

## Capturing photoexcited states of tungsten trioxide by pump-probe X-ray absorption fine structure (XAFS) in SACLA

The production of hydrogen ( $H_2$ ) from water ( $H_2O$ ) using sunlight is an ideal and ultimate process for producing an energy resource with neither extra energy consumption nor by-products. The conversion of  $H_2O$  to  $H_2$  is a key technology for realizing a sustainable human society, and it is one of the most important subjects of modern science and technology. A photocatalyst plays a central role in hydrogen production from sunlight. Many photocatalysts have been developed for decades and new photocatalysts are still being developed. Tungsten trioxide ( $WO_3$ ) has drawn much attention as a promising photocatalyst. A catalytic system combining  $WO_3$  and TaON shows the potential to decompose  $H_2O$  into  $H_2$  and  $O_2$  using sunlight; such catalysts are called 'Z-scheme catalysts' [1].

The photocatalytic properties of  $WO_3$  can be understood from its band structure. The band structure of  $WO_3$  is shown in Fig. 1. When  $WO_3$  is irradiated by light whose energy is greater than its band gap (about 2.6–2.8 eV), electrons in the valence band are excited to the conduction band. Photoelectrons emerge in the conduction band and photoholes emerge in the valence band. The photoelectrons promote reduction and the photoholes promote oxidation. The catalytic activity of  $WO_3$  depends on the energy levels of the valence band and conduction band relative to the redox potential of  $H_2O$  and the lifetimes of photocarriers.

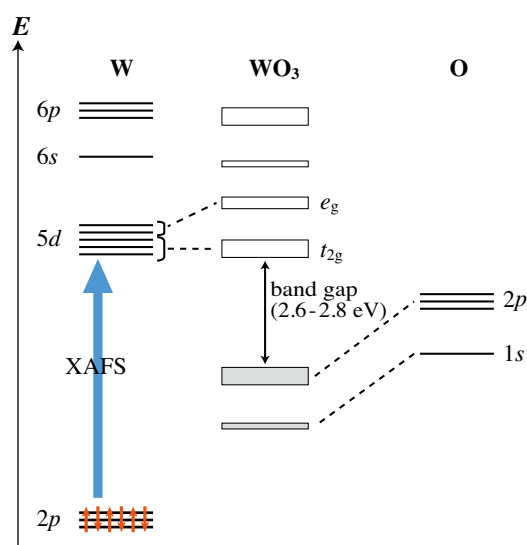


Fig. 1. Energy diagram of the band structure of  $WO_3$ .

The band structure and energy positions have been studied by density functional theory (DFT) [2] and the lifetimes of photocarriers have been observed by spectroscopic techniques using visible or infrared light as a probe [3].

Despite the development of photocatalytic materials and the fundamental studies of photocatalysts for many years, mechanisms of photocatalytic reactions are not well understood. It is difficult to determine where the photocarriers reside during a photocatalytic reaction, which is vital for understanding the reaction mechanism. The local structures and electronic states of photocatalysts in excited states can give crucial information related to the reaction mechanisms. In this study, we performed pump-probe XAFS experiments at SACLA to observe the changes in the local structure and electronic state of  $WO_3$  to determine the photoexcited state of  $WO_3$  [4]. XAFS gives element specific information (in this case, W). The W  $L_{III}$ -edge XAFS spectrum was measured. The W oxide produces a strong peak called a white line, which originates from the transition of inner electrons from  $2p$  states to  $5d$  states (see Fig. 1). The XAFS spectra were measured 500 fs to hundreds of picoseconds after a suspended  $WO_3$  sample was irradiated by a 400 nm excitation laser to observe the creation and relaxation of the excited states of  $WO_3$ . The time resolution of our experimental setup was 500 fs. The W  $L_{III}$ -edge XAFS spectrum in the excited state gives the changes in  $WO_3$  related to the generation of photoelectrons.

The W  $L_{III}$ -edge XAFS spectrum of  $WO_3$  in the ground state and the difference spectra between the excited state and the ground state of  $WO_3$  at several delay times are shown in Fig. 2. There were three energy values (denoted as A, B and C) where the X-ray absorption of the excited state changes considerably from the ground state. The increase in X-ray absorption at position A originates from a redshift of the absorption edge of W. This implies that  $W^{5+}$  species were created by photoabsorption. The increase in X-ray absorption at position A was observed 700 ps after the sample was irradiated by the excitation laser. The peak at position C was also seen shortly after the laser excitation. This was due to the initial redshift. However, the relaxation process of the peak was different from the process at position A. The peak intensity at position C reached its maximum around 200 ps after the laser excitation. Similar behavior was seen at position B. The increase at position B did not start until several picoseconds

after the laser excitation. The peak intensity changed gradually by 200 ps then recovered to its initial intensity. These results display that the photoexcited state of  $\text{WO}_3$  decayed in multiple processes.

The overall changes of the photoexcited state in  $\text{WO}_3$  are displayed in Fig. 3. We found that the excitation process of  $\text{WO}_3$  consists of three processes. The first process was the formation of  $\text{WO}_3^*$  due to photoabsorption, which should be in less than 500 fs. The second process is the change in the initial excited state  $\text{WO}_3^*$  to another excited state ( $\text{WO}_3^{**}$ ). This process is considered to be a structural transformation around W. The third process is the gradual decay of  $\text{WO}_3^{**}$  to the ground state. The kinetic constants of the second and third processes were estimated from the time evolution of the peak at position C.

The photoexcitation process was observed by pump-probe XAFS method at SACLA BL3. It was found that the relaxation of the excited  $\text{WO}_3$  includes multiple steps. The structural change in  $\text{WO}_3$  should occur after the formation of  $\text{W}^{5+}$ . The process of the structural change was not clarified in our previous

experiments [5]. We are now attempting to determine the structural parameters of  $\text{WO}_3^*$  and  $\text{WO}_3^{**}$  by EXAFS analyses and theoretical calculations. The structural parameters of the photoexcited states can provide fundamental information on the local structures of  $\text{WO}_3$  in the excited states and new insights into the mechanisms of the photocatalytic reaction of  $\text{WO}_3$ .

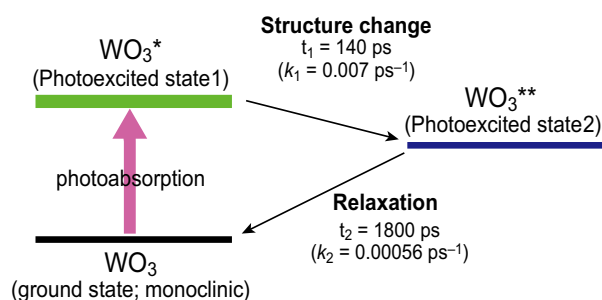


Fig. 3. Diagram of the photoexcitation process of  $\text{WO}_3$ .

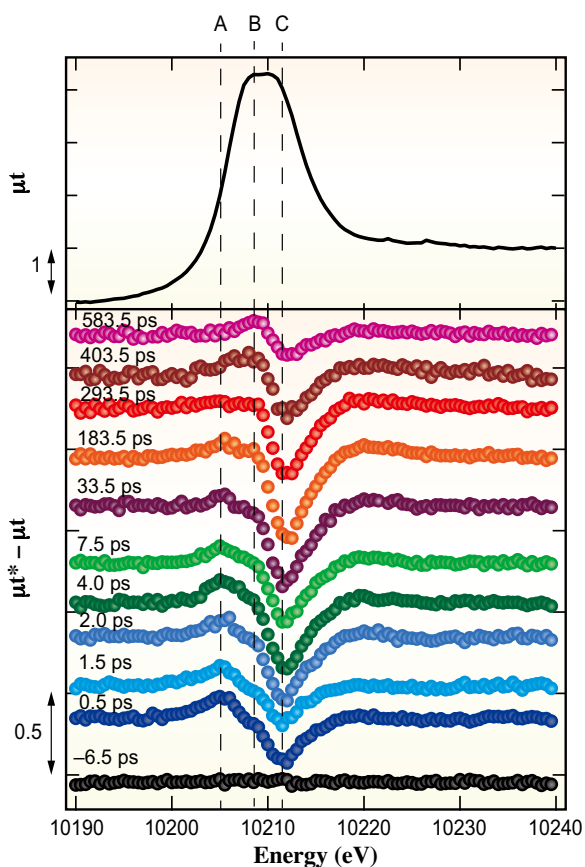


Fig. 2.  $\text{W L}_{\text{III}}$  XAFS difference spectra between the excited state ( $\mu t^*$ ) and the ground state ( $\mu t$ ) at several delay times.

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