1. Introduction

X-ray absorption fine structure is a powerful method to characterize active sites of catalysts. The XAFS has now made big progresses in 4 directions [1]. First progress is to observe the nano region and / or imaging. The second is high energy resolution to detect the precise electron state. The third is to measure the XAFS of the dilute system. The final one it to observe the chemical reaction in the high time resolution under the reaction conditions. High time resolution XAFS can be achieved by Quick XAFS (1 s to ms region) or by Dispersive XAFS (ms to μs). When ns to ps time resolution is necessary, pump-probe approach is usually carried out. In the pump-probe method, the time resolution is limited by the pulse width of pump light and probe light. Laser is usually used for pump light so that the pulse width has reached fs or less. The pulse width of synchrotron radiation is still around 1 ns so that the XAFS pump probe method is limited to ns order. Recently new X-ray source called as XFEL (X-ray Free electron laser) has been developed[1]. It provides a ultra-short pulse with the width of less than 1 ps. We have measured fs pump-probe XAFS using XFEL to follow the photoabsorption processes of photocatalysts such as WO_3 and $BiVO_4$ in order to reveal the local structure and electronic change around cations after the photoabsorption.

2. Experimental

We carried out the pump-probe XAFS measurement in PF-AR NW14A in KEK and SACLA in SPring-8. NW14A was used for the measurements with more than 1ns while SACLA was used for the ps-fs time scale. Photocatalysts were dispersed in the aqueous solution and pumped up to make a flow. The dispersion of photocatalyst was necessary in two ways. One was to adjust the concentration Because the absorption coefficients of UV light were much larger than those of x-ray, we have to reduce the concentration to excite all photocatalysts by UV-light. The other was the damage of laser pulses so that we had to supply the fresh samples constantly.

3. Results and discussion

3.1 Photoabsorption process of WO_3 [2, 3]

WO_3 is a Z scheme type photocatalyst. It absorbs visible light to oxidize the water. We investigated the W local structure and electronic state change by L_3 edges XAFS. Figure 1 shows differential spectra of the photoabsorption process detected by the L_3 edge XAFS. The change of differential spectra could be explained by the electron transfer to W to create W^{5+}, followed by the structure changes.

3.2 Photoabsorption process of $BiVO_4$ [4]

$BiVO_4$ is another photocatalyst. Valence state was composed of Bi 6s states so that the valence hole could be monitored by Bi L_3 edge. As a result of the pump-probe measurement, we could not observe no big edge shift in the Bi L_3 edge as shown in Fig. 2. Rather we observed the excitation of thermal oscillation to produce the structure change. In our analysis first reduction of peak B in 2 ps was due to thermal oscillation between Bi cation and VO_4 unit. Following increases in peaks A and C and further decrease in peak B were due to the elongation of Bi-O bond distances.

4. Future prospects and conclusions.

The pump-probe XAFS provides us local structure and electronic state change in fs-ps. We can expand the measurement range to EXAFS region as shown in Fig.3 which offers the direct structural change information. Time tag method allows us to carry out 100 fs or less time resolution.

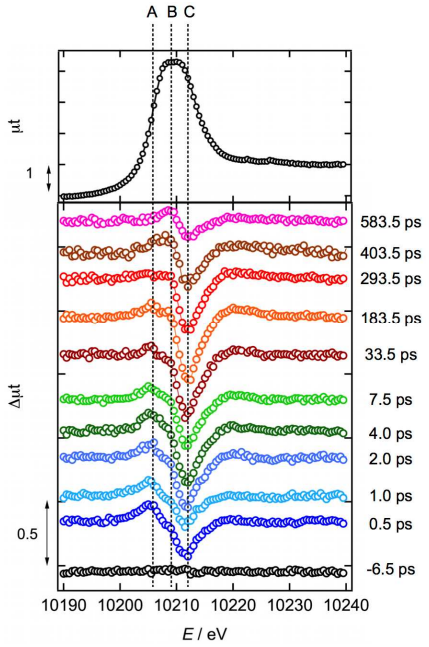

Figure 1 Ultrafast XAFS difference spectra of WO_3.

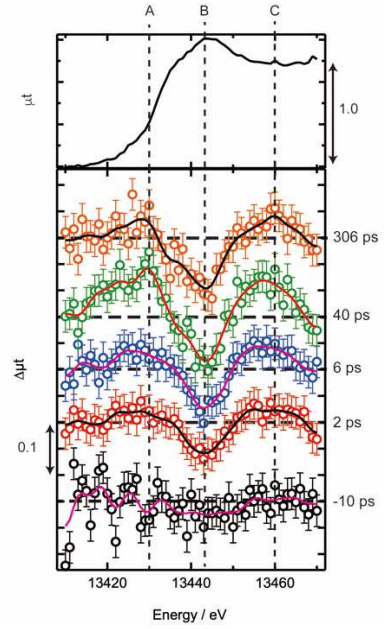

Figure 2 Ultrafast XAFS difference spectra of $BiVO_4$

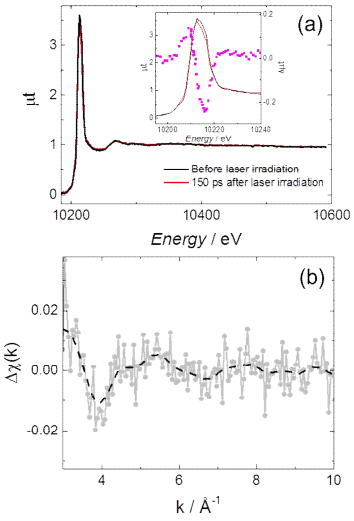

Figure 3 Ultrafast EXAFS measurement of WO_3 after photo absorption.

References

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