Probing excited states of photocatalysts by x-ray spectroscopy in XFELs

Yohei Uemura
European X-ray Free Electron Laser GmbH, Schenenfeld, Germany
yohei.uemura@xfel.eu

Developing a clean and long-standing energy resource is a key issue to establishing an environmentally sustainable society. Producing electricity from the water-splitting reaction using sunlight is an ideal approach to generate electricity without using fossil fuels and producing any harmful by-products. Photocatalysts and photoelectrodes have been developed for decades since they play a central role to promote the water-splitting reaction. Among various kinds of photosensitive materials, metal oxides are good candidates for photocatalysts(ex. TiO_2, α-Fe_2O_3, $BiVO_4$, WO_3). In order to improve their catalytic performances, modifying the energy levels of the conduction band (CB) and the valence band (VB) is an important subject. Fundamental studies such as theoretical calculations, electrochemical methods and spectroscopic studies have been conducted to understand the basic properties of photocatalytic materials to develop new materials. X-ray absorption spectroscopy (XAS) is a newly developed methodology to observe the excited states of such materials. Owing to establishing x-ray free electron lasers (XFELs) in several countries, very fast processes inside photocatalysts after excitation can be observed even within a picosecond.

In this presentation, I would like to introduce recent studies on photocatalytic materials using transient XAS at XFELs. We have measured transient XAS of several different materials(WO_3 [1-3], Fe_2O_3 [4] and $CuWO_4$ [5]) at different facilities. For WO_3, we found that a metastable state is formed after photoexcitation and it includes a significant structural change. In addition, a fast decay process was observed just after the photoexcitation (< 1 ps) owing to the arrival timing monitor which corrects the timing jitter between each x-ray pulse and laser pulse. For α-Fe_2O_3, we employed soft x-ray XAS (Fe L3 edge) at PAL-XFEL (South Korea) to observe the changes in the valence of Fe atoms after photoexcitation directly. The transient changes of the photoexcited Fe atoms were successfully observed by the delay of 10 ps. From the result of the transient Fe L3 XAS, two different kinetic processes were discovered. We also performed resonant inelastic scattering (RIXS) experiments for the photoexcited α-Fe_2O_3 and the modulation of the local structure of Fe was observed during the charge recombination process by the transient RIXS. For $CuWO_4$, the electron density modulation was observed at Cu L3 XAS. This electron modulation does not come from the change of the valence state of Cu but the modulation reflects the charge density changes in neighbouring atoms. We also measured the transient O K-edge XAS of α-Fe_2O_3 and $CuWO_4$. I would also like to present the results of O Kedge XAS.

1. Uemura, Y.; Yokoyama, T., et al., *Appl. Sci.* **2020**, *10*, 7818.
2. Koide, A.; Uemura, Y., et al., *Phys. Chem. Chem. Phys.* **2020**, *22*, 2615-2621.
3. Uemura, Y.; Kido, D., et al., *Angew. Chem. Int. Ed.* **2016**, *55*, 1364-1367.
4. Ismail, A. S. M.; Uemura, Y., et al., *Phys. Chem. Chem. Phys.* **2020**, *22*, 2685-2692.
5. Uemura, Y.; Ismail, A. S. M., et al., *J. Phys. Chem. C* **2021**, *125*, 7329-7336.