Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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Professional Employment

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For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using a ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc.*), deposit materials (metallic and molecular magnets *etc.*) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of near-ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. We have installed nearly ambient pressure (up to ~5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8. We have successfully investigated Pt 3d HAXPES of Pt/C, PtCo/C and PtNi/C cathode catalysts in PEFC under working conditions to reveal degradation mechanism of PEFC. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. Fast time resolved XAFS measurement is difficult since the repetition frequencies of probe SR and pumping lasers are usually far different, requiring pulse picking of the SR probe and resultantly time resolved detection of only energy-integrated x-ray fluorescence. To detect energy- resolved x-ray fluorescence, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
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- Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Wakisaka *et al.*, *Phys. Rev. B* **92**, 184408 (2015).
- K. Eguchi *et al.*, *J. Phys. Chem. C* **119**, 9805 (2015).

1. Ultrafast Structure Determination of Photocarrier in WO_3 Photocatalyst[1)]

The utilization of solar energies is one of the most fascinating and important research subjects to achieve a future society less dependent on fossil fuels. Many photocatalysts have extensively been developed over last several decades in order to produce hydrogen from water without the generation of harmful pollutants. Recently, tungsten trioxide WO_3 has received much attention since its band gap is 2.6–2.8 eV, implying that it functions as an active photocatalyst under visible light irradiation. In the present work, we have investigated femto- and picosecond structure transformation of photoexcited WO_3 by pump-and-probe time-resolved x-ray absorption fine structure (XAFS) spectroscopy using x-ray free electron laser SACLA in Harima and synchrotron radiation PF-AR (single bunch operation) in Tsukuba.

Figure 1 shows the W L_{III}-edge x-ray absorption near edge structure (XANES) of photoexcited WO_3 recorded in SACLA and the time evolution at x-ray energy point C in Figure 1 is depicted in Figure 2. The shift of the edge energy to a lower x-ray energy side is clearly observed, accompanied by the reduction of the white-line intensity. This implies that the W ions are reduced from hexavalent to pentavalent. From Figure 2 and other results of W L_{III}-edge extended x-ray absorption fine structure (EXAFS) and W L_I-edge XANES, we can deduce the photoexcitation process as

1) fast formation of the photocarrier (<0.7 ps)
2) local structural distortion of WO_6 octahedra (140 ps)
3) decay of the photoexcited state (1800 ps).

The local structure distortion of the photocarrier in WO_3 is exemplified, suggesting the usefulness of the time resolved XAFS experiments.

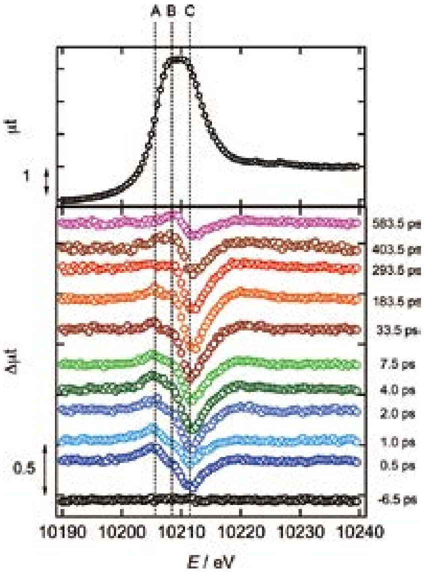

Figure 1. W L_{III}-edge XAFS of the ground state WO_3 and the time evolution of the spectral difference after the photoexcitation (400 nm, 0.070 fs) recorded in SACLA. The time resolving power is ~0.7 ps.

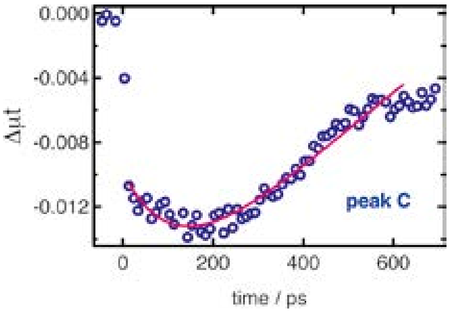

Figure 2. Time evolution of the difference spectra at energy point C in Figure 1.

2. Local Thermal Properties of Functional Materials as Magnetic Alloys[2–4)] and Gold Nanoclusters Studied by Temperature Dependent EXAFS[5)]

We have extensively been studying local thermal properties such as local thermal expansion and local vibrational amplitude between atom pairs by means of the temperature dependent EXAFS technique, together with the computational simulations based on the path-integral effective classical potential theory. In the FeNi invar alloy[2)] that shows almost no thermal expansion up to 400 K, we concluded that the absence of thermal expansion at very low temperature originates from the vibrational quantum effect, and found the different local thermal expansion between Fe and Ni, which cannot be detected with the x-ray diffraction. In the martensitic MnNi alloy,[3)] Mn exhibits large thermal expansion along the tetragonal *a* axis due to the anti-Invar effect and negligibly small thermal expansion along the *c* axis due to the cooperative Invar effect. In metamagnetic FeRh intermetallic compound,[4)] only the Debye-Waller factor of the Fe–Fe pair in the antiferromagnetic phase was found to be enhanced significantly, indicating that the local spin and Fe–Fe distance fluctuations play an important role in driving the metamagnetic transition. In thiolated gold nanoclusters,[5)] we elucidated the hierarchy in the bond stiffness in $Au_{25}(SC_2H_4Ph)_{18}$, $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{144}(SC_2H_4Ph)_{60}$. Longer and more flexible Au–Au bonds locate at the icosahedral-based gold surface, while shorter stiffer Au–Au bonds are distributed along the radial direction and form a cyclic structural backbone of the rigid Au–SR oligomers.

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