

Ultrafast studies of photoinduced dynamics in colloidal nanoparticles: A study on WO₃ nanoparticles

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Hydrogen is an energy carrier that can be converted to electricity without greenhouse gas emissions. However, producing hydrogen still relies heavily on fossil fuels (usually, it is made from fuels). Utilizing hydrogen is not an environmentally friendly energy cycle at all. The water-splitting reaction is an ideal process to produce hydrogen without greenhouse gases. Metal oxides such as TiO₂ or Fe₂O₃ have been studied as photocatalysts/photoelectrodes to promote the water-splitting reaction using sunlight. Although developed for decades, they are still being studied to enhance their catalytic efficiencies. Theoretical calculations, electrochemical methods, and spectroscopic studies have been employed to understand fundamental aspects of the mechanisms of the photocatalysts/photoelectrodes. X-ray absorption spectroscopy (XAS) is a newly employed methodology to understand excited states of photocatalytic materials. Since XAS can address local structures and electronic states of a specific element in a sample, the nature of photocatalysis can be understood from the viewpoint of catalysts. Due to the progress of synchrotrons and x-ray free electron lasers (XFELs), time-resolved XAS can be used to observe the dynamics of metal oxides in the time range from 100 fs to nanoseconds.

We demonstrated that time-resolved x-ray spectroscopy in XFELs is useful to understand dynamic changes in the valence states or local structures of WO₃.^{1, 2} WO₃ is known as a photocatalyst to promote water oxidation, which is a rate-limiting step of the water splitting reaction. We measured pump-probe x-ray absorption spectra (XAS) at SACLA in Japan, and we found that a photoexcited W atom forms a metastable state during its relaxation process. In addition, the metastable state is accompanied by a local structural change 50 ps after photoexcitation². From XAS simulations, the W-O bonds in a specific direction are elongated in the metastable state. We supposed that photoexcited electrons are localised around W atoms, which causes the structural change. Moreover, we measured transient XAS within 1 ps after photoexcitation using the arrival timing monitor³. Our measurements indicate that a fast relaxation process exists in the early stage of the photoexcitation state of WO₃.

We studied the early stage of the photoexcited WO₃ at SACLA using high energy fluorescence detected x-ray absorption spectroscopy method (HERFD-XAS). Despite the indication of the fast kinetics below 1 ps, it was difficult to study further details of the electronic state of the photoexcited WO₃ due to the intrinsic limitation of XAS, which is known as core-hole lifetime broadening. Due to the broadening effect, features of XAS can be smeared out to hinder studying the details of the electronic state of the photoexcited W atoms. Regarding W L_{III} XAS of WO₃, two peaks should be observed corresponding to 2p → 5d(*t*_{2g}) and 2p → 5d(*e*_g), respectively, but they cannot be distinguished in a standard XAS measurement. We successfully observed HERFD-XAS of the photoexcited WO₃ and changes in the electronic states of the photoexcited state W within 1 ps.

References

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