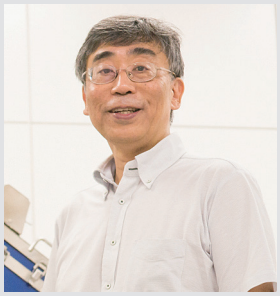
RESEARCH ACTIVITIES
Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions of molecular materials. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells, and field effect transistors are investigated in this department.

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

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. 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 CO_2 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 due to the formation of the metastable polarons. Consequent schematic descriptions of the photoexcited electronic states are summarized in Figure 3.

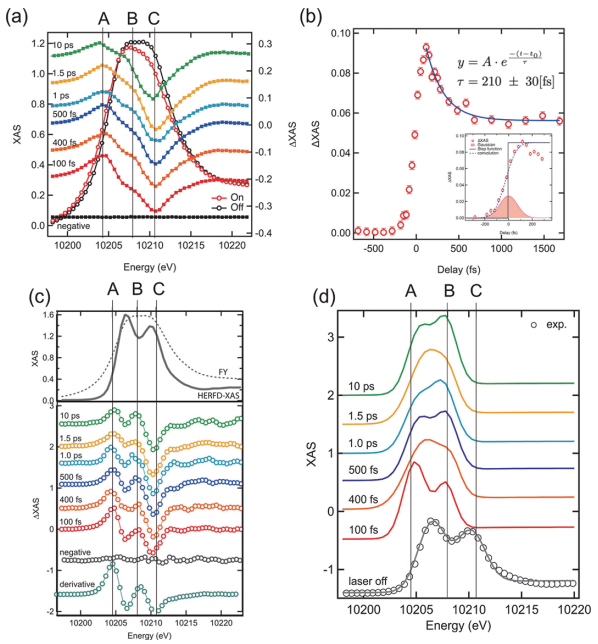


Figure 1. (a) Pump–probe normal energy resolution XAFS spectra and their first derivatives of WO_3 at different time delays. (b) The kinetic trace of XAFS at peak A in (a). (c) Pump–probe HERFD-XAFS and their first derivatives of WO_3 at the corresponding time delays to those in (a). The first derivative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

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.

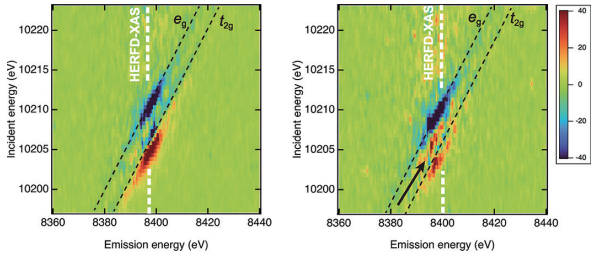


Figure 2. Typical examples of the pump–probe RXES at the delay time of 100 fs (left) and 10 ps (right). The white dash lines imply the energy to form HERFD-XAS in Figure 1(c).

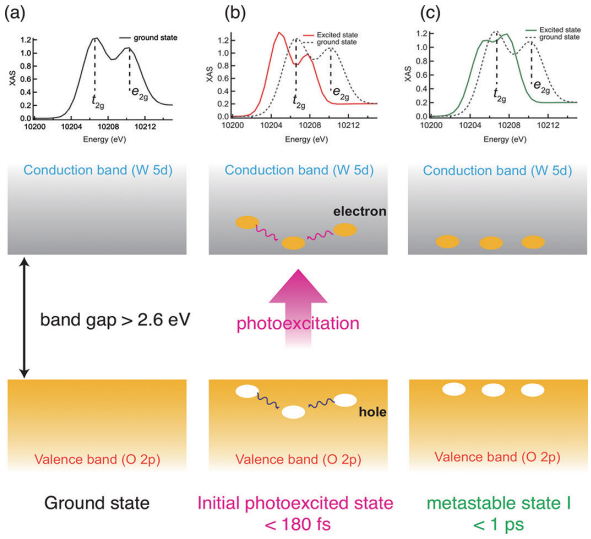


Figure 3. A sketch of proposed photoexcitation and relaxation mechanism: (a) the optical ground state, (b) the initial photoexcited state, (c) the metastable polaron state. After photoexcitation, electrons in the conduction band are delocalized. The HERFD-XAFS spectrum shifts in lower energies due to 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.jpclett.5c01062

2) A. Koide, Y. Uemura *et al.*, *Phys. Chem. Chem. Phys.* **22**, 2615 (2020). DOI: 10.1039/C9CP01332F

3) Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **255**, 1364 (2016). DOI: 10.1002/ange.201509252

4) D. Kido, Y. Uemura, Y. Wakisaka, A. Koide *et al.*, *Chem. Lett.* **51**, 1083 (2022). DOI: 10.1246/cl.220381

Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

Department of Materials Molecular Science
Division of Electronic Structure

SUGIMOTO, Toshiki
Associate Professor
[toshiki-sugimoto@ims.ac.jp]

Education
2007 B.S. Kyoto University
2011 Ph.D. The University of Tokyo

Professional Employment
2012 Assistant Professor, Kyoto University
2016 JST-PRESTO Researcher [Innovative Catalysts] (–2019)
2018 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2019 JST-PRESTO Researcher [Innovative optics and photonics]
2021 Senior Scientific Research Specialist, Ministry of Education, Culture, Sports, Science and Technology

Awards
2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014 39th Vacuum Science Paper Award
2018 PCCP Prize 2018
2018 CSJ Presentation Award 2018
2018 Encouragement Award, The Spectroscopic Society of Japan
2018 Morino Foundation for Molecular Science
2019 12th Young Scientist Awards of the Japan Society for Molecular Science
2019 The 14th Young Scientist Award of the Physical Society of Japan

Member
Research Lecturer
KANAI, Tsuneto
Assistant Professor
SAKURAI, Atsunori
Research Assistant Professor
TAKAHASHI, Shota
SAITO, Hikaru
SATO, Hiromasa
Post-Doctoral Fellow
SETO, Keisuke
LIN, Zhongqiu
Visiting Scientist
SAKAI, Hirofumi
BALTUŠKA, Andrius
Graduate Student
MOCHIZUKI, Tatsuto
JIN, ChengXiang
YOSHIZAWA, Ryu
TSUNEKAWA, Hibiki
TAKAHARA, Yuta
TEZUKA, Harunobu*
KITAYAMA, Taku†
YOSHIMURA, Rihito‡
DOI, Atsushi§
AMANO, Risa‖
TONOMOTO, Yusuke§
Technical Support Staff
SAKAKIBARA, Takayuki
Secretary
URANO, Hiroko
OKUBO Mayuka

Keywords Surface & Interface Science, Nonlinear Optical Spectroscopy, Water Molecules

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning prove microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used phase-sensitive sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\mathrm{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected $\mathrm{Im}\chi^{(2)}$ SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

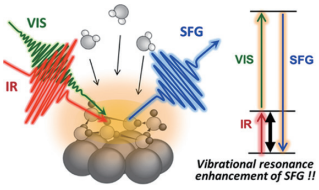


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020). [review]
- H. Sato *et al.*, "Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water," *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
- S. Takahashi *et al.*, "Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity," *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).
- Z. Lin *et al.*, "Positive and Negative Impacts of Interfacial Hydrogen Bonds on Photocatalytic Hydrogen Evolution," *J. Am. Chem. Soc.* **146**, 22276–22283 (2024).
- H. Sato *et al.*, "Direct *operando* Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides," *J. Am. Chem. Soc.* **146**, 24800–24807 (2024).
- A. Sakurai *et al.*, "Tip-Enhanced Sum Frequency Generation for Molecular Vibrational Nanospectroscopy," *Nano Lett.* **25**, 6390–6398 (2025).

1. Tip-Enhanced Sum Frequency Generation for Molecular Vibrational Nanospectroscopy[1)]

We achieved the first detection of vibrational sum-frequency generation (VSFG) signals from molecules at the nanometer scale by developing a tip-enhanced VSFG (TE-SFG) system. Conventional VSFG is a powerful tool for probing molecular structures and orientations at surfaces, but its spatial resolution is restricted by the diffraction limit, yielding ensemble-averaged responses from millions of molecules.

To break this barrier, we integrated femtosecond VSFG spectroscopy with scanning tunneling microscopy. By confining IR and near-IR pulses within the nanogap between a metallic substrate and an STM tip, we detected vibrational signals from molecules adsorbed on the surface. The signal emerged only in the tunneling regime and vanished when the tip–substrate distance exceeded 1 nm, demonstrating localization within ~1 nm. Characteristic vibrational modes of terminal methyl groups were clearly resolved, and analysis of the nonlinear susceptibility revealed their absolute orientation.

Electromagnetic simulations clarified that such extreme localization arises from two synergistic enhancement mechanisms: (i) the antenna effect, which enhances mid-IR absorption at the tip apex, and (ii) plasmonic resonance in the nanogap, which boosts the radiation efficiency of the visible VSFG signal.[2)] Together, these effects yield an enormous effective signal enhancement on the order of 10^{13}, enabling the near-field response from even a single molecule to dominate over far-field background contributions from ~10^8 molecules within a laser focal spot.

This achievement represents the first demonstration of molecular vibrational SFG detection at the nanometer scale. By uniting ultrafast vibrational spectroscopy with scanning probe microscopy, TE-SFG establishes a powerful platform for nonlinear optical nanospectroscopy. The method enables ultrahigh spatial resolution and single-molecule sensitivity, paving the way toward single-molecule ultrafast spectroscopy and molecular imaging beyond the diffraction limit. These capabilities hold strong promise for elucidating interfacial molecular processes in catalysis and materials science, offering a novel route for the rational design of advanced functional materials.

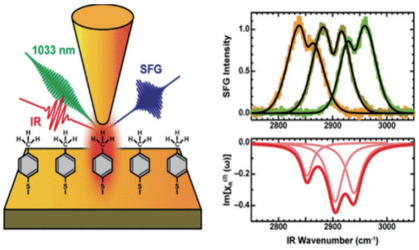


Figure 2. First successful demonstration of near-field tip-enhanced sum-frequency-generation vibrational nanospectroscopy of interfacial molecular systems.

2. Critical Impacts of Metal Cocatalysts on Oxidation Kinetics and Optimal Reaction Conditions of Photocatalytic Methane Reforming[3)]

Photocatalytic activation of methane, the main component of natural gas, is a key process for sustainable energy conversion. In this study, we clarified how metal cocatalysts critically regulate oxidation kinetics and determine optimal reaction conditions in photocatalytic methane reforming under ambient temperature.

Traditionally, noble metal cocatalysts supported on semiconductor photocatalysts have been viewed primarily as electron collectors that promote reduction reactions. Our recent paradigm-shifting work demonstrated, however, that metal cocatalysts can also act as efficient acceptors of photogenerated holes.[4)] Building on this concept, the present study provides the first direct evidence that cocatalyst loading drastically alters the methane pressure dependence of photocatalytic oxidation, shifting the optimal reaction regime to below ambient pressure.

Through systematic kinetic analysis, we revealed that this effect originates from molecular-level congestion of reactive intermediates during the oxidation process, with metal cocatalysts themselves functioning as active sites for oxidation. These findings overturn the conventional view that cocatalysts serve only reductive roles, highlighting their bidirectional contributions to both oxidation and reduction.

This work demonstrates that precise control of metal cocatalysts enables the microscopic design of surface reaction fields and optimization of reaction processes. By redefining the role of cocatalysts in photocatalysis, the study opens a pathway toward rational catalyst engineering for efficient and sustainable methane utilization.

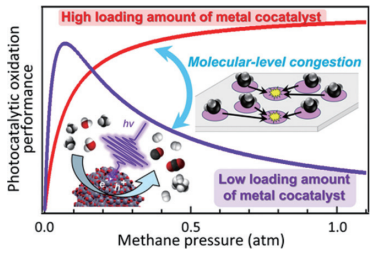


Figure 3. Photocatalytic oxidation kinetics and optimal pressure of methane vary significantly with the loading amount of metal cocatalysts. These variations are well described by kinetic analyses treating molecular-level congestion of oxidation intermediates.

References

1) A. Sakurai, S. Takahashi, T. Mochizuki and T. Sugimoto, *Nano Lett.* **25**, 6390–6398 (2025).
2) S. Takahashi, A. Sakurai, T. Mochizuki and T. Sugimoto, *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).
3) H. Sato and T. Sugimoto, *Chem. Commun.* **61**, 5942–5945 (2025).
4) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).

* carrying out graduate research on Cooperative Education Program of IMS with Waseda University
† carrying out graduate research on Cooperative Education Program of IMS with Tohoku University
‡ carrying out graduate research on Cooperative Education Program of IMS with Keio University
§ carrying out graduate research on Cooperative Education Program of IMS with The University of Tokyo
|| carrying out graduate research on Cooperative Education Program of IMS with Hokkaido University

Exploration of Novel Electronic/Ionic Physical Properties Using Inorganic Thin Films

Department of Materials Molecular Science
Division of Electronic Properties

SHIMIZU, Ryota
Professor
[shimizu-ryota@ims.ac.jp]

Education
2006 B.S. The University of Tokyo
2008 M.S. The University of Tokyo
2011 Ph.D. The University of Tokyo

Professional Employment
2011 Research Associate, Tohoku University
2012 JSPS Reserach Fellowship (PD)
2013 Visiting Researcher, University of California (2013.8–2014.2)
2015 Assistant Professor, Tohoku University
2016 Contract Lecturer, Tokyo Institute of Technology
2017 JST-PRESTO full-time Research Fellowship
2018 Assistant Professor, Tokyo Institute of Technology
2018 JST-PRESTO (Concurrent post, 2018.4–2021.3)
2020 Associate Professor, Tokyo Institute of Technology
2023 Associate Professor, The University of Tokyo
2025 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards
2011 NF-Foundation R&D Encouragement Award
2018 Tokyo Tech Challenging Research Award
2020 The Young Scientists' Award, The Commendation for Science and Technology by MEXT

Member
Research Lecturer
LUSTIKOVA, Jana
Secretary
NODA, Ayaka

Keywords Inorganic Solid-State Chemistry, Surface-Interface Science, Solid-State Electrochemistry

Interface control is a critical issue in both electronic and electrochemical devices. Using thin-film technologies, our group constructs well-defined model interfaces and explore novel electronic and ionic properties.

For electronic devices, we focus on the synthesis and characterization of metastable metal hydrides. Non-equilibrium film growth processes and epitaxial growth techniques enable the realization of functionalities unattainable in bulk materials. By controlling the charge states of hydrogen in solids, we aim to achieve high-transition-temperature superconductivity and develop multifunctional switching devices driven by external fields such as light, heat, and electric fields.

For ionic devices, we are working to improve the performance of fluoride-ion secondary batteries toward high-capacity energy storage. Batteries consist of a cathode, electrolyte, and anode, and operate through the migration of carrier ions between electrodes across the electrolyte. In this process, the electrode–electrolyte interface, where dissimilar materials come into contact, often represents the bottleneck for ion transport. By fabricating model interfaces within thin-film battery and conducting quantitative evaluations, we establish strategies for controlling carrier-ion transport at interfaces.

In addition, to accelerate materials research we are working on the digital transformation (DX) of materials research, including laboratory automation. Conventionally, materials were carefully synthesized and optimized one by one to evaluate their electronic and ionic properties. In this context, we are introducing robots and AI technologies. The use of robots allows experiments to be conducted in extreme environments, such as inert gas atmospheres or X-ray irradiation conditions, where humans cannot enter. Our goal is to advance the automation of experiments and promote the coexistence of humans and robots in materials research.

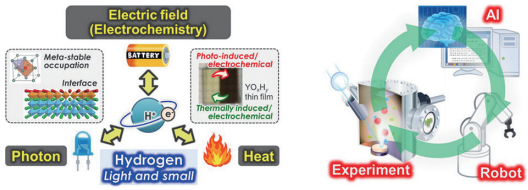


Figure 1. (left): Multiple-field-induced functions of hydride-related materials. (right): Conceptual illustration of experiments combining artificial intelligence (AI) and robots.

Selected Publications

- Y. Komatsu, R. Shimizu *et al.*, "Repeatable Photoinduced Insulator-to-Metal Transition in Yttrium Oxyhydride Epitaxial Thin Films," *Chem. Mater.* **34**, 3616 (2022).
- K. Nishio, R. Shimizu *et al.*, "Immense Reduction in Interfacial Resistance between Sulfide Electrolyte and Positive Electrode," *ACS Appl. Mater. Interfaces* **14**, 34620 (2022).
- M. Haruta, R. Shimizu *et al.*, "Negligible "Negative Space-Charge Layer Effects" at Oxide-Electrolyte/Electrode Interfaces of Thin-Film Batteries," *Nano Lett.* **15**, 1498 (2015).
- R. Shimizu *et al.*, "Autonomous Materials Synthesis by Machine Learning and Robotics," *APL Mater.* **8**, 111110 (2020).
- S. Kobayashi, R. Shimizu *et al.*, "Autonomous Exploration of an Unexpected Electrode Material for Lithium Batteries," *ACS Mater. Lett.* **5**, 10 (2023).

1. Hydrogen Charge-State Control of Multi-Anion Hydrides

The charge state of hydrogen in solids depends on the electronegativity of its bonding partner and can exist as a proton (positively charged), atomic hydrogen (electrically neutral), or a hydride (negatively charged). In this study, we achieved control over protonic and hydridic states in thin-film materials with multi anions with oxygen and nitrogen.

In the calcium–nitrogen–hydrogen system ($Ca_xN_yH_z$), protonic CaNH (imide) and hydridic Ca_2NH (nitrride hydride) are known. However, no synthesis of these compounds in thin-film form had previously been reported, and no guidelines for their fabrication were available. Using reactive magnetron sputtering, we achieved the selective epitaxial growth of both CaNH and Ca_2NH thin films.

To elucidate the selective growth processes, we monitored plasma emission of atomic Ca (422 nm) during the sputtering process. This result revealed that the growth pathway is governed by the relative reaction probabilities of Ca with hydrogen and nitrogen: Under high hydrogen partial pressure, hydrogen reacts preferentially with Ca to form CaH_x, which subsequently converts into CaNH, whereas under low hydrogen partial pressure, hydrogenation and nitrogenation occur simultaneously in a single step to yield Ca_2NH.

Furthermore, by further reducing the hydrogen partial pressure, we successfully synthesized epitaxial thin films of the layered electride Ca_2N. These findings open up new opportunities for controlling physical properties and exploring novel functionalities across proton, hydride, and electride.

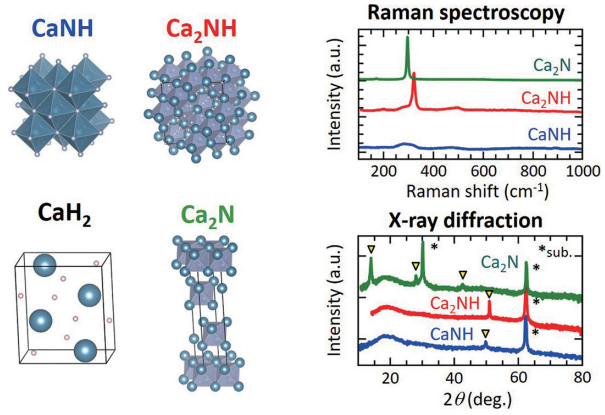


Figure 2. Selective growth of CaNH/Ca_2NH/Ca_2N epitaxial thin films.

2. Electrode/Electrolyte Interface Control of Fluoride Ion Batteries

To realize thin-film fluoride batteries, we fabricated and evaluated liquid-electrolyte cells using BiF_3 thin films as a cathode. When the BiF_3 thin-film electrode surface was directly immersed in the liquid electrolyte, the initial discharge capacity exceeded the theoretical value (~302 mAh g^{-1}), suggesting the occurrence of side reactions. Furthermore, the capacity retention decreased drastically upon cycling.

To address this issue, we applied interfacial control techniques established in Li-ion batteries[2] and introduced a chemically stable LaF_3 solid electrolyte buffer layer onto the BiF_3 electrode surface. As a result, side reactions were effectively suppressed, and the decline in capacity retention during cycling was suppressed. Future studies will focus on evaluations under non-exposure conditions by transferring the cells through vacuum and Ar atmospheres, thereby eliminating the influence of ambient moisture.

This study is collaboration with Dr. Taketoshi Minato of Instrument Center.

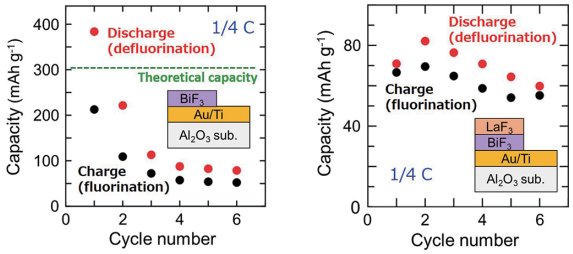


Figure 3. Cycle dependence of charge/discharge capacity. (Left) BiF_3 thin-film electrode in direct contact with liquid electrolyte; (Right) BiF_3 thin-film electrode covered with a LaF_3 solid-electrolyte buffer layer.

3. Format Standardization for Laboratory Automation

In advancing laboratory automation, the standardization of both hardware and software is essential. We have constructed a fully automated and autonomous system for inorganic thin-film synthesis and characterization. In recent years, we have also promoted the standardization of data format generated by automated measurement systems. Here, by employing the MaiML (Measurement, Analysis, Instrument Markup Language) framework—newly standardized as a JIS specification by the Japan Analytical Instruments Manufacturers' Association (JAIMA)—we established a scheme for data sharing on the cloud and successfully applied it to the optimization of synthesis conditions.[3]

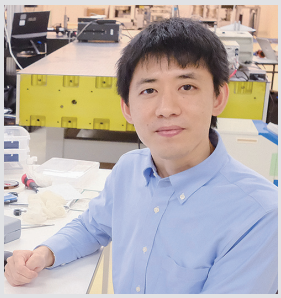
At present, through collaborative research, we are extending such autonomous materials exploration systems to a variety of fields, including spintronics materials and hydrogen storage materials.

References

1) S. Chon, R. Shimizu *et al.*, *J. Phys. Chem. Lett.* **13**, 10169 (2022).
2) S. Kobayashi, R. Shimizu *et al.*, *J. Phys. Chem. C* **127**, 4684 (2023).
3) K. Nishio, R. Shimizu *et al.*, *Digit. Discov.* **4**, 1734 (2025).

Nanostructure Fabrication, Optical Property Control, and Photonic Functionalization of Atomic-Layer Materials

Department of Materials Molecular Science
Division of Electronic Properties



SHINOKITA, Keisuke
Associate Professor
[shinokita@ims.ac.jp]

Education
2008 B.S. Kyoto University
2010 M.S. Kyoto University
2013 Ph.D. Kyoto University

Professional Employment
2010 JSPS Research Fellow (DC1)
2013 Postdoctoral Researcher, University of Groningen
2015 Visiting Researcher, Max Born Institute
2017 Specially Appointed Assistant Professor, Kyoto University
2020 Assistant Professor, Kyoto University
2025 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards
2011 Young Researcher Award, International Symposium on Terahertz Nanoscience (TeraNano 2011), Workshop of International Terahertz Research Network (GDR-I)
2013 Poster Award, International Workshop on Optical Terahertz Science and Technology 2013 (OTST2013)
2020 FY2019 Research Encouragement Award, Institute of Advanced Energy, Kyoto University
2022 18th Osawa Encouragement Award, The Fullerenes, Nanotubes and Graphene Research Society

Member
Graduate Student
OH, Shuto
Secretary
NODA, Ayaka

Keywords Semiconductors, Two-Dimensional Materials, Photophysical Properties

Modern electronic devices are approaching their miniaturization limits, necessitating innovative solutions through the integration of optical and quantum effects. Our research group focuses on atomic layer materials, particularly transition metal dichalcogenides (TMDs), which exhibit remarkable optical properties due to their single-atom thickness.

These materials possess direct bandgaps with strong light–matter interactions and unique electronic properties stemming from their extreme two-dimensionality. By stacking different atomic layers through van der Waals forces, we can create artificial heterostructures. In these structures, excitons—bound pairs of electrons and holes generated by photoexcitation—become spatially confined within periodic moiré potentials.

Our team has successfully observed exciton localization phenomena in $WSe_2/MoSe_2$ heterostructures induced by moiré potentials. Through detailed investigations of interlayer exciton formation and their optical responses, including circular polarization characteristics and quantum coherence measurements, we continue to elucidate the quantum states of moiré excitons. Currently, we are advancing this research by developing nanofabrication techniques for atomic layer materials and precisely controlling light–matter interactions to explore novel optical phenomena and functionalities.

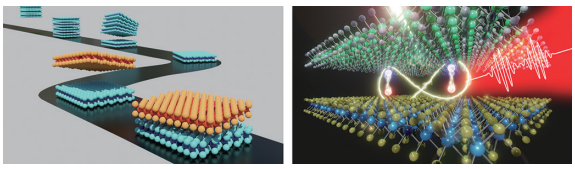


Figure 1. Left: Schematics of nanofabrication process for atomic-layer materials. Right: Visualization of quantum optical phenomena emerging from the engineered atomic-layer nanostructures.

Selected Publications

- H. Wang, H. Kim, D. Dong, K. Shinokita, K. Watanabe, T. Taniguchi and K. Matsuda, "Quantum Coherence and Interference of a Single Moiré Exciton in Nano-Fabricated Twisted Monolayer Semiconductor Heterobilayers," *Nat. Commun.* **15**, 4905 (2024).
- K. Shinokita, K. Watanabe, T. Taniguchi and K. Matsuda, "Valley Relaxation of the Moiré Excitons in a $WSe_2/MoSe_2$ Heterobilayer," *ACS Nano* **16**, 16862 (2022).
- K. Shinokita, Y. Miyauchi, K. Watanabe, T. Taniguchi and K. Matsuda, "Resonant Coupling of a Moiré Exciton to a Phonon in a $WSe_2/MoSe_2$ Heterobilayer," *Nano Lett.* **21**, 5938 (2021).
- K. Shinokita, X. Wang, Y. Miyauchi, K. Watanabe, T. Taniguchi and K. Matsuda, "Continuous Control and Enhancement of Excitonic Valley Polarization in Monolayer WSe_2 by Electrostatic Doping," *Adv. Funct. Mater.* **29**, 1900260 (2019).

1. Tailoring Exciton Dimensionality and Unveiling Prolonged Valley Polarization

Interlayer excitons (IXs) in twisted TMD heterostructures are a promising platform for novel optoelectronic devices. However, the moiré potential arising from the lattice mismatch often traps these IXs, forming zero-dimensional (0D) quantum emitters known as moiré excitons. While interesting for quantum optics, these localized states are less suitable for applications like photodiodes or solar cells, which benefit from mobile two-dimensional (2D) excitons.

To address this, we demonstrated a strategy to tune the dimensionality of IXs in a $MoSe_2/WSe_2$ heterostructure. By inserting an atomically thin hexagonal boron nitride (h-BN) layer as a spacer, we effectively modulated the moiré potential landscape, thereby transforming the trapped 0D moiré excitons into 2D IXs. The transition was unambiguously confirmed through systematic optical spectroscopy, which revealed a significant blue-shift in photoluminescence (PL) energy and a change from nonlinear saturation to linear power dependence of the PL intensity, a hallmark of the transition from a localized to a delocalized system. A remarkable feature of these engineered 2D IXs is their prolonged valley relaxation lifetime, which reaches up to 100 nanoseconds at low temperatures—orders of magnitude longer than the picosecond lifetimes typically observed in monolayer TMDs. This longevity is attributed to the suppression of the electron–hole exchange interaction, a dominant valley depolarization mechanism, which is weakened by the spatial separation of the electron and hole across the h-BN spacer. Our findings provide an effective strategy to tailor exciton dimensionality and harness the long valley lifetime of 2D IXs for future opto-valleytronic applications.

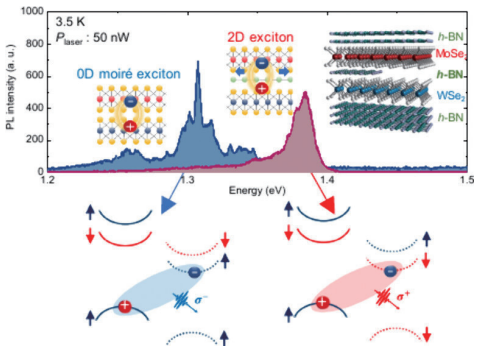


Figure 2. Dimensionality control and valley polarization of interlayer excitons in a $MoSe_2/WSe_2$ heterostructure. The insertion of an h-BN spacer layer (center schematic) transforms 0D moiré excitons with sharp emission peaks (blue spectrum) into 2D excitons with broad emission (red spectrum). These excitons exhibit a unique optical response to circularly polarized light (σ^+/σ^-, bottom schematic), enabling long-lived valley polarization.

2. Observation of Magnetically Switchable Nonlinear Photocurrents

The bulk photovoltaic effect (BPVE), which generates spontaneous photocurrents in non-centrosymmetric materials, offers a pathway to overcome the Shockley-Queisser efficiency limit of conventional solar cells. We investigated these nonlinear photoresponses in a vdW heterostructure that breaks both spatial inversion (P) and time-reversal (T) symmetry, composed of monolayer MoS_2 and the layered antiferromagnet $CrPS_4$. At the hetero-interface, the broken P-symmetry gives rise to a spontaneous photocurrent under illumination, which we identified as a shift current.

More strikingly, we discovered that this photocurrent is highly sensitive to the magnetic state of the $CrPS_4$ layer. The spontaneous photocurrent changed drastically below the Néel temperature of $CrPS_4$ (~40 K), where it transitions into an antiferromagnetic (AFM) phase. This phenomenon is attributed to the emergence of a "magnetic injection current," a distinct nonlinear photocurrent that arises in systems with broken T-symmetry and is superimposed on the existing shift current. We further demonstrated that the net photocurrent can be actively switched with an external magnetic field, which triggers distinct magnetic phase transitions in $CrPS_4$ (*e.g.*, from canted-AFM to ferromagnetic) and alters the contribution of the magnetic injection current. This work demonstrates a magnetic-field-controllable photovoltaic effect and opens a new avenue for "magneto-photovoltaics," a new class of devices that merge magnetism with solar energy conversion.

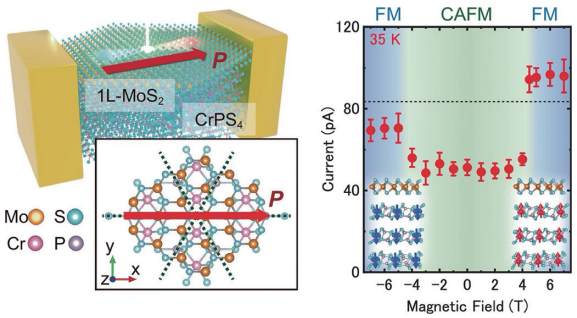


Figure 3. Magnetic field-switching of nonlinear photocurrent at a $MoS_2/CrPS_4$ hetero-interface with broken P- and T-symmetry. In the heterostructure (left schematic), a spontaneous photocurrent is observed. As the magnetic phase of the $CrPS_4$ layer is changed by an external magnetic field (right plot, from canted-AFM to ferromagnetic phase at 35 K), the photocurrent increases in a step-like manner, demonstrating active control of the optical response.

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Solid-State NMR for Molecular Science

Department of Materials Molecular Science
Division of Molecular Functions

NISHIMURA, Katsuyuki
Associate Professor
[nishimur@ims.ac.jp]

Education
1994 B.S. Himeji Institute of Technology (University of Hyogo)
1999 Ph.D. Himeji Institute of Technology (University of Hyogo)

Professional Employment
1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
2001 Assistant Professor, Yokohama National University
2006 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Award
2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

Member
Secretary
YOKOTA, Mitsuyo

Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterizations of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

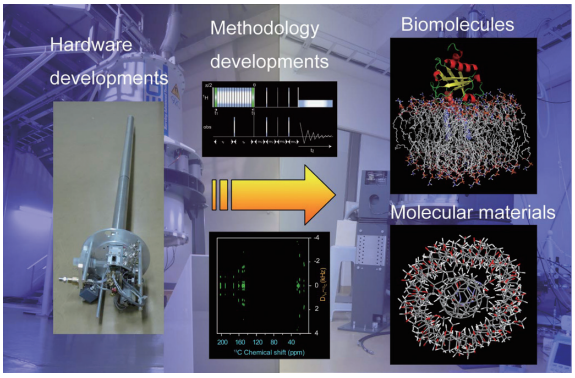

Figure 1. Outline of our studies.

Selected Publications

- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
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- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Huang, L. Zhai, D. E. Coupry, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine and D. Jiang, "Multi-Component Covalent Organic Frameworks," *Nat. Comm.* **7**, 12325 (12 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).
- M. Yagi-Utsumi, S. G. Itoh, H. Okumura, K. Yanagisawa, K. Kato and K. Nishimura, "The Double-Layered Structure of Amyloid-β Assemblage on GM1-Containing Membranes Catalytically Promotes Fibrillization," *ACS Chem. Neurosci.* **14**, 2648–2657 (2023).

1. Developments of Solid-State-NMR Techniques

In rigid organic solids, it is not easy to achieve high resolution ^{1}H NMR spectra in solid-state NMR spectroscopy due to the presence of strong ^{1}H homonuclear dipolar couplings which broaden ^{1}H signals. Therefore, ^{1}H homonuclear dipolar couplings must be decoupled efficiently by applying either magic angle spinning (MAS) at sufficiently high speed larger than 60 kHz or MAS at moderate speed in combination with multiple pulses (MPs). MAS and MPs give perturbations to spatial and spin parts of ^{1}H homonuclear dipolar coupling Hamiltonian, respectively. Furthermore, by using significantly high power radio frequency field (RF), it is still possible to apply MPs under ultra-high speed MAS in which require to keep short cycle time of MPs respect to the MAS period to avoid interference of time averaging effect between spatial and spin parts of ^{1}H homonuclear dipolar coupling Hamiltonian. Even under ultra-high speed MAS, applications of MPs improve spectral resolution furthermore. Therefore, methodology developments of MPs is still one of important research topics. ^{1}H spectral resolution depends on both the efficiency of decoupling and chemical shift scaling factor of MPs. The former factor can be improved through design of MPs enabling the removal of high order correction terms. On the other hand, the latter factor also depends on the design of MPs and larger scaling factor contributes better spectral resolution.

In the last report, we have reported the developed new MP sequence enabling removal of high order correction terms with moderate sequence length to realize efficient ^{1}H homonuclear dipolar decoupling. In this time, we have developed similar but new MPs possessing larger chemical shift scaling factors over previous one. However, the new MPs have twice length of previous one. Therefore, those are suitable to the conventional MAS up to 40 kHz. Such new sequences were evaluated theoretically and their performances will be demonstrated soon.

We have also designed two different types of modules to achieve heteronuclear dipolar recoupling with homonuclear decoupling of irradiated nuclei. The detail of those experiments will be reported. Such new sequences were evaluated theoretically and their performances will be demonstrated soon.

2. Developments of Core Technologies for Solid-State NMR Probes

We have been working on developments of totally original solid-state NMR probes for a couple of years. The probe had been successfully built using originally designed parts except for a spinning module for 400MHz NMR. Then, we have been working on developments of original sample spinning modules for MAS solid-state NMR probes which are fully compatible with Bruker spectrometers and commercial sample tubes. The spinning modules have been designed to fit probes for narrow bore magnet with outer sleeve possessing 38 mm inner diameter. We started the design of a spinning module for a standard 4.0 mm sample tube. After several times of version up, our original spinning module significantly exceeded the spinning performance of the commercial one from Bruker.

The design and build of final version of the spinning module have been finished. Currently, it is under optimization of air bearing black to achieve sufficient stability of spinning at high spinning rate.

Furthermore, the design and build of final version of the original spinning module for 2.5mm sample tube have been finished and it is also optimization of air bearing black.

Currently, we are also working on the design and build of the original spinning module for 1.9 mm sample tube.

3. Characterization of Synthetic Molecules by Solid-State NMR[1)]

Solid-state NMR is one of the efficient techniques to characterize amorphous samples such as synthetic molecules. We have collaborated with many research groups for the characterization of new synthetic molecules using solid-state NMR at the past. During couple of years, we have been collaborated with Associate Prof. Segawa group in IMS for the characterization of their newly developed synthetic molecules which are categorized to covalent organic frameworks (COFs).

Finally, ^{13}C signal solid-state NMR signal assignments had been successfully achieved for two of the new molecules. The obtained results from solid-state NMR together with other experimental data from other experiments sufficiently prove the achievement of the target molecular form of COFs for those samples. This project is also on the way.

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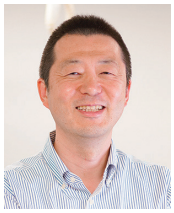
Unveiling Complex Phenomena at Solid–Liquid Interfaces by Scanning Probe Microscopy

Instrument Center



MINATO, Taketoshi
Senior Researcher

The solid–liquid interface serves as a reaction field for a wide range of phenomena, including electro- chemical reactions, dissolution and crystallization, catalysis, and hydrophilicity.[1–3] Despite extensive research, many fundamental aspects of these interfaces remain poorly understood due to their complex and dynamic nature. Scanning probe microscopy (SPM) represents a rare and powerful technique that can directly access the solid–liquid interface, allowing for detailed analysis of geometric structures, mechanical properties, electronic properties, magnetic properties, and even reaction mechanisms with exceptionally high resolution and sensitivity. In our studies, we have applied SPM to investigate electrochemical reactions as well as the physical properties of ice–liquid interfaces, providing new insights into interfacial behavior at the nanoscale.

At the electrode–electrolyte interface in electrochemical systems, the spatial distribution of interfacial structures strongly influences reaction kinetics and mechanisms. However, conventional spectroscopic analyses often fail to provide precise information on local variations in the interfacial structure due to limitations in spatial resolution. To overcome this challenge, we employed force curve measurements using SPM to analyze the local interfacial structure. By examining the distance between plateaus in the force curves, we were able to characterize the distribution of interfacial species (Figure 1). Notably, we observed that changes in the potential of a gold electrode led to significant alterations in the distribution of ionic liquid structures at the interface. This approach demonstrates the potential for probing more complex electrochemical reactions and understanding how local structural changes influence reaction pathways.

In addition to electrochemical systems, we have investigated the interface between ice and liquids. While the physical properties of ice have been extensively studied under ultra-high-vacuum conditions, many ice-related phenomena in nature occur at the interface between ice and liquid. In collaboration with Professor Hiroshi Onishi (Kobe University and IMS), we developed an analytical system based on amplitude-modulation atomic force microscopy to study the interfacial state between ice and liquids. Using this system, we successfully characterized both the structural and mechanical properties of the interface between alcohols and ice.[4–5] To obtain even more detailed information, we further developed a frequency-modulation atomic force microscopy system capable of operating in sub-zero antifreeze liquids. This system was applied to investigate the interface between octanol and graphite, enabling the successful observation of interfacial structures.[6–7] We anticipate that this technique will be widely applicable to studying ice–liquid interfaces and other low-temperature interfacial systems.

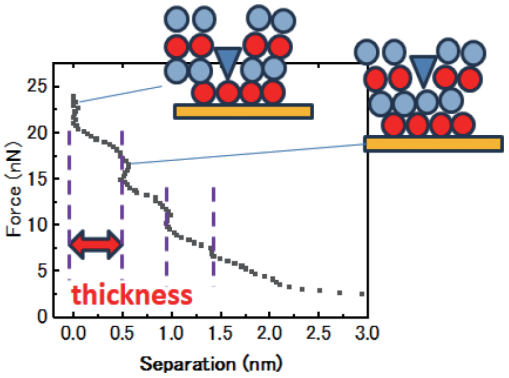


Figure 1. A typical force curve obtained at the interface between an ionic liquid and a gold electrode. The distances between the plateaus correspond to the thickness of the first layer of ionic species.

Our works highlight the importance of combining high-resolution force microscopy with carefully designed experimental systems to advance the understanding of complex interfacial phenomena across a broad range of materials and conditions.

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7) Z. Li, Best Poster Award, The 26th International Conference on Non-Contact Atomic Force Microscopy (2025).

Visiting Professors

Visiting Professor
HAYAMI, Shinya *(from Kumamoto University)*

Molecular Spin Qubits in Spin Crossover Systems

Molecular magnetism is an attractive research area due to its interest as a quantum magnetism, such as single molecule magnets (SMMs) and molecular spin qubits (MSQs). We have attempted to control slow magnetic relaxation by using spin-crossover (SCO) compounds with controllable spin states and molecular distortions. Iron(III) SCO compounds ($S = 5/2 \leftrightarrow S = 1/2$) were prepared and investigated by single crystal analysis, magnetic susceptibility measurements, cw/pulsed electron paramagnetic resonance (EPR) and Mössbauer spectroscopy. The respective distortion parameters (Σ) are compared with those for previously reported SCO iron(III) compounds, and the distortion in HS state is larger than LS state. AC magnetic susceptibility has been also measured for the compounds at 2 K, and show frequency dependency. Pulsed EPR spectra were also measured in the LS state, T_m (coherence time) were estimated. These results are the first attempt to provide molecular design for the development of metal complexes with MSQ by using SCO compounds that can be tuned in the spin states and molecular distortions.

Visiting Associate Professor
MIURA, Hiroki *(from Tokyo Metropolitan University)*

Heterogeneous Catalysts for Sustainable Molecular Transformations

From the perspective of preventing global warming, it is essential to establish advanced carbon-circulation systems that utilize renewable resources such as biomass and waste plastics. Since biomass compounds and polyesters contain numerous C–O bonds, the development of efficient catalysts capable of transforming these bonds is crucial for establishing sustainable processes. Our group has focused on the unique catalysis of supported metal catalysts, in which metal nanoparticles and metal-oxide supports can work in cooperation to activate organic molecules. We recently demonstrated that the cooperation of gold nanoparticles and Lewis acid at the surface of metal oxides enabled highly efficient borylation of unactivated C–O bonds in alkyl esters and alkyl ethers. Furthermore, we found that the strong interaction between gold nanoparticles and organic radicals enabled radical silylation of unactivated C–O bonds in alkyl esters and alkyl ethers. These findings provide important guidelines for the design of highly active heterogeneous catalysts for sustainable molecular transformations.

Visiting Associate Professor
KAWASUGI, Yoshitaka *(from Toho University)*

Phase-Transition Devices Based on Molecular Strongly Correlated Electron Systems

Strongly correlated electron systems consisting of molecular materials are softer and have lower carrier densities than inorganic materials, making them highly sensitive to external fields such as strain and gate electric fields. We have fabricated phase-transition devices utilizing strain and electric fields in organic strongly correlated electron systems. Specifically, we employed bis(ethylenedithio) tetrathiafulvalene [BEDT-TTF] molecules. These devices exhibit a remarkable physical property change, transitioning from an insulator to a superconductor in response to external fields. Recently, we have focused on improving device performance through the fabrication of field-effect transistors using solid electrolyte gates. In solid electrolyte gate transistors, we have successfully observed a field-induced Mott transition where interacting “frozen” electrons dissolve into a conductive liquid state. We have also confirmed that solid electrolytes may possess superior carrier injection capabilities compared to ionic liquids, which are more prone to sample degradation.