

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure



YOKOYAMA, Toshihiko
Professor
[yokoyama@ims.ac.jp]

Education

1983 B.S. The University of Tokyo
1985 M.S. The University of Tokyo
1990 Ph.D. The University of Tokyo

Professional Employment

1987 Research Associate, Hiroshima University
1993 Research Associate, The University of Tokyo
1994 Lecturer, The University of Tokyo
1996 Associate Professor, The University of Tokyo
2002 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Member

Research Assistant Professor
KURAHASHI, Naoya
MAEJIMA, Naoyuki
Secretary
KURITA, Yoshiko

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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 (UVMCD) 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 an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for

polymer electrolyte fuel cells (PEFC) under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time in the world using Beamline 36XU of SPring-8. These works were supported by the NEDO Fuel Cell project. More recently, the apparatus moved to BL46XU and is used for more general chemical reactions on heterogeneous catalysts and electrochemical cells such as CO₂ reduction.

The third subject is applications of the x-ray absorption fine structure (XAFS) spectroscopy, soft x-ray emission spectroscopy, and angle-resolved ultraviolet photoelectron spectroscopy for functional materials. These investigations include femto- and picosecond time resolved XAFS measurements using x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Conventional temperature dependent EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional alloy materials as negative thermal expansion alloys.

Selected Publications

- T. Nakagawa and T. Yokoyama, "Magnetic Circular Dichroism near the Fermi Level," *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, "Anharmonicity and Quantum Effects in Thermal Expansion of an Invar Alloy," *Phys. Rev. Lett.* **107**, 065901 (2011).
- Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, "X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions," *Appl. Phys. Express* **10**, 076603 (2017).
- T. Koitaya, K. Yamamoto, T. Uruga and T. Yokoyama, "Operando Characterization of Copper–Zinc–Alumina Catalyst for Methanol Synthesis from Carbon Dioxide and Hydrogen by Ambient-Pressure Hard X-Ray Photoelectron Spectroscopy," *J. Phys. Chem. C* **127**, 13044–13054 (2023).
- Y. Uemura *et al.*, "Dynamics of Photoelectrons and Structural Changes of Tungsten Trioxide Observed by Femtosecond Transient XAFS," *Angew. Chem., Int. Ed.* **55**, 1364–1367 (2016).

1. Femtosecond Resonant X-Ray Emission Spectra of Photocatalyst WO_3 ¹⁾

Tungsten trioxide WO_3 is one of the well-studied photocatalysts for the solar-assisted photochemical water splitting reaction. Previously we investigated femto- and picosecond time resolved x-ray absorption fine structure (XAFS) spectroscopy to reveal the local geometric and electronic structures of the metastable photoexcited states in WO_3 , using synchrotron radiation from Photon Factory Advanced Ring and the x-ray free electron laser SACLA.^{2–4)} The metastable photoexcited polaron state is found to exhibit more distorted W–O bonds with a reduced W valency compared to the ground state. In the present study, we have performed newly developed femtosecond high-energy-resolution fluorescence detection (HERFD) XAFS and resonant x-ray emission spectra (RXES) measurements for the femtosecond photoexcited state of the WO_3 catalyst using SACLA BL3 EH2.

Figure 1 shows the femtosecond time resolved W L_3 -edge XAFS spectra with normal energy resolution. The HERFD-XAFS spectra were obtained from the RXES as given in Figure 2. By comparing Figures 1(a) and 1(c), the improvement of the energy resolution is quite clear, implying usefulness of the HERFD XAFS measurement. It is found that in the initial state of the visible-light photoexcitation (~ 100 fs), the W L_3 edge $W2p_{3/2} \rightarrow 5d$ absorption shifts to a lower energy side and the W 5d energy levels of the t_{2g} and e_g peaks are modulated due to the photoexcited electrons in the conduction band. The electronic state of the photoexcited W atoms is modified by 500 fs. The crystal field splitting (difference between the W 5d t_{2g} and e_g peak energies) shrinks by 500 fs, which indicates local structural changes around the W atoms

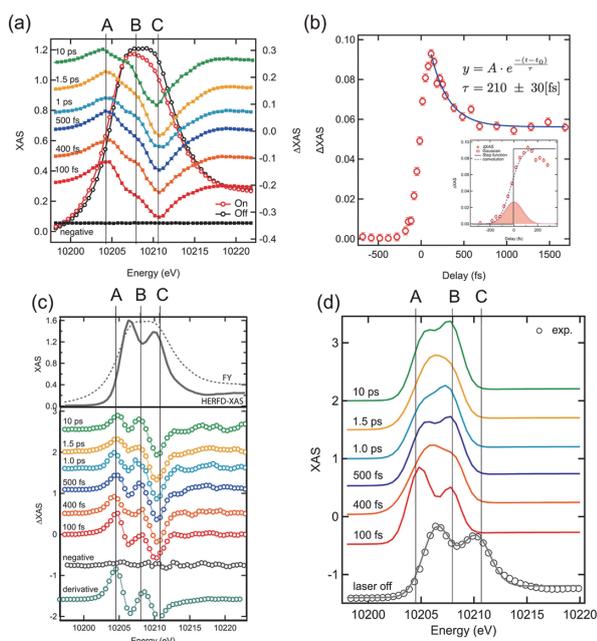


Figure 1. (a) Pump-probe normal energy resolution XAFS spectra and their first derivatives of WO_3 at different time delays. (b) The kinetic trace of XAFS at peak A in (a). (c) Pump-probe HERFD-XAFS and their first derivatives of WO_3 at the corresponding time delays to those in (a). The first derivative of the laser off spectrum is also given. (d) shows the reconstructed excited state spectra.

due to the formation of the metastable polarons. Consequent schematic descriptions of the photoexcited electronic states are summarized in Figure 3.

HERFD-XAS and RXES provide more details about the early stage of the photoexcited states of WO_3 . This work demonstrates that the detailed dynamics of 5d elements in the femtosecond range can be addressed with HERFD-XAS/RXES.

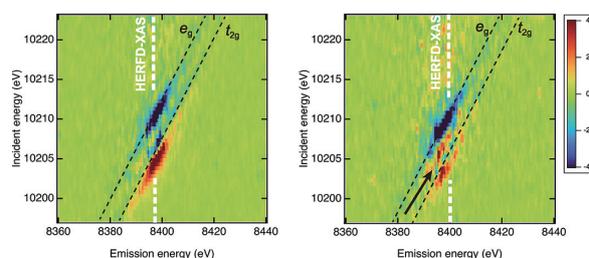


Figure 2. Typical examples of the pump-probe RXES at the delay time of 100 fs (left) and 10 ps (right). The white dash lines imply the energy to form HERFD-XAS in Figure 1(c).

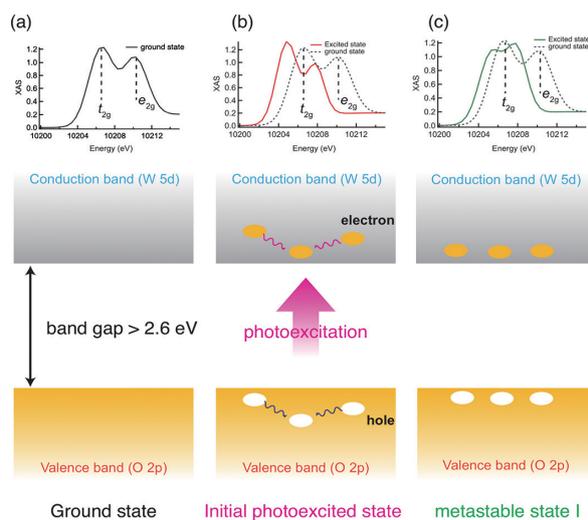


Figure 3. A sketch of proposed photoexcitation and relaxation mechanism: (a) the optical ground state, (b) the initial photoexcited state, (c) the metastable polaron. After photoexcitation, electrons in the conduction band are delocalized. The HERFD-XAFS spectrum shifts in lower energies due to the presence of the electrons in the conduction band. In later delays in Figure 3(c), the electrons are localized, which is supported by the change of the spin-orbit coupling term for the multiplet calculations of W L_3 HERFD-XAFS.

References

- 1) Y. Uemura, K. Yamamoto, Y. Niwa, T. Buttiens, H. Elnaggar, R. -P. Wang, M. Lazemi, F. de Groot, T. Katayama, M. Yabashi, C. J. Milne and T. Yokoyama, *J. Phys. Chem. Lett.* **16**, 6138 (2025). DOI: 10.1021/acs.jpcclett.5c01062
- 2) A. Koide, Y. Uemura *et al.*, *Phys. Chem. Chem. Phys.* **22**, 2615 (2020). DOI: 10.1039/C9CP01332F
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- 4) D. Kido, Y. Uemura, Y. Wakisaka, A. Koide *et al.*, *Chem. Lett.* **51**, 1083 (2022). DOI: 10.1246/cl.220381