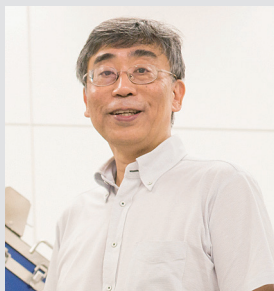# Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

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

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

Member
Assistant Professor
   YAMAMOTO, Kohei*

IMS Research Assistant Professor
   KURAHASHI, Naoya
   MAEJIMA, Naoyuki

Graduate Student
   IZUMI, Yoshiki

Secretary
   KURITA, Yoshiko

Keywords   X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, X-Ray Photoelectron Spectroscopy

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. Although photoelectron spectroscopic measurement is usually done under high vacuum, recent material science often requires ambient pressure measurements 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, more general chemical reactions on heterogeneous catalyst surfaces such as CO_2 hydrogenation using the AP-HAXPES system have been investigating on typical conditions of $\sim 5 \times 10^4$ Pa and ~ 600 K.

The third subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Moreover, conventional temperature dependent EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional 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. 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).

• 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).

1. Metallic Bonds and Thermal Vibration in Brass[1]

Nature of the metallic bond and thermal vibration in brass alloy is investigated from the local structural and thermodynamical points of view by the temperature-dependent Cu and Zn K-edge EXAFS spectroscopy and the path-integral effective classical potential (PIECP) theoretical simulation. It is unexpectedly found that the thermal vibrational amplitude around Zn is a little but meaningfully smaller than that around Cu, although it is usually believed that Zn is a much softer metal than Cu in terms of various thermodynamical physical quantities of elemental metals. Moreover, it is found that the nearest neighbor distance around Zn is almost equivalent to that around Cu (only ~0.01 Å difference), although the metallic radius of Zn commonly used is considerably larger than that of Cu (~0.06–0.09 Å difference). These peculiar findings can be interpreted as a result of confinement of Zn atoms in a smaller space than usual and a significantly larger repulsive potential of Zn than Cu.

Figure 1 shows the mean square relative displacements C_2 for the first-nearest neighbor (NN) shells obtained by the EXAFS experiment and the PIECP simulation. The EXAFS results show slightly smaller temperature dependence around Zn than around Cu, this yielding the Debye temperatures of $\Theta_D(Cu) = 295$ K and $\Theta_D(Zn) = 302$ K. The PIECP results agree with the EXAFS finding qualitatively [$\Theta_D(Cu) = 329$ K and $\Theta_D(Zn) = 348$ K]. This consequence is surprising since it seems to be essentially contradictory to the simple prediction based on the potential stiffness (Cu should be stiffer than Zn). The reason for a smaller thermal vibration and thus a larger force constant in Zn–Zn atom pair is probably ascribed to a steeper repulsive potential at a shorter distance side in the Zn–Zn pair. When the system is really diatomic, the Zn–Zn distance is hardly contracted due to the steep repulsive potential and is easily elongated, resulting in large anharmonic vibrational amplitude in the diatomic Zn_2 molecule. On the contrary, in a closed packed solid like *fcc*, the Zn–Zn distance is hardly elongated due to the existence of other atoms at the opposite side, leading to confinement of the Zn atom. This indicates that the Zn atoms in brass are likely to be confined in a space that is a little too small for Zn and are hardly movable.
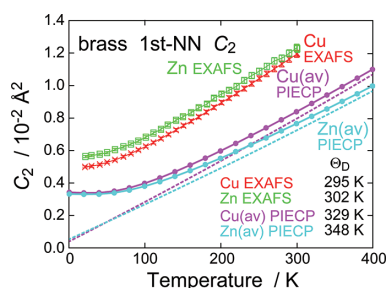

Figure 1. Mean square relative displacements C_2 for the first-nearest neighbor pairs obtained by the EXAFS analysis (with error bars; Cu: Red; Zn: Green) and the PIECP simulations (average Cu: Magenta; average Zn: Light blue; solid line: Quantum; dashed line: Classical), respectively. The corresponding Debye temperatures are also given in the figure.

* Present Address; National Institutes for Quantum Science and Technology

2. Metastable Structure of Photoexcited WO_3 Determined by the Pump–Probe EXAFS Spectroscopy[2]

Photocatalysts have drawn much attention with respect to harvesting sunlight to split water into H_2 and O_2. Usually, the process is understood using the energy band model. In the energy band model, the positions of Fermi level, minimum of the conduction band, and maximum of the valence band are important with respect to the reduction and oxidation potentials for H_2/H_2O and O_2/H_2O. The local structure and electronic state of the photoexcited state need to be elucidated to understand the photocatalysis of water splitting and to improve the performance of water-splitting photocatalysts. In this work, we report the PP-EXAFS results for the structure of the metastable (MS) WO_3 state to clarify the local structure change and to attempt to explain the long formation time for the MS WO_3.

The WO_3 aqueous solution jet was supplied to the cross point of the laser used for photoexcitation (mode-lock Ti-sapphire laser with a 1 ps pulse width, 945 Hz repetition rate, and 400 nm wavelength) and the X-ray beam emitted from the Photon Factory Advanced Ring (single bunch operation with pulse width of 100 ps, and pulse interval of 1.26 µs). The fluorescence X-rays were monitored using a scintillation counter with a Cu filter to attenuate the elastic X rays. The local structure of WO_3 photocatalyst in the photoexcited MS state created 150 ps after laser irradiation as well as the ground state (GS) one has been determined by pump–probe EXAFS and constrained thorough search EXAFS analysis. As shown in Figure 2, a highly distorted octahedral local structure was found, especially one of the shortest W–O was further shortened. We have discussed some contradiction with theoretical calculation and propose a possible structure for the metastable state.
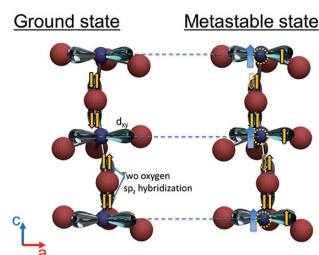

Figure 2. The local structure change in the ground state (GS) WO_3 and the metastable (MS) WO_3. Large red and small blue circles represent O and W atoms, respectively. Yellow broken circles indicate the position of W in GS. Thick blue arrows show the movement of W atoms in the MS WO_3. W atoms along the *c*-axis move in the direction corresponding to W=O contraction. Orange filled and empty arrows in the orbitals correspond to electrons with spin and holes, respectively. Grey filled circles indicate holes. The unpaired electron spins are all parallel in the polaron cluster.

References

1) T. Yokoyama, *Phys. Chem. Chem. Phys.* **25**, 3413–3419 (2023).
2) D. Kido, Y. Uemura, Y. Wakisaka, A. Koide, H. Uehara, Y. Niwa, S. Nozawa, K. Ichiyanagi, R. Fukaya, S. Adachi, T. Sato, H. Jenkins, T. Yokoyama, S. Takakusagi, J. Hasegawa and K. Asakura, *Chem. Lett.* **51**, 1083–1086 (2022).