

High S/N ratio XAFS to investigate ultrafast changes in the local electronic states and structures of WO₃

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1 Introduction

Water splitting photocatalysts are attractive materials to produce hydrogen(H₂) and oxygen(O₂) using sunlight and water(H₂O). The water decomposition with sunlight is an process to produce energy resource since it produces H₂ without any harmful byproducts. Various kinds of photocatalysts have been developed for decades. However, their catalytic efficiencies are not enough for practical use. Fundamental understandings of photocatalyst, especially its local structures and electronic states at excited states, are essential to its further developments.

We have successfully observed photo excited states of WO₃ nanoparticles by a pump-probe XAFS method at NW14A. A large bleaching was found around the white line peak of W L₃ edge 150 ps after excitation. The bleaching was caused by the edge shift of W L₃ XANES spectrum due to the formation of W⁵⁺. Moreover, it was turned out that the structural changes followed the changes in electronic states of W from pump-probe XAFS experiments at XFEL.

Although the kinetics of the decay of the photo excited WO₃ have been understood, the structure of photo excited WO₃ remains unknown. In this study, we performed pump-probe XAFS experiments of WO₃ in order to find the structure of WO₃ at the excited state. W L₁ XANES was measured to observe the changes of conformation of a WO₆ unit. We tried to measure W L₁ XANES before. The signal to noise ratio(S/N) of differential between the excited state and ground state was poor since its low probabilities of X-ray fluorescence. At this time, we applied the high-repetition laser system built in NW14A to measure W L₁ XANES of the excited state.

2 Experiment

All the experiments were performed at the beamline NW14A, PF-AR. W L₁ and edges XAFS spectra were measured in a fluorescence mode. A photomultiplier tube with a plastic scintillator was employed as a detector. A 400-nm laser, whose repetition rate was 1 kHz, was employed to excite WO₃ for EXAFS experiments. A high-repetition laser was employed for W L₁ XANES experiments. The wave length of the high-repetition laser was 343 nm. The fluence of the 400-nm laser was about 280 mJ/cm² whereas the fluence of the 343-nm laser was 31 mJ/cm². A differential XAFS spectrum was calculated

as an unexcited XAFS spectrum was subtracted from photo excited spectrum. WO₃ nanoparticles whose particle size between 50 - 200 nm were dispersed in the distilled water. The concentration of WO₃ was about 2 mM. The suspension was circulated by a pump to suppress its damage from the excitation laser.

3 Results and Discussions

W L₁ XANES spectra of WO₃ at the excited state and the ground state are exhibited in Fig. 1. The data in Fig. 1 (a) were obtained by the high-repetition laser system and the data in Fig. 1 (b) were obtained by the 1-kHz laser system. The repetition rate of X-ray pulses in PF-AR is about 800 kHz. However, the fluorescence X-ray emitted by the X-ray pulses coming from PF-AR which are synchronized with the 1-kHz laser were selected in the 1-kHz laser system. Most of X-ray pulses were lost when the data Fig. 1 (b). It took more than 6 hours to obtain the differential in Fig. 1 (b). By using the high-repetition laser system it took less than 1 hour to obtain the differential with much higher S/N ratio in Fig. 1 (a). It was clearly seen that the pre-edge peak appearing around 12110 eV increased after the excitation. The increasing of the pre-edge peak of W L₁ implies that the conformation of WO₆ units in WO₃ was deformed. It was supposed that the bond length between W-O changed at the excited state.

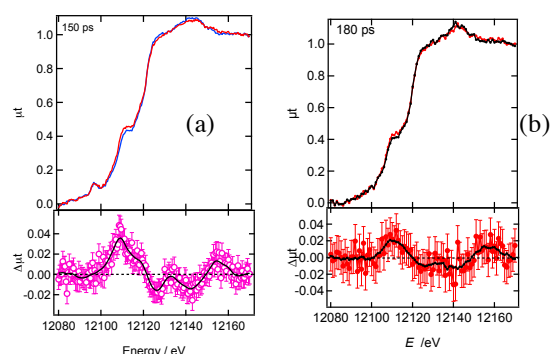


Fig. 1 (a) top: W L₁ edge XAFS spectra of WO₃ at the excited state and the ground state measured by the high-repetition laser system. bottom: the differential between the excited state and the ground state. (b) top: W L₁ edge XAFS spectra of WO₃ at the excited state and the ground state obtained by the 1-kHz laser system. bottom: the differential between the excited state and the ground state.

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