

Elucidation of local structure change of photocatalysts during the photoabsorption process by use of fs-ps pump-probe XAFS method

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Introduction

The local structure and electronic states of metal in photocatalysts were rarely investigated during the photoabsorption processes though such information is quite important to understand the role of the central metal atoms in the photocatalysis and to design the photocatalysts in a rational way. The pump-probe XAFS is the most suitable technique to elucidate the information about the local structure and electronic state change of the central atoms. In the photocatalysis, the photoabsorption is discussed in the band theory where valence electron is excited to d empty state of the central metals in fs time scale. We applied the pump probe to L-edge absorption of WO_3 which allows us to directly monitor the number of d electron vacancy by $2p_{3/2}$ to 5d transition. We also measured the pump-probe XANES of BiL_3 edge of BiVO_4 . We discussed the merit and demerit of the pump-probe XAFS method. [1-3].

Experimental details

The pump-probe experiments were carried out in PF-AR NW14A and EH2 unit of BL3 SACLA in Spring-8. The Si(111) monochromator was used and XAFS spectra were measured in a fluorescence mode. The sample was excited by the Ti-Sapphire laser with wavelength of 400 nm. The maximum time resolutions of PF-AR and SACLA were about 100 ps and 100fs, respectively. The WO_3 powder was suspended in pure water and supplied to the laser-and-X-ray cross point as a stream flow to reduce the damage.

Results and discussion

The XFEL (X-ray Free Electron Laser) pump-probe XANES clearly showed ultrafast change in the electron structure followed by the structure change. In the fast 500 fs W in WO_3 was reduced to 5+ by the photoabsorption to excite the oxygen electron to W 5d state. It induced the edge shift and the filling of the bottom of the d band by the excited electron. Then the local structure started to change to stabilize the W^{5+} . The structure change ceased at about 150 ps and then the total system started to relax the ground state. In case of BiVO_4 , it was assumed that Bi 6s electron was excited to V 3d. The Bi L_3 edge revealed the 6s electron of Bi was not excited. XANES showed the excitation of vibrational modes of Bi-O followed by structural relaxation.

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Reference

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