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# In Situ Observation of a Photoexcited State of $WO_3$ by 100-ps XAFS Experiments

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## 1 Introduction

Photocatalysts are attractive materials to produce energy resources from sunlight and in demand to build a sustainable society. $WO_3$ is one of the most promising catalysts to produce $H_2$ and $O_2$ from water using visible light with high catalytic efficiency. Many researches focus on developing its catalytic performance. A mechanism of photocatalytic reactions can be explained as follows: Photocatalytic reactions can proceed when electron-hole pairs are produced inside $WO_3$. The valence band of $WO_3$ mainly consists of O 2p orbitals and the conduction band is made from W 5d orbitals. Electrons in the valence band are transferred to the conduction band when absorbing light. The electron-hole pairs promote decomposition of water. Although there have been many researches on developing its catalytic performances, its excited states have not been studied much. Especially, there is little information about chemical states of W after photo-excitation. In this study, we employed XAFS to observe chemical states of W after photo-excitation. A time resolution of XAFS is 100 ps, which is the duration of X-ray pulses of PF-AR. A drastic change of W L3 edge XAFS spectra was found after photo-excitation.

## 2 Experiment

All the experiments were performed at the beamline NW14A, PF-AR. W $L_3$ edge XAFS spectra were measured in a fluorescence mode. A photomultiplier tube with a plastic scintillator was employed as a detector. A 400-nm laser was employed to excite $WO_3$. Electrons in the valence band can be excited by this laser since the band gap of $WO_3$ is 2.6 - 2.8 eV and the photon energy of the laser exceeded the band gap of $WO_3$. The laser was operated about 1 kHz, which was synchronized with the X-ray pulses from PF-AR. The fluence of each laser pulse was about 280 mJ/cm$^2$. Photoexcited and unexcited XAFS spectra were measured in every measurement. A differential XAFS spectrum was calculated as an unexcited XAFS spectrum was subtracted from photoexcited spectrum. $WO_3$ nanoparticles whose particle size between 50 - 100 nm were dispersed in the distilled water. The concentration of $WO_3$ was 0.65 mM. The suspension was circulated by a pump to supress its damage from the excitation laser.

## 3 Results and Discussion

Photoexcited and ground state XAFS spectra are shown in Fig. 1 (a). A big difference between photoexcited and ground state spectrum can be seen around 10216 eV. The difference is clearly seen in the difference spectrum at 150 ps after photoexcitation. On the other hand, there is no peak in the difference spectrum at 300 ps before laser excitation. Comparing these two spectra, the spectrum change in 150 ps after excitation should be caused by photoabsorption of $WO_3$. Fig. 1 (b) shows 2nd derivative spectrum of W $L_3$ edge XAFS. A W atom in $WO_3$ is surrounded by 6 O atoms (octahedral coordination) and W 5d orbitals are split into $t_{2g}$ and $e_g$ orbitals. A 2nd derivative of W $L_3$ XAFS spectrum indicate an energy split between $t_{2g}$ and $e_g$ orbitals of W. The lower peak in the 2nd derivative is assigned to $t_{2g}$ and the higher peak is to $e_g$. The peak in the difference spectrum at 150 ps after excitation is around the $e_g$ peak position. This implies that $e_g$ orbitals seemed to be partially occupied after laser excitation.

The intensity of absorption at 10216 eV was observed changing the timing between the X-ray pulses and the laser pulses. The change of the absorption can show the lifetime of the excited state. The excited state can be described as a single exponential function and the lifetime of the excited state was estimated as 2 ns. This lifetime is much larger than the photoelectrons which vanishes by collision with photocreated holes, which would happens within a picoseconds and whose decay cannot be described as a single exponential function. The excited state found in this experiments has more long lifetime and different decay process from the collisions of electron-hole pairs.

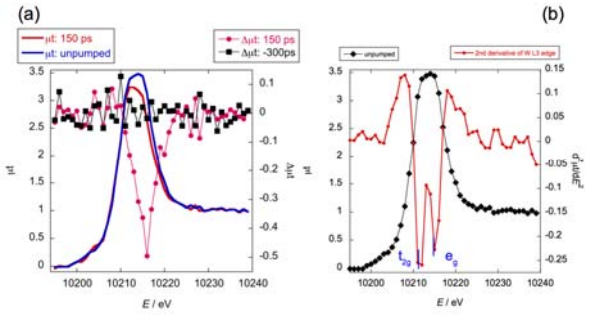


Fig. 1 (a) L3 XAFS spectra of $WO_3$: (left axis) 150 ps after laser excitation(blue), unpumped(pink), (right axis) differential spectra of 150 ps and -300 ps.
(b) L3 XAFS spectrum (black) and 2nd derivative of XAFS (orange)