RESEARCH ACTIVITIES

Division of Advanced Molecular Science

The division consists of two sections. In the first one, scientists of the first water are invited as "distinguished professors," and the environment, in which they can devote themselves to their own research, is provided. The research in this section should be the last word in the field of molecular science.

In the second section, we invite researchers in the universities performing unique researches in the field of molecular science as cross-appointment faculty members, and provide the research environment to enable research activity with advanced facilities in IMS.

Self-Assembling Molecular Systems Based on Coordination Chemistry

Division of Advanced Molecular Science

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Education

1980	B.S. Chiba University
1982	M.S. Chiba University
1987	Ph.D. Tokyo Institute of Technology

Professional Employment

1982	Researcher, Sagami Chemical Research Center
1988	Assistant Professor to Associate Professor, Chiba University
1997	Associate Professor, Institute for Molecular Science
1999	Professor, Nagoya University
2002	Professor, The University of Tokyo
2018	Distinguished Professor, Institute for Molecular Science
2019	Distinguished Professor, The University of Tokyo

Awards

1994	Progress Award in Synthetic Organic Chemistry, Japan
2000	Division Award of Chemical Society of Japan (Organic Chemistry)
2001	Tokyo Techno Forum 21 Gold Medal
2001	Japan IBM Award
2003	Nagoya Silver Medal
2004	Izatt-Christensen Award
2006	G. W. Wheland Award (Chicago University Lectureship Award)
2010	The Reona Esaki Award
2010	The JSCC Award
2011	3M Lectureship Award (University of British Columbia)
2012	Thomson Reuters Research Front Award 2012
2013	The Chemical Society of Japan (CSJ) Award
2013	Arthur C. Cope Scholar Award (ACS National Award)
2013	Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)
2014	ISNSCE 2014 Nanoprize
2014	Medal with Purple Ribbon
2014	Fred Basolo Medal (Northwestern University)
2018	Wolf Prize in Chemistry
2019	The Imperial Prize and the Japan Academy Prize
2020	The 73rd Chunichi Cultural Award
2020	Clarivate Citation Laureates (Chemistry)
2020	“Major Results” of Nanotechnology Platform, MEXT

Member

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Visiting Scientist
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GONDO, Keisuke

Graduate Student
JUNG, Youngcheol*

Secretary
MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

Our research is based on the design of new self-assembled molecular systems using coordination chemistry. We not only create the new self-assembled molecular systems but also try to utilize the created system for various purpose. One example is a molecular system called crystalline sponge (CS).

The CS is a porous crystal of a coordination network, into which various kinds of small molecules could be introduced. Notably, we can know structures of the small molecules accommodated in the pore of the CS by X-ray crystallography, because the CS has the accommodated small molecules periodically aligned. Thus, the CS can be utilized for the structure analysis, and this technique is called the CS method. This method has some advantages; i) only nanogram to microgram scale of analytes is required, ii) the absolute stereochemistry can be determined, iii) even oily substances can be analyzed by X-ray crystallography. Because of these fascinating features, the CS method attracts the interests of many people not only in academia but also in industry.

Currently, we are improving the CS method in various ways. At the same time, we also try to apply the CS method to other field of science. For example, we use the CS method for the studies on natural product chemistry.

Selected Publications

- Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, “X-Ray Analysis on the Nanogram to Microgram Scale Using Porous Complexes,” *Nature* **495**, 461–466 (2013).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, “Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components,” *Nature* **540**, 563–566 (2016).

Here, we show our recent attempts to improve the performance of the CS method and deepen understanding of this method. These studies would broaden the range of compounds, which can be analyzed by the CS method, and provide information helpful for people who want to try this method. We hope these studies encourage many people who needs to analyze the structure of small molecules to use the CS method for their own works and studies.

1. Solvent Effect in the Crystallin Sponge Method[1)]

Recently, we found that a choice of a solvent used in the CS method is important, especially when we want to heighten the quality of data obtained by this method. Before the analytes are introduced into the CS, the pore of the CS is filled with solvents. When the analytes come into the CS, the solvents go out, but a part of the solvents still remain in the pore. Previously, non-polar solvents are frequently used in the CS method, because the non-polar solvents exhibit only limited interactions with the CS, and are easily replaced with analytes. However, in this study, we tried to use various kinds of polar solvents. As a result, we found that the polar solvents are sometimes better than the non-polar solvents. Since the polar solvents remained in the pore show stronger interactions with both analyte and the CS, it can mediate the interaction between the analytes and the CS (Figure 1). It would result in an inhibition of disorder of analyte in the pore of the CS and an improvement of the quality of data.

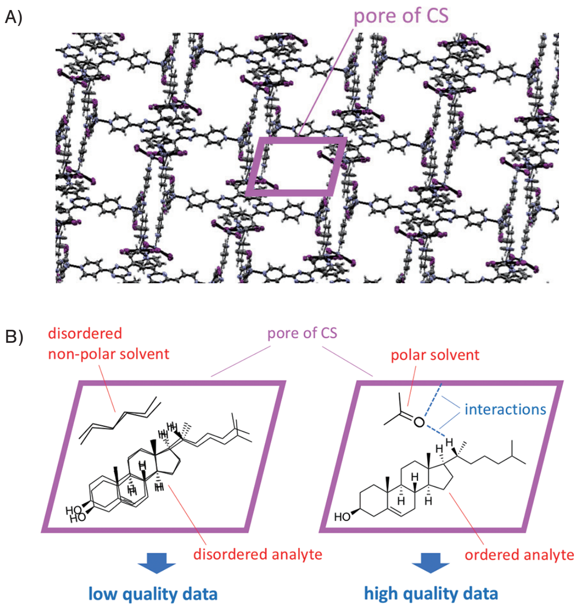

Figure 1. A) Structure of the CS. B) Image of the solvent effect in the CS method.

2. Crystalline Sponge Method Is Suitable for the Structure Analysis of Halogenated Compounds[2)]

The CS method could be used for the structure analysis of a broad range of small molecules. However, it is worth knowing which kinds of analytes is suitable for the analysis using the CS method. We recently found that the halogenated compounds are easily analyzed by the CS method in many cases. For example, we successfully analyzed a series of halogenated compounds classified as persistent organic pollutants (POPs), which are important compounds from the point view of environmental problem. The analysis of the POPs using the CS method revealed that halogen atoms of the analytes effectively interact with the CS (Figure 2). We consider that these interactions help the alignment of the halogenated compounds inside the pore of the CS.

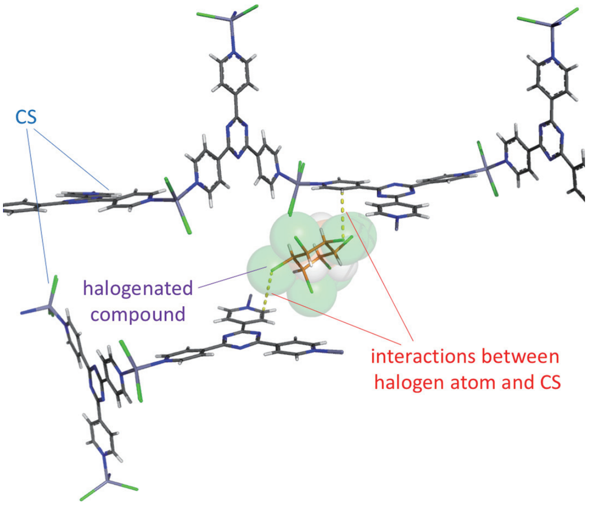

Figure 2. One example of interaction between the CS and a halogenated compound.

References

1) N. Wada, K. Kageyama, Y. Jung, T. Mitsuhashi and M. Fujita, *Org. Lett.* **23**, 9288–9291 (2021).

2) J. Chen, T. Kikuchi, K. Takagi, H. Kiyota, K. Adachi, T. Mitsuhashi and M. Fujita, *Chem. Lett.* **51**, 85–87 (2022).

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Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

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Education

1988	B.S. Tohoku University
1990	M.S. Tohoku University
1991	Ph.D. Tohoku University

Professional Employment

1991	JSPS Postdoctoral Fellow, Tohoku University
1993	Research Associate, Kobe University
1993	Research Associate, Institute for Molecular Science
1998	Associate Professor, Kobe University
2002	Associate Professor, Institute for Molecular Science
2013	Professor, Osaka University
2020	Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	Young Incentive Award, Japanese Society for Synchrotron Radiation Research
2008	The Commendation for Science and Technology by MEXT, Japan Science and Technology Prize (Research Field)
2008	Morita Memorial Prize

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KURITA, Yoshiko

Keywords Condensed Matter, Electronic Structure, Synchrotron Radiation

Physical and chemical properties of solids, such as conductivity, magnetism, superconductivity and chemical reactions originate from microscopic electronic structure, lattice/molecular vibrations, and molecular movements based on quantum mechanics in materials and their interactions. By revealing the microscopic states, we can learn about the origin of physical and chemical properties and hidden functionalities. Also, the microscopic information is helpful for the creation of novel functional properties. To visualize hidden microscopic information, we develop novel spectroscopic techniques using synchrotron radiation, high brilliant electron beams, and other so-called quantum beams. We are now developing a new electron spectroscopy technique, Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS), with bulk-sensitive primary energies of 0.3–1.5 keV, as shown in Figure 1, in order to detect spin-selective element-specific bulk plasmons. Based on the obtained information of electronic structures, we aim to develop novel physical properties of new materials.

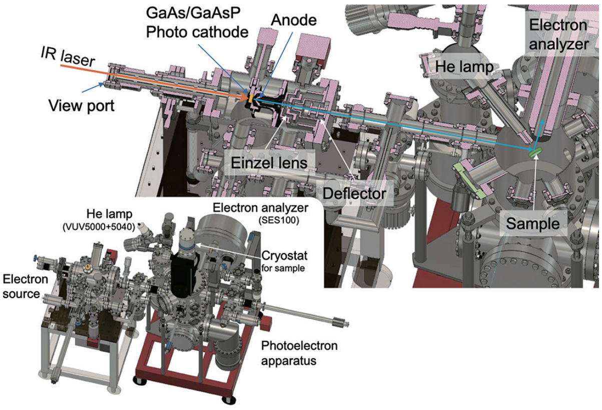

Figure 1. Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

Selected Publications

- Y. Ohtsubo, Y. Yamashita, K. Hagiwara, S. Ideta, K. Tanaka, R. Yukawa, K. Horiba, H. Kumigashira, K. Miyamoto, T. Okuda, W. Hirano, F. Iga and S. Kimura, "Non-Trivial Surface States of Samarium Hexaboride at the (111) Surface," *Nat. Commun.* **10**, 2298 (7 pages) (2019).
- K. Hagiwara, Y. Ohtsubo, M. Matsunami, S. Ideta, K. Tanaka, H. Miyazaki, J. E. Rault, P. Le Fèvre, F. Bertran, A. Taleb-Ibrahimi, R. Yukawa, M. Kobayashi, K. Horiba, H. Kumigashira, K. Sumida, T. Okuda, F. Iga and S. Kimura, "Surface Kondo Effect and Non-Trivial Metallic State of the Kondo Insulator YbB_{12}," *Nat. Commun.* **7**, 12690 (7 pages) (2016).
- S. Kimura and H. Okamura, "Infrared and Terahertz Spectroscopy of Strongly Correlated Electron Systems under Extreme Conditions," *J. Phys. Soc. Jpn.* **82**, 021004 (28 pages) (2013). [review]
- S. Kimura, T. Iizuka, H. Miyazaki, A. Irizawa, Y. Muro and T. Takabatake, "Electronic-Structure-Driven Magnetic Ordering in a Kondo Semiconductor $CeOs_2Al_{10}$," *Phys. Rev. Lett.* **106**, 056404 (4 pages) (2011).

1. Optical Study of the Electronic Structure of Locally Noncentrosymmetric $CeRh_2As_2$[1)]

The electronic structures of the heavy-fermion superconductor $CeRh_2As_2$ with local inversion symmetry breaking and the reference material $LaRh_2As_2$ have been investigated using experimental optical conductivity [$\sigma_1(\omega)$] spectra and first-principles density functional theory calculations. The low-temperature $\sigma_1(\omega)$ spectra of $LaRh_2As_2$ revealed a broad peak at ~0.1 eV and a sharp peak at ~0.5 eV after subtracting the Drude contribution of free carriers. The peak features and the background intensity were nicely reproduced in calculated $\sigma_1(\omega)$ spectra from DFT calculations, implying a conventional metallic nature. In $CeRh_2As_2$, two mid-IR peaks at about 0.12 and 0.4 eV corresponding to the unoccupied Ce $4f_{5/2}$ and $4f_{7/2}$ states, respectively, were strongly developed with decreasing temperature as shown in Figure 2, which suggests the emergence of hybridization states between the conduction and 4*f* electrons. We compared the temperature dependence of the mid-IR peaks of $CeRh_2As_2$ with corresponding data from $CeCu_2Si_2$ and $CeNi_2Ge_2$ in a $ThCr_2Si_2$-type structure to examine the possible impact of local inversion symmetry breaking on electronic structures. We also clarify the local and itinerant character in the electronic structure by investigating the temperature dependence in the $\sigma_1(\omega)$ spectra of various Ce and Yb compounds with a tetragonal $ThCr_2Si_2$-type crystal structure.[2)] The temperature variation in the $\sigma_1(\omega)$ spectrum is still present in the more localized case, even though the Kondo effect is strongly suppressed.

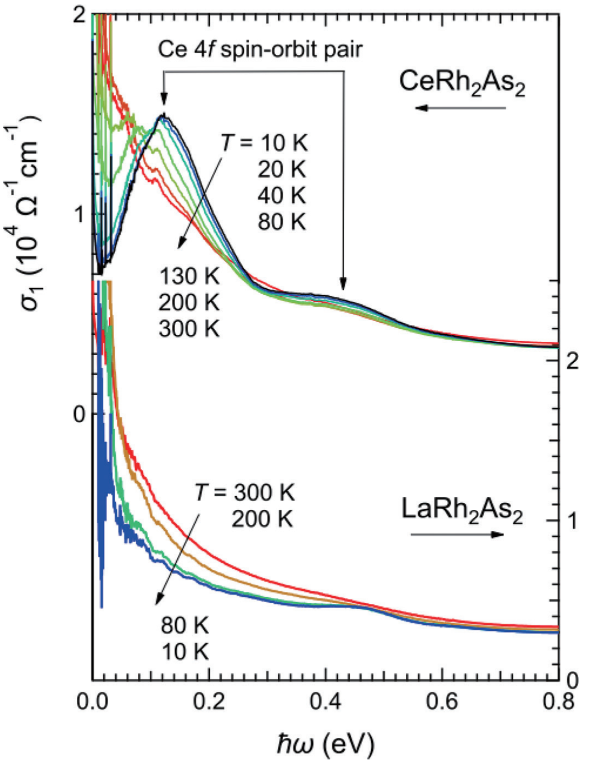

Figure 2. Temperature-dependent optical conductivity [$\sigma_1(\omega)$] spectra of $CeRh_2As_2$ and $LaRh_2As_2$.

2. Bulk-Sensitive Spin-Resolved Resonant Electron Energy-Loss Spectroscopy (SR-rEELS): Observation of Element- and Spin-Selective Bulk Plasmons[3)]

We have developed spin-resolved resonant electron energy-loss spectroscopy (SR-rEELS) with the primary energy of 0.3–1.5 keV, which corresponds to the core excitations of 2*p*–3*d* absorption of transition metals and 3*d*–4*f* absorption of rare-earths, with the energy resolution of about 100 meV using a spin-polarized electron source as a GaAs/GaAsP strained superlattice photocathode. Element- and spin-selective carrier and valence plasmons can be observed using the resonance enhancement of core absorptions and electron spin polarization. The Ni 2*p*–3*d* rEELS of nickel monoxide NiO as an example is shown in Figure 3. Furthermore, bulk-sensitive electron energy-loss spectroscopy spectra can be obtained because the primary energy corresponds to the mean free path of 1–10 nm. The methodology is expected to provide us with novel information about elementary excitations by resonant inelastic x-ray scattering and resonant photoelectron spectroscopy.

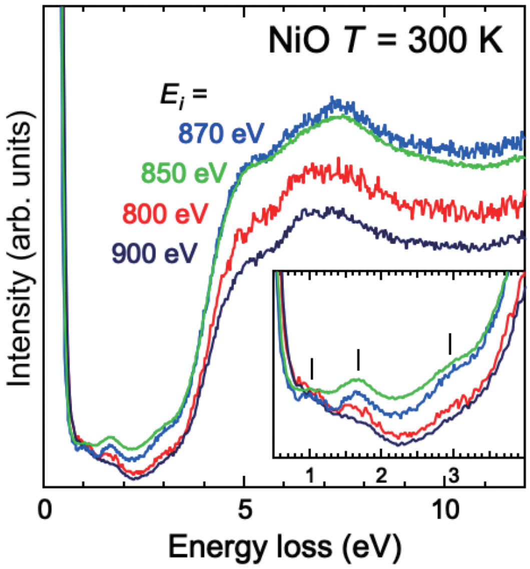

Figure 3. Resonant EELS spectra of nickel monoxide NiO with the primary energies (E_i) of 800–900 eV. The overall spectral intensity is enhanced at E_i = 850 and 870 eV near the Ni 2*d*–3*d* absorption edge. (Inset) Enlarged view of the Ni *d*–*d* excitations (indicated by vertical lines) below the lowest charge transfer excitation energy of about 4 eV.

References

1) S. Kimura, J. Sichelschmidt and S. Khim, *Phys. Rev. B* **104**, 245116 (7 pages) (2021).
2) S. Kimura, Y. S. Kwon, C. Krellner and J. Sichelschmidt, *Electron. Struct.* **3**, 024007 (8 pages) (2021).
3) S. Kimura, T. Kawabata, H. Matsumoto, Y. Ohta, A. Yoshizumi, Y. Yoshida, T. Yamashita, H. Watanabe, Y. Ohtsubo, N. Yamamoto and X. Jin, *Rev. Sci. Instrum.* **92**, 093103 (8 pages) (2021).

Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

Division of Advanced Molecular Science (Department of Materials Molecular Science, Electronic Structure)

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Professor
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Education

1985	B.S. The University of Tokyo
1993	Ph.D. The University of Tokyo

Professional Employment

1989	Assistant Professor, The University of Tokyo
1997	Associate Professor, The University of Tokyo
1999	Project Leader, Kanagawa Academy of Science and Technology
2004	Professor, Kobe University
2021	Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	Young Scientist Award , Catalysis Society of Japan
2002	Nano-Probe Technology Award, Nano-Probe Technology Committee, JSPS
2003	Technical Award, Surface Science Society of Japan
2004	Yazaki Award, Yazaki Foundation
2019	Society Award, Japan Society of Vacuum and Surface Science

Member
Secretary
ISHIKAWA, Azusa
KURITA, Yoshiko

Keywords Reactions at Interfaces, Catalysis, Energy-Related Chemistry

We are proud of our international-compatible studies of liquid–solid interfaces, *e.g.* photocatalysts for artificial photosynthesis and lubricants for smooth tribology. Characterization with frequency-modulation AFM, time-resolved ATR-IR spectroscopy, soft X-ray absorption, and microelectrode-based amperometry are being developed. We are pleased to collaborate with researchers in academic and industrial organizations to reveal science behind material conversion and energy dissipation at liquid–solid interfaces.

A new era of molecular science should be revealed in liquid–solid interfaces of finite thickness (Figure 1). The molecular interface is the place of reaction where molecules of interest collide with or interact with other molecules. We need to observe individual molecules there. On the other hand, the molecular interface is connected to liquid and solid. Materials and energy come from/to the two condensed phases, since functional interfaces are always open to the environment. In addition, operando characterization is definitely required for investigating the interface in its working state.

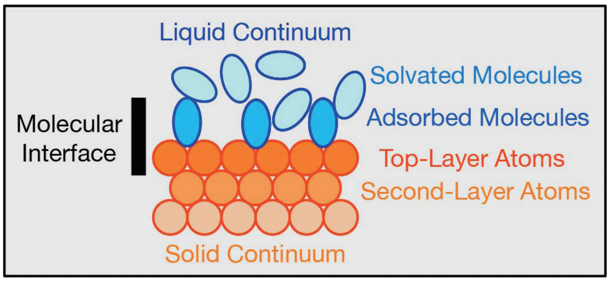

Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- T. Kosaka, Y. Teduka, T. Ogura, Y. Zhou, T. Hisatomi, H. Nishiyama, K. Domen, Y. Takahashi and H. Onishi, "Transient Kinetics of O_2 Evolution in Photocatalytic Water-Splitting Reaction," *ACS Catal.* **10**, 13159–13164 (2020).
- S. Xue, A. Sasahara and H. Onishi, "Atom-Scale Imaging of TiO_2(110) Surface in Water by Frequency-Modulation Atomic Force Microscopy," *J. Chem. Phys.* **152**, 054703 (7 pages) (2020).
- T. Fujiwara, A. Sasahara, N. Happo, K. Kimura, K. Hayashi and H. Onishi, "Single-Crystal Model of Highly Efficient Water-Splitting Photocatalysts: A $KTaO_3$ Wafer Doped with Calcium Cations," *Chem. Mater.* **32**, 439–1447 (2020).
- S. Moriguchi, T. Tsujimoto, A. Sasahara, R. Kokawa and H. Onishi, "Nanometer-Scale Distribution of Lubricant Modifier on Iron Films: A Frequency-Modulation Atomic Force Microscopy Study Combined with Friction Test," *ACS Omega* **4**, 17593–17599 (2019).
- H. Onishi, "Sodium Tantalate Photocatalysts Doped with Metal Cations: Why Are They Active for Water Splitting?" *ChemSusChem* **12**, 1825–1834 (2019).
- H. Imada, K. Kimura and H. Onishi, "Water and 2-Propanol Structured on Calcite (104) Probed by Frequency-Modulation Atomic Force Microscopy," *Langmuir* **29**, 10744–10751 (2013).

1. Microelectrode-Based Transient Amperometry of O_2 Adsorption and Desorption on a $SrTiO_3$ Photocatalyst Excited under Water

Oxygen evolution at water–solid interfaces is a key reaction for sustainable energy production. Although some intermediate states have been detected in transient absorption spectroscopy, the O_2 evolution kinetics after the multi-step, four-electron oxidation of water remain unknown. In this study,$^{1)}$ transient amperometry with a microelectrode was applied to *operando* O_2 detection over Al-doped $SrTiO_3$ particles doubly loaded with $RhCrO_x$ and CoO_y cocatalysts, an efficient photocatalyst for the overall water-splitting reaction. A platinum electrode (radius: 10 μm) was moved close to the particles in an electrolyte solution. Molecular oxygen was released on the particles, diffused across the electrode–particle gap, and converted to a current on the electrode (Figure 2).

Electrochemical O_2 detection at intervals of 0.1 s, which was thereby achieved, unexpectedly indicated instantaneous O_2 adsorption and desorption in addition to steady, photocatalytic O_2 evolution on the photocatalyst modified under intense light irradiation. We hypothesized that electrons excited in the conduction band were transferred to O_2 in water thorough Ti cations neighboring an oxygen anion vacancy on the modified Al-doped $SrTiO_3$. The negatively charged O_2 was then bound to the Ti cations. It was neutralized and released when shaded through electron back-transfer to the conduction band. The hypothesized mechanism for O_2 adsorption and desorption was compared with the photoinduced O_2 desorption known to occur on anion vacancies of $TiO_2(110)$. The microelectrode-based transient amperometry demonstrated here will be applied to many other phenomena at liquid–solid interfaces.

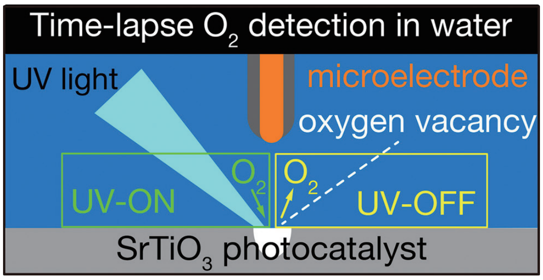

Figure 2. Transient amperometry for detection of molecular oxygen released into water.

2. Long-Life Electrons in Metal-Doped Alkali-Metal Tantalate Photocatalysts Excited under Water

Conversion of materials for artificial photosynthesis is completed in milliseconds or seconds by assembling atoms over semiconductor photocatalysts. Bandgap-excited electrons and holes reactive on this time scale are key for efficient atom assembly to yield the desired products. In this study,$^{2)}$ attenuated total reflection of infrared (IR) light was applied to characterize the electronic absorption of long-life charge carriers excited under water. This was a difficult task since water absorbs IR light for probing, while excitation light is absorbed by photocatalyst particles. An attenuated total reflection (ATR) assembly with a diamond prism is key for guiding the excitation light to the volume probed by IR light (Figure 3).

Under excitation, $NaTaO_3$ and $KTaO_3$ photocatalyst particles doped with Sr or La cations absorbed IR light. A broad absorption band appeared with a maximum at 1400 cm^{-1}, which was enhanced by the addition of hole scavengers (*e.g.*, methanol and Na_2SO_3) and disappeared in the presence of electron scavengers (*e.g.*, $FeCl_3$, $NaIO_3$, and H_2O_2). This absorption corresponded to the electronic transition of bandgap-excited electrons accommodated in mid-gap states. In anaerobic *n*-decane, the electron absorption was enhanced by the excitation light power, *P*, with absorbance being proportional to $P^{1/2}$. The observed 1/2-order power law suggested de-excitation via recombination of electrons and holes. When the excitation light was stopped, the absorbance decreased as a function of time with a second-order rate law, as expected in the case of recombinative de-excitation. In addition, the 1/2-order power law and second-order decay rate law were observed in anaerobic water, with an accelerated decay rate, which was possibly due to a water-related electron-consuming reaction. This study demonstrated that long-life electrons contribute to surface redox reactions over semiconductor photocatalysts for artificial photosynthesis.

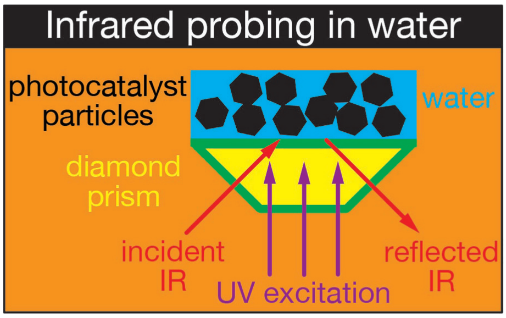

Figure 3. An attenuated total reflection assembly with a diamond prism for guiding ultraviolet light to the volume probed by IR light.

References
1) T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, *Phys. Chem. Chem. Phys.* **23**, 19386–19393 (2021).
2) Z. Fu, T. Hirai and H. Onishi, *J. Phys. Chem. C* **125**, 26398–26405 (2021).

Award

ONISHI, Hiroshi; 2021 HOT PCCP article [T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, *Physical Chemistry Chemical Physics* **23**, 19386–19393 (2021)] (2021).

Innovative Catalysis Development Based on Radiant Light Spectroscopy

Division of Advanced Molecular Science
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(–February, 2022)
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Education

1993	B.S. Osaka University
1995	M.S. Osaka University
1998	Ph.D. Osaka University

Professional Employment

1995	JSPS Research Fellow
1998	Assistant Professor, Osaka University
2002	Guest Scientist, Scripps Research
2008	Associate Professor, Kyoto University
2019	Associate Professor (Cross Appointment), Institute for Molecular Science
2022	Professor, Teikyo University of Science

Awards

2001	N.E. CHEMCAT Award in Synthetic Organic Chemistry, Japan
2008	The 22nd Special Young Lecturer in the 88th CSJ Annual Meeting
2012	Theme Chemistry Journal Award
2015	BCSJ Award, The Chemical Society of Japan
2019	BCSJ Award, The Chemical Society of Japan

Member
Secretary
HAGIWARA, Hisayo

Keywords Organometallic Catalyst, Peptide-Based Material, X-Ray Spectroscopy

For future sustainable development, we promote research development of advanced catalysts based on element strategy criteria. Non-precious metal such as iron, nickel, cobalt, and cupper catalysts are investigated for synthetic transformation of various organic molecules related to pharmaceutical and photoelectronic materials. To elucidate the precise catalytic properties and mechanism, X-ray absorption spectroscopy (XAS) and various radiant right spectroscopies provided at UVSOR are used, where development of a solution-phase in situ XAS spectroscopic techniques and system will be intensively conducted for the study of homogeneous organometallic catalysts. Multidisciplinary research covered on DFT and XAS spectroscopy is also conducted to achieve an efficient structural determination technique being never accessible by the conventional XAS-based structural analysis. Using these cutting-edge spectroscopic technologies, we aim to promote innovative catalyst research which enable us highly efficient transformation of extremely unreactive organic molecules such as simple aromatic compounds, CO_2, and biomass into valuable functional materials.

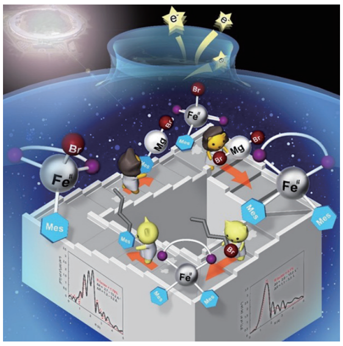


Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

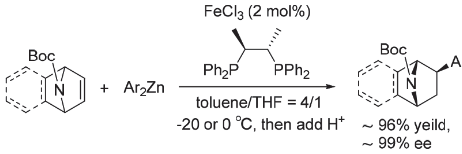
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada–Tamao–Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).
- R. Agata, H. Takaya, T. Iwamoto, T. Hatakeyama, K. Takeuchi, N. Nakatani and M. Nakamura, "Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and Fe^{II}/Fe^{IV} Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations," *Bull. Chem. Soc. Jpn.* **92**, 381–390 (2019).
- Y. Kanazawa, T. Mitsudome*, H. Takaya* and M. Hirano*, "Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate: Synchrotron Radiation Sheds Light on the Cu Cycle Mechanism," *ACS Catal.* **10**, 5909–5919 (2020).
- L. Adak, M. Jin, S. Saito, T. Kawabata, T. Itoh, S. Ito, A. K. Sharma, N. J. Gower, P. Cogswell, J. Geldsetzer, H. Takaya, K. Isozaki and M. Nakamura*, "Iron-Catalysed Enantioselective Carbometalation of Azabicycloalkenes," *Chem. Commun.* **57**, 6975–6978 (2021).

1. DFT-XAS-Based Mechanistic Investigation of Transition-Metal-Catalyzed Reaction in Homogeneous Phase[1,2]

Mechanistic study on transition-metal complex-catalyzed reaction in homogeneous phase mostly carried out by means of solution-phase NMR analysis. However, studies on base metal catalysts being essential for SDGs achievement often suffer from difficulties due to their paramagnetic property which provide unusual large paramagnetic shifts with significant peak broadening. To solve the problems in mechanistic study of base metal-catalyzed reaction, we performed XAS measurement which enables element specific analysis to determine the oxidation state and the geometry of catalytic species without interference from the paramagnetic property.

Recently, we have successfully elucidated the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate where the oxidation states and the local coordination geometries of catalytic intermediates were determined under the stoichiometric conditions of each reaction path.[1] DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is the first to provide a clear answer to the long-term debate on the reaction mechanism in the last three decades and demonstrated that XAS is the powerful tool for the mechanistic study on homogeneous paramagnetic transition-metal complex-catalyzed reactions being difficult by means of the conventional solution-phase NMR analysis.

Effectiveness of the DFT-XAS-based mechanistic study on paramagnetic transition-metal complex-catalyzed reaction was clearly demonstrated in iron-catalyzed enantioselective carbometallation of azabicycloalkenes (eq. 1).[2] In this study, formation of diphosphine ligand-coordinated tetrahedral iron species, which is a key species for chiral recognition of substrate, was successfully identified with the molecular structure in the reaction mixture.



(1)

2. XAFS-Based Structural Study on Flexible Organometallic Systems[3–6]

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal bearing sufficient size and quality for X-ray crystallography. We conducted DFT-XAS-based structural analysis of such flexible molecule. Recently, Prof. Uemura and Benjamin found a flexible MOF prepared from $[Zn_2(BDC)_2(DABCO)]_n$ and polystyrene which has a polymer-threaded multi-layered structure after removing the DABCO pillar ligand. The polymer-threaded extremely flexible molecular scaffolds showed no clear diffraction pattern except for a broad peak. To determine the molecular structure of this flexible MOF system, we carried out Zn K-edge and O K-edge XAS. A DFT-based simulation of both XAS spectra clearly demonstrated that $[Zn_2(BDC)_2]_n$-monolayer was preserved well in the turbostratic phase without DABCO pillar.[3]

Another successful application was achieved in the structure determination of double-decker type iron porpyrin/phtalocyanine dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials or iron-oxo linkage.[4] Fe K-edge XAS-based structural analysis supproted with DFT-MD-based simulation succefully provides the precise local coordionation geometry of iron centers in highly flexible supramolecular system.

Another successful example of the DFT-XAS-based structural study was demonstrated by the molecular strucutre detertmination of an anionic homoleptic organo–transition metal complex of $[Li(12\text{-crown-}4)_2][MPh_6\{Li(thf)\}_2]$ (M = Rh and Ir) in THF solution which are the first examples of hexaaryl complexes of d6 metals with a partially contacted ion pair structure of Ir^{2-}-Li^+ in solution-phase.[5]

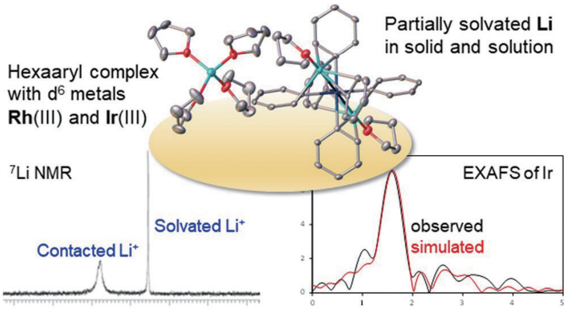


Figure 2. The molecular structure determination of $[Li(12\text{-crown-}4)_2]$ $[MPh_6\{Li(thf)\}_2]$.

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