

Observing dynamics in photoexcited states of photocatalysis/photoelectrodes studied by transient XAS in XFELs

Tuesday, 29 October 2019 14:30 (30 minutes)

Photocatalysts and photoelectrodes play an important role to promote the decomposition of water to hydrogen (H_2) and oxygen (O_2). Various kinds of photocatalysts/photoelectrodes have been proposed for the last several decades. However, new materials are still explored to enhance its catalytic efficiency for our daily use. Fundamental studies on the mechanisms of photocatalysts/photoelectrodes have been based on theoretical calculations, electrochemical methods and spectroscopic studies. Although these studies have achieved important discoveries on photocatalytic materials, the detailed mechanisms of the photocatalytic materials are not well understood yet. X-ray absorption spectroscopy (XAS) is relatively a new methodology to understand the excited states of photocatalytic materials. XAS can address local structures and electronic states of a target element, which can provide different information from optical spectroscopies. Recently, x-ray free electron lasers (XFELs) have been established in some countries (USA, Japan, Germany, South Korea, Switzerland) and they have been utilized for time-resolved experiments because they provide ultrashort x-ray pulses (<10 fs).

We have already demonstrated that time-resolved x-ray absorption spectroscopy (tr-XAS) in XFELs are useful to understand dynamic changes in the valence states or local structures of photocatalytic materials. In WO_3 , there were different two kinetic processes observed after the photoexcitation.¹ It was found that an intermediate state was formed after the photoexcitation and it recovered to its ground state with a lifetime of 2 ns. In $BiVO_4$ ², it was found that a structural change occurred after the photoexcitation, which could be induced by coherent oscillations. Recently, we have measured time-resolved XAS of several different materials: WO_3 , $CuWO_4$ and Fe_2O_3 . For WO_3 , we employed the arrival timing monitor to correct the timing jitter between each x-ray pulse and laser pulse and a fast decay process was observed just after the photoexcitation (< 1 ps). For $CuWO_4$, we employed both the hard x-ray (SACLA, Japan) and soft x-ray XAS (PAL-XFEL, South Korea) and successfully observed the changes in the valence state of Cu. Our hard x-ray and soft x-ray results give new insights into the origin of photoexcited electrons in $CuWO_4$. For Fe_2O_3 , we employed soft x-ray XAS and 2p3d resonant inelastic x-ray scattering (RIXS) to understand the changes in Fe_2O_3 . In addition to XAS, RIXS for the photoexcited Fe_2O_3 was successfully observed. RIXS can give more information about the changes of the photoexcited Fe and the interactions between the Fe and the surrounding atoms. In this presentation, we would like to discuss these new XFELs based time-resolved studies.

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1. Y. Uemura et al. *Angew. Chem. Int. Ed.* 2016, **55**, 1364-1367
2. Y. Uemura et al. *Chem. Comm.* 2018, **53**, 7314-7317

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Session Classification: Poster session

Track Classification: Poster