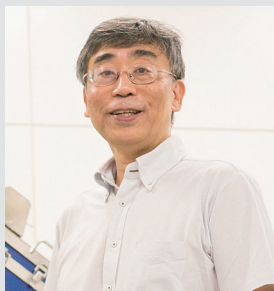


Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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Keywords

X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard 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 (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 an 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 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. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. This work was supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved measurements using x-ray. Time-resolved x-ray absorption fine structure spectroscopy of photocatalysts WO_3 and BiVO_4 was performed and we have investigated those local geometric and electronic structures. Time-resolved measurement can be also applied to investigate the dynamics of magnetic materials with XMCD and other magneto-optical effects. We captured XMCD spectra of the photoinduced transient state. The real space image of magnetic domains can be retrieved from the diffraction patterns. We succeeded in capturing diffraction from magnetic domains and now considering the possibility of its application for time- and space-resolved imaging.

Recently, new assistant professors Drs. Koitaya and Yamamoto joined our group. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).
- Y. Takagi *et al.*, *Acc. Chem. Res.* **51**, 719 (2018).
- L. Yu *et al.*, *J. Phys. Chem. C* **123**, 603 (2019).

1. Quick *Operando* Ambient Pressure Hard X-Ray Photoelectron Spectroscopy for Reaction Kinetic Measurements of Polymer Electrolyte Fuel Cells¹⁾

Polymer electrolyte fuel cells (PEFCs) are currently one of the most promising electrochemical energy conversion and storage technology. To achieve more highly efficient PEFC with longer life time, a continuous supply of more powerful materials and a further detailed understanding of the electrochemical properties of PEFC are essentially important. We have been investigating the degradation and poisoning mechanisms of PEFC using near ambient pressure *operando* HAXPES of PEFC under working conditions. To study catalytic reaction mechanisms, it is generally quite important to investigate reaction kinetics with time-resolved experimental techniques.

In this work, we have designed and constructed a quick *operando* ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) measurement system for the investigations of reaction kinetics in electrochemical cells under working conditions. The HAXPES measurements can be performed at typical pressures of 1×10^4 Pa (maximum 1×10^5 Pa) with the typical time resolution of ~ 200 ms. To accumulate time-resolved spectra with sufficient signal-to-noise ratios, repeated cycles of the chemical reactions are conducted based on the repeated-cycle time-tagged method, requiring the identity of each event and the time trigger. As demonstrative experiments, we have successfully observed time-resolved *operando* Pt $3d_{5/2}$ and S $1s$ HAXPES from the Pt/C cathode catalyst of PEFCs. In the Pt $3d_{5/2}$ HAXPES, we have evaluated the reaction kinetics of the Pt oxidation/reduction processes at the cathode upon abrupt change of the cathode–anode bias voltage between 0.4 and 1.2 V. In the S $1s$ HAXPES for measurements of S species poisoning fuel cells, we have studied the contaminated anionic S adsorption and desorption kinetics on the Pt nanoparticles at the cathode. The results are comparatively discussed with previous findings.

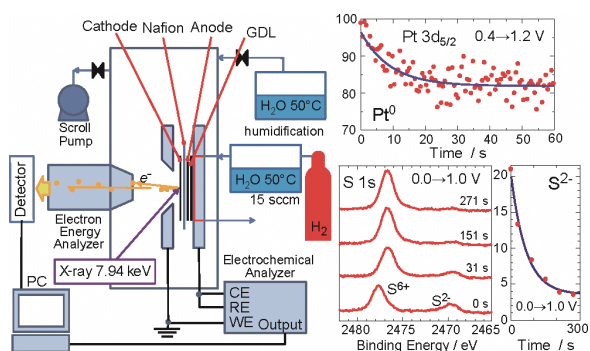


Figure 1. (left) Schematic view of the quick *operando* HAXPES measurement system installed at hard x-ray undulator station BL36XU of SPring-8. (right) Examples of time dependence of the HAXPES results. The upper panel depicts the Pt oxidation process upon an abrupt step of the bias voltage. The lower panel gives the Pt-adsorbed S desorption process upon a similar bias voltage variation.

2. Photoinduced Anisotropic Distortion as the Electron Trapping Site of WO_3 Studied by Ultrafast W L_1 -Edge X-Ray Absorption Spectroscopy with Full Potential Multiple Scattering Calculations²⁾

Understanding excited states of photocatalysts is significant to improve their activity for water splitting reaction. X-ray absorption fine structure (XAFS) spectroscopy using X-ray free electron lasers (XFEL) is a powerful method to address dynamic changes in electronic states and structures of photocatalysts in the excited state in ultrafast short time scales. The ultrafast atomic-scale local structural change in photoexcited WO_3 was observed by W L_1 edge XAFS spectroscopy using an XFEL. An anisotropic local distortion around the W atom could reproduce well the spectral features at a delay time of 100 ps after photoexcitation based on full potential multiple scattering calculations. The distortion involved the movement of W to shrink the shortest W–O bonds and elongate the longest one. The movement of the W atom could be explained by the filling of the d_{xy} and d_{zx} orbitals, which were originally located at the bottom of the conduction band with photoexcited electrons.

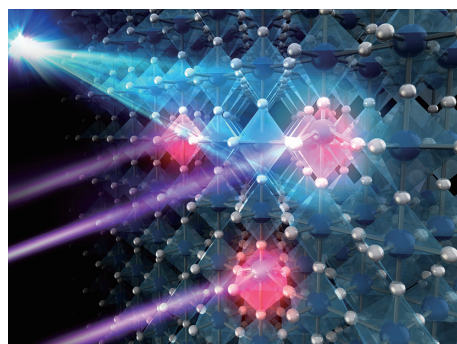


Figure 2. Schematic view of the ultrafast dynamics of WO_3 after ultraviolet laser excitation studied by the x-ray free electron laser.

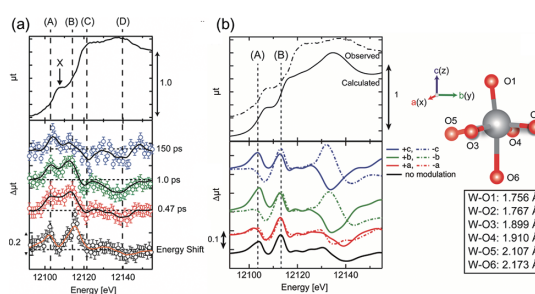


Figure 3. Experimental and calculated time-dependent W L_1 -edge XAFS spectra of WO_3 . Significant more distortion of the local structure around W in the photoexcited state is elucidated.

References

- 1) T. Nakamura *et al.*, *J. Phys. Chem. C* **124**, 17520–17527 (2020).
- 2) A. Koide *et al.*, *Phys. Chem. Chem. Phys.* **22**, 2615–2621 (2020).

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University