Title: Ultrafast structural changes of photocatalysts studied by transient XAFS

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Developing efficient catalysts to promote water splitting reactions with sunlight is one of the most important issues to build a sustainable society. Semiconductor materials such as $BiVO_4$, WO_3 α-Fe_2O_3 attract more attentions as promising photocatalysts or photoelectrodes in practical use since its bandgap is narrow enough to excite electrons in the valence band to the conduction band by sunlight. Although the basic properties of such materials have been studied by ultrafast spectroscopies or ab initio calculations, its catalytic reaction mechanisms remain unknown. In order to understand reaction mechanisms of photocatalysts, grasping the nature of photocarriers such as holes and electrons are inevitable. The transient XAFS method gives opportunities to address ultrafast changes of local charges and structures of such materials. The time resolution of the conventional transient XAFS spectroscopy performed in synchrotron facilities are about 100 ps. The transient XAFS method cannot be applied to observation of ultrafast phenomena with in 100 ps. However, x-ray free electron lasers have been established for last ten years and can provide short and intense x-ray pulses, which enables to study ultrafast dynamics in femtoseconds and picoseconds. We have already demonstrated by using the technique that a metastable state exists in photoexcitation of WO_3 [1]. Our ultrafast XAFS studies imply that the local structure around W should be different from its ground state.

In order to study the ultrafast structural changes, we performed transient XAFS studies at SPring-8 Angstrom Compact Laser (SACLA), which is the x-ray free electron laser (XFEL) in Japan, and Photon Factory Advanced Ring(PF-AR). For WO_3, we measured W L_1 edge XANES whose features is affected by the local structure of W more than W L_3 edge. We analysed the W L_1 XANES with theoretical calculations conducted FPMS code. From the results of L_1 edge XANES and the theoretical calculations, the local structural change around W is not isotropic but the local structure changes in specific directions. A W atom is surrounded by 6 oxygen atoms and the length of each W-O is different. After the photoexcitation, the structural change occurs in the direction of b or c axis of the crystal structure of WO_3. The L_1 edge result also was confirmed by the transient EXAFS of W L_3 edge.

In addition to WO_3, we measured transient XAFS spectra of Bi L_3 edge of $BiVO_4$, which is another promising photocatalyst.[2] We found that there were three energy positions in the Bi L_3 XANES spectra of the photoexcited $BiVO_4$. These changes are not related to the edge shift of Bi L_{III} caused by the valence change. The changes at 2 ps after the laser excitation is induced by local oscillations in the photoexcited states while a structural distortion following the oscillations caused the changes in the later delay times. The structural change was also confirmed and evaluated by transient of Bi L_3 edge EXAFS analyses.

Ultrafast structural changes of WO3 and BiVO4 were successfully analysed by transient XAFS spectroscopy. The photoexcited state of both the sample convert to a metastatble state after the initial photoexcitation. The local structure around W or Bi is distorted.

References

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