

RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

The goal of the Department is understanding and prediction of static and dynamic properties, reactions, and functions in condensed phase including biomolecular and heterogeneous catalytic systems by developing novel theories and computational methodologies based on theories in quantum mechanics, statistical mechanics, and solid state physics. The Department collaborates with Research Center for Computational Science on researches.

Theoretical Studies of Reactions, Functions, and Fluctuations in Many-Body Molecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I



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Education

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1995 Ph.D. The Graduate University for Advanced Studies

Professional Employment

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1994 Research Associate, Nagoya University
1998 Associate Professor, Nagoya University
2005 Professor, Institute for Molecular Science
2006 Professor, The Graduate University for Advanced Studies

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Keywords Reactions, Functions, Fluctuations

Many-body molecular systems, such as (supercooled) liquids and biomolecules, exhibit complex fluctuations. Furthermore, in these systems, various physical properties and biological functions are created and chemical reactions proceed under the fluctuations. We aim to elucidate the properties, functions, and reactions by investigating fluctuations and dynamics of the many-body molecular systems.

We have investigated fluctuations and dynamics of liquids by developing computational method for multi-dimensional nonlinear spectroscopy that can reveal detailed dynamical information not available from conventional linear spectroscopy. Consequently, we revealed the molecular origins of the ultrafast energy relaxation and time evolution of inhomogeneous fluctuations in liquid water. In supercooled liquids, rare and non-uniform structural changes, called dynamic heterogeneity, are induced by fluctuations. We elucidated the relationship between the lifetime of the dynamic heterogeneity and the fragility using the three-time correlation function of density fluctuations.

We study the molecular origin of anomalous properties of liquid water. We revealed that the anomalies of liquid water are related to the structural and dynamical instabilities hidden in the experimentally inaccessible region and the physical reason of the low glass transition of liquid water. Now we

investigate how rare but persistent structural relaxations proceed at low temperatures towards the glass transition temperature.

Complex conformational fluctuations and changes are also found in biomolecular systems. In addition, the conformational dynamics are considered to be essential for biological functions. We examine the relationship between fluctuation and biomolecular function found in the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. We investigate dynamic effects of enzymatic reactions, and find the importance of prearranged states for the rare but persistent enzymatic reactions. Furthermore, we examine dynamic disorder in conformational changes of proteins at the molecular level.

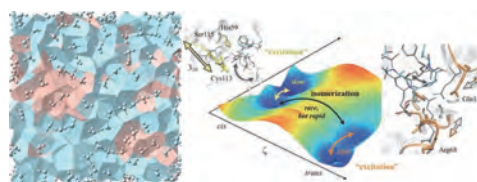


Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013).
- T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019), C. R. Baiz *et al.*, *Chem. Rev.* **120**, 7152–7218 (2020).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018), S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019).
- T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).
- S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).

1. Molecular Mechanism of Acceleration and Retardation of Collective Orientation Relaxation of Water Molecules in Aqueous Solutions¹⁾

The collective orientation relaxation (COR) of water molecules in aqueous solutions is faster or slower with an increase in the concentration of the solutions than that in pure water; for example, acceleration (deceleration) of the COR is observed in a solution of sodium chloride (tetramethyl ammonium chloride) with increasing concentration. However, the molecular mechanism of the solution and concentration dependence of the relaxation time of the COR has not yet been clarified. We theoretically investigate the concentration dependence of the COR of water molecules in solutions of tetramethylammonium chloride (TMACl), guanidinium chloride (GdmCl), and sodium chloride (NaCl). Based on the Mori–Zwanzig equation, we identify two opposing factors that determine the COR of water molecules in any aqueous solution: The correlation of dipole moments and the single-molecule orientation relaxation. We reveal the molecular mechanism of the concentration dependence of the relaxation time of the COR in the TMACl, GdmCl, and NaCl solutions in terms of these two factors.

2. Effects of Interfaces on Structure and Dynamics of Water Droplets on a Graphene Surface: A Molecular Dynamics Study²⁾

The structure and dynamics of water droplets on a bilayer graphene surface are investigated using molecular dynamics simulations. The effects of solid/water and air/water interfaces on the local structure of water droplets are analyzed in terms of the hydrogen bond distribution and tetrahedral order parameter. It is found that the local structure in the core region of a water droplet is similar to that in liquid water. On the other hand, the local structure of water molecules at the solid/water and air/water interfaces, referred to as the interface and surface regions, respectively, consists mainly of three-coordinated molecules that are greatly distorted from a tetrahedral structure. This study reveals that the dynamics in different regions of the water droplets affects the intermolecular vibrational density of states: It is found that in the surface and interface regions, the intensity of vibrational density of states at $\sim 50\text{ cm}^{-1}$ is enhanced, whereas those at ~ 200 and $\sim 500\text{ cm}^{-1}$ are weakened and redshifted. These changes are attributed to the increase in the number of molecules having fewer hydrogen bonds in the interface and surface regions. Both single-molecule and collective orientation relaxations are also examined. Single-molecule orientation relaxation is found to be marginally slower than that in liquid water. On the other hand, the collective orientation relaxation of water droplets is found to be significantly faster than that of liquid water because of the destructive correlation of dipole moments in the

droplets. The negative correlation between distinct dipole moments also yields a blue-shifted libration peak in the absorption spectrum. It is also found that the water–graphene interaction affects the structure and dynamics of the water droplets, such as the local water structure, collective orientation relaxation, and the correlation between dipole moments. This study reveals that the water/solid and water/air interfaces strongly affect the structure and intermolecular dynamics of water droplets and suggests that the intermolecular dynamics, such as energy relaxation dynamics, in other systems with interfaces are different from those in liquid water.

3. Microscopic Insights into Dynamic Disorder in the Isomerization Dynamics of the Protein BPTI³⁾

Understanding the dynamic disorder behind a process, *i.e.*, the dynamic effect of fluctuations that occur on a timescale slower or comparable with the timescale of the process, is essential for elucidating the dynamics and kinetics of complicated molecular processes in biomolecules and liquids. Despite numerous theoretical studies of single-molecule kinetics, our microscopic understanding of dynamic disorder remains limited. In the present study, we investigate the microscopic aspects of dynamic disorder in the isomerization dynamics of the Cys14–Cys38 disulfide bond in the protein bovine pancreatic trypsin inhibitor, which has been observed by nuclear magnetic resonance. We use a theoretical model with a stochastic transition rate coefficient, which is calculated from the 1-ms-long time molecular dynamics trajectory obtained by Shaw *et al.* [*Science* **330**, 341–346 (2010)]. The isomerization dynamics are expressed by the transitions between coarse-grained states consisting of internal states, *i.e.*, conformational sub-states. In this description, the rate for the transition from the coarse-grained states is stochastically modulated due to fluctuations between internal states. We examine the survival probability for the conformational transitions from a coarse-grained state using a theoretical model, which is a good approximation to the directly calculated survival probability. The dynamic disorder changes from a slow modulation limit to a fast modulation limit depending on the aspects of the coarse-grained states. Our analysis of the rate modulations behind the survival probability, in relation to the fluctuations between internal states, reveals the microscopic origin of dynamic disorder.

References

- 1) N. Moritsugu, T. Nara, S.-i. Koda, K. Tominaga and S. Saito, *J. Phys. Chem. B* **124**, 11730–11737 (2020).
- 2) M. Manish, A. K. Metya, J. K. Singh and S. Saito, *J. Chem. Phys.* **154**, 164704 (12 pages) (2021).
- 3) Y. Matsumura and S. Saito, *J. Chem. Phys.* **154**, 224113 (11 pages) (2021).

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Theoretical Studies on Novel Physical Properties Arising from Many-Body Interaction

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Education

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Professional Employment

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2015 Lecturer, The University of Tokyo
2019 Associate Professor, Institute for Molecular Science
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Awards

2008 L'Oréal-UNESCO Japan National Fellowships for Women in Science
2011 Best Poster Award in ISSS-6 Internal Symposium on Surface Science
2017 Young Scientist Award of the Physical Society of Japan
2019 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize
2020 The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science
2021 The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan

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Keywords

Quantum Many-Body Interaction, Density Functional Theory, Quantum Field Theory

Quantum many-body interaction is a source of novel physical properties in the condensed matters. In our group, we develop theoretical methods by combining quantum field theory and density functional theory, and carry out collaborative research with experimental groups. As specific targets, we focus on magnetism in nanostructure and energy dissipation.

For magnetism in nanostructure, we are interested in the Kondo effect and spin-orbit interaction. The Kondo effect arises from the interaction between the localized spin and conduction electrons, which forms a characteristic many-body state so called the Kondo singlet state. The spin-orbit interaction originating from relativistic effect constrains the direction of magnetic moment to specific direction. We investigate the possibility of novel physical phenomena induced by these interactions in the nanostructure and molecules on surfaces.

For energy dissipation, we focus on the effect of electron-phonon interaction. The electron-phonon interaction is one of

the most fundamental interactions in the condensed matter physics, and the quantitative evaluation in realistic materials is highly demanding. We adopt the ab-initio calculation to analyze the signal of electron-phonon coupling in surface spectroscopy and thermal properties in various kind of solids.

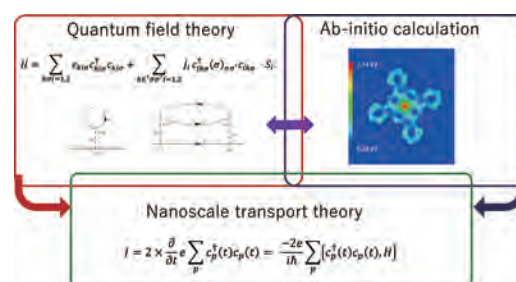


Figure 1. Schematic image of the theoretical method developed in our group.

Selected Publications

- E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi and M. Kawai, "Symmetry-Driven Novel Kondo Effect in a Molecule," *Phys. Rev. Lett.* **109**, 086602 (2012).
- E. Minamitani, R. Arafune, N. Tsukahara, Y. Ohda, S. Watanabe, M. Kawai, H. Ueba and N. Takagi, "Surface Phonon Excitation on Clean Metal Surfaces in Scanning Tunneling Microscopy," *Phys. Rev. B* **93**, 085411 (2016).
- E. Minamitani, N. Takagi and S. Watanabe, "Model Hamiltonian Approach to the Magnetic Anisotropy of Iron Phthalocyanine at Solid Surfaces," *Phys. Rev. B* **94**, 205402 (2016).
- R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai and N. Takagi, "Single-Molecule Quantum Dot as a Kondo Simulator," *Nat. Commun.* **8**, 16012 (2017).
- E. Minamitani, R. Arafune, T. Frederiksen, T. Suzuki, S. M. F. Shahed, T. Kobayashi, N. Endo, H. Fukidome, S. Watanabe and T. Komeda, "Atomic-Scale Characterization of the Interfacial Phonon in Graphene/SiC," *Phys. Rev. B* **96**, 155431 (2017).
- E. Minamitani, M. Ogura and S. Watanabe, "Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential," *Appl. Phys. Express* **12**, 095001 (2019).

1. Ab Initio Investigation for Initial Process of Joule Heating in Semiconductor

Joule heating in semiconductors is a fundamental problem in solid-state physics. The resulting thermal damage, reduction in operational reliability, and power consumption of nanoscale transistors have become increasingly critical as the device size decreases. The macroscopic definition of the Joule heating is the dot product of the electric field and the current density. The microscopic process of Joule heating in a steady state is described as the energy balance between the electron and phonon intermediated by electron–electron, electron–impurity, electron–phonon, and phonon–phonon interactions under nonequilibrium conditions in the presence of a high electric field. Until recently, the empirical treatment of the band structure and the electron–phonon coupling prevents us from understanding the detail of relaxation process induced by these scattering process quantitatively and microscopically.

We propose a methodology for quantitative investigation of the energy relaxation process with the ab initio treatment of electronic states and electron–phonon interactions by approximating the nonequilibrium electron distribution function as being in equilibrium with an effective temperature.¹⁾ This approximation is known as the two-temperature model because the electrons and phonons are described by different effective temperatures, the electron temperature (T_e) and lattice temperature (T_l). The two-temperature model becomes reasonable if the electron equilibration time is sufficiently shorter than the time required for energy relaxation from electrons to phonons. Under such conditions, the Joule heating process can be described by the following three steps: First, electrons accelerated by an electric field are scattered elastically by electron–electron and electron–impurity interactions with a short relaxation time. This process randomizes the electron energy and momentum, and consequently, the electron distribution becomes isotropic in \mathbf{k} -space, which can be described by a Fermi distribution with T_e . Second, the inelastic electron–phonon scattering with a longer energy relaxation time occurs, and the energy is transferred from the hot electrons to the cold phonons specified by T_l . Finally, the excited phonons are thermalized by the slow phonon–phonon interaction, and the heat energy is radiated to the environment or transported to a thermal bath such as a substrate and/or electrode by thermal phonons. We focus on the second energy transfer process as the initial step of Joule heating and develop a method to evaluate this process based on ab initio calculations.

Recent progress in ab initio calculations by combining density functional theory and the Wannier interpolation technique has enabled the evaluation of electron–phonon coupling with high precision. This technique has been employed to evaluate the transport properties of semiconducting materials. Here, we combine the ab initio calculation of the transport

properties with the two-temperature concept. We applied this theoretical approach to bulk Si as a specific target.

As result, we found that the microscopic initial process of Joule heating differed in the electron and hole carriers. Figures 2 (a)–(d) show the phonon dispersion and decomposition of the energy relaxation rates into the contributions from the phonons with <27 meV, <50 meV, and >50 meV energy at low and high T_l as functions of E . The contributions from the phonons with medium energy, the LA and TO modes at the zone boundary, differ for the electron and hole carriers. For the electron carriers, there is a substantial contribution from medium-energy phonons at both low and high T_l . In particular, the relaxation via medium-energy phonons is dominant at low E at low T_l . In contrast, for the hole carriers, the contribution from medium-energy phonons is minor compared to that from the TO and zone center LO modes, except at a very low E at a low T_l . The origin of the differences can be attributed to the presence/absence of the intervalley scattering process and the isotropic/anisotropic band structures in the electron and hole carriers. The important factors that govern the energy relaxation process can be controlled by strain. A detailed ab initio investigation of the energy relaxation rate in a strained structure remains a topic for future research.

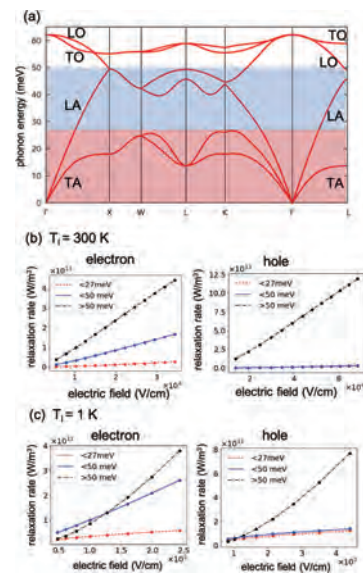


Figure 2. (a) Phonon band structure of bulk Si. The energy relaxation rates of electron and hole carriers are decomposed into contributions from phonons in the three energy ranges at (b) $T_l = 300$ K and (c) $T_l = 1$ K.

2. Other Ongoing Projects: - Thermal Properties in Amorphous Solids

Reference

- 1) E. Minamitani, *Phys. Rev. B* **104**, 085202 (2021).

Awards

MINAMITANI, Emi; The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science (2020).

MINAMITANI, Emi; The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan (2021).

SHITADE, Atsuo; 15th Young Scientist Award of the Physical Society of Japan (2021).

MIWA, Kuniyuki; 15th Young Scientist Award of the Physical Society of Japan (2021).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Professional Employment

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2013 Fellow 2012–2013, Wissenschaftskolleg zu Berlin
2016 Professor, Institute for Molecular Science
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Visiting professor, Nagoya University

Awards

2015 10th Condensed-Matter Science Prize, Japan
2016 10th Young Scientist Award of the Physical Society of Japan
2016 18th Sir Martin Wood Prize
2017 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize
2020 JSPS Prize
2020 Japan Academy Medal

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Keywords

Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

Essentially, any quantum systems can never be regarded as “isolated systems.” Quantum systems are always in contact with “the outside world,” and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spec-

troscopic signals. Therefore, theoretical tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

- (1) Developments of condensed phase quantum dynamic theories
- (2) Quantum theories to describe dynamical and transport processes in materials and biological systems
- (3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

Selected Publications

- A. Ishizaki and G. R. Fleming, “Quantum Coherence in Photosynthetic Light Harvesting,” *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, “Using Coherence to Enhance Function in Chemical and Biophysical Systems,” *Nature* **543**, 647–656 (2017).
- T. P. Nguyen and A. Ishizaki, “Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering,” *J. Phys. Chem. Lett.* **9**, 1243 (2018).
- A. Kato and A. Ishizaki, “Non-Markovian Quantum-Classical

Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases,” *Phys. Rev. Lett.* **121**, 647 (2018).

- Y. Fujihashi, R. Shimizu and A. Ishizaki, “Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules,” *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, “Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy,” *J. Chem. Phys.* **153**, 051102 (2020). [Editor’s Pick]

1. Probing Excited-State Dynamics with Quantum Entangled Photons

Quantum light is a key resource for promoting quantum technology. One such class of technology aims to improve the precision of optical measurements using engineered quantum states of light. In this study, we investigate transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping. It was further demonstrated that the signal corresponds to the spectral information along anti-diagonal lines of, for example, two-dimensional Fourier-transformed photon echo spectra. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.¹⁾

2. Achieving Two-Dimensional Optical Spectroscopy with Temporal and Spectral Resolution Using Quantum Entangled Three Photons

Recent advances in techniques for generating quantum light have stimulated research on novel spectroscopic measurements using quantum entangled photons. One such spectroscopy technique utilizes non-classical correlations among entangled photons to enable measurements with enhanced sensitivity and selectivity. In this work, we investigated spectroscopic measurement utilizing entangled three photons generated through cascaded parametric down-conversion. In this measurement, time-resolved entangled photon spectroscopy with monochromatic pumping [A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (2020)] is integrated with the frequency-dispersed two-photon counting technique, which suppresses undesired accidental photon counts in the detector and thus allows one to separate the weak desired signal. This time-resolved frequency-dispersed two-photon counting signal, which is a function of two frequencies, is shown to provide the same information as that of coherent two-dimensional optical spectra. The spectral distribution of the phase-matching function works as a frequency filter to selectively resolve a specific region of the two-dimensional spectra, whereas the excited-state dynamics under investigation are temporally resolved in the time region longer than the entanglement time. The signal is not subject to Fourier limitations on the joint temporal and spectral resolution, and therefore, it is expected to be useful for investigating complex molecular systems in which multiple electronic states are present within a narrow energy range.²⁾

3. Insights into Photosynthetic Energy Transfer Gained from Free-Energy Structure: Coherent Transport, Incoherent Hopping, and Vibrational Assistance Revisited

Giant strides in ultrashort laser pulse technology have enabled real-time observation of dynamical processes in complex molecular systems. Specifically, the discovery of oscillatory transients in the two-dimensional electronic spectra of photosynthetic systems [G. S. Engel, *et al.*, *Nature* **446**, 782 (2007)] stimulated a number of theoretical investigations exploring the possible physical mechanisms of the remarkable quantum efficiency of light harvesting processes. In this work, we revisited the elementary aspects of environment-induced fluctuations in the involved electronic energies and present a simple way to understand energy flow with the intuitive picture of relaxation in a funnel-type free-energy landscape. The presented free-energy description of energy transfer reveals that typical photosynthetic systems operate in an almost barrierless regime. The approach also provides insights into the distinction between coherent and incoherent energy transfer and the criteria by which the necessity of the vibrational assistance is considered.³⁾

4. Direct and Ultrafast Probing of Quantum Many-Body Interaction and Mott-Insulator Transition through Coherent Two-Dimensional Spectroscopy

Interactions between particles in quantum many-body systems play a crucial role in determining the electric, magnetic, optical, and thermal properties of the system. The recent progress in the laser-pulse technique has enabled the manipulations and measurements of physical properties on ultrafast timescales. In this work, we proposed a method for the direct and ultrafast probing of quantum many-body interaction through coherent two-dimensional (2D) spectroscopy. Up to a moderate interaction strength, the inter-particle interaction manifests itself in the emergence of off-diagonal peaks in the 2D spectrum before all the peaks coalesce into a single diagonal peak as the system approaches the Mott-insulating phase in the strongly interacting regime. The evolution of the 2D spectrum as a function of the time delay between the second and third laser pulses can provide important information on the ultrafast time variation of the interaction.⁴⁾

References

- 1) A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (7 pages) (2020). [Editor's Pick]
- 2) F. Fujihashi and A. Ishizaki, *J. Chem. Phys.* **155**, 044101 (13 pages) (2021).
- 3) A. Ishizaki and G. R. Fleming, *J. Phys. Chem. B* **125**, 3286–3295 (2021).
- 4) T. P. Nguyen and Q. T. Pham, *arXiv:2009.08598* (2021).

Awards

FUJIHASHI, Yuta; 15th Young Scientist Award of the Physical Society of Japan (2021).
ISHIZAKI, Akihito; Research Award of Quantum Life Science Society (2021).

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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Education

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Professional Employment

1993 Postdoctoral Fellow, Institute for Fundamental Chemistry
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1994 Visiting Researcher, Heidelberg University (–1995)
1995 Assistant Professor, Kyoto University
2002 Associate Professor, Kyoto University
2006 Theoretical Research Division Supervisor, Kyoto University (–2008)
2008 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2012 Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009 APATCC Pople Medal
2009 QSCP Prize CMOA

Member

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Graduate Student
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HATORI, Atsuya
Secretary
SUGIMOTO, Yukari

Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at hetero-junction of Ag nanocluster supported by alumina surface in terms of H₂ activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy

Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump-probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, "SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution," *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, "Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser," *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, "CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions," *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, "Cooperative H₂ Activation at Ag Cluster/θ-Al₂O₃ Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Mechanistic Studies on Photoinduced Catalytic Olefin Migration Reactions at the Pd(II) Centers of a Porous Crystal, Metal-Macrocyclic Framework¹⁾

Porous crystals with well-defined active metal centers on the pore surface have high potential as heterogeneous metal catalysts. We have recently demonstrated that a porous molecular crystal, metal-macrocyclic framework (MMF), catalyzes olefin migration reactions by photoactivation of its Pd^{II}Cl₂ moieties exposed on the crystalline channel surface. Herein we report a mechanistic study of the photoinduced olefin migration reactions at the Pd^{II} active centers of MMF. Several experiments, including a deuterium scrambling study, revealed that olefin migration is catalyzed *via* an alkyl mechanism by *in situ* generated Pd-H species on the channel surface during photoirradiation. This proposed mechanism was further supported by DFT and ONIOM calculations.

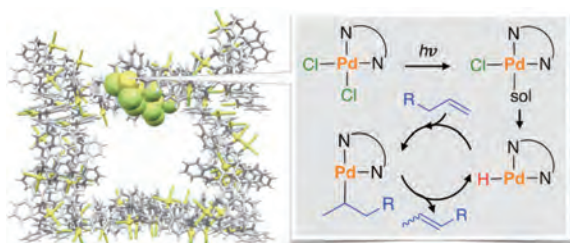


Figure 1. Porous Crystal Metal-Macrocyclic Framework show characteristic photoinduced olefin migration reaction at the Pd^{II} active centers.

2. Selective Catalytic Reduction of NO with NH₃ over Cu-Exchanged CHA, GME, and AFX Zeolites: A Density Functional Theory Study²⁾

Density functional theory calculations have been applied to study the selective catalytic reduction of NO by NH₃ over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages. The Cu^I, Cu^{II}, and [Cu^{II}(OH)]⁺ ions are considered as the active sites to study both the reduction and oxidation processes during the catalytic cycle. In the case of the reduction process, the NH₂NO formation at the [Cu^{II}(OH)]⁺ site possesses high barriers in the three frameworks, while the lower barriers are found at the Cu^{II} site. Importantly, it is found that the barriers are largely decreased at the solvated [Cu^{II}(NH₃)₄]²⁺ site for the *cha* and *aft* frameworks, while the barrier is only slightly decreased for the *gme* cage. As for the oxidation, the nitrate formation has similar reaction barriers at the Cu^I site of the three frameworks, which are lower than the following nitrite formation. In particular, the smallest *gme* cage possesses the highest barrier for the nitrite formation. Calculations on the O₂ activation by the NH₃-solvated Cu dimer revealed that the *cha* and *aft* cages have better performance than the *gme* cage, and the much smaller adsorption energy of O₂ in the *gme* cage indicates the unfavorable O₂ insertion. Therefore, the selectivity caused by the cage size is identified during the reaction process, and the *cha* and *aft* cages are more favorable.

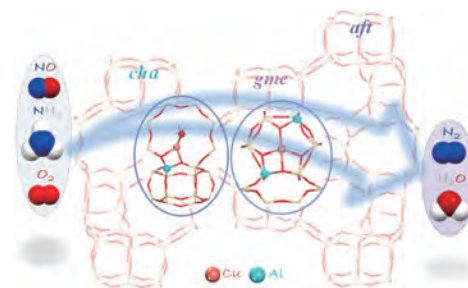


Figure 2. Density functional theory calculations on selective catalytic reduction of NO by NH₃ over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages revealed the selectivity caused by the cage size during the reaction process.

3. Facet-Dependent Catalytic Activity of Anatase TiO₂ for the Selective Catalytic Reduction of NO with NH₃: A Dispersion-Corrected Density Functional Theory Study³⁾

Recently, the facet-dependent catalytic activity of anatase TiO₂ for the selective catalytic reduction of NO with NH₃ (NH₃-SCR) has been observed experimentally. In this study, the NH₃-SCR of NO on the TiO₂ (001) and (101) surfaces was systematically investigated using dispersion-corrected density functional theory. We propose that the surface-assisted mechanism is predominant on the (001) surface, which involves the oxygen active sites playing a crucial role in facilitating the reaction. The NH₃ dissociation step reveals the largest activation energy barrier (E_a) of 61 kJ/mol on the (001) surface, whereas the NH₂NO decomposition step has the largest barrier, $E_a \approx 156$ kJ/mol, on the (101) surface. The results obtained by calculation are consistent with the experimental results, which have shown that a TiO₂ nanosheet with a dominant (001) facet shows superior catalytic performance in NH₃-SCR of NO compared to TiO₂ nanoparticles with dominant (101) facet.

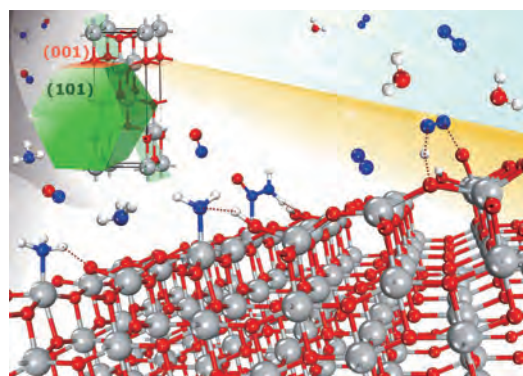


Figure 3. NH₃-SCR of NO on the (001) facet of anatase TiO₂.

References

- 1) H. Yonezawa, T. Shiraogawa, M. Han, S. Tashiro, M. Ehara and M. Shionoya, *Chem. –Asian J.* **16**, 202–206 (2021).
- 2) P. Zhao, B. Boekfa, K. Shimizu, M. Ogura and M. Ehara, *Catal. Sci. Technol.* **11**, 1780–1790 (2021).
- 3) A. Junkaew, M. Ehara, L. Huang and S. Namuangruk, *Appl. Catal., A* **623**, 118250 (2021).

Molecular Dynamics Simulations of Disease-Related Biomolecules

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Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. The conventional canonical-ensemble molecular dynamics (MD) simulations tend to get trapped in a few of the local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as replica-permutation method. We apply these methods to proteins and peptides and try to predict the native structures of proteins as in Figure 1.

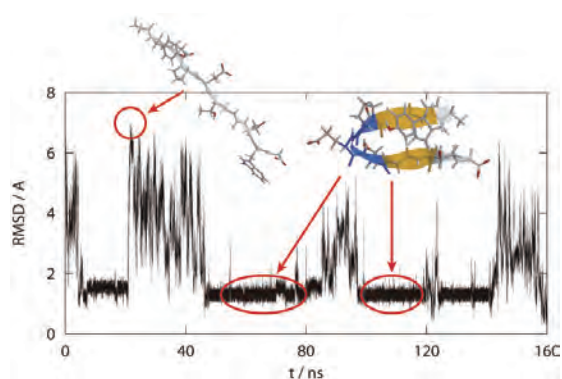


Figure 1. Time series of protein folding simulation.

We are also interested in disease-related biomolecules. For example, protein aggregates such as spherical substances called oligomers and acicular substances called amyloid fibrils (Figure 2) cause more than 30 kinds of diseases. Alzheimer's disease is thought to be caused by aggregated amyloid- β ($A\beta$) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of $A\beta$ peptides. We perform such MD simulations of oligomers and amyloid fibrils.

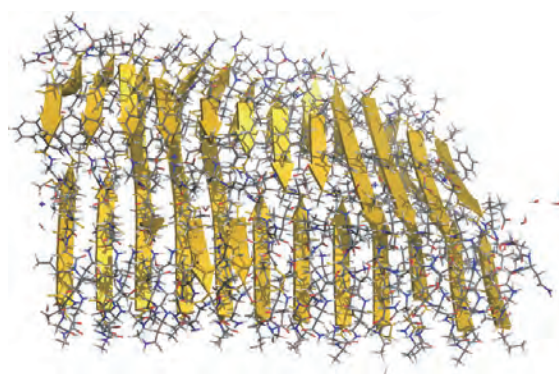


Figure 2. Snapshot of an $A\beta$ amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- H. Okumura and S. G. Itoh, "Structural and Fluctuational Difference between Two Ends of $A\beta$ Amyloid Fibril: MD Simulation Predicts Only One End Has Open Conformations," *Sci. Rep.* **6**, 38422 (9 pages) (2016).
- S. G. Itoh and H. Okumura, "Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method," *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- S. G. Itoh and H. Okumura, "Oligomer Formation of Amyloid- β (29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* **120**, 6555–6561 (2016).

1. Role of Water Molecules in the Laser-Induced Disruption of Amyloid Fibrils Observed by Nonequilibrium Molecular Dynamics Simulations

Water plays a crucial role in the formation and destruction of biomolecular structures. The mechanism for destroying biomolecular structures was thought to be an active breaking of hydrogen bonds by water molecules. However, using nonequilibrium molecular dynamics simulations, in which an A β amyloid fibril was destroyed via infrared free-electron laser (IR-FEL) irradiation, we discovered a new mechanism, in which water molecules disrupt protein aggregates,¹⁾ as shown in Figure 3. The intermolecular hydrogen bonds formed by C=O and N-H in the fibril are broken at each pulse of laser irradiation. These bonds usually spontaneously reform after the irradiation in many cases. However, when a water molecule happens to enter the gap between C=O and N-H, it inhibits the reformation of the hydrogen bonds. Such sites become defects in the regularly aligned hydrogen bonds, from which all hydrogen bonds in the intermolecular β -sheet are broken as the fraying spreads. This role of water molecules is entirely different from other known mechanisms. This new mechanism can explain the recent experiments showing that the amyloid fibrils are not destroyed by laser irradiation under dry conditions. Additionally, we found that helix structures form more after the amyloid disruption; this is because the resonance frequency is different in a helix structure. Our findings provide a theoretical basis for the application of IR-FEL to the future treatment of amyloidosis.

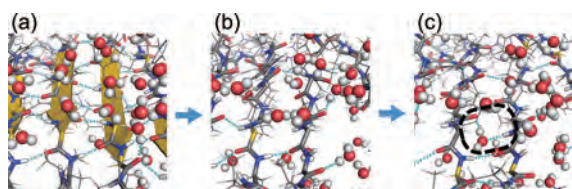


Figure 3. Snapshots of the disruption process of the hydrogen bonds between the A β peptides. (a) Hydrogen bonds are formed between A β peptides. (b) These hydrogen bonds are broken by the IR-FEL. (c) Water molecule enters the gap between C=O and N-H, it inhibits the reformation of the hydrogen bonds.

2. Replica-Permutation Molecular Dynamics Simulations of an Amyloid- β (16–22) Peptide and Polyphenols

Polyphenols are known to inhibit the aggregation of A β peptides. We performed all-atom replica-permutation molecular dynamics simulations of an A β fragment, A β _{16–22}, and two kinds of polyphenols, myricetin and rosmarinic acid in explicit water solvent.²⁾ We found that glutamic acid E22 of the A β _{16–22} peptide has the highest probability to bind to the polyphenols and specified the hydroxyl groups and carboxyl groups of polyphenols that contribute to the binding.

3. “Bucket Brigade” Using Lysine Residues in RNA-Dependent RNA Polymerase of SARS-CoV-2

The RNA-dependent RNA polymerase (RdRp) of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is a promising drug target for coronavirus disease 2019 (COVID-19) because it plays the most important role in the replication of the RNA genome. Nucleotide analogs such as remdesivir and favipiravir are thought to interfere with the RNA replication by RdRp. More specifically, they are expected to compete with nucleoside triphosphates, such as adenosine triphosphate (ATP). However, the process in which these drug candidates and nucleoside triphosphates are taken up by RdRp remains unknown. We performed all-atom molecular dynamics simulations to clarify the recognition mechanism of RdRp for these drug candidates and ATP that were at a distance.³⁾ The ligand recognition ability of RdRp decreased in the order of remdesivir, favipiravir, and ATP. We also identified six recognition paths. Three of them were commonly found in all ligands, and the remaining three paths were ligand-dependent ones. In the common two paths, it was observed that the multiple lysine residues of RdRp carried the ligands to the binding site like a “bucket brigade,” as shown in Figure 4. In the remaining common path, the ligands directly reached the binding site. Our findings contribute to the understanding of the efficient ligand recognition by RdRp at the atomic level.

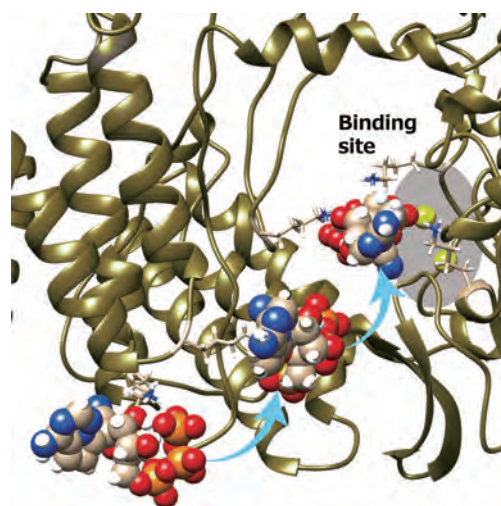


Figure 4. Remdesivir (shown in the sphere model) is transferred to two Mg²⁺ ions (yellow-green spheres) at the binding site of the RNA polymerase while being passed from one lysine residue (shown in the stick model) to another.

References

- 1) H. Okumura, S. G. Itoh, K. Nakamura and T. Kawasaki, *J. Phys. Chem. B* **125**, 4964–4976 (2021).
- 2) L. Le Nguyen Ngoc, S. G. Itoh, P. Sompornpisut and H. Okumura, *Chem. Phys. Lett.* **758**, 137913 (7 pages) (2020).
- 3) S. Tanimoto, S. G. Itoh and H. Okumura, *Biophys. J.* **120**, 3615–3627 (2021). DOI: 10.1016/j.bpj.2021.07.026

Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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Keywords Theoretical Biophysics, Biomolecular Machines, Molecular Motors

Biomolecular machines, such as molecular motors and transporters in the cell, are known to change their structure when they function. For example, ATP synthase, which synthesizes ATP in mitochondria, is a molecular motor that uses chemical energy to rotate. Transporters, which transport substrate molecules across the cell membrane, perform substrate transport by changing their structure between an inwardly and outwardly open structure relative to the membrane. Our goal is to elucidate the mechanism of these elaborate and dynamic nanomachines created by nature at the atomic and molecular level, and to control their functions based on our findings.

We would like to understand the mechanism of biomolecular machines by “seeing” the motion of biomolecular machines at the moment they function, on a computer at the molecular level. However, this is not an easy task, because biomolecular machines are huge molecules, and their functioning time scale is slow (for a molecular scale) at milliseconds or longer. Conventional atomistic molecular dynamics (MD) simulations cannot cover millisecond-long functional dynamics, especially for a large system like typical biomolecular machines. Therefore, we are trying to capture the motion at the moment of function by using methods such as an

importance sampling technique, or coarse-graining multiple atoms together.

We have been working on biomolecular motors such as ATP synthase. ATP synthase is a rotary motor that produces most of ATP required in the cell. It is composed of two rotary motors: F_0 and F_1 . F_0 motor is embedded in the membrane driven by proton gradient, while F_1 motor is driven by ATP hydrolysis reaction. We clarified how the rotation of F_1 motor is driven by a key chemical step, P_i release after ATP hydrolysis reaction, by accelerating atomistic MD simulations with external forces.

Transporters are membrane proteins that transport their substrates across the membrane. We have studied Na^+/H^+ antiporter that exchanges sodium ions and protons inside and outside the cell. The ion transport by the Na^+/H^+ antiporter was simulated in atomic detail with the transition path sampling technique to capture the moment of the ion transports. The simulations predicted the mutation that can speed up the ion transport. The mutation was tested in experiments and shown to speed up the ion transport twice faster than the wild type. Therefore, we succeeded in controlling the function of the transporter based on mechanism obtained from simulations.

Selected Publications

- K. Okazaki and G. Hummer, “Phosphate Release Coupled to Rotary Motion of F_1 -ATPase,” *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).
- K. Okazaki and G. Hummer, “Elasticity, Friction, and Pathway of γ -Subunit Rotation in F_0F_1 -ATP Synthase,” *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, “Mechanism of the Electroneutral Sodium/Proton Antiporter PaNhaP from Transition-Path Shooting,” *Nat. Commun.* **10**, 1742 (2019).

1. Mechanism of Unidirectional Motions of Chitinase

Processive cellulase and chitinase recently have been cast new light as a different type of biomolecular motors that use hydrolysis energy of polysaccharides for their unidirectional movements. We used single-molecule trajectories to estimate an underlying diffusion model with chemical-state-dependent free energy profile.¹⁾ To consider nonequilibrium trajectories driven by the chemical energy consumed by biomolecular motors, we developed a novel framework based on a hidden Markov model, wherein switching among multiple energy profiles occurs reflecting the chemical state changes in motors. The chemical-state-dependent free energy profile underlying the burnt-bridge Brownian ratchet mechanism of processive chitinase was determined.¹⁾

2. Mechanism of Na⁺/H⁺ Antiporter and Engineering of a Faster Transporter

Na⁺/H⁺ antiporters control pH and Na⁺ concentration in the cell by exchanging sodium ions and protons across lipid membranes. They belong to the cation/proton antiporter (CPA) superfamily, and prevail in all domains of life. The archaeal Na⁺/H⁺ antiporters PaNhaP from *Pyrococcus abyssi* and MjNhaP1 from *Methanocaldococcus jannaschii* as well as human NHE1, which is linked to a wide spectrum of diseases from heart failure to autism and has no structure solved yet, are electroneutral antiporters of the CPA1 family, exchanging one proton against one sodium ion. As a model system in mechanistic studies of electroneutral Na⁺/H⁺ exchange, we studied the transport mechanism of PaNhaP.²⁾

Na⁺/H⁺ antiporters use the gradient of either sodium ion or proton to drive the uphill transport of the other ion (Figure 1A). The conformational transition of the transporter makes the ion-binding site accessible from either side of the membrane in the alternating manner. For PaNhaP, the inward-open conformation was obtained by X-ray crystallography, while the outward-open conformation is not known experimentally. We modelled the outward-open conformation by MDFF flexible fitting to the low-resolution outward-open structure of the homologous MjNhaP1 from cryo-EM, followed by the long equilibrium MD simulations. It was shown that the transporter domain moves ~3.5 Å in the direction normal to the membrane to take the outward-open state.

By applying the transition path sampling technique, we sampled unbiased transition paths between the inward- and outward-open states. In analysis of the transition paths, we found hydrophobic gates above and below the ion-binding site, which open and close in response to the domain motions (Figure 1B). From the reaction coordinate analysis, it was shown that open-close motion of the outside gate (Ile163-Tyr255) is a rate-limiting step of the alternating-access conformational change. Based on this result, we weakened the outside gate by mutating the residues to both alanine. It was expected that this mutation lowers the barrier and makes the

ion transport faster. It was confirmed by experiments that the ion-transport speed of the mutant is indeed twice faster than the wild-type transporter.

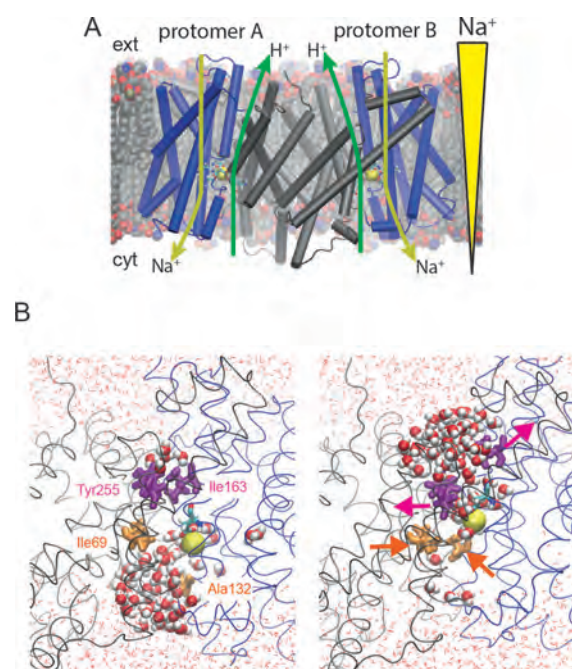


Figure 1. (A) PaNhaP dimer structure. (B) The outside (purple) and inside (orange) gates found in the transition path simulations.

3. Mechanism of Membrane Remodeling by F-BAR Protein Pacsin1

F-Bin/Amphiphysin/Rvs (F-BAR) domain proteins play essential roles in biological processes that involve membrane remodelling, such as endocytosis and exocytosis. Notably, Pacsin1 from the Pacsin/Syndapin subfamily has the ability to transform the membrane into various morphologies: striated tubes, featureless wide and thin tubes, and pearling vesicles. We clarified the membrane curvature induction and sensing characteristics of Pacsin1 by combining all-atom (AA) and coarse-grained (CG) MD simulations.³⁾ By matching structural fluctuations between AA and CG simulations, a CG protein model called “Gō-MARTINI” was developed and optimized.⁴⁾ The model should prove useful for describing protein dynamics that are involved in membrane remodeling processes.

References

- 1) K. Okazaki, A. Nakamura and R. Iino *J. Phys. Chem. B* **124**, 6475–6487 (2020).
- 2) K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, *Nat. Commun.* **10**, 1742 (2019).
- 3) M. I. Mahmood, H. Noguchi and K. Okazaki, *Sci. Rep.* **9**, 14557 (2019).
- 4) M. I. Mahmood, A. B. Poma and K. Okazaki, *Front. Mol. Biosci.* **8**, 619381 (2021).

Theoretical Studies on Molecular Aggregates

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Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates can exhibit remarkable optical and electronic properties that are not observed in isolated molecules. We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship. Our research also include the developments of theoretical and computational methods.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave functions can be delocalized over many molecules by intermolecular electronic couplings. By contrast, the wave functions can be localized because of the static disorder and interactions with nuclear degree of freedom. Therefore, successful theoretical descriptions require the inclusions of electronic couplings, static disorder, and electron–phonon or electron–vibration interaction. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. Electronic states of an aggregate are obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian is used for simulating energy or charge dynamics by a quan-

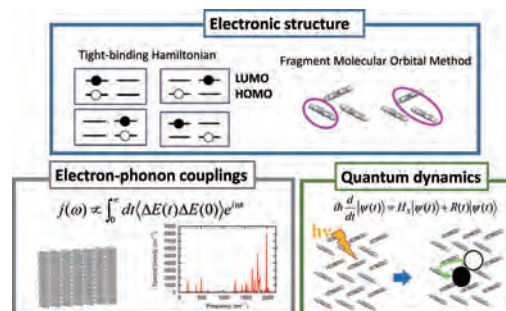


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

tum dynamics method, which incorporates finite-temperature effects and electron–vibration interactions. The combined computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

We currently investigate electronic states and quantum dynamics at organic interfaces. We also develop the many-body perturbation theory to predict electronic levels at higher accuracy.

Selected Publications

- T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, “Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2′3′-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization,” *J. Phys. Chem. Lett.* **7**, 1374–1380 (2016).
- T. Fujita and Y. Mochizuki, “Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems,” *J. Phys. Chem. A* **122**, 3886–3898 (2018).

1. Fragment-Based Excited-State Calculations Using the GW Approximation and Bethe–Salpeter Equation¹⁾

Accurate calculations of electronic states are essential for the computational studies of organic semiconductor materials, toward understanding of electronic processes in organic devices. The electronic processes in organic electronic devices, such as charge injection and electron–hole separation, are governed by the energies of the charged and neutral excited states. Although the Kohn–Sham (KS) density functional theory (DFT) has been established to be accurate for investigating the ground-state properties, a more sophisticated method is required for excited states. The many-body Green’s function method within the GW approximation has been established as a standard approach for the first-principle computation of the charged excitations in condensed matter. Further, neutral excited states can be computed using the Bethe–Salpeter equation (BSE) within the GW approximation, *i.e.*, the GW/BSE method. In particular, the GW/BSE method can yield the correct long-range asymptotic behaviors of the charge-transfer excited states in both gas and condensed phases, which is in contrast to the standard time-dependent DFT.

In this study, we present a fragment-based approach for calculating the charged and neutral excited states in molecular systems, based on the many-body Green’s function method within the GW approximation and Bethe–Salpeter equation. Our implementation relies on the many-body expansion of the total irreducible polarizability in the basis of fragment molecular orbitals. The GW quasiparticle energies in complex molecular environments are obtained by the GW calculation for the target fragment plus induced polarization contributions of the surrounding fragments at the static Coulomb-hole plus screened exchange level. In addition, we develop a large-scale GW/BSE method for calculating the delocalized excited states of molecular aggregates, based on the fragment molecular orbital method and the exciton model. The accuracy of fragment-based GW and GW/BSE methods were evaluated on the molecular clusters and molecular crystal. We found that the accuracy of the total irreducible polarizability can be improved systematically by including two-body correction terms, and the fragment-based calculations can reasonably reproduce the results of the corresponding unfragmented calculations with a relative error of less than 100 meV. The proposed approach enables the efficient excited-state calculations for large molecular systems with reasonable accuracy.

2. Excited-State Dynamics Based on the FMO and Wavepacket Propagation Method²⁾

We develop a method to investigate the excited-state dynamics in organic molecular aggregates. Our approach is based on three components: (i) FMO-based electronic coupling calculations, (ii) derivations of model Hamiltonians, and (iii) a wavepacket dynamics method. Using the electronic couplings obtained from an FMO calculation for an aggregate, we derive a model Hamiltonian that describes a charge carrier or an exciton in the aggregate. From a theoretical viewpoint, an *ab initio* many-electron Hamiltonian can be mapped into a reduced one-body or two-body Hamiltonian through the FMO calculation. The time evolution of the model Hamiltonian is then simulated using a wavepacket propagation method. We attempt to understand photophysical and optoelectronic processes in a molecular aggregate as the quasiparticle dynamics described by the model Hamiltonian. We have implemented the electronic coupling calculations and model Hamiltonian derivations into the ABINIT-MP program. In view of computations, an FMO calculation by the ABINIT-MP program provides Hamiltonian matrix elements. The matrix data are then passed to other software that simulates the time propagation.

We investigated the excited-state dynamics in the DNTT thin film and the C₆₀/pentacene (PEN) interface. In particular, we highlight the spatial extents of the electron and hole wave functions that constitute exciton states. We show that the dynamics of the electron and hole wave functions play essential roles in optoelectronic processes, such as the exciton relaxation dynamics and charge separation. Because the extent of delocalization is determined by the interplay among electronic couplings, structural disorder, and finite-temperature effects, the combined approach based on the FMO and wavepacket dynamics is indispensable. Although we have focused on the organic materials, our approach is general and can be applied to other molecular systems. Potential applications include functional supramolecular systems and bio-inspired materials, as well as organic electronic materials.

References

- 1) T. Fujita and Y. Noguchi, submitted.
- 2) T. Fujita and T. Hoshi, *Recent Advances of the Fragment Molecular Orbital Method*, Y. Mochizuki, S. Tanaka and K. Fukuzawa, Eds., Springer; Singapore, pp. 547–566. (2021).

Theory and Computation of Reactions and Properties in Solutions and Liquids

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We focus on the projects on ionic liquids (ILs). ILs' projects include both the unique dissolution process of cellulose polysaccharides and the investigation of static and dynamical properties on ionic liquids.

1. Investigations of Dissolution and Decomposition Mechanisms of a Cellulose Fiber in Ionic Liquids¹⁾ with Molecular Dynamics Simulation

We carried out the studies of dissolution and decomposition mechanisms of cellulose (I_{β}) polymers in ILs. In order to investigate motion of cellulose fibers and intermolecular interactions between cellulose molecules and cationic and anionic species in ILs. We employed the 1-ethyl-3-methylimidazolium acetate IL solvent for target system. From molecular dynamics simulation results, it was found out that the intermolecular interaction energy between cellulose polymers in the IL are reduced, comparing with that in water. Also, our

results suggest that the enhancement of the flexibility of rigid cellulose chains triggered by the breakage of intrachain H-bonds due to anions starts decomposition processes accompanied by dissolution processes due to the intercalation of cations, synergistically, and, then, both dissolution and decomposition processes are executed simultaneously.

2. Researches on Static and Dynamical Properties of Ionic Liquids: Molecular Origin of Low-k Peak of ILs and Dynamical Heterogeneity

We have investigated the molecular level origin of low-k peak ($< 0.5 \text{ \AA}^{-1}$) in the structure factor in ILs. In particular, we found out that the structure factor of heterocyclic ring parts in cations largely contribute to low-k peak in ILs. Also, we are going to carry out the study of dynamical properties of ILs, dynamical heterogeneity in ILs at room temperature with molecular dynamics simulation procedure.

Reference

1) T. Ishida, *J. Phys. Chem. B* **124**, 3090–3102 (2020).

Visiting Professors



Visiting Professor
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Electronic Structure Informatics for Designing Functional Liquid Materials

Mixed liquids exhibit various chemical functions depending on their composition and mixing ratio. Contrary to its fundamental scientific importance, however, the chemistry of mixing is an area where molecular level knowledge is not still enough. With the backgrounds, we have been challenging the predictive chemistry of functional liquid materials by developing a novel *ab initio* molecular simulation method with conventional computational cost (Effective fragment potential molecular dynamics; EFP-MD) and a data science approach. In fiscal 2020, we worked on the prediction of Henry's constant values related to the absorption of various industrial exhaust gases for non-aqueous mixed solutions (mixed ionic liquids, ionic liquids/organic solvent mixtures) which supports environmental chemical engineers shortly. We will proceed with our research aiming at the construction of statistical thermodynamic theory for real systems that predict mixed thermodynamics.



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YANASE, Youichi (from Kyoto University)

Theoretical Study of Exotic Quantum Phases

We are working on theoretical studies of exotic quantum phases such as unconventional superconductivity, parity-violating magnet, quantum liquid crystal, and topological states of matter. In particular, our recent interest focuses on quantum phases lacking global or local space inversion symmetry. This year, we studied exotic superconductivity such as odd-parity superconductivity, odd-frequency superconductivity, noncentrosymmetric superconductivity, and ferroelectric superconductivity. Target materials include transition metal dichalcogenides such as MoS₂, heavy fermion superconductors such as UTe₂ and CeRh₂As₂, and perovskite oxides such as SrTiO₃. Interestingly, most of them are candidates of topological superconductors. We also explored new functionalities of superconductors and magnets. For instance, superconducting diode effect, giant surface Edelstein effect in d-wave superconductors, chiral photocurrent generation in parity-violating antiferromagnet, and nonlinear electric transport have been theoretically clarified, and candidate materials have been proposed.



Visiting Associate Professor
HIGASHI, Masahiro (from Kyoto University)

Theoretical Study on the Excited-State Reactions in Condensed Phases

We are theoretically investigating chemical reactions and physical properties in condensed phases such as solutions and proteins. In particular, we are focusing on the excited-state reactions in condensed phases. The excited-state reaction dynamics of large systems are still one of most challenging subjects in theoretical chemistry due to the high computational cost of quantum chemical calculations for excited states and adequate statistical samplings required for molecular dynamics simulations. To overcome these difficulties, we have been developing several efficient methods combining quantum chemical calculations and molecular dynamics simulations. Recently, we analyzed the excitation energy transfer in a light-harvesting complex by using our developed methods and found that the efficient excitation energy transfer is achieved by the site-dependent fluctuations. We are now investigating the primary charge separation in photosynthetic reaction centers and the photoexcited charge separation in organic solar cells. We will reveal molecular mechanisms of environmental effects in both systems.

RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction of atoms and molecules with optical fields with its possible applications to active control of atomic and molecular functionality and reactivity. We also develop novel light sources to promote those studies. Two research facilities, the Center for Mesoscopic Sciences and the UVSOR Synchrotron Facility, closely collaborates with the Department.

The core topics of the Department include attosecond coherent control of gas- and condensed-phase atoms and molecules, high-resolution optical microscopy applied to nanomaterials, synchrotron-based spectroscopy of core-excited molecules and solid-state materials, vacuum-UV photochemistry, and the development of novel laser- and synchrotron-radiation sources.

Ultrafast Quantum Simulator and Computer

Department of Photo-Molecular Science Division of Photo-Molecular Science II



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Professional Employment

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2007 Visiting Professor, Tokyo Institute of Technology (–2008)
2009 Visiting Professor, The University of Tokyo (–2011)
2012 Visiting Professor (Humboldt Awardee), University of Heidelberg
2014 Visiting Professor, University of Strasbourg (–2016)

Awards

1998 Award by Research Foundation for Opto-Science and Technology
2007 JSPS Prize
2007 Japan Academy Medal
2008 Norman Hascoe Distinguished Lecturer, University of Connecticut, USA
2009 Fellow of the American Physical Society
2012 Humboldt Research Award
2017 Hiroshi Takuma Memorial Prize of Matsuo Foundation
2018 Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan

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Keywords

Quantum-Classical Boundary, Quantum Simulation, Quantum Computing

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.¹⁾ This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as “collapse” in quantum theory, is often accepted as a discontinuous change, but a basic question arises: When and how the delocalized wave function becomes localized? Our objective is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this objective in mind, we have developed coherent control with precisions on the picometer spatial and atto-second temporal scales. Now we apply this ultrafast and ultrahigh-precision coherent control to delocalized wave functions of macroscopic many-particle systems such as an array of ultracold rubidium (Rb) Rydberg atoms, as depicted

schematically in Figure 1 and named “ultrafast quantum simulator,” envisaging the quantum-classical boundary connected smoothly.

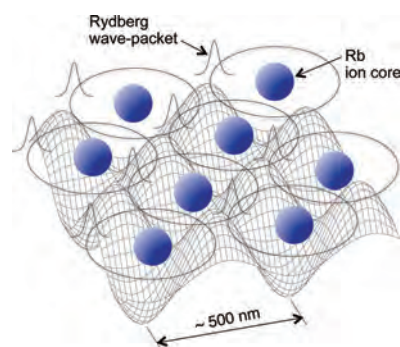


Figure 1. Metal-like quantum gas. A schematic of the many-body quantum simulator with ultracold Rydberg atoms, named “ultrafast quantum simulator,” where electronic wave functions spatially overlap between neighboring atoms.^{2,7)}

Selected Publications

- H. Katsuki *et al.*, “Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference,” *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, “Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales,” *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, “Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule,” *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, “Strong-Laser-Induced Quantum Interference,” *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, “All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth,” *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, “Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas,” *Nat. Commun.* **7**, 13449 (2016).
- C. Liu *et al.*, “Attosecond Control of Restoration of Electronic Structure Symmetry,” *Phys. Rev. Lett.* **121**, 173201 (2018).
- M. Mizoguchi *et al.*, “Ultrafast Creation of Overlapping Rydberg Electrons in an Atomic BEC and Mott-Insulator Lattice,” *Phys. Rev. Lett.* **124**, 253201 (2020).

1. Development of an “Ultrafast Quantum Simulator” by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales^{3–10}

Quantum many-body problems are at the heart of a variety of physical functionalities including superconductivity and magnetism in solid materials. It is extremely hard, however, to solve such quantum many-body problems. In solving the Hubbard model with 1000 particles, for example, the diagonalization would take 10 to the power of 573 years even with the world’s fastest supercomputers. In this project, we develop a novel quantum simulator that can simulate quantum many-body dynamics for more than 1000 particles within one nanosecond, combining our two unique experimental resources: “coherent control with attosecond precision”⁸) and “a strongly-correlated ultracold Rydberg gas.”^{7,9,10}

We have completed a standard hardware of this ultrafast quantum simulator composed of an array of ultracold Rb atoms trapped in an optical lattice and excited to Rydberg levels with a coherent picosecond (ps) laser pulse, as schematically illustrated in Figure 2.^{3,4,6,7,10} The broad bandwidth of the ps laser pulse has allowed us to excite the atoms in the neighboring lattice sites to Rydberg levels simultaneously for the first time. With this standard hardware, we have succeeded in creating an exotic electronic state with spatially overlapping wavefunctions as shown schematically in Figures 1 and 2.^{2,4,7,10} The degree of spatial overlap is actively tuned with ~ 50 nanometer precision. This exotic metal-like quantum gas under exquisite control opens up a completely new regime of many-body physics for simulating ultrafast many-body electron dynamics dominated by Coulomb interactions.^{7,10}

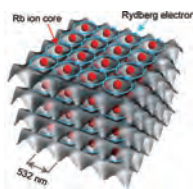


Figure 2. Schematic of the standard hardware of the ultrafast quantum simulator.^{3,4,6,7,10}

We have also completed a readout interface of our ultrafast quantum simulator, which is the time domain Ramsey interferometry of ultracold Rydberg atoms with attosecond precision, whose contrast is almost 100% as shown in Figure 3.⁵) The phase and visibility of this Ramsey interferogram are highly sensitive to the nature and strength of many-body interactions among the Rydberg atoms.

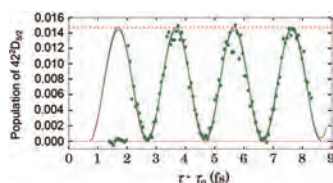


Figure 3. Time domain Ramsey interferometry of ultracold ^{87}Rb atoms with attosecond precision to be used as a readout interface of the ultrafast quantum simulator. Population of the $42^2\text{D}_{5/2}$ Rydberg state is plotted as a function of the delay τ between two laser pulses, where $\tau_0 \sim 50$ ps.⁵)

2. Application of an “Ultrafast Quantum Simulator” to Quantum Computing^{3,10}

We are developing a cold-atom based quantum annealer with the hardware of the ultrafast quantum simulator.¹¹) The cold-atom quantum annealer has advantages against the one with the superconducting qubits. Those advantages include scalability and efficiency. All to all connections among physical bits necessary for quantum annealing could also be easier with cold atoms than superconducting qubits.

So far we have developed arbitrary two dimensional optical trap arrays for cold atoms, which are necessary for quantum annealing,¹¹) in tight collaborations with Hamamatsu Photonics K.

K.^{3,10}) Their examples are shown in Figure 4, the world’s smallest arbitrary trap arrays whose nearest neighbor distance is only ~ 1 micron, which used to be typically ~ 4 micron in previous works.¹²)

We have recently succeeded in loading a single atom into each trap of those arbitrary arrays, and reassembling those atoms with an optical tweezer. Accordingly we can prepare an array of atoms we desire, as exemplified in Figure 5.

These techniques mentioned above are also being applied to the development of gate-based quantum computing with cold atoms.

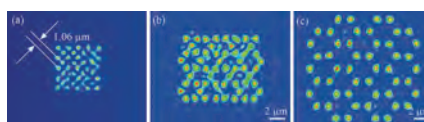


Figure 4. Examples of the world’s smallest arbitrary arrays of optical traps. (a) Square lattice; (b) Kagome Lattice; (c) Hexagonal (Honeycomb) lattice.¹⁰

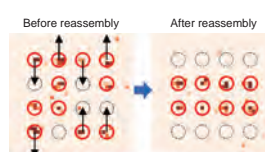


Figure 5. Assembly of an arbitrary array of single Rb atoms.¹⁰

3. Engineering Quantum Wave-Packet Dispersion with a Strong Nonresonant Femtosecond Laser Pulse^{13,14}

A non-dispersing wave packet has been attracting much interest from various scientific and technological viewpoints. However, most quantum systems are accompanied by anharmonicity, so that retardation of quantum wave-packet dispersion is limited to very few examples only under specific conditions and targets. Here we demonstrate a conceptually new and universal method to retard or advance the dispersion of a quantum wave packet through “programmable time shift” induced by a strong non-resonant femtosecond laser pulse. A numerical simulation has verified that a train of such retardation pulses stops wave-packet dispersion.^{13,14})

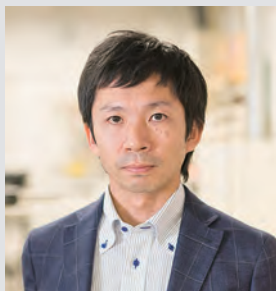
Our ultrafast quantum simulator and computer operates with atomic Rydberg levels,^{3–10}) whose level structure is anharmonic, so that its wave packet is dispersed and broadened quickly. The new control method for wave-packet dispersion developed here would serve as an enabling technology for our ultrafast quantum simulator and computer to enhance their functionalities.

References

- 1) K. Tonomura *et al.*, *Am. J. Phys.* **57**, 117 (1989).
- 2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
- 3) Patent “Quantum Simulator and Quantum Simulation Method,” H. Sakai (Hamamatsu Photonics K.K.), K. Ohmori (IMS) *et al.* (US 2020, JP 2021).
- 4) White Paper 2018 on Manufacturing Industries published by Ministry of Economy Trade and Industry, JAPAN.
- 5) C. Liu *et al.*, *Phys. Rev. Lett.* **121**, 173201 (2018).
- 6) Highlighted in “Quantum-Technology Innovation Strategy” by the Cabinet Office of Japan, January 2020.
- 7) M. Mizoguchi *et al.*, *Phys. Rev. Lett.* **124**, 253201 (2020).
- 8) H. Katsuki *et al.*, *Acc. Chem. Res.* **51**, 1174–1184 (2018).
- 9) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).
- 10) S. Sugawa *et al.*, *Solid State Physics* **56**, 243 (2021). (Invited Paper/Cover-Page Highlight)
- 11) A. W. Glaetzle *et al.*, *Nat. Commun.* **8**, 15813 (2017).
- 12) D. Barredo *et al.*, *Science* **354**, 1021 (2016).
- 13) H. Katsuki *et al.*, *Phys. Rev. Res.* **3**, 043021 (2021).
- 14) Y. Ohtsuki *et al.*, *Phys. Rev. A* **104**, 033107 (2021).

Electronic Property of Functional Organic Materials

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Keywords

Photoelectron Spectroscopy, Molecular Assemble, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However, the mechanisms and the origin of various device characteristics are still under debate. Scientific discussions have been redundant because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is essential to investigate precisely the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the

electronic states is very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

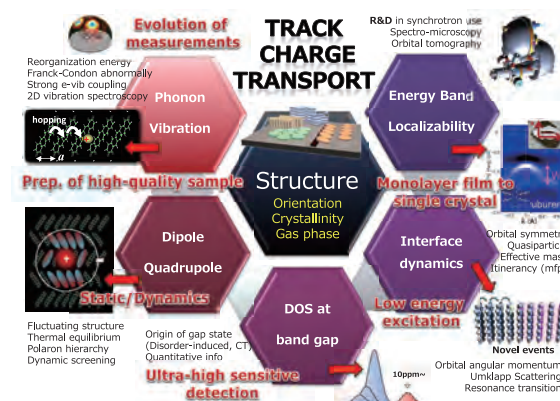


Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- Y. Nakayama, S. Kera and N. Ueno, *J. Mater. Chem. C* **8**, 9090–9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
- S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Experimental Observation of Anisotropic of Valence Band Dispersion in the Organic Semiconductor Crystal (DNTT)¹⁾

Organic semiconductors based on the aromatic compounds having wide π -conjugation are attracting the attention of researchers because of their applications in various electronic devices. One of the central interests of these materials considering their physicochemical properties is their charge transport mechanism. In general, the conduction of charge carriers in most of the organic semiconductor solids is happening through the intermolecular hopping processes among the discrete molecular orbitals. However, some organic semiconductors with high charge-carrier mobility such as pentacene and rubrene exhibit continuous energy dispersion of valence bands, and the characteristics of the so-called “band transport” have been proposed.

The molecule focused on in this study is dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT). Although it has been proposed that the transport mechanism of DNTT is a band transport, the valence band dispersion has not yet been observed experimentally. In this study, we elucidate the valence band structure of DNTT single crystals using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) along three inequivalent crystallographic directions in the surface Brillouin zone. The valence band maximum is verified to be positioned at the Γ point, and the ionization energy of a DNTT single crystal is determined to be 5.02 eV at the VBM. The effective mass of hole is derived from the curvature of the experimental valence band at the Γ point in all three directions, where the lowest value of $2.6m_0$ is measured along the Γ -S direction.

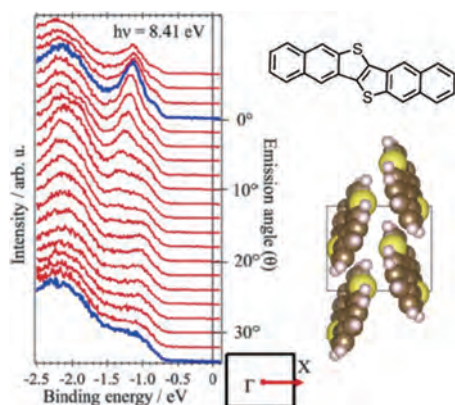


Figure 2. X-ray photoelectron spectroscopy (XPS) spectra of the DNTT single crystal taken along Γ -X direction. The figure is after ref 1).

2. Accessing the Conduction Band Dispersion in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Single Crystal²⁾

The conduction band dispersion in methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), which is a potential candidate for photovoltaic absorbers due to its high-light absorption coefficient,

long carrier lifetime and diffusion length, low exciton binding energy, and easy fabrication, was studied both by angle-resolved two photon photoelectron spectroscopy (AR-2PPE) with low photon intensity (~ 0.0125 nJ/pulse) and angle-resolved low-energy inverse photoelectron spectroscopy (AR-LEIPS). Clear energy dispersions of the conduction band along Γ -M direction are observed by these independent methods under different temperatures for the first time, and the dispersion is found to be consistent with band calculation under a cubic phase. The effective mass of the electrons at Γ point is estimated to be $(0.20 \pm 0.05)m_0$ at 90 K. The observed energy position is significantly different between the AR-LEIPS and AR-2PPE, which is ascribed to the electronic-correlation effects depending on the difference of initial/final state probing processes. The present results also indicate that the surface structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is given by a $\text{CH}_3\text{NH}_3 + \text{I}$ plane, which provides the cubic dominated electronic property even at lower temperatures.

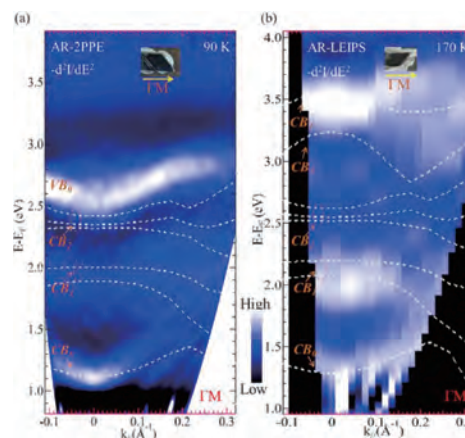


Figure 3. Second-derivative intensity maps of (a) AR-2PPE spectra and (b) AR-LEIPS spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal. The figure is after ref 2).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope are developing at BL6U.³⁾

References

- 1) R. Takeuchi, S. Izawa, Y. Hasegawa, R. Tsuruta, T. Yamaguchi, M. Meissner, S. Ideta, K. Tanaka, S. Kera, M. Hiramoto and Y. Nakayama, *J. Phys. Chem. C* **125**, 2938–2943 (2021).
- 2) J. Yang, H. Sato, H. Orio, X. Liu, M. Fahlman, N. Ueno, H. Yoshida, T. Yamada and S. Kera, *J. Phys. Chem. Lett.* **12**, 3773–3778 (2021).
- 3) S. Makita, H. Matsuda, Y. Okano, T. Yano, E. Nakamura, Y. Hasegawa, S. Kera, S. Suga and F. Matsui, *e-J. Surf. Sci. Nanotechnol.* **19**, 42–47 (2021).

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Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Beam Physics, Synchrotron Radiation

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz waves to the soft X-rays. Although it was constructed nearly 40 years ago, its performance is still in the world top level particularly among the low energy synchrotron light sources. This is the result of the continuous efforts on improving the machine. Our research group has been developing and introducing new accelerator technologies toward producing brighter synchrotron light with high stability, such as low emittance electron beam optics, novel insertion devices or state-of-the-art beam injection scheme. We have been developing novel light source technologies, such as free electron laser, coherent synchrotron radiation, optical vortices and laser Compton gamma-rays. We have been investigating beam physics which would be the basis of the future developments of the facility.



Figure 1. UVSOR-III Electron Storage Ring and Synchrotron Radiation Beamlines.

Selected Publications

- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, "Tunable Narrowband Terahertz Emission from Mastered Laser–Electron Beam Interaction," *Nat. Phys.* **4**, 390–393 (2008).
- M. Shimada, M. Katoh, M. Adachi, T. Tanikawa, S. Kimura, M. Hosaka, N. Yamamoto, Y. Takashima and T. Takahashi, "Transverse-Longitudinal Coupling Effect in Laser Bunch Slicing," *Phys. Rev. Lett.* **103**, 144802 (2009).
- M. Katoh, M. Fujimoto, H. Kawaguchi, K. Tsuchiya, K. Ohmi, T. Kaneyasu, Y. Taira, M. Hosaka, A. Mochihashi and Y. Takashima, "Angular Momentum of Twisted Radiation from an Electron in Spiral Motion," *Phys. Rev. Lett.* **118**, 094801 (2017).
- Y. Taira, T. Hayakawa and M. Katoh, "Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light," *Sci. Rep.* **7**, 5018 (2017).
- S. Matsuba, K. Kawase, A. Miyamoto, S. Sasaki, M. Fujimoto, T. Konomi, N. Yamamoto, M. Hosaka and M. Katoh, "Generation of Vector Beam with Tandem Helical Undulators," *Appl. Phys. Lett.* **113**, 021106 (2018).
- Y. Hikosaka, T. Kaneyasu, M. Fujimoto, H. Iwayama and M. Katoh, "Coherent Control in the Extreme Ultraviolet and Attosecond Regime by Synchrotron Radiation," *Nat. Commun.* **10**, 4988 (2019).
- T. Kaneyasu, Y. Hikosaka, M. Fujimoto, H. Iwayama and M. Katoh, "Electron Wave Packet Interference in Atomic Inner-Shell Excitation," *Phys. Rev. Lett.* **126**, 1132202 (2021).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have been developing light source technologies at the UVSOR-III electron storage ring using a dedicated experimental station BL1U, which was constructed under the support of Quantum Beam Technology Program of JST/MEXT aiming to develop novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beamline consisting of mirrors and a monochromator whose arrangement can be flexibly changed according to the types of the experiments.

In these years, we are focusing on generation of spatially structured light, such as optical vortex beams and optical vector beams from undulators, in collaboration with Hiroshima Univ. and Nagoya Univ. We have succeeded in producing such novel photon beams and are exploring their applications. More recently, we have started exploring the possibility utilizing the temporal structure of undulator radiation, in collaboration with Saga Light Source and Toyama Univ. So far, we have been demonstrated the coherent controls of atoms by using radiation from two undulators arranged in tandem. More recently, we have succeeded in observing ultrafast change of an electronic state of an atom, by using tandem undulator radiation.

We have been developing a laser Compton scattering gamma-ray source at BL1U, which is capable of producing monochromatic and energy-tunable gamma-rays. Now we are exploring their applications such as isotope imaging based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and QST, photon-induced positron annihilation lifetime spectroscopy in collaboration with Yamagata Univ. and AIST and an experimental verification on Delbruck scattering in collaboration with QST, AIST and Kyoto Univ. Theoretically we have proven that vortex photons carrying orbital angular momentum can be produced by non-linear Compton scattering of circularly polarized photons. We are planning its experimental demonstration at BL1U in collaboration with AIST.

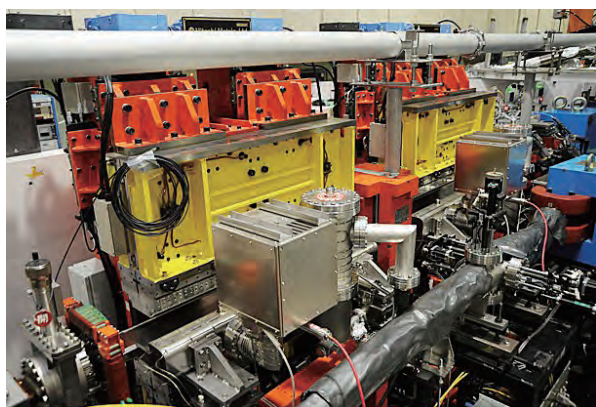


Figure 2. Twin Polarization-variable Undulators/Optical Klystron at UVSOR-III.

2. Accelerator Technology Developments for Electron Synchrotrons

We carried out several upgrade plans on UVSOR electron synchrotron since 2000. We designed a special beam optics intended to higher brightness. We developed necessary accelerator components, reconstructed the accelerator and commissioned it. We have constructed and commissioned six undulators successfully. Moreover, we have been continuously introducing new accelerator technologies such as the top-up operation in which the electron beam intensity is kept quasi-constant at a high beam current, 300mA, and the novel beam injection scheme with a pulsed sextupole magnet. As the result of all these efforts, now, the machine is one of the brightest synchrotron light sources among the low energy machines below 1GeV in the world.

Currently, the storage ring is stably operated for many of the users, however, the requirements from the users for the stability is getting higher and higher. As a near-term upgrade plan, we are considering replacing some of the undulators to fit the changes of the users' requirements on the wavelength. Also, we are seeking a possibility to reduce the emittance with the present magnet configuration. So far, we have found a few beam optics which would give lower emittance around 10 nm. Although they are not compatible with the operation of the narrow gap undulators, they may be used for special experiments which requires lower emittance. For a long-term plan, we continue the design study on a new light source facility. We have been investigating various accelerator systems such as a diffraction-limited synchrotron, an energy recovery linear accelerator and so on. Currently we are focusing on designing a synchrotron with the electron energy of 1 GeV and the circumference of around 70 m. We have designed a synchrotron which would give low emittance of around 6 nm under the achromatic condition.

We are collaborating with Nagoya Univ. and developing new technologies for the future plan. Accelerator magnets based on permanent magnets are being developed, which would contribute to the power consumption saving. New pulsed multipole magnet is also being developed to realize a novel beam injection scheme.

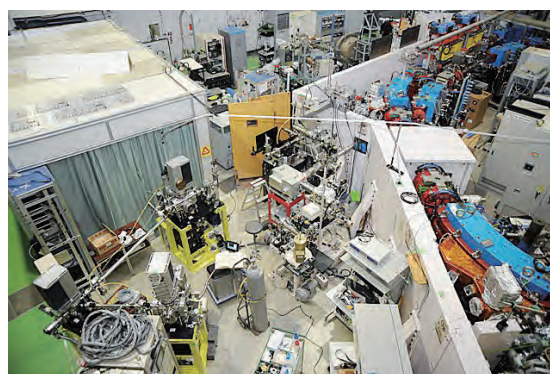
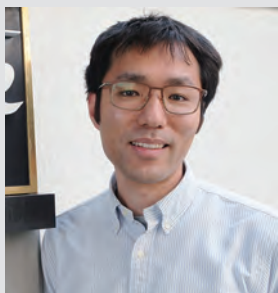


Figure 3. UVSOR BL1U experimental station for source development studies.

Development and Utilization of Novel Quantum Beam Sources Using a High Energy Electron Beam

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Professional Employment

2011 JSPS Research Fellow
2012 Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST)
2018 Senior Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST)
2020 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards

2010 Student Presentation Award, The 23rd Annual Meeting of the Japanese Society for Synchrotron Radiation Research
2010 Young Researcher Best Presentation Award, The 53rd Annual Meeting of the Japanese Society of Radiation Chemistry
2011 Nagoya University Outstanding Graduate Student Award
2012 Oral Presentation Award, The 9th Annual Meeting of Particle Accelerator Society of Japan
2012 Young Researcher Best Poster Award, 12th International Symposium on Radiation Physics
2013 Young Scientist Award of the Physical Society of Japan
2015 Young Researcher Best Presentation Award, Beam Physics Workshop 2015

Member

Assistant Professor
SUGITA, Kento
Post-Doctoral Fellow
SALEHI, Elham
Graduate Student
KOYAMA, Kazuki*
YAMAMOTO, Ryohei*

Keywords Electron Beams, Synchrotron Radiation, Gamma-Rays

Our group develop new electromagnetic wave sources using a high energy electron beam. In the UVSOR-III electron storage ring at the Institute for Molecular Science, a 750-MeV electron beam can be generated. Electromagnetic waves in a wide frequency range from ultraviolet waves to gamma-rays are emitted by interacting the electron beam with magnetic fields and lasers.

Laser Thomson (Compton) scattering is a method to generate a high energy gamma-ray by the interaction between a high energy electron and a laser. We have developed ultra-short pulsed gamma-rays with the pulse width of sub-ps to ps range by using 90-degree laser Thomson scattering (Figure 1). We applied this ultra-short pulsed gamma-rays to gamma induced positron annihilation lifetime spectroscopy (GiPALS).

A positron is an excellent probe of lattice defects in solids and of free volumes in polymers at the sub-nm to nm scale. GiPALS enables defect analysis of a thick material in a few cm because positrons are generated throughout a bulk material via pair production. Our group is conducting research on improving the properties of the material by using GiPALS.



Figure 1. Schematic illustration of 90-degree laser Thomson scattering.

Selected Publications

- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultra-Short-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696 (2011).
- Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, "Photon-Induced Positron Annihilation Lifetime Spectroscopy Using Ultrashort Laser-Compton-Scattered Gamma-Ray Pulses," *Rev. Sci. Instrum.* **84**, 053305 (2013).
- Y. Taira, T. Hayakawa and M. Katoh, "Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light," *Sci. Rep.* **7**, 5018 (2017).
- Y. Taira and M. Katoh, "Gamma-Ray Vortices Emitted from Nonlinear Inverse Thomson Scattering of a Two-Wavelength Laser Beam," *Phys. Rev. A* **98**, 052130 (2018).
- Y. Taira, M. Fujimoto, S. Ri, M. Hosaka and M. Katoh, "Measurement of the Phase Structure of Elliptically Polarized Undulator Radiation," *New J. Phys.* **22**, 093061 (2020).

1. Gamma-Induced Positron Annihilation Lifetime Spectroscopy (GiPALS)

Positron lifetime spectrum is calculated by measuring the time difference between a reference signal and a detector output for the annihilation gamma-rays, which is emitted when a positron annihilates with an electron inside material. A reference signal is the output of a photodiode located near the injection position of a laser. A BaF₂ scintillator and a photomultiplier tube is utilized to detect the annihilation gamma-rays. Two detectors are arranged at 180 degrees because two annihilation gamma-rays are generated at 180-degree direction. The annihilation gamma-rays are generated to whole solid angle. Therefore array detectors are effective to increase the count rate of the annihilation gamma-rays and to reduce the measurement time. We have developed the array detector using 10 detectors with a help of Equipment Development Center (Figure 2).

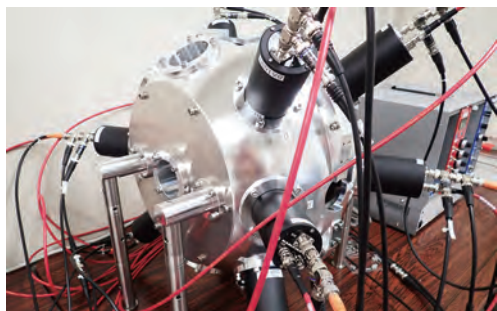


Figure 2. Positron lifetime measurement system using 10 detectors.

Users can currently utilize GiPALS at BL1U in UVSOR-III. A result of defect analysis for a GAGG scintillator was published in 2020.¹⁾ We are also developing a new measurement method, gamma ray-induced age-momentum correlation (GiAMOC). On the other hand, we are planning to develop other measurement technique for the annihilation gamma-rays, such as a three-dimensional distribution imaging technique for defects, coincidence Doppler broadening, and spin polarized positrons generated from circularly polarized gamma-rays.

A new laser injection vacuum chamber was installed to the UVSOR-III electron storage ring in April 2021. As both the incoming and outgoing sides of the vacuum chamber are optical windows, the laser can be focused down to 10 micrometers. We have confirmed that the intensity of gamma-rays at the generation point has been improved by a factor of 40.

2. Short Wavelength Optical Vortices

An optical vortex is an electromagnetic wave with a helical phase structure. When an optical vortex beam is viewed in a plane transverse to the direction of propagation, an

annular intensity profile is observed due to the phase singularity at the center axis. An important consequence of the optical vortex is that it carries orbital angular momentum (OAM) due to the helical phase structure.

While fundamental and applied research on optical vortices using visible wavelength lasers is widely studied, much less has been done in ultraviolet, X-rays, and gamma-rays energy ranges. We have proposed for the first time a method to generate a gamma-ray vortex using nonlinear inverse Thomson scattering of a high energy electron and an intense circularly polarized laser.²⁾ In our method, the circularly polarized laser is important because the helical phase structure arises from the transverse helical motion of the electron inside the circularly polarized laser field. When peak power of a laser achieves terawatt class, high harmonic gamma-rays are generated. Only gamma-rays more than the first harmonic carry OAM. High harmonic gamma-rays show the annular intensity distribution due to this characteristic.

There are few facilities in the world, where can carry out the experiment for the nonlinear inverse Thomson scattering using an intense circularly polarized laser in terawatt class. We carried out the experiment at Kansai Photon Science Institute in Japan, where a 150 MeV microtron and a petawatt laser are available. Although we were not able to achieve the measurement of an annular intensity distribution of high harmonic gamma-rays, we plan to continue the experiment this year.

On the other hand, optical vortices in the ultraviolet wavelength range can be generated using a helical undulator. Similar with a nonlinear inverse Thomson scattering, an electron obeys a helical trajectory inside an undulator. Therefore, high harmonic radiation emitted from a helical undulator forms the helical phase structure.

Generation of an optical vortex from a helical undulator has been demonstrated at UVSOR-III. Recently, we newly revealed that undulator radiation with the phase structure can be generated from an elliptically polarized undulator.²⁾ We derived the analytic expressions for the emitted electric fields were fully derived and the radiation's phase structure was found to change according to polarization. Average phase gradients of the undulator's radiation were measured using a double slit interferometer. The measured phase gradients of the first through third harmonics were compared with the calculated results.

References

- 1) K. Fujimori, M. Kitaura, Y. Taira, M. Fujimoto, H. Zen, S. Watanabe, K. Kamada, Y. Okano, M. Katoh, M. Hosaka, J. Yamazaki, T. Hirade, Y. Kobayashi and A. Ohnishi, *Appl. Phys. Express* **13**, 085505 (4 pages) (2020).
- 2) Y. Taira, M. Fujimoto, S. Ri, M. Hosaka and M. Katoh, *New J. Phys.* **22**, 093061 (2020).

Award

TAIRA, Yoshitaka; The Outstanding Presentation Award of the 64th Annual Meeting of the Japanese Society of Radiation Chemistry (2021).

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

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

UVSOR Synchrotron Facility Division of Advanced Solid State Physics



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Education

2000 B.S. The University of Tokyo
2005 Ph.D. The University of Tokyo

Professional Employment

2005 Postdoctoral Fellow, Stanford University and Lawrence Berkeley National Laboratory
2008 Assistant Professor, Osaka University
2013 Associate Professor, Osaka University
2014 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Member

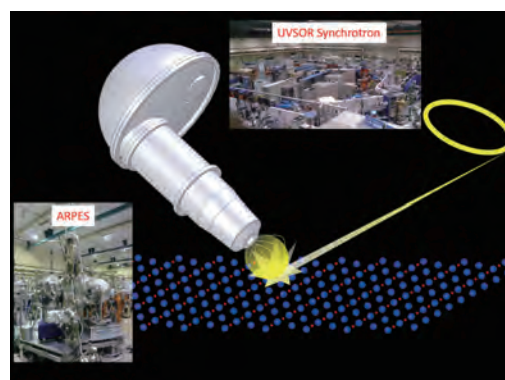
Assistant Professor
IDETA, Shin-ichiro*
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Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials has attracted more attentions in the last few decades because of their unusual and fascinating properties such as high- T_c superconductivity, giant magnetoresistance, heavy fermion and so on. Those unique properties can offer a route toward the next-generation devices. We investigate the mechanism of the physical properties as well as the electronic structure of those materials by using angle-resolved photoemission spectroscopy (ARPES). ARPES is a powerful experimental technique, directly measuring the energy (E) and momentum (k) relation, namely the band structure of solids. In the last quarter of a century, the energy resolution and angular resolution of ARPES have improved almost three order of magnitude better, which makes us possible to address the fine structure of the electronic structure near the Fermi level: Superconducting gap, kink structure and so on. The main target materials of our group is high- T_c superconductors, such as cuprates and iron pnictides and use UVSOR-III as a strong light source.

Our group is also developing high-efficiency spin-resolved ARPES system. Spintronics is a rapidly emerging field of science and technology that will most likely have a significant

impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin-resolved ARPES is one of the most powerful experimental techniques to investigate the magnetic properties of such materials.



Selected Publications

- K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* **450**, 81–84 (2007).
- K. Tanaka, N. Hieu, G. Vincini, T. Masui, S. Miyasaka, S. Tajima and T. Sasagawa, "Quantitative Comparison between Electronic Raman Scattering and Angle-Resolved Photoemission Spectra in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Superconductors: Doping Dependence of Nodal and Antinodal Superconducting Gaps," *J. Phys. Soc. Jpn.* **88**, 044710 (2019).
- S. Ideta, N. Murai, M. Nakajima, R. Kajimoto and K. Tanaka, "Experimental Investigation of the Suppressed Superconducting Gap and Double-Resonance Mode in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$," *Phys. Rev. B* **100**, 235135 (7 pages) (2019).

1. Development of Spin-Resolved ARPES with Image-Spin Detection

Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin- and angle-resolved photoemission spectroscopy (spin-resolved ARPES) is one of the most powerful experimental techniques to investigate the magnetic properties of such materials, where one can know the “complete” information of the electronic states of materials; energy, momentum, and spin direction. Recent development of high energy and angle resolved photoelectron analyzer as well as the contemporary light sources such as third generation synchrotron radiation make it possible for the photoemission spectroscopy to investigate not only band structures but many body interactions of electrons in solids. However, appending the spin resolution to photoemission spectroscopy is quite difficult because of an extremely low efficiency (10^{-4}) of Mott-type spin detectors. Recently, very-low-energy-electron-diffraction (VLEED-type) spin detector with 100 times higher efficiency than that of conventional Mott-type has been developed and spin-resolved ARPES has been started to be realized. So far, most of the spin-resolved ARPES systems in the world are using the single-channel detector and efficiency is still a problem.

Beamline BL5U at UVSOR has been totally reconstructed by our group, and opened for users as high photon flux and high energy resolution ARPES beamline since 2017. As a new function for this beamline, we have started high-efficient spin-resolved ARPES project with multi-channel detection (we call “image-spin” detection). The goal of this project is to realize

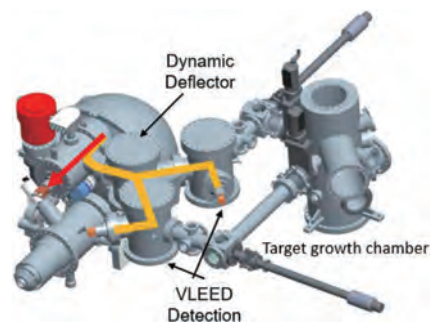


Figure 1. Current setup of image-spin ARPES.

the 100 times better efficiency and the 10 times better momentum resolution than the current spin-resolved ARPES system in the world, which can be a breakthrough in this field.

In 2020, we set up the spin detection system and finished the adjustment of the electron lens parameters of the spin detection part (Figure 1). Finally, we successfully obtained spin-resolved signal of Au(111) surface as shown in Figure 2. According to the rough estimation, the efficiency is 100 times better and the momentum resolution is several times better than the current spin-resolved ARPES system in the world.

2. Strong Relationship between ARPES Superconducting Spectral Weight and T_c ^{1,2)}

Our recent ARPES study on high- T_c cuprate superconductors $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Bi2212) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi2223) indicated strong relationship between the superconducting spectral weight and the critical temperature T_c . To see the detail, we are performing temperature and carrier concentration dependent measurements on several kinds of high- T_c cuprate superconductors.

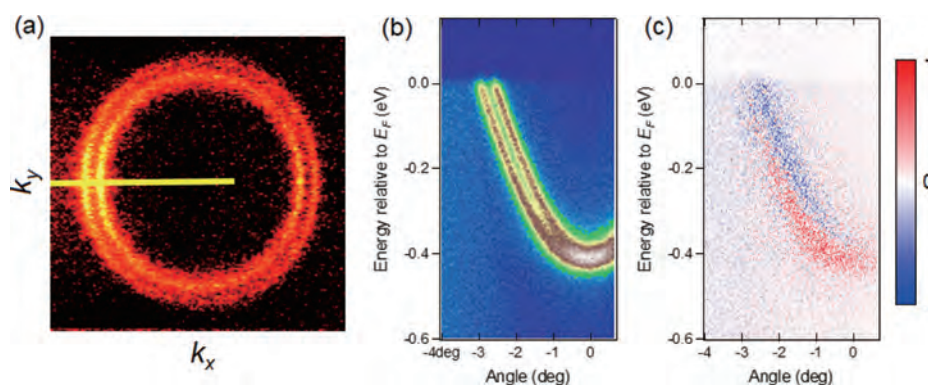


Figure 2. (a) Fermi surface of Rashba spin splitting in Au(111) surface states and (b) image plot of normal ARPES at yellow bar in (a). (c) Spin-resolved ARPES showing the spin polarization (blue–red scale).

References

- 1) G. Vincini *et al.*, *Supercond. Sci. Technol.* **32**, 113001 (2019).
- 2) K. Tanaka *et al.*, *J. Phys. Soc. Jpn.* **88**, 044710 (2019).

* Present Address; Hiroshima University

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

Photoemission Imaging in k and r Spaces

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



MATSUI, Fumihiko
Senior Researcher

Complete measurements of photoelectron, including three-dimensional spin degrees of freedom are challenging techniques for pioneering electron spin physics and spintronics. We are developing a new system that combines a photoelectron momentum microscope (PMM), two-dimensional spin filter, and a synchrotron light source. Our goal is to achieve reliable electronic structure analysis by complete photoelectron measurement of band dispersion and core levels, and link it to developments and applications of materials and devices.

1. Photoelectron Momentum Microscope

We have built a new PMM station for 3D momentum-resolved photoelectron spectroscopy with a microscopic field of view at the soft X-ray beamline BL6U of UVSOR. The details of the specification evaluation result are described elsewhere.¹⁾ In brief, the energy, spatial, and momentum resolutions of the analyzer were estimated to be 20 meV, 50 nm, and 0.012 \AA^{-1} , respectively. Samples can be cooled down to 8 K and heated up to 400 K.

A gold checkerboard pattern on a Si wafer imaged by a microscopy mode is shown in Figure 1. Elemental specific information is obtained by spectro-microscopy as shown in Figure 1(b) and (c). Figure 2 shows an example of 3D valence band dispersion imaging by a momentum mode.

With a photon energy range up to 800 eV covered by the BL6U, core-level excitation of a variety of important elements including C, N, O and transition metals is possible. Specific atomic sites and electronic states can be selectively characterized by the resonant Auger process. Resonant momentum-resolved photoelectron spectroscopy is a method unique to this

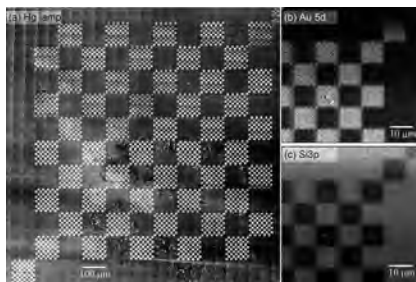


Figure 1. Real-space valence photoelectron images of a gold checkerboard pattern observed using (a) Hg lamp and (b)–(c) synchrotron radiation ($h\nu = 60 \text{ eV}$) as excitation.²⁾

station that opens the door to elemental- and orbital-selective valence band dispersion analysis.

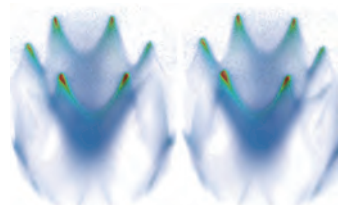


Figure 2. (a) Stereograph of valence band dispersion of graphite crystal surface. A parabolic π band with six Dirac points is imaged.

2. Original Analyzers towards Spin Imaging

Furthermore, we are aiming at highly efficient and comprehensive measurement of spin distribution as the final goal. *Omnidirectional photoelectron acceptance lens* (OPAL)³⁾ together with *Projection-type electron spectroscopy collimator analyzer* (PESCATORA)⁴⁾ enables photoelectron holography measurement of the full hemisphere. Moreover, we invented *Right angle deflection imaging analyzer* (RADIAN)⁵⁾ for spin vector analysis with k/r -space resolution. We are expanding the MM system based on our original inventions.

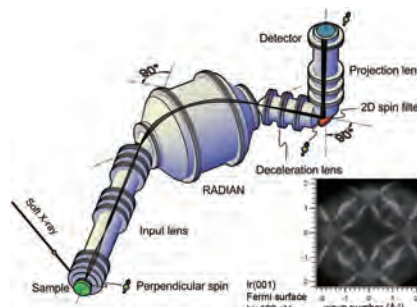


Figure 3. Schematic diagram of 3D-spin distribution projection analysis system.⁵⁾ Inset is the Fermi surface of the Ir(001) thin film for a 2D spin filter target measured by UVSOR-PMM.

References

- 1) F. Matsui *et al.*, *Jpn. J. Appl. Phys.* **59**, 067001 (2020).
- 2) S. Makita, F. Matsui, *et al.*, *e-J. Surf. Sci. Nanotechnol.* **19**, 42 (2021).
- 3) H. Matsuda and F. Matsui, *Jpn. J. Appl. Phys.* **59**, 046503 (2020).
- 4) F. Matsui and H. Matsuda, *Rev. Sci. Inst.* **92**, 073301 (2021).
- 5) H. Matsuda and F. Matsui, *J. Electron Spectrosc. Relat. Phenom.* **245**, 147001 (2020).

Award

MATSUI, Fumihiko; NAGAI Foundation for Science & Technology Encouragement Award (2021).

Soft X-Ray Absorption Spectroscopy for Observing Chemical Processes in Solution

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) observes local structures of liquids with different light elements. We have developed liquid cells and devices with precise absorbance control and observed several chemical processes in solution by using *operando* XAS.¹⁾ In this year, we have developed an ultrathin liquid cell for XAS of liquids in the low-energy region below 200 eV.

1. Development of the Ultrathin Liquid Cell for XAS in the Low-Energy Region

XAS below 200 eV is important for chemical research since it includes K-edges of Li and B and L-edges of Si, P, S, and Cl. Recently, we have established soft X-ray transmission argon gas window that is effective from 60 to 240 eV.²⁾ From soft X-ray transmission calculations, soft X-rays below 200

eV can transmit argon gas with the optical length of 2.6 mm. As shown in Figure 1, we have developed the ultrathin liquid cell that realize the 2.6 mm optical length of argon gas. XAS spectra of 2 M LiCl aqueous solution at Li K-edge and Cl L-edge were successfully obtained by using this liquid cell.

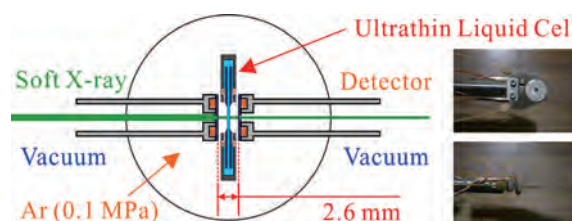


Figure 1. The schematic and photographs of the ultrathin liquid cell for XAS measurements of liquids in the low-energy region.

References

- 1) M. Nagasaka and N. Kosugi, *Chem. Lett.* **50**, 956–964 (2021).
- 2) M. Nagasaka, *J. Synchrotron Radiat.* **27**, 959–962 (2020).

Distribution of Biological Molecules in a Cell Nucleus Analyzed by 3-Dimensional Spectro-Microscopy

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

Scanning transmission X-ray microscopy (STXM) is a promising tool to analyze 2-dimensional chemical state of a sample with high spatial resolution around 30 nm. We have been developing computer tomography (CT) for STXM to perform 3-dimensional spectro-microscopy.^{1,2)} An isolated cell nucleus of a HeLa S3 cell was used as a sample. 50 datasets of 2-dimensional

X-ray absorption spectra (2D XAS) of the sample around O K-edge was acquired with rotating the sample 3.6° each (180° rotation in total). 3D XAS of the cell nucleus is reconstructed from 50 datasets of 2D XAS. Distributions of DNA (red) and protein (green) are obtained by fitting reference spectra to the 3D XAS by single value decomposition algorithm (Figure 1). In cross sectional images, nucleoli and network structure of protein around them can be distinguished clearly. A goal of

this research is to elucidate chemical and morphological change of biological molecules through a process of apoptosis.

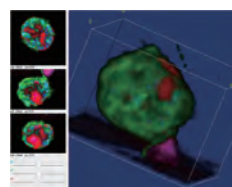


Figure 1. 3-dimensional distributions of DNA (red) and protein (green) in a HeLa S3 cell nucleus. Left panels are cross sectional images and a right panel is volume rendering image.

References

- 1) T. Ohigashi, A. Ito, K. Shinohara, S. Toné, Y. Inagaki, H. Yuzawa and N. Kosugi, *Microsc. Microanal.* **24**, 400–401 (2018).
- 2) T. Ohigashi, Y. Inagaki, A. Ito, K. Shinohara and N. Kosugi, *J. Phys.: Conf. Ser.* **849**, 012044 (2017).

Mesoscopic Structures of Liquid-Crystal Molecules Probed by Resonant Soft X-Ray Scattering

UVSOR Synchrotron Facility
Division of Advanced Photochemistry



IWAYAMA, Hiroshi
Assistant Professor

We study soft matters such as liquid-crystal materials with soft x-ray, whose energy region covers K-edge energies of carbon, nitrogen and oxygen. Soft matters exhibit their intriguing properties due to mesoscopic physical structures by self-organizations. To understand properties of soft matters, we need to investigate their structure in the mesoscopic scale.

1. Resonant Soft X-Ray Scattering Method

Resonant soft x-ray scattering measurements can probe mesoscopic structures and periodic spatial variations of the orientation of molecules with both elemental and chemical

environment sensitivity and have orders of magnitude scattering intensity enhancement over conventional small angle (non-resonant) x-ray scattering, which is sensitive only to the electron density modulations.

In this year, we performed RSoXS experiments at UVSOR BL3U for the first time. Our sample is S-MHPOBC, which is a chiral smectic liquid crystal molecule and shows ferro- and antiferroelectric phases depending on its temperature.

We successfully obtained diffraction images at the wavelength of 4.34 nm (285 eV), which correspond to C 1s-to- π^* core excitations. From the analysis of images, we found a resonant enhancement of diffractions corresponding to a period length of 6.4 nm. Considering single molecular length of 3 nm, this shows the sample is antiferroelectric under the measurement conditions. We investigate intermediate phases between ferro- and antiferroelectric one by changing sample temperatures.

Visiting Professors



Visiting Professor
FUKUI, Ken-ichi (from *Osaka University*)

Ionic Liquid/Organic Semiconductor Film Interfaces for Efficient Carrier Transport

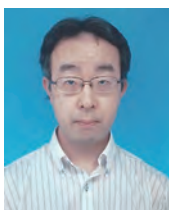
Local analyses of electrolyte/organic semiconductor electrode interfaces at controlled electrode potentials are of fundamental importance to understanding the origin and properties of the electric double layer (EDL) at the interfaces, which is necessary for their application to EDL-organic field effect transistors (OFETs). Ionic liquids (ILs) gated EDL-OFETs can be operated with ultralow threshold voltage (~ 0.1 V), and high electric field of the EDL restricts the hole carrier at the organic molecular facing the interface, thus a few molecular layer film works as the efficient device. By adopting newly developed electrochemical ATR-FUV (EC-ATR-FUV) system for the analyses of electronic states of the device consisting of a two-layer-thick C9-DNBDT-NW film and an IL (EMIM-FSA), we have succeeded in obtaining the hole carrier density as low as 1/500 hole per a C9-DNBDT-NW molecule. The spectrum analyses also provided the information of interaction between the organic thin film and the IL. Further analyses of the system using UVSOR are in progress.



Visiting Professor
SHIMADA, Kenya (from *Hiroshima University*)

High-Resolution Angle-Resolved Photoemission Study of Topological Materials

By means of high-resolution angle-resolved photoemission spectroscopy (ARPES), we clarify electronic structures of solids (band structures, Fermi surface, spin polarization) to understand their physical properties from the microscopic point of view. This year, we have examined the antiferromagnetic topological insulator families $(\text{Bi}_2\text{Te}_3)_n\text{MnBi}_2\text{Te}_4$ ($n = 1, 2$). We have observed the electronic band structures specific to the surface termination, which are fully consistent with detailed density functional theory (DFT) calculations. It indicates the surface termination is important for the surface states on $(\text{Bi}_2\text{Te}_3)_n\text{MnBi}_2\text{Te}_4$. We have also examined the spin texture of a photocatalyst BiOI. There are two Bi-I sectors connected via the centrosymmetric point, and we found that the topmost iodine layer had a helical spin texture with a spin polarization up to $\sim 80\%$. Based on the detailed theoretical considerations, the high spin polarization on each sector is protected by the non-symmorphic lattice symmetry (P4/nmm) together with the strong spin-orbit interaction. We have confirmed that the spin-momentum-layer locking effect in BiOI. To improve the spatial resolution of high-resolution ARPES on the HiSOR beamline, we have introduced a highly precise XYZ translator with the absolute accuracy of $< 1\mu\text{m}$ and developed the spatial mapping mode.



Visiting Associate Professor
KATSUKI, Hiroyuki (from *Nara Institute of Science and Technology*)

Coherent Control in Condensed Systems

Coherent control is a technique to manipulate quantum states of a target system utilizing the interference of wavefunctions. Highly designed ultrashort laser pulses, both temporally- and spatially-modulated, are used to manipulate the amplitudes and phases of the target wavefunctions. Current my research is focused on the coherent control in various condensed phase systems including strongly coupled systems composed of cavity photons and molecular excited states. Especially, vibrational polaritons which are composed of the molecular vibrational states and mid-infrared cavity photons are of great interest due to the possibility to manipulate the dynamics of chemical reactions. This is possible since the ground state potential surface is locally modulated by the formation of polaritons. Now we are preparing a femtosecond pump-probe and other nonlinear spectroscopic setups to track the ultrafast dynamics of such strongly coupled vibrational polariton systems.

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. 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
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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

Assistant Professor
KOITAYA, Takanori
YAMAMOTO, Kohei
Secretary
ISHIKAWA, Azusa

Keywords

X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard and Soft 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 apparatus is extensively open for public usage. Recently, assistant professor Kohei Yamamoto is developing the soft x-ray resonant magnetic reflectivity (SXRMR) system for the clarification of depth resolved magnetism of magnetic thin films with the atomic layer resolution scale, and is conducting coherent diffraction imaging (CDI) experiments for the observation of magnetic domain structures of magnetic thin films, using highly coherent SR x-rays from SPring-8 hard x-ray

undulators and x-ray free electron laser SACLA. By combining the SXRMR and CDI experiments, the magnetic structures along both the vertical and lateral directions can be revealed with atomic to nm spatial resolution.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although photoelectron spectroscopic measurement is usually done under 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. Moreover, we designed and constructed the subsecond time resolved AP-HAXPES measurement system, and successfully investigated electrochemical reaction dynamics for the cathode Pt oxidation/reduction and the S^2 -adsorption/desorption processes upon an abrupt step of the cathode-anode bias voltages. These works were supported by the NEDO Fuel Cell project. More recently, assistant professor, Takanori Koitaya, has been investigating various kinds of surface chemical reactions such as methane activation and CO_2 hydrogenation using the AP-HAXPES system combined with the near ambient pressure soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8.

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).
- T. Nakamura *et al.*, *J. Phys. Chem. C* **124**, 17520 (2020).
- S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866 (2021).

1. Sulfur Poisoning Pt and PtCo Anode and Cathode Catalysts in PEFC Studied by *operando* AP-HAXPES¹⁾

In practical performance of polymer electrolyte fuel cells (PEFC), the Pt₃Co alloy electrode is known to be superior to the pure Pt electrode because of a longer life time and a less amount of noble Pt metal. In this work, in order to evaluate the tolerance of S poisoning between Pt₃Co and Pt electrodes comparatively, we have investigated the S adsorption behaviours on Pt (average particle size ~2.6 nm) and Pt₃Co (~3.0 nm) anode and cathode electrode catalysts in PEFC under working conditions for the fresh state just after the aging process and also the degraded state after accelerated degradation tests (ADT), by recording near ambient pressure HAXPES.

The S 1s HAXPES of both the anode and cathode electrodes show not only the principal S species from the sulfonic acid group (-SO₃H) in the Nafion electrolyte (~2478 eV in the left panel of Figure 1) but also other characteristic S species such as zero-valent S (S⁰) adsorbed on the carbon support (~2471 eV) and anionic S (S²⁻) adsorbed on the Pt electrode (~2470 eV). The S²⁻ species on Pt should be ascribed to S contamination poisoning the Pt catalyst electrode. The S²⁻ species on the cathode can be oxidatively removed by applying a high cathode–anode bias voltage (≥ 0.8 V) to form SO₃²⁻, while at the anode the S²⁻ species cannot be eliminated because of reductive environment in hydrogen gases. The important finding is the different S adsorption behaviour between the Pt/C and Pt₃Co/C electrodes after ADT. After ADT, the Pt/C anode electrode exhibits much larger S²⁻ adsorption than the Pt₃Co/C anode electrode. This indicates that the Pt₃Co/C anode is more desirable than the Pt/C one from the view point of S poisoning.

The reason for more tolerance of the Pt₃Co/C anode catalyst against S poisoning after ADT can be ascribed to more negative charge of the surface Pt atoms in the Pt₃Co/C catalyst than the Pt/C one, this yielding weaker interaction between the surface Pt and the anionic S species as S²⁻, SO₃²⁻, and SO₄²⁻.

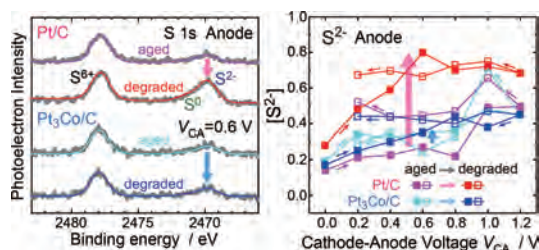


Figure 1. (left) Typical S 1s HAXPES from the anode Pt/C and Pt₃Co/C electrodes at the cathode–anode voltage $V_{CA} = 0.6$ V for the aged (before ADT) and degraded (after ADT) PEFC. The S²⁻ peak intensity (~2470 eV) is found to increase significantly in Pt/C, while it is not so much in Pt₃Co/C. (right) The relative amount of S²⁻ with respect to S⁶⁺ originating from Nafion -SO₃H, for the aged and degraded anode Pt/C and Pt₃Co/C electrodes, as a function of V_{CA} . It is clearly exemplified that the Pt₃Co/C anode electrode is more tolerant against S poisoning than the Pt/C.

Award

KOITAYA, Takanori; 2021 Vacuum and Surface Science Journal Award of the Japan Society of Vacuum and Surface Science (2021).

A similar behaviour was observed also in the cathode catalyst. The present findings will nevertheless provide important information to design novel Pt-based PEFC electrodes with higher performance and longer durability.

2. Negative Thermal Expansion of Zinc-Blende CdTe from the View Point of Local Structure

Since the discovery of anomalously large negative thermal expansion (NTE) in ZrW₂O₈ over an extremely wide temperature range in 1996, NTE has revived as a hot topic in structural solid-state chemistry and physics. The origin of zero thermal expansion and/or NTE is known to be categorized into two mechanisms. The first one is a so-called Invar effect as observed in the Fe₆₄Ni₃₆ Invar alloy, in which the electronic structure of some atoms in the system is temperature dependent. The second one is derived from vibrational anomaly. The materials with zinc blende or diamond structure mostly show NTE at low temperature due to the presence of vibrational anomaly. In this work, thermal expansion of zinc-blende CdTe was investigated from the view point of local structure using the extended x-ray absorption fine structure (EXAFS) spectroscopic data and the path-integral effective classical potential (PIECP) Monte Carlo computational simulations. Figure 2 shows the experimental (EXAFS as orange open circles and XRD as light-blue filled circles) and theoretical (PIECP as solid lines and classical MC as dashed lines). Although the origin of NTE is known as a result of classical vibrational anomaly within the Newton dynamics theory, the quantum statistical simulation is found to be essential to reproduce the negative thermal expansion of CdTe. It is emphasized that the vibrational quantum effect and classical anharmonicity are of great importance for the understanding of low-temperature thermal expansion as well as the elastic constants.

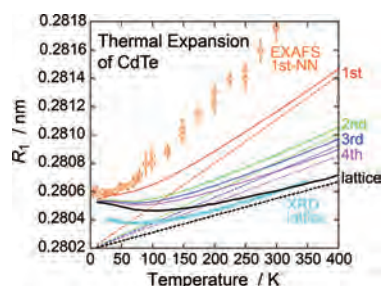


Figure 2. Experimental and theoretical thermal expansion of CdTe. Experimental XRD result for the lattice constant (light-blue closed circles) gives small NTE at <100 K, while experimental EXAFS result for the 1st nearest neighbor shell (orange open circles with error bars) provides quite normal thermal expansion even at low temperature. Computational PIECP results (solid lines) agree qualitatively well with both the experimental EXAFS and XRD data, while the classical MC results failed in the reproduction of the NTE (see black dashed lines).

Reference

1) S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866–3873 (2021).

Exotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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Professional Employment

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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 14th Young Scientist Award of the Physical Society of Japan

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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 probe 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 recently developed heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\text{Im}\chi^{(2)}$ 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 $\text{Im}\chi^{(2)}$ 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.

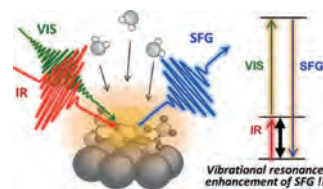


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji *et al.*, “Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice,” *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- K. Shirai *et al.*, “Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO₂ Photocatalyst,” *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Top-most Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).
- F. Kato *et al.*, “Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice,” *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
- T. Sugimoto *et al.*, “Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces,” *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).

1. Interface Engineering of the Thermodynamic Properties of Strongly Correlated Many-Body Protons in Crystalline Ice¹⁾

The static and dynamic behavior of strongly correlated protons play crucial roles in rendering exotic properties and enabling a wide range of applications of nanoscale hydrogen-bonded (HB) materials in physics, chemistry and biology. However, because of the difficulty in probing and manipulating the proton configuration in nanomaterials, controlling the cooperative behavior of many-body protons has not been realized.

In this study, we demonstrate the possibility of designing and controlling the physical properties of strongly correlated many-body protons through systematic sum-frequency generation (SFG) spectroscopy of crystalline-ice nanofilms. Since the second-order nonlinear susceptibility tensor $\chi^{(2)}$ is nonzero for non-centrosymmetric systems, the homodyne-detected SFG intensity $|\chi^{(2)}|^2$ increases with increasing the number of water molecules with net orientational preference, and thus can be used as the signature of the emergence of ferroelectric proton ordering. Because of the strong correlation of many-body protons imposed by the ice rules,^{2,3)} protons in the hydrogen-bond (HB) network of crystalline ice provide an interesting platform for studying fundamental emergent properties of strongly correlated proton systems. Here, we employ SFG spectroscopy of heteroepitaxial crystalline-ice nanofilms grown on Pt(111) surface precovered by a well-defined single layer of either carbon monoxide (CO) molecules or oxygen (O) atoms to study the effects of interface termination on mesoscopic characteristics of many-body protons.

The intensities of the $|\chi^{(2)}|^2$ -SFG spectra were shown as a function of ice thickness for these substrates (Figure 1). We found that the SFG signal derived from ice film on CO precovered Pt(111) continues to increase as that on bare Pt(111).^{2,3)} In contrast, negligibly small $|\chi^{(2)}|^2$ -SFG intensity (Figure 1) suggests that ice film on oxygen precovered Pt substrate is paraelectric. Our observations on the two different types of intercalated layer directly demonstrate that the thermodynamic properties of emergent ferroelectric proton ordering are extensively tuned by the interface engineering at the angstrom scale.

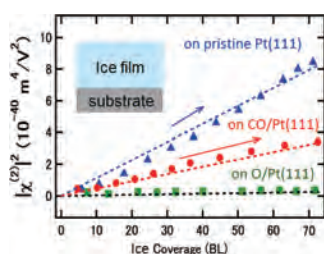


Figure 2. Thickness dependence of the $|\chi^{(2)}|^2$ -SFG intensity of crystalline ice films on pristine Pt(111), CO- and O-precovered Pt(111) at 140 K.¹⁾

2. Operando FT-IR Spectroscopy of Steam-Methane-Reforming Photocatalyst under Irradiation of Intensity Modulated UV Light⁴⁾

Photocatalytic steam-methane reforming is an attractive

chemical technology for hydrogen production from abundant resources of methane and water. In the case of photocatalytic reaction, photo-generated electron plays key roles in hydrogen production. However, the dynamics of photogenerated electrons under reaction condition have been unclear. To uncover the behavior of reactive photo-excited electrons, we conducted *operando* FT-IR spectroscopy of metal loaded Ga_2O_3 photocatalysts under irradiation of intensity modulated UV light. We succeeded in observing a correlation between the reaction activity and a broad mid-infrared absorption band derived from the photo-generated electrons shallowly trapped at the photocatalyst surfaces.

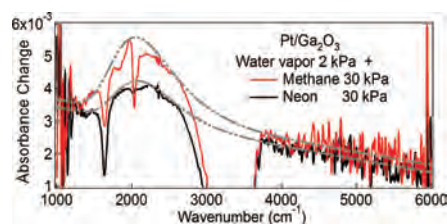


Figure 3. Comparison of the IR absorbance spectra measured in the non-reactive Ne gas and the reactive methane gas environment for Pt loaded Ga_2O_3 photocatalysts.⁴⁾

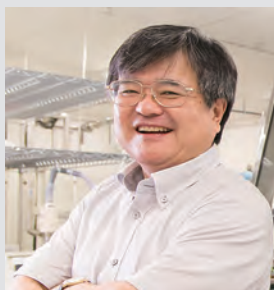
3. Critical Role of Interfacial Water Molecules on the Photocatalytic Methane Activation⁵⁾

Recent expectations for effective use of natural gas have led to an interest in chemical technology for methane activation. Photocatalytic approach has a potential to convert methane at ambient conditions. However, the microscopic understanding on photocatalytic reaction mechanism, especially robust C–H bond activation mechanism, remains an open question. Here, combining *in-situ* MS-IR spectroscopy and systematic reaction measurements under various partial pressures of methane and water, we demonstrate that photo-activated interfacial water molecules facilitate the first C–H dissociation and shift the rate-determining step. Our reaction observation on typical three photocatalysts (Ga_2O_3 , NaTaO_3 , TiO_2) clarified the existence of critical partial pressure of methane at approximately 0.5 atm, around which the reaction rates markedly increased with methane partial pressure. *Operando* IR measurements showed that H atom extraction from methane by photo-activated water was accelerated at the same critical partial pressure of methane, suggesting that the first C–H activation and adsorption of methane was directly assisted by interfacial water.

References

- 1) N. Aiga and T. Sugimoto, submitted.
- 2) T. Sugimoto *et al.*, *Nat. Phys.* **12**, 1063–1068 (2016).
- 3) T. Sugimoto and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).
- 4) H. Sato and T. Sugimoto, *Vac. Surf. Sci.* **63**, 476–481 (2020).
- 5) H. Sato, T. Higashi, K. Takeyasu, A. Ishikawa and T. Sugimoto, submitted.

Organic Solar Cells

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Professional Employment

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Awards

2021 Outstanding Achievement Award, Molecular Electronics & Bioelectronics Division, Japan Society of Applied Physics
2017 Fellow Award of Japan Society of Applied Physics
2006 Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
2006 Research and Education Award, Osaka University
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Keywords

Organic Semiconductors, ppm-Doping, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc.* Last year, we proposed a novel concept of the structure of organic solar cell, namely, a lateral multilayered junction (Figure 1). An essential point is that the photo-generated holes and electrons are laterally transported and extracted to the respective electrodes. We also investigated the reduction of open-circuit voltage (V_{oc}) loss due to non-radiative recombination in organic solar cells by using high-mobility organic semiconductors. We observed the V_{oc} reaching to thermodynamic (Shockley-Queisser) limit (Figure 2, double red dot). On the other hand, we have been focused on the research on the ppm-level doping effects in organic semiconductor films and organic single crystals for organic solar cells. So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s^{-1} , in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

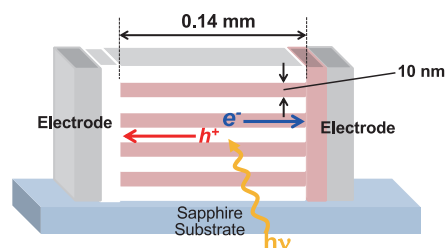


Figure 1. Lateral multilayered junction.

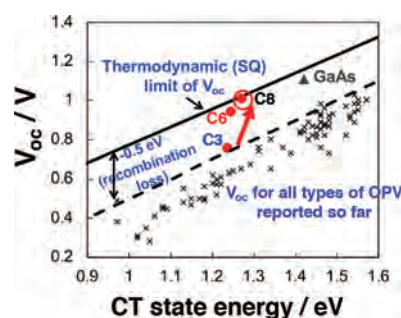


Figure 2. V_{oc} vs. Charge Transfer (CT) state energy of donor/acceptor type organic solar cells. By using high carrier mobility organic semiconductors, V_{oc} reaching SQ-limit was observed (double red dot).

Selected Publications

- M. Kikuchi, M. Hirota, T. Kunawong, Y. Shinmura, M. Abe, Y. Sadamitsu, A. M. Moh, S. Izawa, M. Izaki, H. Naito and M. Hiramoto, "Lateral Alternating Donor/Acceptor Multilayered Junction for Organic Solar Cells," *ACS Appl. Energy Mater.* **2**, 2087–2093 (2019).
- S. Izawa, N. Shintaku, M. Kikuchi and M. Hiramoto, "Importance

of Interfacial Crystallinity to Reduce Open-Circuit Voltage Loss in Organic Solar Cells," *Appl. Phys. Lett.* **115**, 153301 (2019).

- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* **30**, 1801236 (15 pages) (2018). [Invited Progress Report]

1. Efficient Solid-State Photon Up-conversion Enabled by Spin Inversion at Organic Semiconductor Interface¹⁾

Energy of photons, *i.e.* the wavelength of light, can be upgraded through interactions with materials—a process called photon upconversion (UC). Although UC in organic solids is important for various applications, such as in photovoltaics and bioimaging, conventional UC systems, based on intersystem crossing (ISC), suffer from low efficiency.

In this study, we report a novel UC mechanism at heterojunctions of organic semiconductors in bilayer structures. The UC occurs through spin inversion during the charge separation and recombination at the interface (Figure 3(a)). This spin inversion can efficiently convert the incident photons to triplets without relying on the ISC, whose rate is typically accelerated by the heavy-atom effect. As a result, a solid-state UC system is achieved with an external efficiency of two orders of magnitude higher than those of the conventional systems. Using this result, efficient UC, from near-infrared to visible light, can be realized on flexible organic thin films under a weak light-emitting diode-induced excitation, observable by naked eyes (Figure 3(b)).

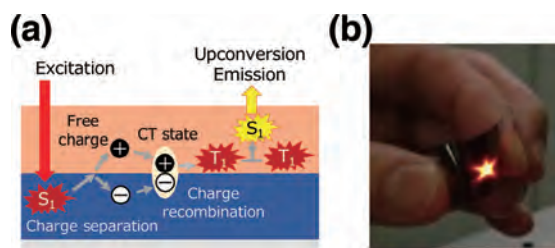


Figure 3. (a) Up-conversion (UC) emission by star-shaped patterned NIR LED irradiation. (b) Photographs of UC emission by a star-patterned NIR LED irradiation (750 nm, 71.7 mW/cm²) on a flexible thin film.

2. Photovoltaic Behavior of Centimeter-Long Lateral Organic Junctions²⁾

Recently, we reported a lateral alternating multilayered junction using a high mobility organic semiconductor.¹⁾ In this

study, we fabricated lateral junction cells having lateral distance (L) reaching cm order (Figure 4(a)). A donor [C8-BTBT (hole mobility: 43 cm²V⁻¹s⁻¹)]–acceptor [PTCDI-C8 (electron mobility: 1.7 cm²V⁻¹s⁻¹)] combination was used. Buffer layers of BCP and MoO₃ were used for the selective carrier collection of electrons and holes, respectively. Surprisingly, even lateral cells with $L = 1.8$ cm (Figure 4(b)) showed clear photovoltaic behavior (Figure 4(c), red curve). Figure 4(d) shows the L dependence of observed J_{sc} (red curve) and calculated J_{sc} (blue curve) obtained from diffusion lengths of electrons (4.7 mm) and holes (5.5 mm), which are dominated by traps. These diffusion lengths were obtained by the experiments using the moving photomask covering the irradiated surface from respective electrodes. Thus, considerable decrease in photocurrent is attributed to the trap-assisted recombination indicated by the blue curve. A further difference between the observed and calculated curves is due to bimolecular recombination and its effect is small. Thus, we concluded that trap-assisted recombination can be the main reason for photocurrent loss of the long lateral cells. Hence, identifying and removing the defects acting as traps can be done to improve cell performance.

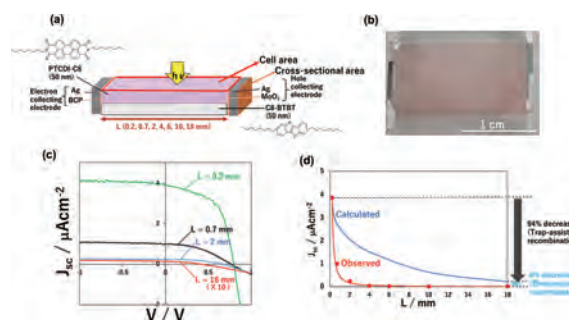


Figure 4. a) Structure of a lateral junction cell. (b) Photograph of a cell with $L = 18$ mm. (c) J-V curves of cells with $L = 0.2$, 0.7 and 18 mm. (d) Dependence of short-circuit photocurrent (J_{sc}) on L .

References

- 1) S. Izawa and M. Hiramoto, *Nat. Photonics*, in press (2021).
- 2) J. P. Ithikkal, A. Girault, M. Kikuchi, Y. Yabara, S. Izawa and M. Hiramoto, *Appl. Phys Express* **14**, 094001 (2021).

Awards

HIRAMOTO, Masahiro; Outstanding Achievement Award, Molecular Electronics and Bioelectronics Division, Japan Society of Applied Physics (2021).

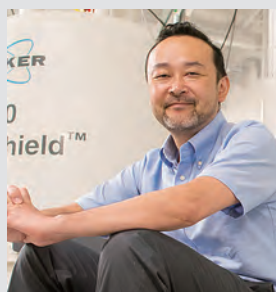
IZAWA, Seichiro; The Young Scientist Award, Molecular Electronics and Bio Electronics Division in the Japan Society of Applied Physics (2021).

IZAWA, Seichiro; Konica Minolta Imaging Science Encouragement Award (2021).

IZAWA, Seichiro; The Outstanding Presentation Award of the 31st Japan OLED Forum (2021).

Solid-State NMR for Molecular Science

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Education

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Professional Employment

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2001 Assistant Professor, Yokohama National University
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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 characterization 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.

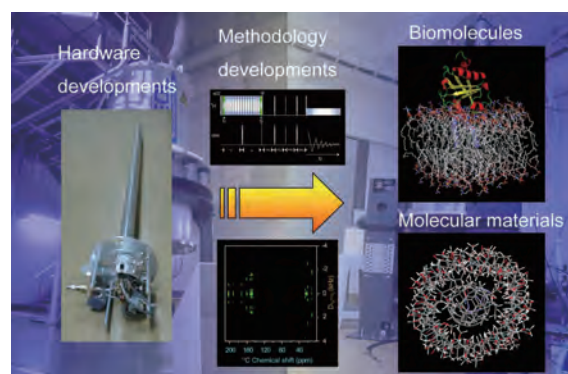


Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C- δ 1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, " ^2H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^1H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β -Sheet Structures by High Resolution ^1H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C- δ 1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- 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. 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).

1. Structural Characterization of Amyloid- β Protein Oligomer Promoted on Model Neuronal Cell Membranes Using State NMR

Amyloid β (A β) protein is disordered in solutions under diluted conditions, however it conforms insoluble amyloid fibrils, which are found in senile plaque as a hallmark of Alzheimer's disease. Although molecular structures of amyloid fibrils have been determined, its molecular process for fibrillation in vivo has not been clarified yet. However, accumulated evidences suggest that the fibrillation process may be promoted on neuronal cell membrane. Especially, it has been reported that A β specifically interacts with ganglioside GM1 which is one of the key lipids in lipid raft. Therefore, GM1 embedded into lipid bilayers composed of neutral lipid DMPC may be considered to be the most simplified model neuronal cell membrane. In order to clarify the role of GM1 in the fibrillation process, first, we have successfully determined the oligomeric structure of A β (1-40) induced on DMPC bilayers based on solid-state NMR.¹⁾ We have been collaborated with Prof. Kato group in IMS for those A β studies.

In the current study, A β (1-40) oligomer induced on model neuronal cell membranes consisting of GM1 and DMPC have been attempted to characterize using solid-state NMR. Based on information of intra- and intermolecular distances and torsion angles of back bone obtained from solid-state NMR analyses, precise molecular structure of A β oligomer was determined from restrained molecular dynamics simulations in collaboration with Prof. Okumura group in IMS.

The determined A β structure conforms disordered N-terminus followed by center and C-terminus β -sheets. A β takes intermolecular configuration of antiparallel β -sheet among adjacent molecules, in which different from A β fibrils prepared in solution and also A β oligomer induced on DMPC bilayers.¹⁾ Those suggest specific roles of GM1 for the formation of A β oligomers. We expect the significant contribution of our determined A β oligomer structure to reveal the molecular mechanism of A β fibrils on neuronal cell membranes, and thus understanding of Alzheimer's disease. The manuscript of this study is under preparation.

2. Characterizations of Lipid Binding of Prion Fragment Based on Solid-State NMR

"Prion" protein is amyloid protein responsible for class of neurodegenerative diseases such as Bovine spongiform encephalopathy, (BSE), Creutzfeldt-Jakob disease (CJD) of human, scrapie of sheep. Those are collectively known as transmissible spongiform encephalopathies (TSEs). The onset of TSEs has been considered to be arisen by conformational conversion of the native monomeric cellular prion protein (PrP^c) into misfolded β -sheet rich form (PrP^s), resulting in their insoluble aggregations. Recent studies suggest that those processes are facilitated through interactions with biomembranes, in particular, through binding with ganglioside GM1 in lipid raft. Despite of many studies of prion, molecular mechanism of structural conversion of prion protein and the cytotoxicity have not been clarified yet.

Ultimate goal of this project is provision of molecular basis

of prion disease through the characterizations of molecular structure of prion and their interactions with specific lipids based on solid-state NMR analyses. As the first stage, we start study of PrP(106-126) fragment which has been considered as minimum prion fragment to understand their fibrillation mechanism, because of conservations of important properties of formation of amyloid fibrils, membrane binding ability and cytotoxicity. We explore to clarify PrP(106-126) specific binding site in GM1 has been explored through the analyses of chemical shift perturbations of ¹³C signals from GM1 in POPC/GM1 vesicles from the comparisons of ¹³C-solid-state NMR spectra in the presence and absence of PrP(106-126). None of ¹³C signals from POPC exhibited peak shift, but several signals in GM1 exhibited peak shifts due to PrP(106-126) bindings, suggesting specific interactions of PrP(106-126) with GM1 in GM1/POPC lipid bilayers. Further detail is under investigation.

3. Characterization of Protein Using Solid-State NMR

The secretary abundant heat soluble protein (SAHS) from water bear which has ability of torpor under dry-condition, and recovery from torpor by water supply. The biological functions of SAHS at dry-state has not been identified yet, but SAHS has been considered to play key roles during torpor. This is collaboration project with Prof. Kato group in IMS. SAHS consisting of more than 200 amino acid residues and its dry-state is expected to be inhomogeneous. Therefore, in order to investigate structural homogeneity and obtain local conformational information, 2D ¹³C-homonuclear correlation solid-state NMR measurements were carried out for the dry-state SAHS protein which only isoleucine residues are specifically ¹³C and ¹⁵N isotope labeled. The 6 sets of signals were observed and assigned successfully.

4. Development of Solid-State NMR Probe

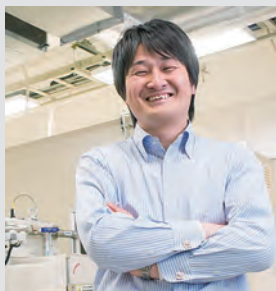
We have built a variety of solid-state NMR probes such as static and MAS ¹H-X double resonance probes for 400 MHz NMR, and a variable temperature ¹H-X double resonance MAS probe for 920 MHz ultra-high field NMR at past. During the past few years, we have been working on building an original solid-state NMR probe which is fully compatible with commercial instruments currently used. Those developed probes were built with originally designed parts except for spinning and spinning rate detection modules which were purchased from NMR company. To replace remained commercial modules, we attempted to design original spinning module. At first stage, two different types of original spinning modules were designed for 4.0 mm sample tube. Those exhibited moderate performances but slightly lower performance respect to commercial module. Based on various tests, we identified the key parts to govern the performance of the spinning. The improved version of spinning module is under developments.

Reference

- 1) M. Yagi-Utsumi, K. Kato and K. Nishimura, *PLoS One* **11**, 0146405 (10 pages) (2016).

Study on Hydride Ion Conductive Materials for Novel Electrochemical Devices

Department of Materials Molecular Science
Division of Molecular Functions



KOBAYASHI, Genki
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Education

2006 B.E. Kanazawa University
2008 M.E. Tokyo Institute of Technology
2010 D.S. Tokyo Institute of Technology

Professional Employment

2010 Postdoctoral Fellow, Tokyo Institute of Technology
2011 Assistant Professor, Kanagawa University
2012 JST-PRESTO Researcher (Additional post)
2013 Research Associate Professor, Institute for Molecular Science
2018 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards

2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018 The 39th Honda Memorial Young Researcher Award, The Honda Memorial Foundation
2018 The 7th Ishida Award, Nagoya University
2019 Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan
2019 Morino Foundation for Molecular Science

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Keywords Solid State Ionics, H⁻ Conductor, Battery

Hydrogen has a charge flexibility and can take various charge states such as proton (H⁺), atomic hydrogen (H⁰), and hydride (H⁻) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H⁰, H⁺ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H⁻ is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H⁻ has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties ($E^\circ(\text{H}^-/\text{H}_2) = -2.35 \text{ V vs. SHE}$), its electrochemical applications have not been considered. Against this back-

ground, we developed a series of H⁻ conductive oxyhydrides, $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$, in 2016 and found its function as an H⁻ solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H⁻ conductors and the development of novel electrochemical devices utilizing H⁻ conduction phenomena.

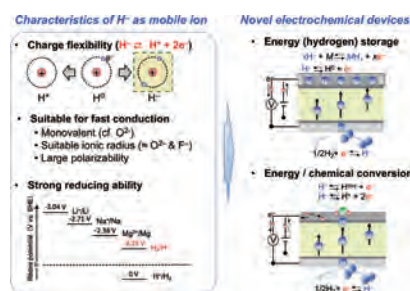


Figure 1. Our research concept toward realization of electrochemical devices utilizing hydrogen charge flexibility.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**(2), 88–92 (2017).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- N. Matsui, G. Kobayashi, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- H. Nawaz, F. Takeiri, A. Kuwabara and M. Yonemura and G. Kobayashi, *Chem. Commun.* **56**, 10373–10376 (2020).
- T. Uchimura, F. Takeiri, K. Okamoto, T. Saito, T. Kamiyama and G. Kobayashi, *J. Mater. Chem. A* **9**, 20371–20374 (2021).

1. Study on H⁻ Conductive Oxyhydrides¹⁻³⁾

In 2016, we synthesized a series of K₂NiF₄-type oxyhydrides, La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2 upper) and demonstrated pure H⁻ conduction properties in the oxyhydrides.¹⁾ The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH₂ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H⁻ conduction phenomena.

More recently, we synthesized novel H⁻ conductive oxyhydrides, Ba₂MHO₃ (M = Sc, Y),^{2,3)} with the K₂NiF₄-type structure and confirmed its unique site selectivity for H⁻. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba₂MHO₃ selectively occupied the rock-salt layer, in contrast to those of the observed isostructural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O led to the formation of the [Ba₂H₂] layers. These results indicate that anion ordering in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H⁻ conducting materials.

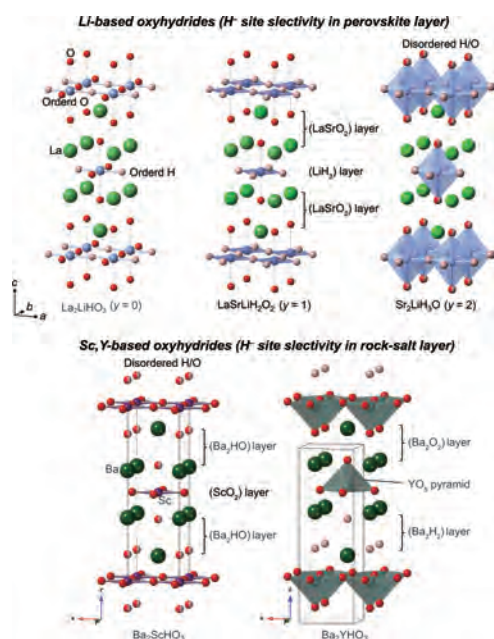


Figure 2. Crystal structures of H⁻ conductive oxyhydrides La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} (x = 0, y = 0, 1, 2) and Ba₂MHO₃ (M = Sc, Y).

2. Materials Processing of Oxyhydrides for Electrochemical Applications⁴⁻⁶⁾

Synthesizing oxyhydrides usually requires unique methods such as solid-state reactions at high-pressure and topochemical reactions using CaH₂ reductant. Since the former method is a

sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an O²⁻/H⁻ exchange reaction using oxides as precursors and is useful for preparing metastable phases that the conventional sintering process cannot obtain. However, the low synthesis volume in the high-pressure method and less reproducibility of composition due to complicated multi-step processes such as washing in CaH₂ reduction have prevented expanding the study on oxyhydrides to applicable research for electrochemical devices. To resolve the above problems, we have been trying to establish a suitable synthesis method for oxyhydrides.

For Li-based oxyhydrides (LSLHO) with the K₂NiF₄-type structure, we have successfully established the solid-state reaction method under ambient-pressure.^{4,5)} Electromotive force measurements using hydrogen concentration cells became possible by preparing the LSLHO sintered pellets with sufficient size.

We have also succeeded in direct synthesis of barium titanium oxyhydride BaTiO_{3-x}H_x by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of oxyhydrides. We also confirmed that the prepared polycrystalline BaTiO_{3-x}H_x worked as a hydrogen-permeable electrode. This result suggests that H⁻/e⁻ mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices (Figure 3).⁶⁾

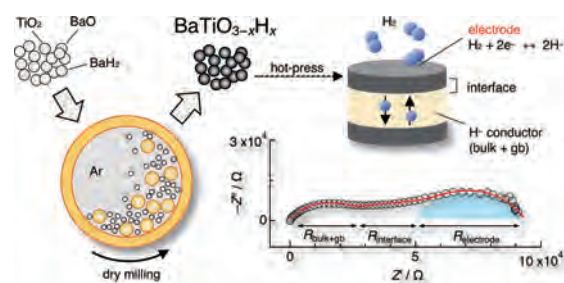


Figure 3. BaTiO_{3-x}H_x synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

References

- 1) G. Kobayashi* *et al.*, *Science* **351**, 1314–1317 (2016).
- 2) F. Takeiri, G. Kobayashi* *et al.*, *Inorg. Chem.* **58**, 4431–4436 (2019).
- 3) H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* **56**, 10373–10376 (2020).
- 4) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85**, 88–92 (2017).
- 5) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- 6) T. Uchimura, G. Kobayashi* *et al.*, *J. Mater. Chem. A* **9**, 20371–20374 (2021).

* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization

Clarification of the Energy Conversion Mechanism at the Surface and Interface by Scanning Probe Microscopy

Instrument Center



MINATO, Taketoshi
Senior Researcher

At the interface between solid and liquid, energy conversion reactions in the physical, chemical, and biological process proceed. The details of such a energy conversion process is yet to be clarified completely.^{1,2)} Scanning probe microscopy (SPM) is a powerful method to clarify such mechanisms because it can explore structural, mechanical, electric and electronic properties in atomic (or molecular) scales. As shown in an atomic resolved SPM image of $\text{CaCO}_3(104)$ surface in 5 mM NaCl aqueous solution (Figure 1), atomic scale properties are investigated by SPM.

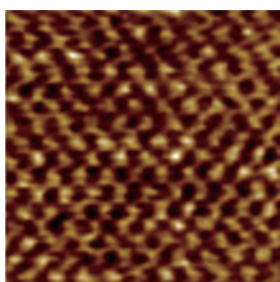


Figure 1. An atomically resolved friction image of $\text{CaCO}_3(104)$ surface in 5 mM NaCl aqueous solution. image size: $5 \text{ nm} \times 5 \text{ nm}$.

Rechargeable battery plays an important role in the development of new systems of energy storage and transfer. Currently, lithium-ion batteries have been widely used for energy systems. Recent demands for rechargeable batteries require more developments in the capacity, cyclic performance and lifetime. For these developments, the clarification of the reaction mechanism at the interface between electrode and electrolyte during the charge and discharge reactions is crucial.

During the charge and discharge reactions of rechargeable battery, solvent, carrier ions, additive and solute produce specific states at the interface between electrode and electrolyte. The interface states are believed to change the physical properties depending on the potential and strongly correlate the battery performances. However, detecting the interface states is challenging. By setting up SPM system which can operate in electrochemical conditions, we detected and the investigated physical properties of interface states. Figure 2

shows force curves obtained at the interface between organic electrolyte for lithium-ion battery and gold electrode. The force curve was changed by the sample potential between +1.0 (blue) and -1.0 V (red) (vs Pt). The changes of the force curves were caused by the interface states, exhibiting the evidence of the formation of the thick interface states by electrolyte at -1.0 V. By the analysis of the force curves, the mechanical properties of the interface states were also clarified. The analysis of the electrode/electrolyte interface will be applied to innovative battery systems³⁻⁵⁾ that can overcome current battery performances.

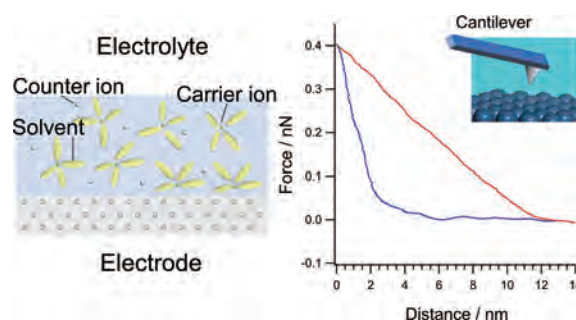
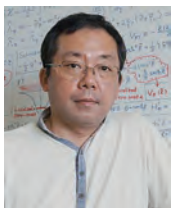


Figure 2. A schematic model of electrode/electrolyte interface in a rechargeable battery and force curves obtained by electrochemical SPM systems at the interface between organic electrolyte for lithium-ion battery and gold electrode with changing the sample potential. The blue and red curve were obtained at +1.0 and -1.0 V (vs. Pt), respectively. The force curves were measured during the approaching the tip to the interface. The distance was determined from the point detecting 0.4 nN.

References

- 1) T. Minato and T. Abe, *Prog. Surf. Sci.* **92**, 240–280 (2017).
- 2) T. Minato, K.-i. Umeda, K. Kobayashi, Y. Araki, H. Konishi, Z. Ogumi, T. Abe, H. Onishi and H. Yamada, *Jpn. J. Appl. Phys.* (review), **60**, SE0806 (2021).
- 3) T. Minato, H. Konishi, A. Celik Kucuk, T. Abe and Z. Ogumi, *Ceramics Japan* **54**, 637 (2019).
- 4) H. Nakano, T. Matsunaga, T. Mori, K. Nakanishi, Y. Morita, K. Ide, K.-i. Okazaki, Y. Orikasa, T. Minato, K. Yamamoto, Z. Ogumi and Y. Uchimoto, *Chem. Mater.* **33**, 459–466 (2021).
- 5) K. Shimoda, T. Minato, H. Konishi, G. Kano, T. Nakatani, S. Fujinami, A. C. Kucuk, S. Kawaguchi, Z. Ogumi and T. Abe, *J. Electroanal. Chem.* **895**, 115508 (2021).

Visiting Professors



Visiting Professor

KISHINE, Jun-ichiro (from *The Open University of Japan*)

Theoretical Studies on Chiral Material Science

The concept of chirality is ubiquitous in natural sciences. However, until only recently, research fields on chirality had been fragmented into separated branches of physics, chemistry and biology. Even inside physics, a term “chiral” has been used in different meanings in condensed matter and high-energy physics.

One of the most important mission of our project is to integrate the scattered concepts of chirality and make a roadmap toward an attempt at synthesis of chiral material sciences. Let us remind the Laurence Barron’s definition of the true chirality, *i.e.*, true chirality is shown by systems existing in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation. The space inversion is a matter of geometrical symmetry, while time reversal is a matter of dynamical motion. This unambiguous definition clearly indicates that the concept of chirality ties geometry and dynamics. Conversion of geometry into dynamics naturally leads to material functionalities. The main purpose of this research project is to integrate these concepts in a unified manner. During this one year, we have focused on theoretical description of the chirality-induced phonon in non-centrosymmetric crystals.



Visiting Associate Professor

FURUKAWA, Ko (from *Niigata University*)

Advanced ESR Study of Molecule-Based Functional Materials

To develop the high-efficiency molecule-based device, it’s vital to clarify the mechanism of the functional molecules/materials. We investigate the mechanism of the solid-state functional materials in terms of advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, time-resolved ESR, pulsed-ESR and so on. Recently, our themes are following three (I) spin dynamics

study of molecule-based materials with the complex function combined to photoconductivity and photo-induced magnetic properties, (II) operand ESR study of the novel oxygen reduction reaction (ORR) catalyst for fuel cell, and (III) the soil environments were investigated by using ESR spectroscopy for the vegetable food such as the rice and tea leaves.



Visiting Associate Professor

OSHIMA, Yugo (from *RIKEN*)

Development of ESR Probe for Molecular Field-Effect Transistor (FET) Devices

Recently, a novel type of ferromagnet (Et-4BrT)[Ni(dmit)₂]₂ has been developed by Kusamoto Group and Yamamoto Group in IMS (dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and Et-4BrT is ethyl-4-bromothiazolium). We have found that this ferromagnet is the first realization of the Nagaoka-Penn ferromagnetism, where the ferromagnetism is achieved by the light hole-doping of the insulating Ni(dmit)₂ layer owing to the internal dipole moment of the monovalent cation Et-4BrT (*Sci. Rep.* **11**, 1332 (2021)).

Our latest interest is whether the ferromagnetism of this material can be controlled by electrical doping or not. In collaboration with Yamamoto Group, we have newly developed an ESR sample holder for field-effect transistors (FETs), so that we can control precisely the electrical doping of (Et-4BrT)[Ni(dmit)₂]₂ by means of FET structure. We will investigate the magnetic properties of (Et-4BrT)[Ni(dmit)₂]₂ by carrier doping from ESR spectroscopy.

RESEARCH ACTIVITIES

Life and Coordination-Complex Molecular Science

Department of Life and Coordination-Complex Molecular Science is composed of two divisions of biomolecular science, two divisions of coordination-complex molecular science, and one adjunct division. Biomolecular science divisions cover the studies on functions, dynamic structures, and mechanisms for various biomolecules such as sensor proteins, metalloproteins, biological-clock proteins, glycoconjugates, antibodies, and motor proteins. Coordination-complex divisions aim to develop molecular catalysts and functional metal complexes for transformation of organic molecules, and molecular materials with photonic-electronic-magnetic functions and three-dimensional complex structures. Interdisciplinary alliances in this department aim to create new basic concepts for the molecular and energy conversion through the fundamental science conducted at each division.

Bioinorganic Chemistry of Metalloproteins Responsible for Metal Homeostasis and Signal Sensing

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions



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Professor
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Education

1982 B.S. Tokyo Institute of Technology
1987 Ph.D. Tokyo Institute of Technology

Professional Employment

1988 Postdoctoral Fellow, Georgia University
1989 Assistant Professor, Tokyo Institute of Technology
1994 Associate Professor, Japan Advanced Institute of Science and Technology
2002 Professor, Institute for Molecular Science
Professor, Okazaki Institute for Integrative Bioscience (-2018)
Professor, The Graduate University for Advanced Studies
2018 Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Member

Assistant Professor
MURAKI, Norifumi
IMS Research Assistant Professor
TAKEDA, Kouta
Post-Doctoral Fellow
NAM, Dayeon
TOHDA, Rei
Technical Fellow
MURAKI, Megumi
Secretary
NAKANE, Kaori

Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

Transition metal ions and metalloproteins play crucial roles in meeting the energy demands of the cell by playing roles in intermediary metabolism and in signal transduction processes. Although they are essential for biological function, metal ion bioavailability must be maintained within a certain range in cells due to the inherent toxicity of all metals above a threshold. This threshold varies for individual metal ions. Homeostasis of metal ions requires a balance between the processes of uptake, utilization, storage, and efflux and is achieved by the coordinated activities of a variety of proteins including extracytoplasmic metal carriers, ion channels/pumps/transporters, metal-regulated transcription and translation proteins, and enzymes involved in the biogenesis of metal-containing cofactors/metalloproteins. In order to understand the processes underlying this complex metal homeostasis network, the study of the molecular processes that determine the protein-metal ion recognition, as well as how this event is transduced into a functional output, is required. My research interests are focused on the elucidation of the structure and

function relationships of metalloproteins responsible for the regulation of biological homeostasis.

I am also working on gas sensor proteins. Gas molecules such as O₂, NO, CO and ethylene are present in the environment and are endogenously (enzymatically) produced to act as signaling molecules in biological systems. Sensing these gas molecules is the first step in their acting as signaling molecules. Sensor proteins are usually required. Input signals generated by gas sensing have to transduce to output signals that regulate biological functions. This is achieved by biological signal-transduction systems. Recognition of the cognate gas molecules is a general mechanism of functional regulation for gas sensor proteins. This induces conformational changes in proteins that controls their activities for following signal transductions. Interaction between gas molecules and sensor proteins is essential for recognition of gas molecules. Metal-containing prosthetic groups are widely used. In my research group, our research focuses on transition metal-based gas-sensor proteins and the signaling systems working with them.

Selected Publications

- M. Nishinaga, H. Sugimoto, Y. Nishitani, S. Nagai, S. Nagatoishi, N. Muraki, T. Tosha, K. Tsumoto, S. Aono, Y. Shiro and H. Sawai, "Heme Controls the Structural Rearrangement of Its Sensor Protein Mediating Bacterial Survival," *Commun. Biol.* **4**, 467 (12 pages) (2021).
- N. Muraki, K. Takeda, D. Nam, M. Muraki and S. Aono, "Structural Characterization of Thermoglobin from a Hyperthermophilic Bacterium *Aquifex aeolicus*," *Chem. Lett.* **50**, 603–606 (2021).
- N. Muraki, C. Kitatsuji, Y. Okamoto, T. Uchida, K. Ishimori and S. Aono, "Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria," *Chem. Commun.* **55**, 13864–13867 (2019).
- N. Muraki, K. Ishii, S. Uchiyama, S. G. Itoh, H. Okumura and S. Aono, "Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase," *Commun. Biol.* **2**, 385 (12 pages) (2019).
- A. Pavlou, H. Yoshimura, S. Aono and E. Pinakoulaki, "Protein Dynamics of the Sensor Protein HemAT as Probed by Time-Resolved Step-Scan FTIR Spectroscopy," *Biophys. J.* **114**, 584–591 (2018).
- A. Pavlou, A. Loullis, H. Yoshimura, S. Aono and E. Pinakoulaki, "Probing the Role of the Heme Distal and Proximal Environment in Ligand Dynamics in the Signal Transducer Protein HemAT by Time-Resolved Step-Scan FTIR and Resonance Raman Spectroscopy," *Biochemistry* **56**, 5309–5317 (2017).

1. Structural Characterization of Thermoglobin from a Hyperthermophilic Bacterium *Aquifex aeolicus*

Globins are heme-binding proteins, which show a variety of biological functions such as oxygen transport, oxygen storage, redox catalysis and gas sensing. In bacteria, four distinct globins are identified; single domain hemoglobin (sdHb), truncated hemoglobin (tHb), flavohemoglobin (fHb) and globin-coupled sensor (GCS). Truncated hemoglobins (tHbs) are shorter than the canonical vertebrate hemoglobins by 20–40 residues. Whereas the canonical hemoglobins, sdHb, fHb and GCS are composed of eight α -helices (A–H), that fold into a 3-on-3 α -helical sandwich structure, tHbs form a 2-on-2 α -helical sandwich in which helices B and E lie over helices G and H. The physiological function of some sdHb, tHb, and fHb is proposed to provide resistance to nitrosative stress such as reactive nitrogen species. In this work, the structural characterization of AaTgb was carried out by X-ray crystallography.

We have determined the crystal structure of Y29F-AaTgb in the imidazole-bound form. Y29F-AaTgb shares the structural similarity to known bacterial sdHb structures; *Campylobacter jejuni* Hb (CjHb, 44% sequence identity), *Methylobacterium thermophilum* Hb known as hell's gate globin I (HGbl, 32% sequence identity) and *Vitreoscilla stercoraria* Hb (VsHb, 43% sequence identity). sdHb was discovered from *Vitreoscilla stercoraria*, which shares approximately 30% amino acid sequence identity with the globin domain of fHb that functions as nitric oxide dioxygenase. Based on the amino acid sequence homology, it is assumed that sdHb also acts as nitric oxide dioxygenase. Indeed, *Campylobacter jejuni* Hb and *Helicobacter pullorum* Hb have been reported to contribute to remove nitric oxide.

The superposition between the C α atoms of Y29F-AaTgb and CjHb (PDB ID: 2wy4), HGbl (PDB ID: 3s1i) and VsHb (PDB ID: 3vhh) shows a root mean square deviation of 0.89 Å, 1.04 Å and 1.18 Å, respectively. By using a structural homology search in Structure Navigator in PDBj, Y29F-AaTgb has the highest structural homology to the globin domain of nitric oxide dioxygenase from *Rhodothermus marinus* (RmaNOD, UniProt ID: D0MGT2). The superposition between the C α atoms of Y29F-AaTgb and the globin domain of RmaNOD (PDB ID: 6wk3) shows a root mean square deviation of 0.60 Å with 48% sequence identity. The structural similarity of AaTgb to sdHb and RmaNOD suggests a possibility that AaTgb is also responsible for NO detoxification, though further studies must be required to confirm this hypothesis.

The heme environmental structure of Y29F-AaTgb is shown in Figure 1. In Y29F-AaTgb, the heme iron is coordinated by His82 and imidazole in the proximal and distal side, respectively. The distances between iron and nitrogen atom are 2.17 and 2.13 Å for His82 and imidazole, respectively. ND1 of His82 forms hydrogen bonds with OH of Tyr92 and OE2 of Glu132. These hydrogen bonds will fix the orientation of imidazole ring of His82. These amino acids and hydrogen bonds network in the proximal site are conserved in sdHbs except to HGbl.

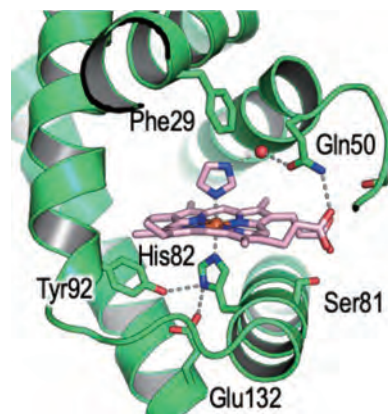


Figure 1. Heme environmental structure of Y29F-AaTgb in the imidazole-bound form. Hydrogen bonds are shown in dashed lines. Nitrogen and oxygen atoms are shown in blue and red, respectively. Red sphere in the heme pocket shows the water molecule W.

Imidazole bound to heme participate in a hydrogen bonding network in the distal heme pocket. A well-defined water molecule (W) present in the distal heme pocket forms hydrogen bonds with imidazole and Gln50. Gln50 forms a hydrogen bond with a propionate group of heme. This hydrogen bonding network will stabilize and fix the orientation of imidazole ligand. On the other hand, Phe29 was 3.41 Å from nitrogen of imidazole and 3.69 Å from the water molecule W.

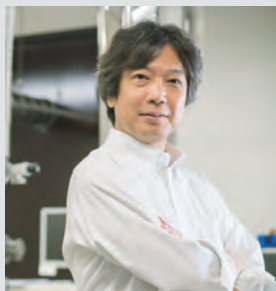
The binding affinity of imidazole (K_d) to the ferric form of AaTgb was 4.1 and 5.7 μ M for the wild type and Y29F variant, respectively, which were determined by measuring absorbance changes upon imidazole titration. Similar binding affinity of imidazole will be achieved as a loss of the hydrogen bond between Tyr29 and imidazole in Y29F variant is compensated by the hydrogen bond between the water molecule W and imidazole.

2. Structural and Functional Analyses of Heme Sensing Transcriptional Regulator PefR

Hemes (iron-porphyrins) are critical for biological processes in all organisms. In this work, structural, functional and spectroscopic analyses of the heme-responsive sensor protein PefR from *Streptococcus agalactiae*, were carried out to elucidate the molecular mechanisms of how heme molecule regulates the functional activity of PefR. The crystal structures of apo-PefR, apo-PefR/DNA complex, and heme-bound (holo-) PefR were determined at 2.6, 2.5 Å, and 1.7 Å resolutions, respectively. Structural comparison of the apo-PefR/DNA complex and holo-PefR reveals that conformational change occur around the heme-binding site, which is induced by the coordination of His114 of one subunit to heme followed by the coordination of the N-terminal amino group of the other subunit. Rigid-body motion of the α 1 helix in association with heme accommodation alters the relative orientation of the DNA-binding domain in holo-PefR from the apo form, resulting in a conformational change in the DNA-binding domain.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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Professional Employment

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Awards

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Keywords Biomolecule Organization, NMR

Living systems are characterized as dynamic processes of assembly and disassembly of various biomolecules that are self-organized, interacting with the external environment. The omics-based approaches developed in recent decades have provided comprehensive information regarding biomolecules as parts of living organisms. However, fundamental questions still remain unsolved as to how these biomolecules are ordered autonomously to form flexible and robust systems (Figure 1). Biomolecules with complicated, flexible structures are self-organized through weak interactions giving rise to supramolecular complexes that adopt their own dynamic, asymmetric architectures. These processes are coupled with expression of integrated functions in the biomolecular systems.

Toward an integrative understanding of the principles behind the biomolecular ordering processes, we conduct multidisciplinary approaches based on detailed analyses of



Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

dynamic structures and interactions of biomolecules at atomic level, in conjunction with the methodologies of molecular and cellular biology along with synthetic and computational technique.

Selected Publications

- H. Yagi, S. Yanaka and K. Kato, “Structural and Functional Roles of the *N*-Glycans in Therapeutic Antibodies,” in *Comprehensive Glycoscience, 2nd edition*, J. Barchi, Ed., Elsevier; Oxford, **vol. 5**, pp. 534–542 (2021).
- S. Yanaka, R. Yogo and K. Kato, “Biophysical Characterization of Dynamic Structures of Immunoglobulin G,” *Biophys. Rev.* **12**, 637–645 (2020).
- T. Satoh and K. Kato, “Structural Aspects of ER Glycoprotein Quality-Control System Mediated by Glucose Tagging,” in *Glycobiophysics*, Y. Yamaguchi and K. Kato, Eds., Springer Nature; Singapore, pp. 149–169 (2018).
- K. Kato, H. Yagi and T. Yamaguchi, “NMR Characterization of the Dynamic Conformations of Oligosaccharides,” in *Modern Magnetic Resonance, 2nd Edition*, G. A. Webb, Ed., Springer International Publishing, pp. 737–754 (2018).
- T. Yamaguchi and K. Kato, “Molecular Dynamics of Gangliosides,” in *Gangliosides*, S. Sonnino and A. Prinetti, Eds., Methods in Molecular Biology, Humana Press; New York, **vol. 1804**, pp. 411–417 (2018).
- K. Kato and T. Satoh, “Structural Insights on the Dynamics of Proteasome Formation,” *Biophys. Rev.* **10**, 597–604 (2018).

1. Methodological Advancements for Analysis of Conformational Dynamics and Interactions of Biomolecules

During the past year, we have made significant progresses in our methods for investigating conformational dynamics and interactions of biomolecules, especially oligosaccharides and glycoproteins. Oligosaccharides play versatile roles in various biological systems but are difficult to characterize from a structural viewpoint due to their remarkable degrees of freedom in internal motion. Therefore, molecular dynamics simulations have been widely used to delineate the dynamic conformations of oligosaccharides. However, hardly any methods have thus far been available for the comprehensive characterization of simulation-derived conformational ensembles of oligosaccharides. We developed a theoretical approach for comprehensive characterization of oligosaccharide conformational ensembles with conformer classification by free-energy landscape via reproductive kernel Hilbert space.¹⁾ This methodology will open opportunities to explore oligosaccharides' conformational spaces, and more generally, molecules with high degrees of motional freedom.

In addition, we sophisticated our experimental methods for stable-isotope-assisted measurements of nuclear magnetic resonance (NMR) and small-angle neutron scattering (SANS) using immunoglobulin G (IgG) as a model glycoprotein. This enabled us to achieve NMR spectral assignments of the N-linked oligosaccharides as well as polypeptide backbones of the Fc portion of IgG.^{2,3)} Moreover, we combined inverse contrast-matching SANS method with size exclusion chromatography and thereby successfully observed SANS from the non-deuterated IgG glycoprotein in complex with its binding partners with 75% deuteration, which were unobservable in terms of SANS in D₂O.⁴⁾ Furthermore, we revealed residual structure of unfolded ubiquitin by employing a dimethylsulfoxide-quenched hydrogen/deuterium-exchange NMR technique with the use of spin desalting columns.⁵⁾

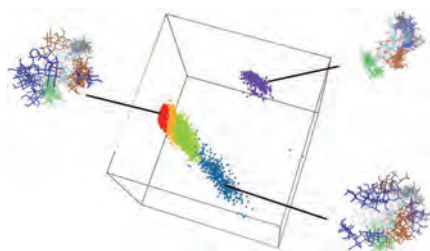


Figure 2. A kernel method for the comprehensive characterization of conformational ensembles of oligosaccharides in association with the conformational free-energy landscape.

Awards

YAGI-UTSUMI, Maho; 10th Young Researcher Award, National Institutes of Natural Sciences (2021).

YANAKA, Saeko; Award for Young Scientists, the Division of Physical Sciences of the Pharmaceutical Society of Japan (2021).

UMEZAWA, Fumiko; Young Scientist Award, Japanese Biochemical Society Chubu Branch (2021).

SAITO, Taiki; the Young Scientist Award, the 16th Forum of the Glycoscience Base for Chubu (2021).

2. Integrative Approaches for Characterizing Biomolecular Assembly Systems

We characterized various biomolecular assembling systems using integrative approaches. Cold atmospheric plasma (CAP) has attracted much attention in the fields of biotechnology and medicine owing to its potential utility in clinical applications. Recently accumulating evidence has demonstrated that CAP influences protein structures. However, there remain open questions regarding the molecular mechanisms behind the CAP-induced structural perturbations of biomacromolecules. In view of this situation, we investigated the potential effects of CAP irradiation of amyloid β (A β).⁶⁾ Based on NMR, mass spectrometry, and kinetics analyses, we demonstrated that the CAP irradiation results in selective oxidation of the methionine residue at position 35 of A β , which suppresses amyloid fibril formation. This modification is made by H₂O₂ generated in the plasma-irradiated buffer solution, rather than by the direct action of the plasma.

We also conducted a cryo-electron microscopic study of the proteasome α 7 subunit, which self-assembles into a homotetradecamer consisting of two layers of α 7 heptameric rings.⁷⁾ Our observations suggest that the α 7 double-ring structure was significantly different from the previously reported crystallographic model and fluctuates considerably in solution.

In addition, we contributed to an IMS Joint Research lead by Dr. Ryo Ohtani (Kyushu University) on two-dimensional coordination polymers as *pseudo-membrane jackets*, which achieve visible phase separation in cell membrane.^{8,9)} This system opens new avenues for the application of metal complex lipids toward controlling lipid distributions in fluid membranes.

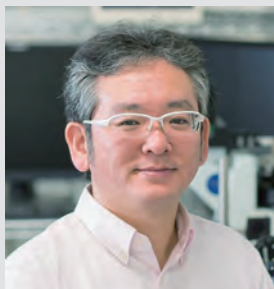
References

- 1) T. Watanabe *et al.*, *Phys. Chem. Chem. Phys.* **23**, 9753–9760 (2021).
- 2) H. Yagi *et al.*, *Biomolecules* **10**, 1482 (2020).
- 3) S. Yanaka *et al.*, *Biomol. NMR Assignments* **15**, 187–192 (2021).
- 4) N. Sato *et al.*, *J. Biochem.* **169**, 701–708 (2021).
- 5) M. Yagi-Utsumi *et al.*, *Biophys. J.* **119**, 2029–2038 (2020).
- 6) M. Yagi-Utsumi *et al.*, *Int. J. Mol. Sci.* **22**, 3116 (2021).
- 7) C. Song *et al.*, *Int. J. Mol. Sci.* **22**, 4519 (2021).
- 8) R. Ohtani *et al.*, *Angew. Chem., Int. Ed.* **61**, 13603–13608 (2021).
- 9) R. Ohtani *et al.*, *Angew. Chem., Int. Ed.* **59**, 17931–17937 (2020).

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Operation and Design Principles of Biological Molecular Machines

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Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by various molecular machines made of proteins. Protein molecular machines are tiny, but show very high performance, and are superior to man-made machines in many aspects. One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces and torques that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane.

We unveil operation principles of molecular motors with advanced single-molecule functional analysis. With the help of site-saturation mutagenesis and robot-based automation, we also engineer non-natural molecular motors to understand their design principles.

Selected Publications

- A. Visootsat, A. Nakamura, P. Vignon, H. Watanabe, T. Uchihashi and R. Iino, "Single-Molecule Imaging Analysis Reveals the Mechanism of a High-Catalytic-Activity Mutant of Chitinase A from *Serratia marcescens*," *J. Biol. Chem.* **295**, 1915–1925 (2020).
- J. Ando, T. Shima, R. Kanazawa, R. Shimo-Kon, A. Nakamura, M. Yamamoto, T. Kon and R. Iino, "Small Stepping Motion of Processive Dynein Revealed by Load-Free High-Speed Single-Particle Tracking," *Sci. Rep.* **10**, 1080 (2020).
- J. Ando, A. Nakamura, M. Yamamoto, C. Song, K. Murata and R. Iino, "Multicolor High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles," *ACS Photonics* **6**, 2870–2883 (2019).
- T. Iida, Y. Minagawa, H. Ueno, F. Kawai, T. Murata and R. Iino, "Single-Molecule Analysis Reveals Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V₁-ATPase,"



Figure 1. Protein molecular machines. (Left) A linear molecular motor chitinase A. (Center and Right) Rotary molecular motors F₁-ATPase and V₁-ATPase, respectively.

J. Biol. Chem. **294**, 17017–17030 (2019).

- J. Ando, A. Nakamura, A. Visootsat, M. Yamamoto, C. Song, K. Murata and R. Iino, "Single-Nanoparticle Tracking with Angstrom Localization Precision and Microsecond Time Resolution," *Biophys. J.* **115**, 2413–2427 (2018).
- A. Nakamura, K. Okazaki, T. Furuta, M. Sakurai and R. Iino, "Processive Chitinase is Brownian Monorail Operated by Fast Catalysis after Peeling Rail from Crystalline Chitin," *Nat. Commun.* **9**, 3814 (2018).
- A. Nakamura, T. Tasaki, Y. Okuni, C. Song, K. Murata, T. Kozai, M. Hara, H. Sugimoto, K. Suzuki, T. Watanabe, T. Uchihashi, H. Noji and R. Iino, "Rate Constants, Processivity, and Productive Binding Ratio of Chitinase A Revealed by Single-Molecule Analysis," *Phys. Chem. Chem. Phys.* **20**, 3010–3018 (2018).

1. Domain Architecture Divergence Leads to Functional Divergence in Binding and Catalytic Domains of Bacterial and Fungal Cellobiohydrolases¹⁾

Cellobiohydrolases directly convert crystalline cellulose into cellobiose and are of biotechnological interest to achieve efficient biomass utilization. As a result, much research in the field has focused on identifying cellobiohydrolases that are very fast. Cellobiohydrolase A from the bacterium *Cellulomonas fimi* (CfCel6B) and cellobiohydrolase II from the fungus *Trichoderma reesei* (TrCel6A) have similar catalytic domains (CDs) and show similar hydrolytic activity. However, TrCel6A and CfCel6B have different cellulose-binding domains (CBDs) and linkers: TrCel6A has a glycosylated peptide linker, whereas CfCel6B's linker consists of three fibronectin type 3 domains. We previously found that TrCel6A's linker plays an important role in increasing the binding rate constant to crystalline cellulose. However, it was not clear whether CfCel6B's linker has similar function. Here we analyze kinetic parameters of CfCel6B using single-molecule fluorescence imaging to compare CfCel6B and TrCel6A. We find that CBD is important for initial binding of CfCel6B, but the contribution of the linker to the binding rate constant or to the dissociation rate constant is minor. The crystal structure of the CfCel6B CD showed longer loops at the entrance and exit of the substrate-binding tunnel compared with TrCel6A CD, which results in higher processivity. Furthermore, CfCel6B CD showed not only fast surface diffusion but also slow processive movement, which is not observed in TrCel6A CD. Combined with the results of a phylogenetic tree analysis, we propose that bacterial cellobiohydrolases are designed to degrade crystalline cellulose using high-affinity CBD and high-processivity CD.

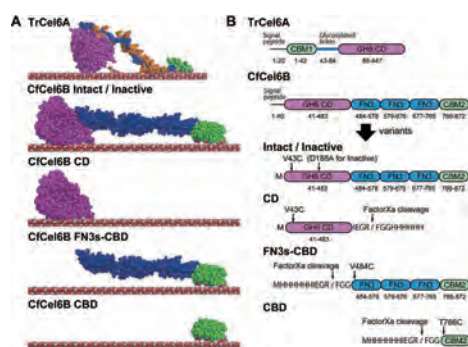


Figure 2. Structures of TrCel6 and CfCel6B. A, model structures of Intact TrCel6A, CfCel6B, and CfCel6B domain constructs used in this study. TrCel6A structure is the same as in the previous report. For CfCel6B, structure of CD is X-ray crystal structure (PDB code 7CBD), and FN3s and CBD are modeled by SWISS-MODEL server. Figures were prepared by PyMOL. B, detailed descriptions of domain compositions for each construct. Positions of mutation sites, histidine tags, and FaXa cleavage sites and estimated amino acid numbers for each domain are shown.

Award

OTOMO, Akihiro; Best Presentation Award, 2020 Annual Meeting of the Biophysical Society of Japan Chubu Branch Meeting (2020).

2. Combined Approach to Engineer a Highly Active Mutant of Processive Chitinase Hydrolyzing Crystalline Chitin²⁾

Serratia marcescens chitinase A (SmChiA) processively hydrolyzes recalcitrant biomass crystalline chitin under mild conditions. Here, we combined multiple sequence alignment, site-saturation mutagenesis, and automated protein purification and activity measurement with liquid-handling robot to reduce the number of mutation trials and shorten the screening time for hydrolytic activity improvement of SmChiA. The amino acid residues, which are not conserved in the alignment and are close to the aromatic residues along the substrate-binding sites in the crystal structure, were selected for site-saturation mutagenesis. Using the previously identified highly active F232W/F396W mutant as a template, we identified the F232W/F396W/S538V mutant, which shows further improved hydrolytic activity just by trying eight different sites. Importantly, valine was not found in the multiple sequence alignment at Ser538 site of SmChiA. Our combined approach allows engineering of highly active enzyme mutants, which cannot be identified only by the introduction of predominant amino acid residues in the multiple sequence alignment.

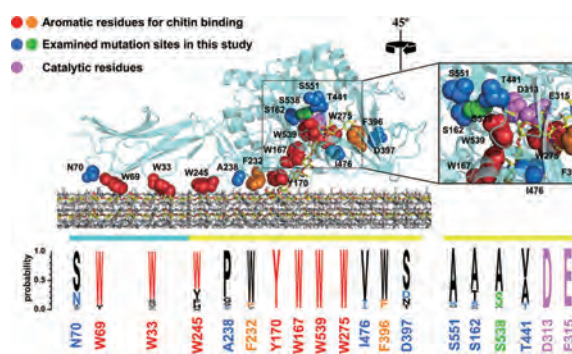


Figure 3. Model structure of SmChiA bound to crystalline chitin, important residues for binding and catalysis, and residues mutated in this study. (Top) A crystal structure of SmChiA (PDB entry 1CTN; ribbon model) aligned with the crystalline chitin chains (stick model). Amino acid residues responsible for binding to chitin (red and orange), catalytic residues (pink), and examined mutation sites (blue and green) are highlighted with sphere models. An expanded image around the catalytic site (transparent box in the left structure) is also shown in the right-hand-side box with 45° turn from the left structure. The cyan and yellow bars under the structure indicate the binding and catalytic domains, respectively. (Bottom) Result of multiple sequence alignment for amino acid residues highlighted in the top. The residues of SmChiA are shown in the same color as the top.

References

- 1) A. Nakamura *et al.*, *J Biol. Chem.* **295**, 14606–14617 (2020).
- 2) A. Visootsat *et al.*, *ACS Omega* **5**, 26807–26816 (2020).

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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Awards

1991 Eisai Award, Synthetic Organic Chemistry
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Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).

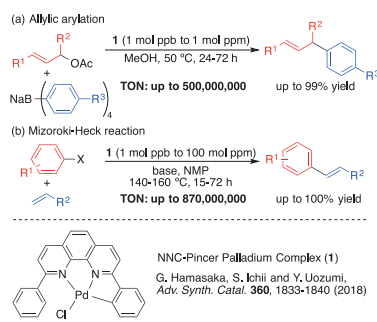


Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Complexes.

Selected Publications

- R. David and Y. Uozumi, “Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review),” *Adv. Synth. Catal.* **360**, 602–625 (2018).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, “Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin,” *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, “Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels,” *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, “Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex,” *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, “Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Palladium Catalyst Supported on Amphiphilic Resin,” *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, “A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water,” *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, “Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane,” *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. C–H Arylation of Thiophenes with Aryl Bromides by a Parts-per-Million Loading of a Palladium NNC-Pincer Complex¹⁾

A palladium NNC-pincer complex efficiently catalyzed the direct arylation of thiophene derivatives with extremely low palladium loadings of the order of parts per million. Thus, the reaction of various thiophenes with aryl bromides in the presence of 25–100 mol ppm of chlorido[(2-phenyl- κ -C²)-9-phenyl-1,10-phenanthroline- κ -2-*N,N'*]palladium(II) NNC-pincer complex, K₂CO₃, and pivalic acid in *N,N*-dimethylacetamide afforded the corresponding 2- or 5-arylated thiophenes in good to excellent yields. A combination of the present C–H arylation and Hiyama coupling with the same NNC-pincer complex provides an efficient synthesis of unsymmetrical 2,5-thiophenes with catalyst loadings at mol ppm levels.

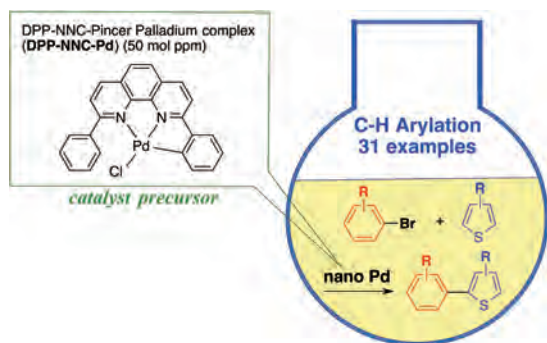


Figure 2. C–H Arylation of Thiophenes with Aryl Bromides by a Parts-per-Million Loading of a Palladium NNC-Pincer Complex.

2. A Convolutated Polyvinylpyridine-Palladium Catalyst for Suzuki-Miyaura Coupling and C–H Arylation²⁾

The development of highly active and reusable supported catalysts for Suzuki-Miyaura coupling and catalytic C–H arylation is important for fundamental and applied chemistry, with these reactions being used to produce medical compounds and functional materials. We found that a mesoporous composite made of a linear poly(4-vinylpyridine) and tetrachloropalladate acted as a dual-mode catalyst for a variety of cross-coupling reactions, with both Pd nanoparticles and a Pd complex catalyst being observed under different conditions. The polyvinylpyridine-palladium composite was readily prepared via the molecular convolution of poly(4-vinylpyridine) and sodium tetrachloropalladate to provide a hardly soluble polymer-metal composite. The Suzuki-Miyaura coupling and the C–H arylation of aryl chlorides and bromides with arylboronic acids, thiophenes, furans, benzene, and anisole proceeded in the presence of 0.004 mol% (40 mol ppm) to 1 mol% Pd to afford the corresponding coupling products in high yields. Furthermore, the catalyst was reused without an

appreciable loss of activity. Pharmaceutical compounds and functional materials were synthesized via the coupling reactions. N₂ gas adsorption/desorption analysis indicated that the catalyst had a mesoporous nature, which played a crucial role in the catalysis. In the Suzuki-Miyaura couplings, in situ generated palladium nanoparticles in the polymer matrix were catalytically active, while a polymeric Pd(II) complex was crucial in the C–H arylations. These catalytic species were investigated via XAFS, XPS, far-infrared absorption, and Raman spectroscopies, as well as DFT calculations.

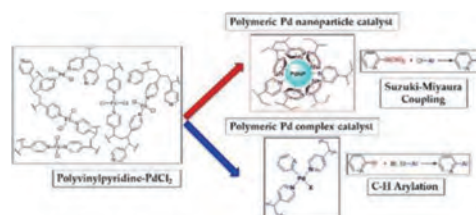


Figure 3. Polyvinylpyridine-Palladium Catalyst for Suzuki-Miyaura Coupling and C–H Arylation.

3. Synthesis of α -Tertiary Amines by the Ruthenium-Catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters³⁾

We demonstrated a ruthenium-catalyzed regioselective allylic amination of tertiary allylic esters with various amines using [Cp*Ru(CH₃CN)₃][PF₆]/5,5'-dimethyl-2,2'-bipyridine (5,5'-diMe-2,2'-bpy) and related ruthenium catalytic systems, and successfully obtained a diverse range of α -tertiary amines as single regioisomers. The present ruthenium catalytic system was effective for reactions with various types of amines.

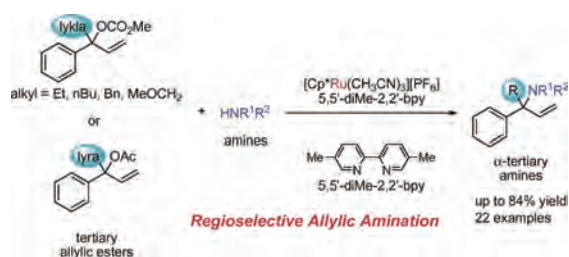


Figure 4. Ruthenium-catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters.

References

- 1) A. E. Purta, S. Ichii, A. Tazawa and Y. Uozumi, *Synlett* **31**, 1634–1638 (2020).
- 2) A. Ohno, T. Sato, T. Mase, Y. Uozumi and Y. M. A. Yamada, *Adv. Synth. Catal.* **362**, 4687–4698 (2020).
- 3) S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. Lett.* **49**, 645–647 (2020).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Keywords Synthetic Chemistry, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, “metal” has been frequently used as the activation center, and conformationally rigid catalyst framework has been preferably components for the catalyst design. To develop new type of molecular catalysis, we have focused on the use of hydrogen and halogen atom as activation unit, and have utilized non-covalent interactions as organizing forces of catalyst framework in the molecular design of catalyst, which had not received much attention until recently. We hope that our approach will open the new frontier in chiral organic molecules from chiral molecular chemistry to chiral molecular science.

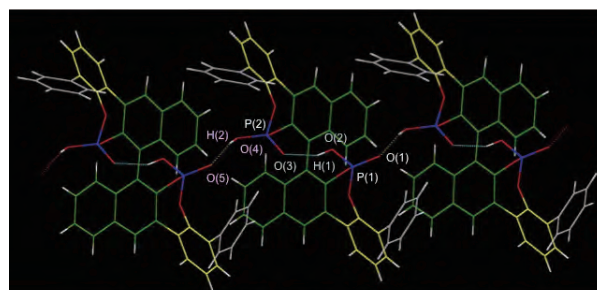


Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3-arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl-phenyl axis.

Selected Publications

- T. P. Yoon and E. N. Jacobsen, *Science* **299**, 1691–1693 (2003).
- N. Momiyama and H. Yamamoto, “Brønsted Acid Catalysis of Achiral Enamine for Regio- and Enantioselective Nitroso Aldol Synthesis,” *J. Am. Chem. Soc.* **127**, 1080–1081 (2005).
- N. Momiyama, H. Tabuse and M. Terada, “Chiral Phosphoric Acid-Governed Anti-Diastereoselective and Enantioselective Hetero-Diels–Alder Reaction of Glyoxylate,” *J. Am. Chem. Soc.* **131**, 12882–12883 (2009).
- N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, “Design of Chiral Bis-Phosphoric Acid Catalyst Derived from (*R*)-3,3'-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels–Alder Reaction of α,β -Unsaturated Aldehydes with Amidodienes,” *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
- N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, “Molecular Design of a Chiral Brønsted Acid with Two Different Acidic Sites: Regio-, Diastereo-, and Enantioselective Hetero-Diels–Alder Reaction of Azopyridine-carboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid–Monophosphoric Acid,” *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).

1. Brønsted Acid Catalyzed Asymmetric Rearrangement: Asymmetric Synthesis of Linear Homoallylic Amines

Allylation of imines with allylic metal reagents has been one of the most valuable tools to synthesize enantioenriched homoallylic amines. Due to the inherent nature of allylic metal reagent, however, regioselectivity has been a long-standing subject in this area. To develop the synthetic reaction for enantioenriched linear homoallylic amines, we discovered chirality transferred formal 1,3-rearrangement of ene-aldimines in the presence of Brønsted acid, and developed it as synthetic method for variety of enantioenriched linear homoallylic amines.¹⁾ Furthermore, we studied details of reaction mechanism and succeeded catalytic asymmetric version of this rearrangement.²⁾ On the basis of this study, catalytic asymmetric version of this reaction was developed.³⁾ To the best of our knowledge, our discovery is the first example of catalytic asymmetric methylene migration.

2. Design of Chiral Brønsted Acid Catalyst

Chiral Brønsted acid catalysis has been recognized as one of the useful tools in asymmetric synthesis. We have contributed to this area by focusing on the use of perfluoroaryls and C_1 -symmetric design.

Perfluorinated aryls have emerged as an exquisite class of motifs in the design of molecular catalysts, and their electronic and steric alterations lead to notable changes in the chemical yields and the stereoselectivities. We developed the perfluoroaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deliver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino-ene reaction using aldehydes and FmocNH₂.⁴⁾

We have developed (*R*)-3,3'-di(2-hydroxy-3-arylphenyl)binaphthol derived chiral bis-phosphoric acid which efficiently catalyzed enantioselective Diels–Alder reaction of acroleins with amidodienes.^{5,6)} We demonstrated that two phosphoric acid groups with individually different acidities can play distinct roles in catalyst behavior through hydrogen bonding interactions. Therefore, we developed a Brønsted acid with two different acidic sites, aryl phosphinic acid-phosphoric acid.⁷⁾ Furthermore, molecular design of a chiral Brønsted acid with two different acidic sites, chiral carboxylic acid-cyclic mono-phosphoric acid, was identified as a new and effective concept in asymmetric hetero-Diels–Alder reaction of 2-azopyridinoester with amidodienes.⁸⁾

3. Design of Catalysis with Halogen Bond for Carbon–Carbon Bond Forming Reactions

Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of the type R–X (X = Cl, Br, I) and Lewis bases LBs. It has been known

that strong halogen bonds are realized when “R” is highly electronegative substituents such as perfluorinated alkyl or aryl substituents. We recently developed synthetic methodology for perfluorinated aryl compounds and applied it for the development of chiral Brønsted acid catalysts. On the basis of our achievements, we have examined it to develop catalysis with halogen bond for carbon–carbon bond forming reactions.⁹⁾

We found that perfluorinated iodoaryls are able to catalyze the allylation reaction to *N*-activated heteroaromatics. On the basis of this discovery, a quantitative approach was studied using 4-substituted perfluorinated iodobenzene.¹⁰⁾ Examination of the electrostatic potential surfaces showed that substituent R groups significantly affected the charge density of iodine, fluorine, and carbon on the benzene ring. ¹⁹F NMR titrations were used to determine the binding constants *K* for chloride, and their catalytic activities were evaluated in the allylation reaction. We revealed that the log *K* and product yields were linearly correlated, and that they were dependent on the Hammett substituent parameter, σ_{meta} . This linear correlation provided a quantitative predictive model for both the binding constant and the reaction yield. Concomitantly, this efficiently permitted the development of a highly active anion-binding catalyst, namely 4-CNC₆F₄I. The catalytic activity of 4-CNC₆F₄I was established in the allylation and crotylation of silatrane reagents to *N*-activated isoquinolines.

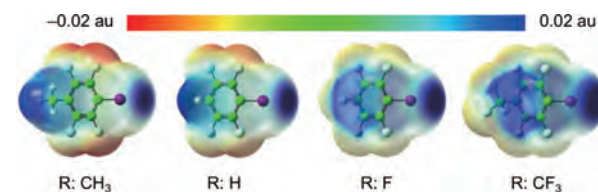


Figure 2. Molecular electrostatic potential surfaces of 4-RC₆F₄I (R: CH₃, H, F, and CF₃) at the M06-2X-D3/6-311+G(d,p)-SDD level of theory.

References

- 1) C. Jongwohan, Y. Honda, T. Suzuki, T. Fujinami, K. Adachi and N. Momiyama, *Org. Lett.* **21**, 4991–4995 (2019).
- 2) N. Momiyama, Y. Honda, T. Suzuki and C. Jongwohan, *Asian J. Org. Chem.* **10**, 2205–2212 (2021). [Invitation only] doi: 10.1002/ajoc.202100302
- 3) N. Momiyama *et al.*, submitted.
- 4) N. Momiyama, H. Okamoto, J. Kikuchi, T. Korenaga and M. Terada, *ACS Catal.* **6**, 1198–1204 (2016).
- 5) N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
- 6) N. Momiyama, K. Funayama, H. Noda, M. Yamanaka, N. Akasaka, S. Ishida, T. Iwamoto and M. Terada, *ACS Catal.* **6**, 949–956 (2016).
- 7) N. Momiyama, T. Narumi and M. Terada, *Chem. Commun.* **51**, 16976–16979 (2015).
- 8) N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamashiki, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).
- 9) N. Momiyama, *et al.*, Two communications & Two articles under revision; five manuscripts under preparation for submission.
- 10) N. Momiyama, A. Izumiseki and N. Ohtsuka, *ChemPlusChem* **6**, 913–919 (2021). [Invitation only, special issue for ISXB-4]

Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

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Keywords

Radical, Open-Shell Electronic States, Photonic-Electronic-Magnetic Properties

The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of its rarity and low chemical (photo-)stability. We have developed highly photostable luminescent organic radicals, PyBTM and its analogues, and investigated photofunctions attributed to their open-shell electronic states. We have discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence at RT with $\phi_{em} = 89\%$, which is exceptionally high in radicals, (ii) radical-doped crystals and radical-based coordination polymers exhibit drastic changes in the emission spectra by applying a magnetic field. These are the first demonstrations of magnetoluminescence in radicals, and are attributed to interplay between the spin and the luminescence. Our studies provide novel and unique concepts in molecular photonics,

electronics, and spintronics, and also bring innovative ideas in the development of light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

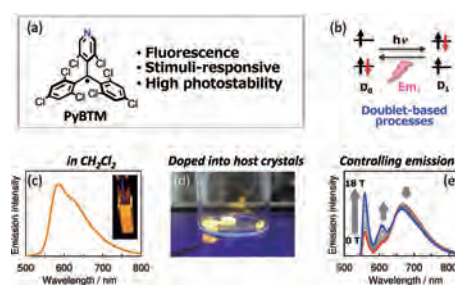


Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2 . (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, "An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice and Triangular Organic Radical," *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).
- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).

1. An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice Based on Triangular Radical

Two-dimensional (2D) open-shell coordination polymers (CPs) with honeycomb lattices have attracted growing interest because of the exotic electronic structures and physical properties derived from their structural topology. Employing organic radicals as building blocks is a promising approach to produce open-shell CPs. However, radical-based CPs with honeycomb lattices reported generally have low chemical stability or poor crystallinity. Accordingly, high crystallinity and persistence are in strong demand in this class of compounds. In this study, we developed a novel triangular organic radical tris(3,5-dichloro-4-pyridyl)methyl radical (trisPyM) possessing three pyridyl groups.¹⁾ trisPyM demonstrates photoluminescence ($\lambda_{\text{em}} = 700$ nm, $\phi_{\text{em}} = 0.85\%$, $\tau = 3.0$ ns in dichloromethane) and high photostability with its half-life upon UV irradiation 10000 times that of TTM, a conventional luminescent radical. Complexation of trisPyM with $\text{Zn}^{\text{II}}(\text{hfac})_2$ afforded single crystals of a novel 2D CP, trisZn, possessing a honeycomb lattice with graphene-like spin topology (Figure 2). The coordination structure of trisZn is stable under evacuation at 60 °C. trisZn exhibits photoluminescence below 79 K at $\lambda_{\text{em}} = 695$ nm. Importantly, trisZn displays magnetoluminescence below 20 K.²⁾ This is the first example showing magnetoluminescence as pure (*i.e.*, non-doped) radical compounds. Our results indicate that trisPyM can be a promising building block in the construction of a new class of 2D honeycomb CPs with spin-correlated novel photofunctions.

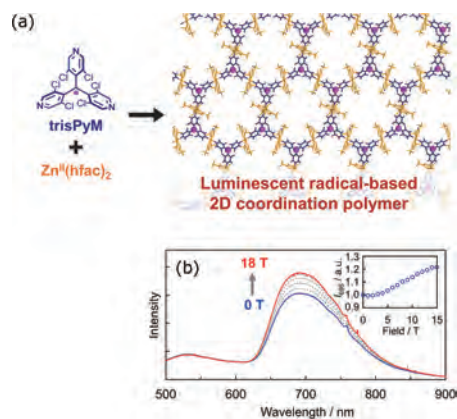


Figure 2. (a) Chemical structure of trisPyM and crystal structure of trisZn. (b) Emission spectra of trisZn at 4.2 K under a magnetic field.

2. Solid-State Room-Temperature Near-Infrared Photoluminescence of a Stable Organic Radical

Luminescent organic radicals have been shown to demonstrate unique emission properties in solvents or in host materials. On the other hand, the luminescent properties of radicals in the

fully aggregated pure solid state have rarely been investigated, especially at room temperature. In this study, a novel luminescent radical with a 3-pyridyl moiety, the (2,4-dichloro-3-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (metaPyBTM) was prepared and the optical properties were investigated in detail.³⁾ metaPyBTM exhibits distinct near-infrared photoluminescence in its crystalline state at room temperature, in spite of the fact that the electronic structure and photophysical properties in solution are similar to those of the analogues radicals. The solid-state luminescence properties of metaPyBTM are modulated strongly by temperature and the degree of aggregation. metaPyBTM in the moderately aggregated state displays magnetic-field responsive luminescence, magnetoluminescence, whereas no magnetic field effect was detected in the emission spectrum of purely crystalline metaPyBTM. These results suggest that controlling the manner of interactions between radicals is an important factor for achieving magnetoluminescence.

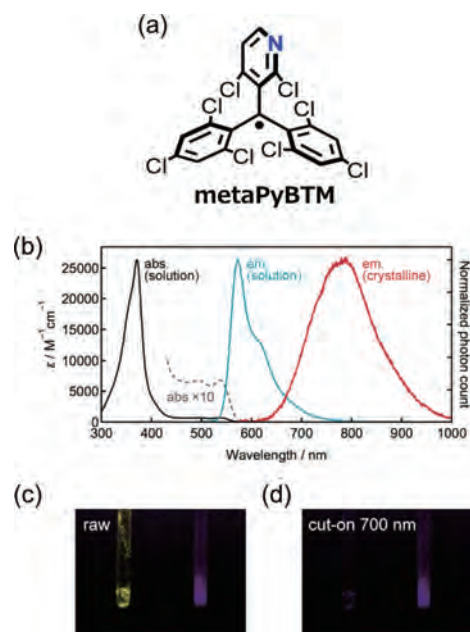


Figure 3. (a) Chemical structure of metaPyBTM. (b) Absorption and emission spectra of metaPyBTM in dichloromethane (black, pale blue) and in crystalline state (red). (c,d) Vis-NIR photographs of pure metaPyBTM (right) and metaPyBTM-doped α H-metaPyBTM crystals under UV light at $\lambda = 365$ nm with (d) and without (c) a longpass filter (cut-on: 700 nm). Photos were taken by BIZWORKS Yubaflex digital camera.

References

- 1) S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).
- 2) S. Kimura, R. Matsuoka, S. Kimura, H. Nishihara and T. Kusamoto, *J. Am. Chem. Soc.* **143**, 5610–5615 (2021).
- 3) R. Matsuoka, S. Kimura and T. Kusamoto, *ChemPhotoChem* **5**, 669–673 (2021).

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π -Conjugated Molecules, Molecular Topology, 3D Network Polymer

Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights.

To achieve our purpose, this group will start electron-diffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~ 0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultra-small crystals (1 μm or less). There are many fields such as covalent organic crystals with a three-dimensional structure

and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

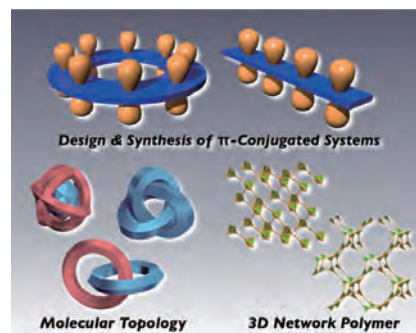


Figure 1. Design and synthesis of π -conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, "Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes," *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).
- K. Y. Cheung, K. Watanabe, Y. Segawa and K. Itami, "Synthesis of a Zigzag Carbon Nanobelt," *Nat. Chem.* **13**, 255–259 (2021).
- Y. Saito, K. Yamanoue, Y. Segawa and K. Itami, "Selective Transformation of Strychnine and 1,2-Disubstituted Benzenes by C–H Borylation," *Chem* **6**, 985–993 (2020).
- Y. Segawa, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," *Acc. Chem. Res.* **52**, 2760–2767 (2019).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).

1. Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes

The layered structures of graphite and related nanographene molecules play a key role in their physical and electronic properties. The well-ordered molecular alignment of nanographenes and its structural determination are of interest in order to gain insight into a variety of carbon materials. It is well known that the one-dimensional (1D) assembly of planar nanographenes can be achieved by introducing suitable peripheral substituents that tune solubility. The 1D assembly of bowl-shaped nanographenes was also achieved by convex-concave π - π stacking along with non-covalent interactions. However, the stacking modes of negatively curved nanographenes remain unclear, owing to the lack of suitable nanographene molecules.

We developed the synthesis and 1D self-assembly of a newly designed nanographene **1-H** ($C_{68}H_{28}$), a negatively curved nanographene with 12 carbon atoms fewer than WNG (Figure 2a).¹⁾ Serendipitously, we discovered that **1-H** self-assembles in various organic solvents and works as a highly efficient gelator that forms organic gels at concentrations of <1 wt% (Figure 2b). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements confirm that **1-H** forms fibers with diameters of ~ 2.8 nm. The presence of efficient π - π interactions in the fiber structures is supported by a bathochromic shift in the fluorescence spectrum of the gel state relative to that of dilute solutions of **1-H**. Finally, using three-dimensional electron diffraction crystallography, the double-helix π - π stacking mode of **1-H** in the supramolecular nanofiber was revealed (Figure 2c).

Based on this discovery and its revelation of a new guiding principle in supramolecular self-assembly, we expect that a number of negatively curved nanographenes can be developed for new applications in materials science and biology. Moreover, this work not only reports the discovery of an all- sp^2 -carbon supramolecular π -organogelator with negative curvature, but it also showcases the power of 3D electron diffraction crystallography for the structural determination of submicrometer-sized hydrocarbon molecular assemblies.

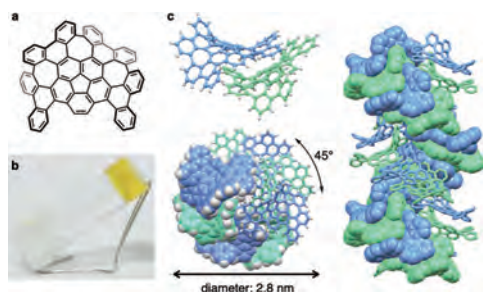


Figure 2. The negatively curved nanographene (**1-H**) that forms double-helix nanofibers. (a) Chemical structure of **1-H**. (b) Photo of organogel made of dichloromethane with 0.3 wt% of **1-H**. (c) The double-helix packing structure of **1-H** revealed by microcrystal electron diffraction crystallography (MicroED).

2. Theoretical Studies on the Strain Energy of Helicene-Containing Carbon Nanobelts

Carbon nanobelts (CNBs), the sidewall segment molecules of carbon nanotubes (CNTs), have attracted growing attention owing to their radial π -conjugation, strain-induced reactivity and potential applications in template CNT synthesis. Various CNB structures have been proposed and investigated by both theoretical and synthetic organic chemists. Recently, our group synthesized armchair-type (n,n) CNB (**A_n**, Figure 3a) and a zigzag-type (18,0)CNB. Apart from these known CNBs, other CNBs with more complex structures can also be designed by cutting the CNTs differently. CNBs with helicene structures (**B_n**–**E_n**, Figure 3b) are the representative examples of these complex structures, and the structural properties of such unexplored CNBs have been of interest.

To estimate the feasibility of synthesizing strained belt-shaped compounds, the calculation of strain energy (SE) is effective. While homodesmotic reaction method using reference molecules is generally used for strained molecules, we previously found that conventional homodesmotic reactions using small reference molecules could not be applied to CNBs.

Here we have successfully estimated the strain energies of CNBs containing helicene moieties.²⁾ Through the calculation of CNB **B_n**, we revealed that our previously reported method is not applicable to helicene-containing CNBs. The newly developed method, combining the conventional homodesmotic reactions and linear regression analysis, was successful for the determination of the strain energies of CNBs **B_n** and **C_n** that have helicene moieties in their side chains. By changing the reference molecules, the strain energies of CNBs with helicene structures in the main chains (**D_n** and **E_n**) were also determined.

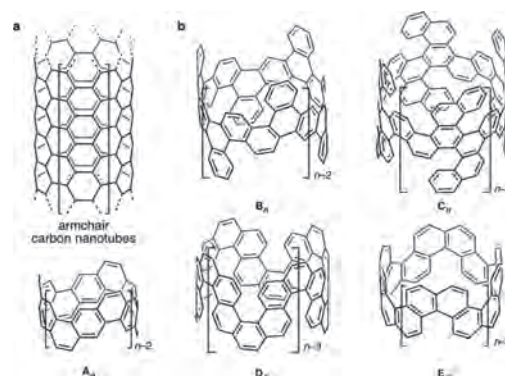


Figure 3. (a) Structures of armchair CNTs and CNBs (**A_n**). (b) CNBs containing helicene structures (**B_n**–**E_n**).

References

- 1) K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).
- 2) K. Watanabe, Y. Segawa and K. Itami, *Chem. Commun.* **56**, 15044–15047 (2020).

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Visiting Professors



Visiting Professor
FUKAZAWA, Aiko (from *Kyoto University*)

Renaissance of Nonbenzenoid π -Conjugated Systems toward Functional Materials

The work of our group has focused on exploring functional organic compounds with unusual with superb optical and/or electronic properties, based on the molecular designs of novel π -conjugated scaffolds as well as unusual functional groups. In particular, we have recently proposed a rational design of stable yet unusual π -conjugated systems based on the characteristics of nonbenzenoid hydrocarbons, *i.e.*, dehydroannulenes, non-alternant hydrocarbons, and fulvalenes, by annulation of weakly aromatic (hetero)arenes. In this year, we have succeeded in synthesizing several thiophene-fused antiaromatic π -systems that exhibit high thermal stability even without bearing bulky substituents while retaining pronounced antiaromatic character. Moreover, we have recently succeeded in synthesizing the fulvalene-based π -conjugated oligomers that exhibit exceptional electron-accepting character as well as the robustness toward multi-electron reduction.



Visiting Professor
WATANABE, Rikiya (from *RIKEN*)

Single Molecule Physiology

Our study aims to understand cellular functions using a bottom-up approach from the single molecule level. To achieve this, we are attempting to elucidate the mechanism by which individual biomolecules or their networks function in a precise manner, by developing novel single-molecule techniques using multidisciplinary approaches, including biophysics, bioMEMS, and chemical biology. In addition, we are developing a methodology to investigate correlations between genetic mutations, dysfunctions, and diseases with single molecule sensitivity, which would provide new insights for biological as well as pharmaceutical studies. Notably, last year, we developed a novel technology that can identify new coronavirus, SARS-CoV-2, at the single molecule level, enabling the world's fastest quantitative detection for early diagnosis.



Visiting Associate Professor
UEDA, Akira (from *Kumamoto University*)

Development of Purely Organic Molecular Materials with Three-Dimensional Electronic Structure

Design and synthesis of novel molecular materials have been a central issue for the development of molecular science. Our group has recently succeeded in the development of a new type of molecular conductor crystal composed of a zwitterionic neutral radical with a partially charge-transferred structure. Single crystal X-ray analysis reveals that this material has a peculiar electronic structure where two-dimensional conducting layers are electronically coupled to each other through the intramolecular interaction of the partially charge-transferred zwitterionic neutral radical. Therefore, one can say that this material has a three-dimensional-like electronic structure different from one- or two-dimensional ones in the conventional molecular conductors. Interestingly, the low-temperature structural analysis and physical property measurements suggest that this material undergoes a phase transition from the charge-uniform state to a three-dimensionally charge-ordered state.

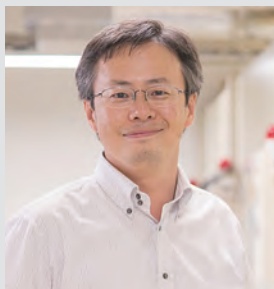
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

The mission of CIMoS is to analyze molecular systems in nature to find the logic behind the sharing and control of information between the different spatiotemporal hierarchies, with the ultimate goal of creating novel molecular systems on the basis of these findings.

Biological Rhythm and Dynamics through Chemistry

Research Center of Integrative Molecular Systems Division of Trans-Hierarchical Molecular Systems



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Education

1997 B.E. Kyoto University
1999 M.E. Kyoto University
2002 Ph.D. Kyoto University

Professional Employment

2001 JSPS Research Fellow
2002 JSPS Postdoctoral Fellow
2003 RIKEN Special Postdoctoral Researcher
2005 JST-PRESTO Researcher
2008 Junior Associate Professor, Nagoya University
2011 Associate Professor, Nagoya University
2012 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards

2016 The 13th (FY2016) JSPS PRIZE
2008 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize
2007 Young Scientist Prize, The Biophysical Society of Japan
2006 SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
2002 The Protein Society Annual Poster Board Award

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OUYANG, Dongyan
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SIMON, Damien
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WASHIO, Midori
TAKAYA, Mari
SUGISAKA, Kanae
WADA, Kotoe
Secretary
SUZUKI, Hiroko

Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

Living organisms on Earth evolved over time to adapt to daily environmental alterations, and eventually acquired endogenous time-measuring (biological clock) systems. Various daily activities that we perform subconsciously are controlled by the biological clock systems sharing three characteristics. First, the autonomic rhythm repeats with an approximately 24-hour (circadian) cycle (self-sustainment). Second, the period is unaffected by temperature (temperature compensation). Third, the phase of the clock is synchronized with that of the outer world in response to external stimuli (synchronization). We seek to explain these three characteristics, and consider the biological clock system of cyanobacteria to be an ideal experimental model.

The major reason that cyanobacteria are considered to be the ideal experimental model is that the core oscillator that possesses the three characteristics of the clock can be easily reconstructed within a test tube. When mixing the three clock proteins KaiA, KaiB, and KaiC with ATP, the structure and enzyme activity of KaiC change rhythmically during a circadian cycle. Taking advantage of this test tube experiment, we used an approach combining biology, chemistry, and physics

to elucidate the means by which the clock system extends from the cellular to atomic levels.

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC reveals the rhythm of autophosphorylation and dephosphorylation; however, the cycle of this rhythm depends on the ATPase activity of KaiC independent of KaiA or KaiB. For example, when the ATPase activity of KaiC doubles as a result of amino acid mutations, the frequencies of both the *in vitro* oscillator and the intracellular rhythm also double (the cycle period is reduced to half). This mysterious characteristic is called a transmurial hierarchy, in which the cycle (frequency) and even the temperature compensation both *in vitro* and *in vivo* are greatly affected (controlled) by the function and structure of KaiC.

How are the circadian activities and temperature compensation features encoded in KaiC and then decoded from it to propagate rhythms at the cellular level? We are committed to better understanding biological clocks and other dynamic systems through the chemistry of circadian **rhythm, structure**, and evolutionary **diversity**.

Selected Publications

- D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
- A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
- A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. Structure: Reasons for Seeking Structure and Dynamics of Circadian Clock Components in Cyanobacteria¹⁻³⁾

A great deal of effort has been devoted to characterizing structural changes in the clock proteins along the circadian reaction coordinate.¹⁾ However, little is known about the mechanism driving the circadian cycle, even for the simple cyanobacterial protein KaiC that has ATPase and dual phosphorylation sites in its N-terminal C1 and C-terminal C2 domains, respectively. Nearly all KaiC structures reported to date share a nearly identical structure, and they do not appear to be suggestive enough to explain the determinants of circadian period length and its temperature compensation. We are studying the structural and dynamical origins in KaiC using high-resolution x-ray crystallography²⁾ and quasielastic neutron scattering,³⁾ respectively.

2. Rhythm: Cross-Scale Analysis of Cyanobacterial Circadian Clock System³⁻⁵⁾

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations and also it is temperature compensated. This unique property has inspired us to develop an ATPase-based screening for KaiC clock mutants⁴⁾ giving short, long, and/or temperature-dependent periods. A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 1). Using the developed device, we are screening a number of temperature-dependent mutants of KaiC.³⁾

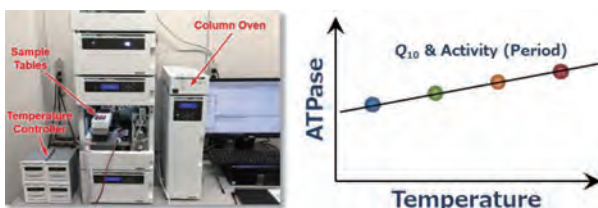


Figure 1. Development of a quick ATPase assay system.

We also collaborated with Drs. Ito-Miwa and Kondo (Nagoya University) to identify a series of KaiC mutations altering circadian periods dramatically, from 0.6 to 6.6 d.⁵⁾

3. beyond Evolutionary Diversity⁶⁾

In the presence of KaiA and KaiB, the ATPase activity of KaiC oscillates on a 24-hour cycle. KaiC is not capable of maintaining a stable rhythm on its own, but its activity was

observed to fluctuate with reduced amplitude over time (Figure 2A). We have identified a signal component that is similar to damped oscillation, and propose that it encodes the specific frequency, equivalent to a 24-hour cycle.¹⁾

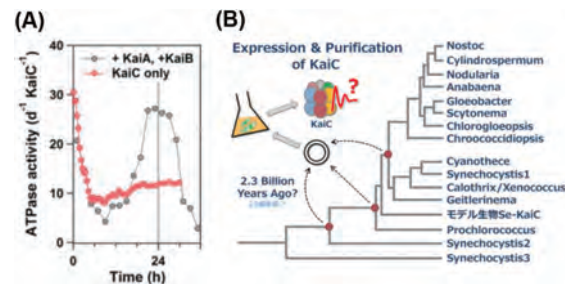


Figure 2. Damped oscillation of KaiC ATPase activity (A) and evolutionary diversity of cyanobacteria (B).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.⁶⁾ Furthermore, some KaiA and KaiB genes are missing in several strains of cyanobacteria. This is understandable to some extent if KaiC possesses the specific frequency. Given our current understanding of this phenomenon, *what specific frequencies are possessed by KaiC homologues in other species and ancestral cyanobacteria?* (Figure 2B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS⁷⁾

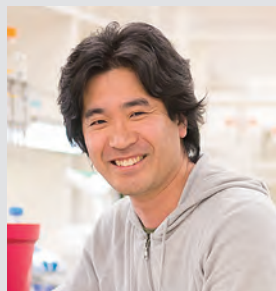
We have supported SAXS users so that they can complete experiments smoothly and publish their results.⁷⁾

References

- 1) S. Akiyama, *Circadian Rhythms in Bacteria and Microbiomes*, 138–145 (2021).
- 2) Y. Furuike, A. Mukaiyama, D. Ouyang, K. Ito-Miwa, D. Simon, E. Yamashita, T. Kondo and S. Akiyama, *bioRxiv* doi: 10.1101/2021.08.30.457330 (2021).
- 3) Y. Furuike, D. Ouyang, T. Tominaga, T. Matsuo, A. Mukaiyama, Y. Kawakita, S. Fujiwara and S. Akiyama, *bioRxiv* doi: 10.1101/2021.08.20.457041 (2021).
- 4) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
- 5) K. Ito-Miwa, Y. Furuike, S. Akiyama and T. Kondo, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 20926–20931 (2020). doi: org/10.1073/pnas.2005496117
- 6) A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
- 7) M. Okumura, S. Kanemura, M. Matsusaki, Y. H. Lee, S. Akiyama and K. Inaba, *Structure* **29**, 1–14 (2021).

Protein Design Using Computational and Experimental Approaches

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Education

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2006 Postdoctoral Fellow, Kobe University
2007 Postdoctoral Fellow, Kyoto University
2007 JSPS Postdoctoral Fellow for Research Abroad
2009 Postdoctoral Fellow, University of Washington
2014 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2014 JST-PRESTO Researcher (additional post) (–2017)
2018 Associate Professor, Exploratory Research Center on Life and Living Systems (EXCELLS)

Awards

2013 Young Scientist Award, The 13th Annual Meeting of the Protein Science Society of Japan
2013 Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan
2018 Morino Foundation for Molecular Science

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KOBAYASHI, Naoya
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MITSUMOTO, Masaya
KAIDA, Shingo
Secretary
SUZUKI, Hiroko

Keywords

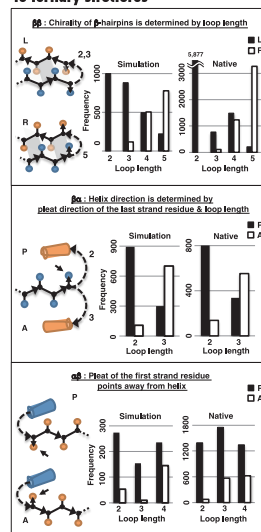
Protein Design for Structure and Function, Protein Folding, Structural Biology

Protein molecules spontaneously fold into unique three-dimensional structures specified by their amino acid sequences from random coils to carry out their functions. Many of protein studies have been performed by analyzing naturally occurring proteins. However, it is difficult to reach fundamental working principles of protein molecules only by analyzing naturally occurring proteins, since they evolved in their particular environments spending billions of years. In our lab, we explore the principles by computationally designing protein molecules completely from scratch and experimentally assessing how they behave.

Protein design holds promise for applications ranging from catalysis to therapeutics. There has been considerable recent progress in computationally designing new proteins. Many of protein design studies have been conducted using naturally occurring protein structures as design scaffolds. However, since naturally occurring proteins have evolutionally optimized their structures for their functions, implementing new functions into the structures of naturally occurring proteins is difficult for most of cases. Rational methods for building any arbitrary protein structures completely from scratch provide us opportunities for creating new functional proteins. In our lab, we tackle to establish theories and tech-

nologies for designing any arbitrary protein structures precisely from scratch. The established methods will open up an avenue of rational design for novel functional proteins that will contribute to industry and therapeutics.

Rules relating local backbone structures to tertiary structures



Selected Publications

- N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, "Principles for Designing Ideal Protein Structures," *Nature* **491**, 222–227 (2012).
- Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T.

Montelione and D. Baker*, "Control over Overall Shape and Size in De Novo Designed Proteins," *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).

1. Robust Folding of a De Novo Designed Ideal Protein Even with Most of the Core Mutated to Valine

De novo designed ideal proteins, which are stabilized completely consistent local and non-local interactions, exhibit a remarkable property of extremely high thermal stability, compared with naturally occurring proteins. Whereas non-local interactions such as tight hydrophobic core packing have been traditionally considered to be crucial for protein folding and stability, the rules suggest the importance of local backbone structures in protein folding. We studied the robustness of folding of de novo designed proteins to the reduction of the hydrophobic core, by extensive mutation of large hydrophobic residues (Leu, Ile) to smaller ones (Val) for one of the designs. Surprisingly, even after 10-residue mutations from all of Leu and Ile to Val, a mutant with most of the core filled with Val was found to not be a molten globule and fold into the same backbone structure as the original design, with high stability. These results highlight the significance of local backbone structures for the folding ability and high thermal stability of designed proteins.

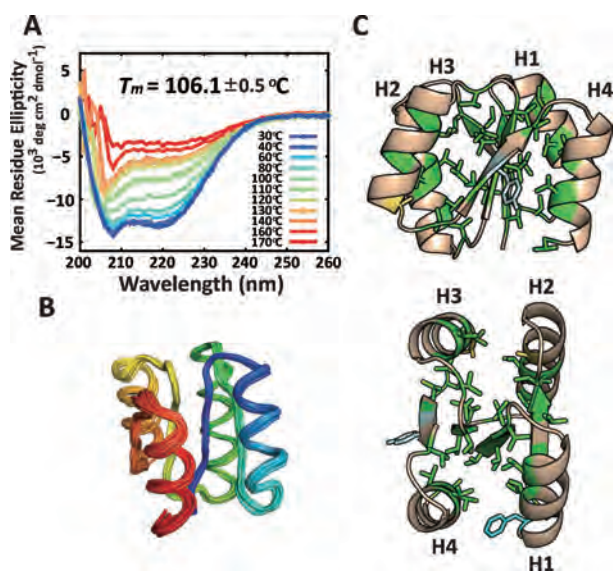


Figure 1. Experimental characterization of the designed protein with most of the core mutated to Val. (A) The far-UV CD spectra at various temperatures. (B) NMR structure. (C) Hydrophobic core side chains are shown in stick. Residues colored in green are valine.

Awards

KOSUGI, Takahiro; The Young Scientist Excellence Award of Protein Science Society of Japan (PSSJ) (2021).

MITSUMOTO, Masaya; The Poster Excellence Award of the 1st Molecular Engine Workshop (2021).

MITSUMOTO, Masaya; The Poster Award of Protein Science Society of Japan (PSSJ) (2021).

KAIDA, Shingo; The Poster Award of Protein Science Society of Japan (PSSJ) (2021).

2. Role of Backbone Strain in De Novo Design of Complex α/β Protein Structures

We have elucidated principles for designing ideal proteins with completely consistent local and non-local interactions which have enabled the design of a wide range of new α/β -proteins with four or fewer β -strands. The principles relate local backbone structures to supersecondary-structure packing arrangements of α -helices and β -strands. Here, we test the generality of the principles by employing them to design larger proteins with five- and six-stranded β -sheets flanked by α -helices. The designs are monomeric in solution with high thermal stability, and the nuclear magnetic resonance (NMR) structure of one was close to the design model, but for two others the order of strands in the β -sheet was swapped. Investigation into the origins of this strand swapping suggests that the global structures of the design models are more strained than the NMR structures. We incorporated explicit consideration of global backbone strain into our design methodology, and succeeded in designing proteins with the original unswapped strand arrangements. These results illustrate the value of experimental structure determination in guiding improvement of de novo design, and the importance of consistency between local, supersecondary, and global tertiary interactions in determining protein topology. The augmented set of principles should inform the design of larger functional proteins.

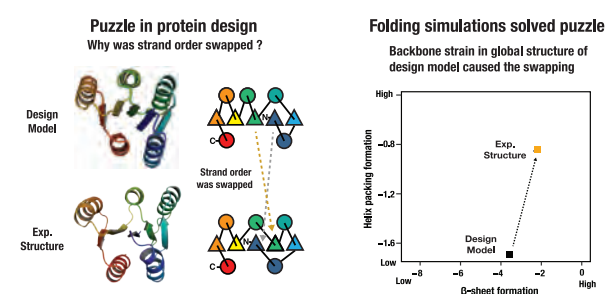


Figure 2. (left) The strand order swapping in de novo design of larger α/β -proteins has been a long-standing problem for the research team. (right) Backbone ensembles generated from folding simulations identified that backbone strain caused the strand swapping.

References

- 1) R. Koga*, M. Yamamoto, T. Kosugi, N. Kobayashi, T. Sugiki, T. Fujiwara and N. Koga*, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 31149–31156 (2020).
- 2) N. Koga*, R. Koga, G. Liu, J. Castellanos, G. T. Montelione and D. Baker*, *Nat. Commun.* **12**, 3921 (12 pages) (2021).

Elucidation of Function, Structure, and Dynamics of Condensed-Phase Molecular Systems by Advanced Ultrafast Laser Spectroscopy

Research Center of Integrative Molecular Systems Division of Trans-Hierarchical Molecular Systems



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Education

2007 B.S. Tokyo Institute of Technology
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Professional Employment

2013 Special Postdoctoral Researcher, RIKEN
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2020 Associate Professor, Institute for Molecular Science
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Awards

2017 The 8th Research Incentive Award of RIKEN
2017 The Spectroscopical Society of Japan Award for Young Scientists
2019 RSC PCCP Prize
2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Award
2020 Morino Foundation for Molecular Science
2020 The 13th Young Scientist Awards of the Japan Society for Molecular Science
2021 The 13th Inoue Science Research Award

Member

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YONEDA, Yusuke
Secretary
ITO, Atsuko

Keywords Ultrafast Spectroscopy, Nonlinear Spectroscopy, Chemical Reaction Dynamics

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study the chemical reaction dynamics of the condensed-phase molecules. In particular, we focus on exploiting unique methodologies based on sub-10-fs pulses (*e.g.*, time-domain impulsive vibrational spectroscopy and multidimensional spectroscopy) and tracking molecular dynamics from electronic and structural viewpoints throughout the chemical reaction with exquisite temporal resolution. We also develop a novel methodology and light source to probe ultrafast dynamics of single molecules in the condensed phase at room temperature, with the aim to understand chemical reaction dynamics at the single-molecule level. Our particular interest rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as proteins,

molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our advanced spectroscopic approaches, we aim to establish a new avenue for the study of chemical reaction dynamics.

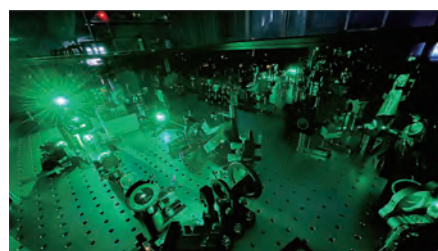


Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi and T. Tahara, "Tracking Ultrafast Structural Dynamics by Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).
- H. Kuramochi, S. Takeuchi, H. Kamikubo, M. Kataoka and T. Tahara, "Fifth-Order Time-Domain Raman Spectroscopy of Photoactive Yellow Protein for Visualizing Vibrational Coupling in Its Excited State," *Sci. Adv.* **5**, eaau4490 (2019).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photoreception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
- T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, "Role of Coherent Low-Frequency Motion in Excited-State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy," *J. Am. Chem. Soc.* **138**, 3942–3945 (2016).
- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* **87**, 043107 (2016).

1. Tracking Ultrafast Dynamics with Time-Domain Raman Spectroscopy

In traditional Raman spectroscopy, narrow-band light is irradiated on a sample, and its inelastic scattering, *i.e.*, Raman scattering, is detected. The energy difference between the Raman scattering and the incident light corresponds to the vibrational energy of the molecule, providing the Raman spectrum that contains rich information about the molecular-level properties of the materials. On the other hand, by using ultrashort optical pulses, it is possible to induce Raman-active coherent nuclear motion of the molecule and to observe the molecular vibration in real time. This time-domain Raman measurement can be combined with femtosecond photoexcitation triggering chemical changes, which enables tracking ultrafast structural dynamics in a form of “time-resolved” time-domain Raman spectroscopy, also known as time-resolved impulsive stimulated Raman spectroscopy (Figure 2). Through our extensive efforts, time-resolved impulsive stimulated Raman spectroscopy now realizes high sensitivity and a wide detection frequency window from THz to 3000 cm^{-1} , and has seen success in unveiling the molecular mechanisms underlying the efficient functions of complex molecular systems. We recently overviewed its application to the study on femtosecond structural dynamics of complex molecular systems such as photoresponsive proteins and molecular assemblies,¹⁾ and reported another application to the ultrafast structural dynamics of a fluorescent protein.²⁾ In the latter, we studied excited-state proton transfer (ESPT) dynamics of LSSmOrange, which has been extensively used for multi-color bioimaging owing to its large Stokes shift. The chromophore of LSSmOrange takes a neutral form in the ground state, but the bright orange fluorescence is emitted from the anionic form that is generated through ESPT upon photoexcitation. This ESPT has been known to proceed in a biphasic manner, but its origin has been unknown. We investigated the chromophore structural dynamics during ESPT and unveiled that the chromophore exists in both *trans* and *cis* forms in the ground state, and they are simultaneously photoexcited and undergo ESPT in parallel with significantly different time scales.

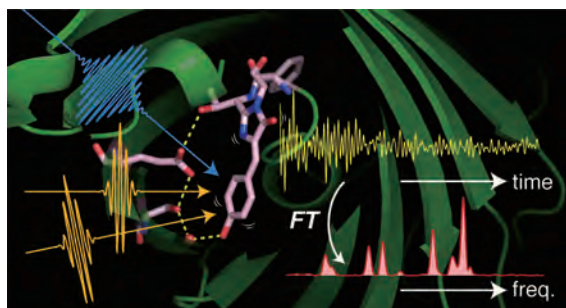


Figure 2. Schematic illustration of time-resolved time-domain Raman spectroscopy. Reprinted with permission from ref. 1. Copyright 2021 American Chemical Society.

2. Generation of Sub-10-fs Pulses with Ultrabroadband Spectral Coverage

Electronic/vibrational coherence has been used as a probe to gain detailed insights into the chemical reaction dynamics. Moreover, it has recently attracted tremendous interest as a control knob for directing and thus enhancing chemical reactions in the desired way. Observing and manipulating such coherences of the condensed phase polyatomic molecules inevitably require extremely short pulses with broad spectral coverage to monitor relevant electronic transitions thoroughly. Nevertheless, generating such ultrashort pulses has been primarily limited in the visible spectral region from the viewpoint of spectroscopic applications, where long-term high stability is required. We developed light sources to generate highly stable sub-10-fs pulses in a broad spectral coverage from UV to NIR. The light source is based on a Yb:KGW regenerative amplifier. Through various nonlinear optical processes such as optical parametric amplification, self-phase modulation, and subsequent sum-frequency mixing, we generate pulses tunable from 300–1400 nm with bandwidths that support the pulse duration well below 10 fs at Fourier transform limit, as shown in Figure 3. We compensate group delay dispersion of these pulses by a combination of chirped mirrors and a pulse shaper, and the intensity profiles of the compressed pulses retrieved from Frequency-Resolved Optical Gating (FROG) measurement show that the compressed pulses have a pulse duration as short as 4.5 fs. Applications of these pulses to ultrafast spectroscopy of functional molecules are now in progress.

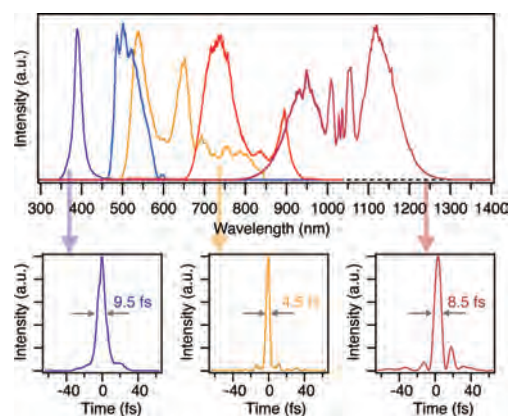


Figure 3. (Top) Typical spectra of the broadband pulses that support Fourier transform limit pulse duration of <10 fs. (Bottom) Intensity profiles of the compressed pulses retrieved from the FROG data.

References

- 1) H. Kuramochi and T. Tahara, *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
- 2) P. Kumar, E. Fron, H. Hosoi, H. Kuramochi, S. Takeuchi, H. Mizuno and T. Tahara, *J. Phys. Chem. Lett.* **12**, 7466–7473 (2021).

Awards

KURAMOCHI, Hikaru; The 13th Inoue Science Research Award (2021).

KURAMOCHI, Hikaru; The 13th Young Scientist Awards of the Japan Society for Molecular Science (2020).

Open up Future Electronics by Organic Molecules

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Education

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Professional Employment

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1999 Special Postdoctoral Fellow, RIKEN
2000 Research Scientist, RIKEN
2007 Senior Research Scientist, RIKEN
2012 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards

2009 RSC Publishing CrystEngComm Prize
2009 Young Scientist Awards, Japan Society for Molecular Science
2010 RIKEN-ASI Award for the Young Scientist
2019 The CSJ Award for Creative Work
2020 NAGAI Foundation for Science & Technology Academic Award

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ISHIKAWA, Yuko

Keywords

Organic Mott Insulator, Field Effect Transistors, Organic Spintronics

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Our group focuses on the development of organic electronics in the next era by providing new mechanism and concepts of the device operation and fabrication. For example, an electronic phase transition is utilized for the ON/OFF switching of our field-effect-transistor (FET). This special FET is called an organic Mott-FET, where the conduction electrons in the organic semiconductor are solidified at the OFF state because of Coulomb repulsion among carriers. In the operation, these solidified electrons can be melted by applying a gate voltage, and show an insulator-to-metal transition so-called Mott-transition to be switched to the ON state. Because of this phase transition, a large electric response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. In addition to this high performance, the Mott-FET is interesting in terms of superconductivity. Because the Mott-transition sometimes accompanies superconducting phase in between metal and insulator, modulation of gate electric field at low temperature may induce superconductivity. In fact, we have achieved first example of field-induced superconductivity in an organic FET. By combining a strain effect that can tune the bandwidth, this type of electric-field-induced superconducting transition can

be utilized for mapping the phase diagram around the Mott-insulator as shown in Figure 1.

Another approach to the future electronics is the development of spintronic devices based on chirality of organic material. We aim to implement chirality-induced spin selectivity (CISS) effect into molecular devices that can generate spin-polarized current. This type of device is expected to realize spintronics devices without magnet or topological insulator.

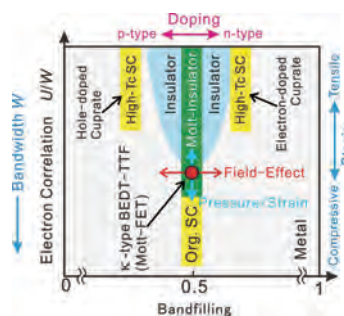


Figure 1. Phase diagram surrounding a Mott-insulator. SC denotes superconductor, while U and W are on-site Coulomb repulsion and bandwidth, respectively.

Selected Publications

- H. M. Yamamoto, "Phase-Transition Transistor Based on Organic Mott Insulators," *Bull. Chem. Soc. Jpn.* **94**, 2505–2539 (2021).
- Y. Kawasugi, K. Seki, S. Tajima, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Two-Dimensional Ground-State Mapping of a Mott-Hubbard System in a Flexible Field-Effect Device," *Sci. Adv.* **5**, eaav7282 (9 pages) (2019).
- M. Suda, Y. Thathong, V. Promarak, H. Kojima, M. Nakamura, T.

Shiraogawa, M. Ehara and H. M. Yamamoto, "Light-Driven Molecular Switch for Reconfigurable Spin Filters," *Nat. Commun.* **10**, 2455 (7 pages) (2019).

- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).

1. Current-Induced Spin-Polarization in a Chiral Crystal CrNb_3S_6 ^{1,2)}

CISS effect has remarkable ability which generates highly polarized spin current even with light element molecules. However, its extension to inorganic chiral materials has not been well investigated. Moreover, detection of CISS effect in metals that show ohmic response is quite interesting because one can discuss the CISS-based spin polarization in terms of band theory if metallic CISS effect in linear response regime is observed. So far, however, CISS experiments have been investigated only in tunnelling conduction regime.

We detected CISS-based spin transport phenomena in a monoaxial chiral dichalcogenide CrNb_3S_6 . This material has chiral structure and metallic conduction, so that we could perform CISS experiments with metallic conduction regime. Spin polarization was detected in this chiral bulk crystal under a charge current flowing along the principal c axis at room temperature without magnetic field. The detection was made by an inverse spin Hall signal which is induced on the tungsten electrode that absorbs polarized spin from the chiral crystal. An inverse response was also observed when applying the charge current into the tungsten electrode, which implied an inverse CISS effect. The signal sign reversed in the device with the opposite chirality, which is consistent with the symmetry required for CISS effect. Furthermore, the spin signals were found over micrometer length scale in a nonlocal configuration. Such a robust generation and protection of the spin-polarized state can be discussed based on a one-dimensional model with an antisymmetric spin-orbit coupling.

In addition to the above experiments, we also detected bulk magnetization generated by applying electric current to the crystal using SQUID magnetometer (Figure 2). When the current amplitude was swept from negative to positive, the current-induced magnetization changed linearly. Directly detecting such magnetization by magnetometry enables one to estimate the number of spin-polarized electrons. Using this

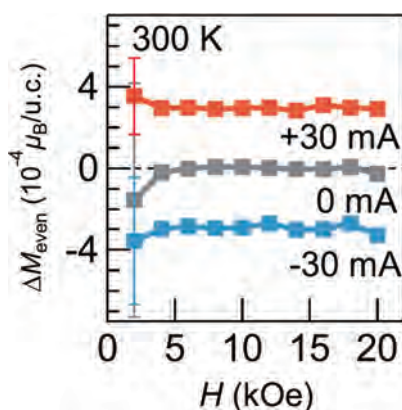


Figure 2. Detection of spin polarization in a chiral metal CrNb_3S_6 . By applying electrical current, electron spins are polarized along the current direction by CISS effect. The amplitude of the magnetization is irrelevant to the applied magnetic field, which strongly supports the current-induced nature of this magnetization.

number, we evaluated the spin polarization rate within the framework of Boltzmann's equation and found that spin polarization generated by CISS effect was enhanced by 10^5 times inside this material. It seemed that effective magnetic field generated by CISS could reach 10^3 T at high current density, which again confirmed the robustness of CISS effect. We also observed that the current-induced magnetization increased in the vicinity of the phase boundary between paramagnetic and forced ferromagnetic phases, which could be attributed to the spin fluctuation associated with the phase transition. (SQUID = superconducting quantum interference device)

2. Spin Current Generation in a Chiral Organic Superconductor

Although centrosymmetric s - and d -wave superconductors are in a spin singlet state, a superconductor with broken mirror symmetry is expected to show spin triplet state, according to a theory developed by Edelstein.³⁾ This means spin polarization can be generated by applying supercurrent in a chiral superconductor, whose magnetization direction depending on the lattice symmetry has been recently calculated by group theory.⁴⁾ We have tested this idea by employing κ -(BEDT-TTF)₂Cu(NCS)₂ (hereafter, κ -NCS) which is an organic superconductor with chiral and polar crystal lattice. The space group of this crystal is $P2_1$, and its handedness is defined by the relative arrangement between the anionic $\text{Cu}(\text{NCS})_2$ and cationic BEDT-TTF. This handedness can be experimentally determined by X-ray diffraction or circular dichroism. After confirming pure enantiomeric lattice system, a thin crystal of κ -NCS has been laminated onto a resin substrate with pre-patterned gold and nickel electrodes. At temperature lower than superconducting T_c , an electrical current was applied to induce spin magnetization. The spin polarization accumulated at the interface between κ -NCS and the magnetic electrode was detected as a voltage that is dependent on the magnetic field. By measuring the angle dependency of this magneto-voltaic signal, the direction of accumulated spin could be determined. The spin polarization direction was dependent on the specific location inside the crystal, and its arrangement was consistent with a magnetic quadrupole structure which has been hypothesized in a chiral molecule with CISS effect. [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

References

- 1) Y. Nabei, D. Hirobe, Y. Shimamoto, K. Shiota, A. Inui, Y. Kousaka, Y. Togawa and H. M. Yamamoto, *Appl. Phys. Lett.* **117**, 052408 (2020).
- 2) A. Inui, R. Aoki, Y. Nishiue, K. Shiota, Y. Kousaka, H. Shishido, D. Hirobe, M. Suda, J. Ohe, J. Kishine, H. M. Yamamoto and Y. Togawa, *Phys. Rev. Lett.* **124**, 166602 (2020).
- 3) V. M. Edelstein, *Phys. Rev. B* **72**, 172501 (2005).
- 4) W.-Y. He and K. T. Law, *Phys. Rev. Res.* **2**, 012073(R) (2020).

RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

In the past few decades, great progress in experimental and theoretical methods to analyze structures, dynamics, and properties of single-component (or single hierarchical) molecules and nanomaterials has been made. Now we should also direct our attention to properties and functions of multi-hierarchical molecular systems. We develop innovative methods of measurements and analysis for molecular and materials systems to elucidate the processes that trigger the functions and reactions of the systems in the mesoscopic regime, that is the regime where micro and macroscopic properties influence each other.

Nano-Optical Imaging and Application to Nanomaterials

Center for Mesoscopic Sciences Division of Supersensitive Measurements



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Professional Employment

1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Award

2012 The Chemical Society of Japan (CSJ) Award for Creative Work
2020 The Commendation for Science and Technology by the MEXT Awards for Science and Technology Research Category

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Keywords Nano Optics, Plasmons, Chirality

Studies of local optical properties of molecular assemblies and materials are the keys to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Nano-optical methods, such as scanning near-field optical microscopy (SNOM), enable optical imaging with spatial resolution beyond the diffraction limit of light. Combination of nano-optical techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterial systems. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies. In the past several years, we suc-

ceeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

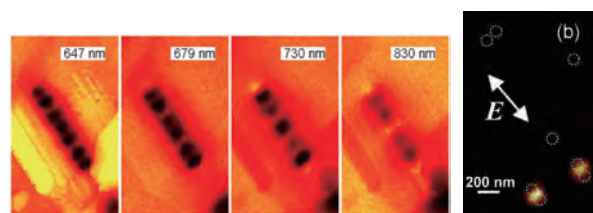


Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20 \text{ nm}^D \times 510 \text{ nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates the incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local

Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).

- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

1. Supramolecular Chirality Synchronization in Thin Films of Plasmonic Nanocomposites¹⁾

Mirror symmetry breaking (chirality) in materials is a fascinating phenomenon that has practical implications for various optoelectronic technologies. Chiral plasmonic materials are particularly appealing due to their strong and specific interactions with light. In this work we broaden the portfolio of available strategies toward the preparation of chiral plasmonic assemblies, by applying the principles of chirality synchronization—a phenomenon known for small molecules, which results in the formation of chiral domains from transiently chiral molecules. We report the controlled co-crystallization of 23 nm gold nanoparticles and liquid crystal molecules yielding domains made of highly ordered, helical nanofibers, preferentially twisted to the right or to the left within each domain. We applied our recently developed precise far-field circular dichroism (CD) microscopy to this system and confirmed that such micrometer sized domains exhibit strong CD signals, even though the bulk material is racemic. We further highlight the potential of the proposed approach to realize chiral plasmonic thin films by using a mechanical chirality discrimination method. Toward this end, we utilized a rapid CD imaging technique based on the use of polarized optical microscopy, which enabled probing the CD signal. The method allows us to extend intrinsically local effects of chiral synchronization to the macroscopic scale, thereby broadening the available tools for chirality manipulation in chiral plasmonic systems.

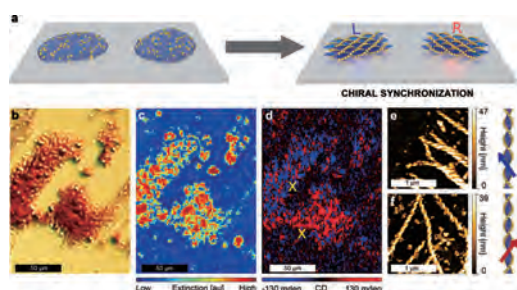


Figure 2. Micrometer-scale circular dichroism measurements of the helical Au nanoparticle assemblies.¹⁾ (a) Graphical representation of the chiral synchronization process. (b) Optical micrograph, (c) extinction intensity map at 550 nm, and (d) CD map at 550 nm from the same region of the sample. (e) AFM height map of a selected region from a left-handed and (f) a right-handed domain, with graphical models of the helical nanofilament. ©ACS 2020

2. Directional Supramolecular Polymerization to Form Nanofibers in a Microflow Reaction System^{2,3)}

Directional chain reactions are common self-assembly processes in nature. However, it has been challenging to achieve such processes in artificial one-dimensional self-assembling systems. In this work, we conducted supramolecular polymerization of perylene bisimide derivatives to form nanofibers. With selectively activating one end of a supramolecular polymer during its growth in a microflow

channel, it realized directional supramolecular polymerization. The dependency of the aggregation efficiency on the flow rate suggested that the shear force facilitated collisions among the monomers to overcome the activation energy required for nucleation. By introducing a solution containing both monomer and polymer, we investigated how the shear force influenced the monomer–polymer interactions. In situ fluorescence spectra and microscopic absorption linear dichroism measurements in the microflow system revealed that growth of the polymers was accelerated only when they were oriented under the influence of shear stress. Upon linear motion of the oriented polymer, polymer growth at that single end became predominant relative to the nucleation of freely diffusing monomers. This strategy—friction-induced activation of a single end of a polymer—should be applicable more generally to directional supramolecular block co-polymerizations of various functional molecules, allowing molecular hetero-junctions to be made at desired positions in a polymer.

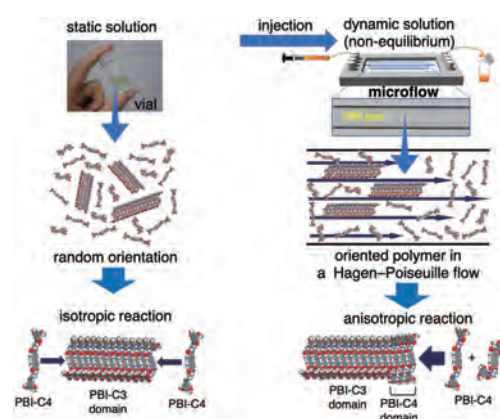


Figure 3. Comparison of general isotropic supramolecular polymerization in a vial (left) and the directional anisotropic supramolecular polymerization in a microflow system (right).²⁾ In the microflow system, the forward-facing terminus of the highly aligned polymer reacts with monomers, thereby leading to anisotropic elongation. ©ACS 2021

3. Optical Trapping of Chiral Metal Nanoparticles

Optical trapping experiments of chiral metal nanoparticles with circularly polarized light were conducted. The analysis of the data to reveal the origin of dissymmetry in optical force is now in progress.

References

- 1) P. Zustakiewicz, N. Kolsut, D. Grzelak, T. Narushima, M. Góra, M. Bagiński, D. Pocięcha, H. Okamoto, L. M. Liz-Marzán and W. Lewandowski, *ACS Nano* **14**, 12918–12928 (2020).
- 2) S. Matoba, C. Kanzaki, K. Yamashita, T. Kusukawa, G. Fukuhara, T. Okada, T. Narushima, H. Okamoto and M. Numata, *J. Am. Chem. Soc.* **143**, 8731–8746 (2021).
- 3) C. Kanzaki, S. Matoba, A. Inagawa, G. Fukuhara, T. Okada, T. Narushima, H. Okamoto and M. Numata, *Bull. Chem. Soc. Jpn.* **94**, 579–589 (2021).

Atomic-Scale Optical Spectroscopy

Center for Mesoscopic Sciences Division of Broadband Multiscale Analysis



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Education

2006 B.S. Ritsumeikan University
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Professional Employment

2008 JSPS Research Fellow, Kyoto University
2011 JSPS Research Fellow, Fritz-Haber Institute
2013 Group Leader, Fritz-Haber Institute
2021 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2020 Guest Professor, Hokkaido University

Awards

2013 Inoue Research Award for Young Scientists
2014 Morino Award for Molecular Science
2016 Gerhard Ertl Young Investigator Award
2020 Gaede Prize (German Physical Society)
2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Award
2020 Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science)

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Keywords Atomic-Scale Optical Spectroscopy, Scanning Probe Microscopy, Nanoscale Science

Optical imaging and spectroscopy at atomic resolution is an overarching goal in modern nanoscale science and technology, allowing us to directly access atomic-scale structures and dynamics in real space and real time. Atomic-scale crystal imperfections, defects and inhomogeneities indeed play a crucial role in physicochemical properties and functions of solid catalysts and semiconductor optoelectronic devices. We have challenged to attain atomic-scale optical spectroscopy by combining advanced low-temperature scanning tunneling microscopy, laser spectroscopy and nanoplasmonics.

Electromagnetic fields can be confined to nanoscale through excitation of localized surface plasmon resonances of metallic nanostructures. Plasmonics is a mature research field, enabling precise control of nanoscale light. Accordingly, nanoscale optical imaging and spectroscopy well below the diffraction limit has become a more routine technique. However, the typical spatial resolution remains a few tens of nanometers, which is still far from the atomistic length scale. More recently, state-of-the-art experiments and theories demonstrated that atomic-scale confinement of electromagnetic fields occurs at

atomistic asperities existing on metallic nanostructures. However, it is an outstanding challenge to precisely manipulate atomically confined light. We have developed advanced experimental techniques to manipulate extremely confined, strong plasmonic fields in scanning tunneling microscope junctions and implemented ultrasensitive and ultrahigh resolution optical spectroscopy. We also investigate intriguing atomic-scale strong light–matter interactions in an atomically well-defined environment.

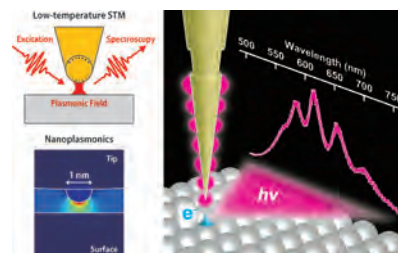


Figure 1. Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

Selected Publications

- S. Liu *et al.*, “Plasmon-Assisted Resonant Electron Tunneling in a Scanning Tunneling Microscope Junction,” *Phys. Rev. Lett.* **121**, 226802 (2018).
- H. Böckmann, S. Liu *et al.*, “Near-Field Manipulation in a Scanning Tunneling Microscope Junction with Plasmonic Fabry-Pérot Tips,” *Nano Lett.* **19**, 3597–3602 (2019).
- S. Liu *et al.*, “Resolving the Correlation between Tip-Enhanced Resonance Raman Scattering and Local Electronic States with 1 nm Resolution,” *Nano Lett.* **19**, 5725–5731 (2019).
- S. Liu *et al.*, “Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation,” *Nano Lett.* **20**, 5879–5884 (2020).
- S. Liu *et al.*, “Atomic Point Contact Raman Spectroscopy of a Si(111)-7×7 Surface,” *Nano Lett.* **21**, 4057–4061 (2021).
- S. Liu *et al.*, “Anti-Stokes Light Scattering Mediated by Electron Transfer Across a Biased Plasmonic Nanojunction,” *Nano Lett.*, in print.

1. Control of Gap-Mode Plasmons in Scanning Tunneling Microscope Junctions

Optical imaging and spectroscopy in plasmonic scanning tunneling microscope junctions rely on gap-mode plasmons whose properties are largely determined by the nanoscale morphology of the tip apex. Although a metallic tip for a scanning tunneling microscope is typically prepared by electrochemical etching, it is hard to precisely control the nanoscale structure of its apex. In order to obtain plasmonic tips in a highly controlled and reproducible manner, we employed focused ion beam milling.¹⁾ Figure 2a displays a scanning electron micrograph of a gold tip with a nanoscopically sharpened apex. Furthermore, we demonstrated that the spectral features of the gap-mode plasmon can be controlled by making nanoscale structures on the tip shaft. As an exemplary case, we produced nanoscopically sharp gold tips with a single groove on the shaft at a distance of a few micrometers from the apex. This structure leads to tunable plasmonic Fabry–Pérot interference. Figures 2b and 2c show the electrodynamic simulation and the scanning tunneling luminescence spectra, respectively, where the modulated spectral response through the interference is observed. Nanofabrication of plasmonic tips will be a key technology to attain highly precise, reproducible nanoscale and atomic-scale optical imaging and spectroscopy.

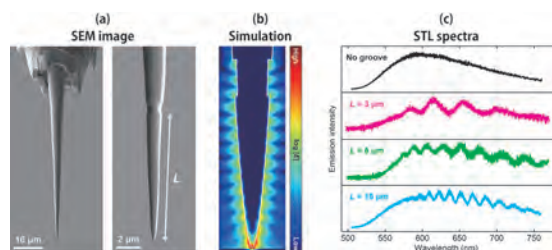


Figure 2. Nanofabrication of plasmonic tip with focused ion beam milling. (a) Scanning electron micrograph of a nanoscopically sharpened gold tip. (b) Simulation of plasmonic Fabry–Pérot tip. (c) Scanning tunneling luminescence spectra of the plasmonic Fabry–Pérot tip.

2. Ultrasensitive and Ultrahigh Resolution Tip-Enhanced Raman Spectroscopy

Raman spectroscopy is a versatile tool widely used in physics, chemistry and biology. Low-temperature tip-enhanced Raman spectroscopy (TERS) enables chemical identification with single-molecule sensitivity and with extremely high spatial resolution even down to the atomic scale.^{2,3)} The large enhancement of Raman scattering obtained in TERS originates from electromagnetic field and/or chemical enhancement mechanisms. Whereas former enhancement requires a strong near-field through excitation of localized surface plasmons, the latter is governed by resonance in the electronic structure of the sample, known as resonance Raman spectroscopy. Recent-

ly we demonstrated tip-enhanced resonance Raman scattering (TERRS) for ultrathin ZnO films epitaxially grown on a Ag(111) surface,⁴⁾ where both electromagnetic and chemical enhancement mechanisms are simultaneously operative, yielding exceptionally high sensitivity. By recording scanning tunneling spectroscopy (STS) in parallel, we also showed that the TERRS intensity is strongly correlated with the nanoscale variation of the electronic resonance. It was found that the spatial resolution of TERRS is dependent on the tip–surface distance and reaches nearly 1 nm in the tunneling regime. This exceptionally high resolution can be rationalized by the extreme confinement of the plasmonic field in the junction. Simultaneous STS and TERRS mapping visualize a correlation between the local electronic resonance and the Raman spectrum at near-atomic resolution. Therefore, TERRS will pave the way to directly observe electron–phonon coupling on the atomic length scale.

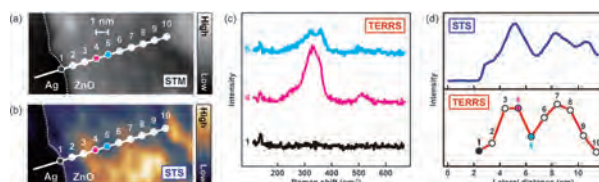


Figure 3. Tip-enhanced resonance Raman spectroscopy of ultrathin zinc oxide films. (a) and (b) STM and STS images of ultrathin zinc oxide film. (c) TERRS spectra obtained at different locations over the zinc oxide film. (d) STS and TERRS intensities along the line indicated in (a) and (b).

Additionally, we discovered that tip-enhanced Raman scattering can be dramatically enhanced through formation of atomic point contacts.^{5,6)} We showed that atomic point contact formation between a silver tip and the surface of a bulk Si sample can lead to the dramatic enhancement of Raman scattering and consequently the phonon modes of the reconstructed Si(111)-7×7 surface can be detected. Furthermore, we demonstrate the chemical sensitivity of this method by probing local vibrations resulting from Si–O bonds on the partially oxidized Si(111)-7×7 surface. This approach will expand the applicability of ultrasensitive tip-enhanced Raman spectroscopy, exceeding the previous measurement strategies that exploit intense gap-mode plasmons, typically requiring a plasmonically resonant substrate.

References

- 1) H. Böckmann, S. Liu *et al.*, *Nano Lett.* **19**, 3597 (2019).
- 2) J. Lee *et al.*, *Nature* **568**, 78 (2019).
- 3) Y. Zhang *et al.*, *Natl. Sci. Rev.* **6**, 1169–1175 (2019).
- 4) S. Liu *et al.*, *Nano Lett.* **19**, 5725 (2019).
- 5) S. Liu *et al.*, *Nano Lett.* **20**, 5859 (2020).
- 6) S. Liu *et al.*, *Nano Lett.* **21**, 4057 (2021).

Awards

KUMAGAI, Takashi; Gaede Prize (German Physical Society) (2020).

KUMAGAI, Takashi; Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science) (2020).

Center for Mesoscopic Sciences as an Interdepartmental Facility

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KUMAGAI, Takashi	Associate Professor
NARUSHIMA, Tetsuya	Assistant Professor
YOSHIZAWA, Daichi	Assistant Professor
NISHIDA, Jun	Assistant Professor
OKANO, Yasuaki	Technical Associate
NOMURA, Emiko	Secretary

As the succeeding organization of former Laser Research Center for Molecular Science, Center for Mesoscopic Sciences continues development of new experimental apparatus and methods to open groundbreaking research fields in molecular science, in collaboration with other departments and facilities. Those new apparatus and methods will be served as key resources in advanced collaboration with the researchers from the community of molecular science. The targets cover:

- novel quantum-control schemes based on intense and ultra-fast lasers

- novel optical imaging and nanometric microscopy and spectroscopy
- novel method of analysis for mesoscopic phenomena and so forth.

The Center also possesses several general-purpose instruments for laser-related measurements (commercial as well as in-house developed), and lends them to researchers in IMS who conduct laser-based studies, so as to support and contribute to their advanced researches.

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
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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

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JUNG, Youngcheol*

Secretary

MASUDA, Michiko

Keywords

Self-Assembly, Nano-Space, Coordination Chemistry

We are designing new self-assembled molecular systems based on coordination chemistry, and trying to apply the molecular system to various research fields.

For example, we applied the self-assembled molecular systems to biological studies and the structure elucidation of small molecules (Figures 1 and 2).

Currently, we are focusing on the following two projects:

(1) Protein encapsulation in self-assembled Coordination cages: In this project, we aim to explore the potential of proteins encapsulated within precisely designed molecular capsules (Figure 1). We envision to 1) control the property of protein (*e.g.*, stability, ligand affinity or selectivity), 2) control enzymatic reactivity (*e.g.*, activity or new function), and 3) develop new analytical methodology (coupled with NMR, X-ray, MS or cryoEM *etc.*).

(2) Crystalline sponge (CS) method: The CS is a porous crystal, which can accommodate various kinds of small molecules, and align the accommodated molecules neatly in its inner space. Actually, we can observe the structure of the

small molecules neatly aligned in the CS by the X-ray crystallography (Figure 2). The method has a potential to accelerate the various kinds of researches, in which the structure elucidation of novel compounds is required. We target to develop new drug discovery using this method.

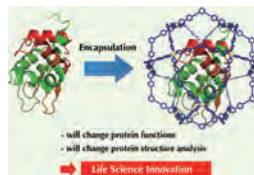


Figure 1. Cartoon presentation for the protein encapsulation.

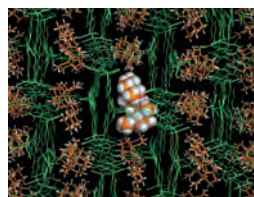


Figure 2. One example of the crystalline sponge method.

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).

1. Protein Stabilization and Refolding in a Gigantic Self-Assembled Cage

Spatial isolation of molecules is often a powerful strategy for regulating their molecular behavior. Biological systems employ such mechanisms well; however, scientists have yet to rival nature, particularly for macromolecular substrates. We demonstrated that the encapsulation of a protein in a molecular cage with an open framework stabilizes the tertiary structure of the protein and improves its enzymatic activity. Particularly, when the three-dimensionally confined enzyme was exposed to an organic solvent, its half-life was prolonged 1,000-fold. Kinetic and spectroscopic analysis of the enzymatic reaction revealed that the key to this stability is the isolated space; this is reminiscent of chaperonins, which use their large internal cavities to assist the folding of client proteins (Figure 3). The single-molecule protein caging affords a new type of protein-based nanobiotechnology that accelerates molecular biology research as well as industrial applications.

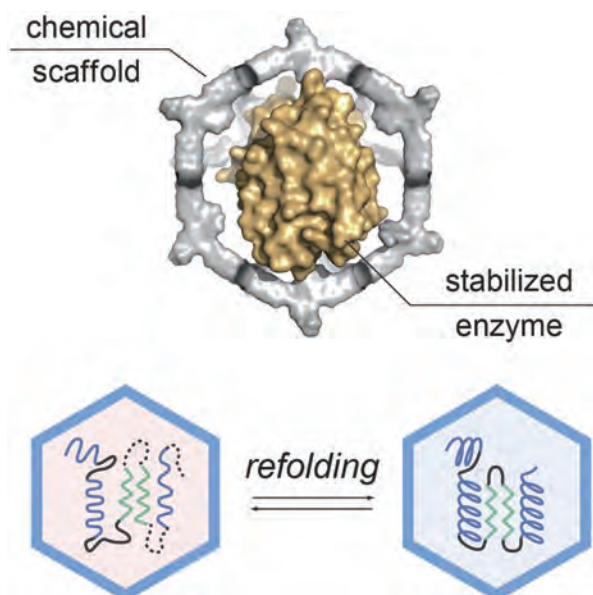


Figure 3. Protein refolding in the cage.

2. Absolute Configuration Determination from Low *ee* Compounds by the Crystalline Sponge Method

When chiral compounds with low enantiomeric excess (*ee*, R:S = *m*:*n*) were absorbed into the void of the CS, enantiomerically pure [(R)_{*m*}(S)_{*n*}] chiral composites were formed,

Awards

FUJITA, Makoto; Clarivate Citation Laureates (Chemistry) (2020).

MITSUHASHI, Takaaki; FUJITA, Makoto; “Major Results” of Nanotechnology Platform, MEXT (2020).

changing the centrosymmetric space group into non-centrosymmetric one (Figure 4). The absolute configuration of the analyte compounds was elucidated with a reasonable Flack (Parsons) parameter value. This phenomenon is characteristic to the “post-crystallization” in the pre-determined CS crystalline lattice, seldom found in common crystallization where the crystalline lattice is defined by an analyte itself. The results highlight the potential of the CS method for absolute configuration determination of low *ee* samples, an often encountered situation in asymmetric synthesis studies, which is important for the development of new drugs.

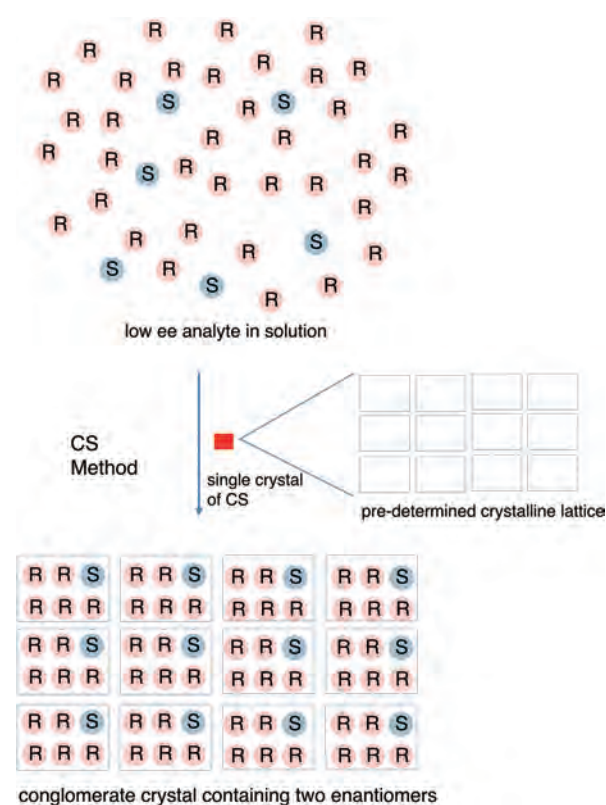


Figure 4. CS method was applied to the analysis of chiral compounds with low enantiomeric excess.

References

- 1) D. Fujita, R. Suzuki, Y. Fujii, M. Yamada, T. Nakama, A. Matsugami, F. Hayashi, J.-K. Weng, M. Yagi-Utsumi and M. Fujita, *Chem* **7**, (2021), in press.
- 2) R. Dubey, K. Yan, T. Kikuchi, S. Sairenji, A. Rossen, S. S. Goh, B. L. Feringa and M. Fujita, *Angew. Chem., Int. Ed.* **60**, 11809–11813 (2021).

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

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Awards

2001 Young Incentive Award, Japanese Society for Synchrotron Radiation Research
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Keywords Condensed Matter, Optical and Photoelectrical Properties, 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, namely 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.

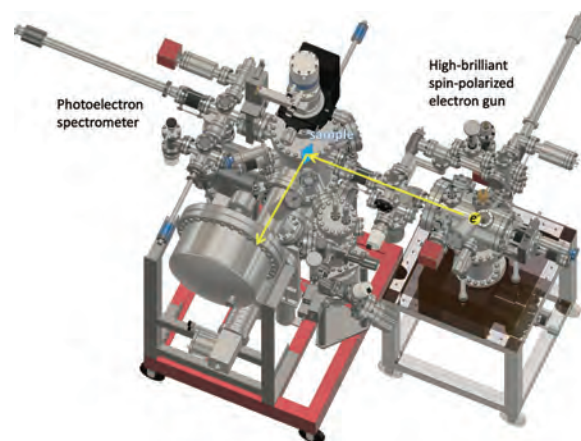


Figure 1. Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

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 YbB₁₂,” *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 CeOs₂Al₁₀,” *Phys. Rev. Lett.* **106**, 056404 (4 pages) (2011).

1. Magneto-Optics of the Weyl Semimetal TaAs in the THz and IR Regions¹⁾

The magnetic-field dependence of optical conductivity [$\sigma(\omega)$] spectra of the ideal type-I Weyl semimetal TaAs has been investigated at the temperature of 10 K in the terahertz (THz) and infrared (IR) regions. The obtained $\sigma(\omega)$ spectrum in the THz region of $\hbar\omega \leq 15$ meV is strongly affected by the applied magnetic field (B): The Drude spectral weight is rapidly suppressed, and an energy gap originating from the optical transition in the lowest Landau levels appears with a gap size that increases in proportion to \sqrt{B} , which suggests linear band dispersions. The obtained THz $\sigma(\omega)$ spectra could be scaled not only in the energy scale by \sqrt{B} but also in the intensity by $1/\sqrt{B}$ as shown in Figure 2, which has been predicted theoretically. In the IR region for $\hbar\omega \geq 17$ meV, on the other hand, the observed $R(\omega)$ peaks originating from the optical transitions in higher Landau levels are proportional to linear- B suggesting parabolic bands. The different band dispersions suggests that the Dirac linear bands transition to the free-electron-like parabolic bands with increasing energy.

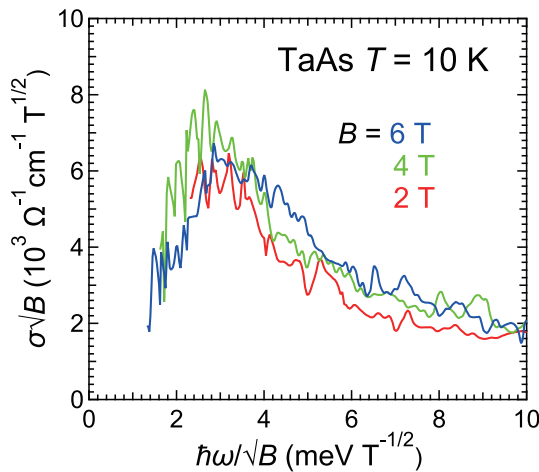


Figure 2. Magnetic-field dependence of optical conductivity [$\sigma(\omega, B)$] spectrum of TaAs in the THz region at the temperature of 10 K. The horizontal and vertical axes are normalized by B and $1/\sqrt{B}$, respectively.

2. One-Dimensionality of the Spin-Polarized Surface Conduction and Valence Bands of Quasi-One-Dimensional Bi Chains on GaSb(110)-(2×1)²⁾

Surface electronic structure and its one-dimensionality above and below the Fermi level (E_F) are surveyed on the Bi/GaSb(110)-(2×1) surface hosting quasi-one-dimensional (Q1D) Bi chains, using conventional (one-photon) and two-photon angle-resolved photoelectron spectroscopy (ARPES) and theoretical calculations. ARPES results reveal that the Q1D electronic states are within the projected bulk band gap. Circular dichroism of two-photon ARPES and density-functional-theory calculation indicate clear spin and orbital polarization of the surface states consistent with the giant sizes of

Rashba-type spin-orbit interaction (SOI), derived from the strong contribution of heavy Bi atoms. The surface conduction band above E_F forms a nearly straight constant-energy contour (Figure 3a), suggesting its suitability for application in further studies of one-dimensional electronic systems with strong SOI. A tight-binding model calculation based on the obtained surface electronic structure successfully reproduces the surface band dispersions (Figures 3b, 3c) and predicts possible one- to two-dimensional crossover in the temperature range of 60–100 K.

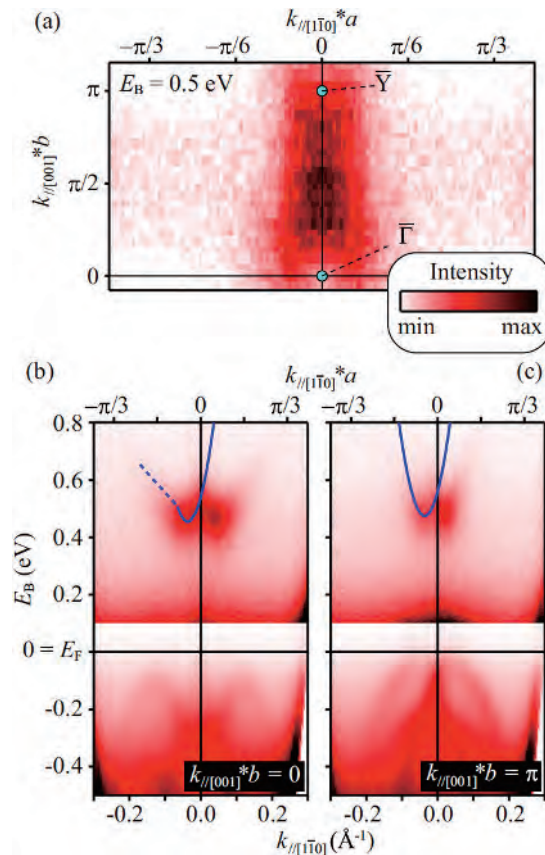


Figure 3. ARPES intensity plots of Bi/GaSb(110)-(2×1) at 25 K taken with two laser pulses. A delay time between the pump and probe pulses was set to 1 ps. The pump pulses ($\hbar\nu = 1.5$ eV) were linearly polarized photons, the electric field vector, which lies in the photon incident plane. The probe ones had the same incident plane as the circular polarization ($\hbar\nu = 6.0$ eV). (a) Constant energy contour at $E_B \sim 0.5$ eV. (b) ARPES intensity plot along $\bar{\Gamma}-\bar{X}$. The photoelectron signals in $E_B > 0.1$ eV are enhanced to make the surface conduction band dispersion visible. (c) Same as (b) but taken along $\bar{Y}-\bar{M}$. Solid and dashed curves in (b) and (c) guide the theoretical band dispersions.

References

- 1) S. Kimura, Y. Yokoyama, Y. Nakajima, H. Watanabe, J. Sichelschmidt, V. Süß, M. Schmidt and C. Felser, *JPS Conf. Proc.* **30**, 011017 (5 pages) (2020).
- 2) Y. Ohtsubo, N. Tokumasu, H. Watanabe, T. Nakamura, P. Le Fèvre, F. Bertran, M. Imamura, I. Yamamoto, J. Azuma, K. Takahashi and S. Kimura, *Phys. Rev. B* **101**, 235306 (8 pages) (2020).

Innovative Catalysis Development Based on Radiant Light Spectroscopy

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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

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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 copper 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 light 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, CO₂, and biomass into valuable functional materials.

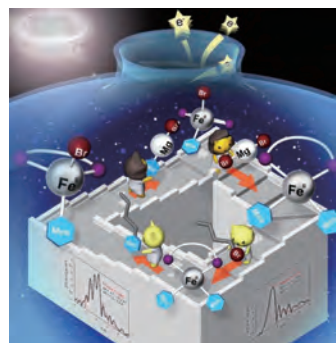


Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

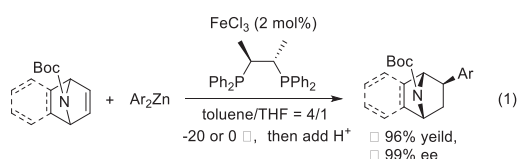
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada-Tamao-Corriu-Type Cross-Coupling Reaction Assisted by 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 Carbometallation of Azabicycloalkenes," *Chem. Commun.* **57**, 6975–6978 (2021).

1. DFT-XAS-based Mechanistic Investigation of Transition-Metal-Catalyzed Reaction in Homogeneous Phase¹⁻⁴

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 conducted to use XAS 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 succeeded to elucidate 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.^{1,2} 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).³ 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.



2. XAFS-Based Structural Study on Flexible Organometallic Systems⁵⁻⁷

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.⁴

Another successful application was achieved in the structure determination of double-decker type iron porphyrin/phtalocyanine dimer in which two units of iron-porphyrin or phtalocyanine were interlocked through highly flexible quadruplet axial or iron-oxo linkage.^{5,6} Fe K-edge XAS-based structural analysis supported with DFT-MD-based simulation successfully provides the precise local coordination geometry of iron centers in highly flexible supramolecular system.

Another successful example of the DFT-XAS-based structural study was demonstrated by the molecular structure determination of an anionic homoleptic organo-transition metal complex of $[Li(12-crown-4)_2][MPh_6\{Li(thf)\}_2]$ (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.⁷

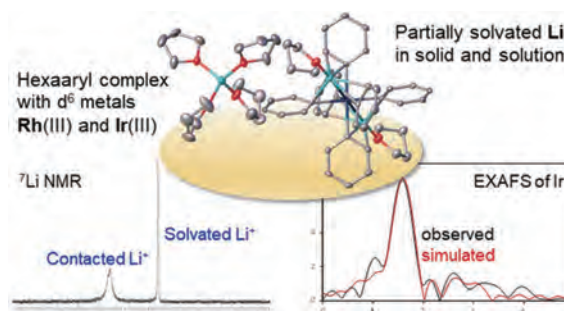


Figure 2. The molecular structure determination of $[Li(12-crown-4)_2][MPh_6\{Li(thf)\}_2]$.

References

- 1) H. Masafumi*, K. Sano, Y. Kanazawa, N. Komine, Z. Maeno, T. Mitsudome and H. Takaya*, *ACS Catal.* **8**, 5827–5841 (2018).
- 2) Y. Kanazawa, T. Mitsudome*, H. Takaya* and M. Hirano*, *ACS Catal.* **10**, 5909–5919 (2020).
- 3) 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*, *Chem. Commun.* **57**, 6975–6978 (2021).
- 4) L. O. Benjamin, H. Takaya and T. Uemura*, *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
- 5) Y. Yamada*, K. Morita, T. Sugiura, Y. Toyoda, N. Mihara, M. Nagasaka, H. Takaya, K. Tanaka, T. Koitaya, N. Nakatani, H. Ariga-Miwa, S. Takakusagi, Y. Hitomi, T. Kudo, Y. Tsuji, K. Yoshizawa and K. Tanaka*, *ChemRxiv* DOI: 10.26434/chemrxiv.14728860.v1 (2021).
- 6) N. Mihara, Y. Yamada*, H. Takaya, Y. Kitagawa, K. Igawa, K. Tomooka, H. Fujii and K. Tanaka*, *Chem. –Eur. J.* **25**, 3369–3375 (2019).
- 7) T. Iwasaki*, Y. Hirooka, H. Takaya, T. Honma and K. Nozaki*, *Organometallics* **40**, 2489–2495 (2021).

RESEARCH ACTIVITIES

Division of Research Innovation and Collaboration

As the open innovation hub managed by IMS and companies, we conduct the research projects in collaboration with Academia, Industry and Government.

Micro Solid-State Photonics

Division of Research Innovation and Collaboration



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Education

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Professional Employment

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1989 Research Associate, Fukui University
1993 Visiting Researcher, Stanford University (-1994)
1998 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2018 Group Director, RIKEN SPring-8 Center
2019 Project Professor, Institute for Molecular Science

Awards

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2012 SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014 IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)
2018 IAPLE (The International Academy of Photonics and Laser Engineering) Fellow
2019 LSJ (The Laser Society of Japan) Fellow

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MATSUDA, Miho
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ONO, Yoko
INAGAKI, Yayoi

Keywords

Solid-State Lasers, Nonlinear Optics, Micro Solid-State Photonics

“Micro Solid-State Photonics” based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro and/or microchip solid-state, ceramic and single-crystal, lasers can provide excellent spatial mode quality and narrow linewidths with enough power. High-brightness nature of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion: The world first laser ignited car, highly efficiency broad frequency conversions from the wavelength of 118nm VUV until 300–500 μ m THz waves, and so on. In addition, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. Lately, we propose a new architecture to realize a monolithic multi-disk laser by the surface activated bonding (SAB). This multiple thin-disk or chip gain medium for distributed face cooling (DFC) structure can manage the high-power and high-field laser with high-gain compact system. Besides, QPM-structured crystal quartz constructed by multiple plate stacking could be promising as a high-power and reliable VUV frequency conversion devices. These downsized and

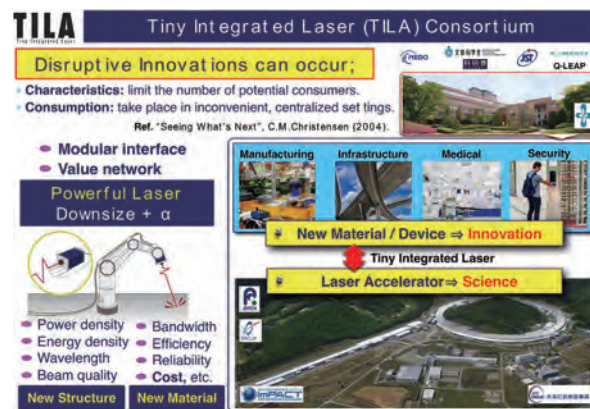


Figure 1. TILA consortium toward “Laser Science and Innovation” by micro solid-state photonics.

modularized **tiny integrated lasers** (TILA) promise the extremely high-brightness lasers to open up the new science, such as laser driven electron accelerator toward table-top XFEL, and innovation by the compact power laser (Figure 1).

Selected Publications

- T. Taira *et al.*, *Opt. Lett.* **16**, 1955 (1991).
- T. Taira *et al.*, *IEEE J. Sel. Top. Quantum Electron.* **3**, 100 (1997).
- T. Taira, *IEEE J. Sel. Top. Quantum Electron.* **13**, 798 (2007).
- T. Taira, *Opt. Mater. Express* **1**, 1040 (2011).
- Y. Sato *et al.*, *Sci. Rep.* **7**, 10732 (2017).
- H. Sakai *et al.*, *Opt. Express* **16**, 19891 (2008).
- M. Tsunekane *et al.*, *IEEE J. Quantum Electron.* **46**, 277 (2010).
- T. Taira *et al.*, *The 1st Laser Ignition Conference '13, OPIC '13*, Yokohama, April 23-26, LIC3-1 (2013).
- R. Bhandari *et al.*, *Opt. Express* **21**, 28849 (2013).
- S. Hayashi *et al.*, *Sci. Rep.* **4**, 5045 (2014).
- L. Zheng *et al.*, *Opt. Mater. Express* **7**, 3214 (2017).
- H. Ishizuki *et al.*, *Opt. Mater. Express* **8**, 1259 (2018).
- N. H. Matlis *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. A* **909**, 27 (2018).
- S.W. Jolly *et al.*, *Nat. Commun.* **10**, 1 (2019).

1. Radiation Dose Rate Effects on the Properties of a Laser-Induced Breakdown Spectroscopy System Developed Using a Ceramics Micro-Laser for Fiber-Optic Remote Analysis¹⁾

Radiation dose rate effects on the properties of a compact fiber-optic laser-induced breakdown spectroscopy (LIBS) system with a monolithic Nd:YAG/Cr:YAG composite ceramics were investigated for remote analysis in a hazardous environment. To investigate radiation effects on the LIBS signal, properties related to the Nd:YAG laser operation such as oscillation threshold, output energy, oscillation timing, temporal pulse shape, and beam profile was measured as a function of the radiation dose rate from 0 to 10 kGy/hr in view of their influences to the signal (Figure 2). LIBS spectra of zirconium metal were measured under irradiation. Although signal intensity decreased considerably by irradiation, informative spectra were well obtained even at the maximum radiation dose rate. From the comparison of the LIBS-related parameters among the laser properties, the signal reduction was mainly ascribed to the pulse energy reduction. Scintillation emission spectra were also measured from the ceramics during the irradiation, where the signal intensity increased linearly with the dose rate. The results show that the developed system is applicable to effective remote elemental analysis and monitoring of radiation dose rate in hazardous environments such as nuclear fuel debris inspection.

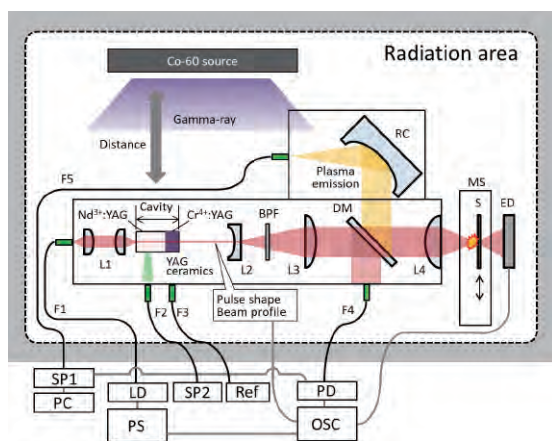


Figure 2. Experimental setup to study the properties of the FO-MC LIBS system in radiation environment.

2. Deformation Properties of Laser Peen Forming Using Sub-Nanosecond Microchip Laser²⁾

A high-power pulsed microchip laser, which has a pulse duration of sub-nanosecond order, had been developed. A focused microchip laser pulse can induce an effective shock wave for deforming the irradiated metal surface plastically. When a sheet metal is scanned by the laser, dieless sheet forming, called laser peen forming, is achieved through the accumulation of such plastic deformations. The authors have applied the method to sheet metal bending (Figure 3). A tamping layer, such as water, on a target surface encourages

laser-induced shock waves. Therefore, the sheet metals were irradiated in water. Several materials were bent, and the feasibility of the process was confirmed. Fundamental deformation properties in terms of forming parameters, such as defocusing, pulse energy, material hardness, and thickness, were examined. It was confirmed that, qualitatively, the process had similar deformation modes to those obtained by peen forming. However, when fluence was greatly increased by focusing the pulse energy, laser absorption by water reduced the bending deformation.



Figure 3. Example of bend workpiece (A1100, $t = 1$ mm).

3. Study on the Specific Heat of $Y_3Al_5O_{12}$ between 129 K and 573 K³⁾

We measured the isopiestic specific heat (C_p) of $Y_3Al_5O_{12}$ (YAG) by the differential scanning calorimetry aiming to obtain thermal parameters under cryogenic and room-temperature (RT) conditions. It was also found that the applicable temperature range of our numerical model for C_p of YAG was updated to the range between 129 K and 573 K with below 3% error. Obtained parameters were verified by the comparative study with the first principles calculations. Discrepancy between the calculation value and measured value at 273 K was 0.017 J/gK in C_p . Figure 4 also shows the reason why reported θ_D of YAG has been varied from 500 K to 900 K. θ_D shows the dependence to gradually decrease T towards 0 K and to gradually increase θ_D over 800 K, and to gradually increase T over 600 K under the isopiestic condition and to gradually decrease θ_D toward below 500 K.

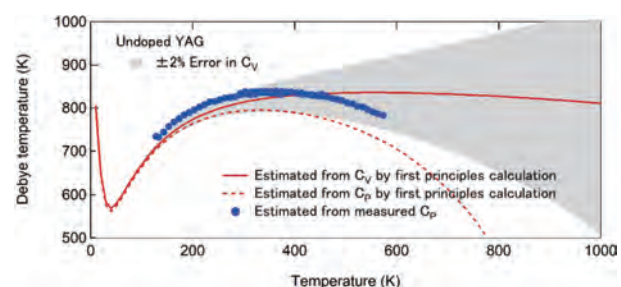


Figure 4. Temperature dependence of θ_D by our model.

References

- 1) K. Tamura, H. Ohba, M. Saeki, T. Taguchi, H. H. Lim, T. Taira and I. Wakaida, *J. Nucl. Sci. Technol.* **58**, 405 (2020). DOI: 10.1080/00223131.2020.1854880
- 2) Y. Sagisaka, T. Kawasaki, V. Yahia, T. Taira and Y. Sano, *Journal of the JSTP* **62**, 8 (2021). (in Japanese). DOI: 10.9773/sosei.62.8
- 3) Y. Sato and T. Taira, *Opt. Mater. Express* **11**, 551 (2021). DOI: 10.1364/OME.416480