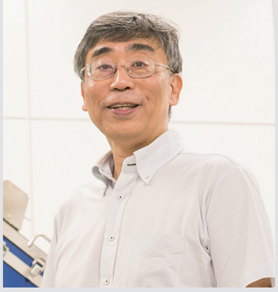
RESEARCH ACTIVITIES

Materials Molecular Science

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

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure



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Education

1983	B.S. The University of Tokyo
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Professional Employment

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1994	Lecturer, The University of Tokyo
1996	Associate Professor, The University of Tokyo
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Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UVMCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time in the world using Beamline 36XU of SPring-8. These works were supported by the NEDO Fuel Cell project. More recently, the apparatus moved to BL46XU and is used for more general chemical reactions on heterogeneous catalysts and electrochemical cells such as CO_2 reduction.

The third subject is applications of the x-ray absorption fine structure (XAFS) spectroscopy, soft x-ray emission spectroscopy, and angle-resolved ultraviolet photoelectron spectroscopy for functional materials. These investigations include femto- and picosecond time resolved XAFS measurements using x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Conventional temperature dependent EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional alloy materials as negative thermal expansion alloys.

Selected Publications

- T. Nakagawa and T. Yokoyama, “Magnetic Circular Dichroism near the Fermi Level,” *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, “Anharmonicity and Quantum Effects in Thermal Expansion of an Invar Alloy,” *Phys. Rev. Lett.* **107**, 065901 (2011).
- Y. Uemura *et al.*, “Dynamics of Photoelectrons and Structural Changes of Tungsten Trioxide Observed by Femtosecond Transient XAFS,” *Angew. Chem., Int. Ed.* **55**, 1364–1367 (2016).
- Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, “X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions,” *Appl. Phys. Express* **10**, 076603 (2017).
- T. Koitaya, K. Yamamoto, T. Uruga and T. Yokoyama, “*Operando* Characterization of Copper–Zinc–Alumina Catalyst for Methanol Synthesis from Carbon Dioxide and Hydrogen by Ambient-Pressure Hard X-Ray Photoelectron Spectroscopy,” *J. Phys. Chem. C* **127**, 13044–13054 (2023).

1. Local Thermal Expansion of Co-Containing Invar Alloys[1)]

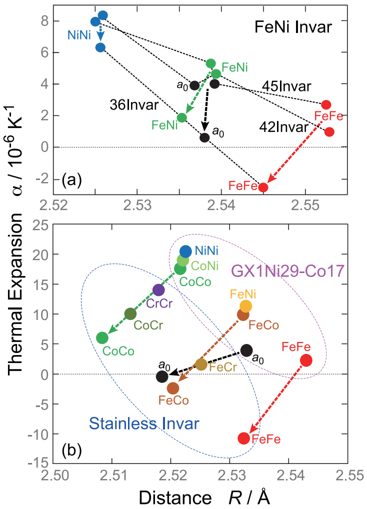

Figure 1. Thermal expansion coefficients α (10^{-6} K^{-1}) at 200 K for the first-NN interatomic distances determined by EXAFS and the lattice constant a_0 versus corresponding distances of (a) FeNi invar and (b) Kovar and stainless invar.

Low thermal expansion materials are quite attractive from the viewpoints of both fundamental science and industrial technology. FeNi invar alloys are quite familiar and have been applied to precision equipment as telescope, microscope, and nanodevice, and also been employed as core cables of electric high-voltage power lines to avoid sagging due to heat on high current conduction. Recently, Fujii *et al.* developed a new stainless invar alloy, which is employed for the cryogenic infrared space telescope in National Astronomical Observatory. In this work, we measured and analyzed EXAFS spectra of Co-containing invar alloys of this newly developed stainless invar, together with Kovar $Fe_{53}Co_{17}Ni_{29}X_1$ for comparison. We will focus our attention on how Co plays a role in the invar effect from the local structure viewpoint, which is often different from the macroscopic points of view.

Two stainless invar foils with 10 µm thickness were prepared and the elemental compositions are found to be $Fe_{38.8}Co_{50.1}Cr_{9.2}Ni_{1.9}$ and $Fe_{37.8}Co_{51.3}Cr_{9.0}Ni_{1.9}$ by the x-ray fluorescence spectra. Cr, Fe, Co, and Ni K-edge EXAFS spectra of commercially available Kovar (10 µm) and the stainless invar foils were recorded with the transmission mode in BL9C of Photon Factory, High Energy Accelerator Research Organization (KEK-PF) at 30–300 K using a He gas-circulating refrigerator installed at the beamline. The lattice thermal expansion coefficients of Kovar and stainless invar were measured by the laboratory dilatometer. We have also recorded Cr, Fe and Ni K-edge EXAFS of FeNi invar alloys $Fe_{64}Ni_{36}$, $Fe_{58}Ni_{42}$, and $Fe_{55}Ni_{45}$, stainless steel SUS304 ($Cr_{18.09}Fe_{71.98}Ni_{9.07}X_{0.86}$) and the Ni spanC Elinvar alloy ($Cr_{5.49}Fe_{49.66}Ni_{42.38}Ti_{2.47}$).

Temperature dependent EXAFS spectra were analyzed with the standard method including the third-order cumulant to yield thermal expansion for the first-nearest neighbor (NN) shells correctly. Since the first-NN shell includes different atom pair contributions, the analysis yields only the average distances. Nevertheless, assuming that the interatomic distance is given as a sum of the atomic radii, all the interatomic distances are evaluated as long as all the corresponding EXAFS spectra provide the average distances. Figure 1 shows the thermal expansion at 200 K thus obtained for the interatomic distances and the lattice constant as a function of corresponding distances. Since the two stainless invar alloys exhibit essentially the same results and the average values are given here. In FeNi invar, the Fe–Fe pair shows significant reduction of the interatomic distance and thermal expansion going from 42 and 45 invar to 36 invar, while the Ni–Ni one exhibits little suppression of thermal expansion and negligible distance contraction. This clearly implies that Fe exclusively contributes to the invar effect in $Fe_{64}Ni_{36}$. In stainless invar in Figure 1(b), it is found that thermal expansions of Fe–Fe, Fe–Co, and Co–Co are significantly smaller than in Kovar, associated with shortening of the corresponding interatomic distances. This implies a much more significant invar effect on Co as well as Fe in stainless invar, while the invar effect on Co is negligibly small in Kovar. The path-integral effective classical potential simulations exhibit qualitative agreement with this finding, indicating that the Co magnetization is more noticeably suppressed with a temperature rise in stainless invar, because of a smaller lattice constant and interatomic distances and also of the presence of Cr in stainless invar, both of which favor antiferromagnetic coupling. The present study clearly demonstrates importance of local structure point of view to understand detailed low thermal expansion mechanism, in which microscopic local thermal expansion noticeably differs from macroscopic lattice thermal expansion.

2. Synchrotron Radiation Based Spectroscopic Characterization of Functional Materials

In FY2023, we have been investigating following research subjects. The first one is continuous collaboration with Prof. Toshio Miyamachi in Nagoya University using high-field, low-temperature and ultrahigh-vacuum XMCD system installed at BL4B in UVSOR-III. Interesting magnetic properties such as magnetic anisotropy of ferromagnetic ultrathin films decorated organic molecules are being studied. Second, AP-HAXPES investigations are being conducted for working electrochemical cells on CO_2 reduction. This is a collaboration with Prof. T. Koitaya in Kyoto University and Dr. Y. Takagi in JASRI (both were previous assistant professors in this research group in IMS). Third, research assistant professor Dr. N. Kurahashi is studying peculiar water motion in Nafion solid electrolyte that shows abrupt phase transformation around 15°, using soft x-ray absorption and emission spectroscopy and AP-HAXPES. Fourth, research assistant professor Dr. N. Maejima is investigating a novel 2-dimensional Dirac-cone-like blue phosphorene using angle-resolved photoelectron spectroscopy and low-energy positron diffraction.

Reference

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Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
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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 prove microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

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

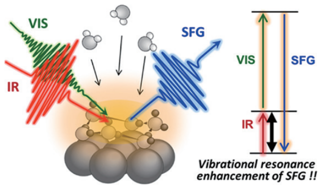

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, "Topologically Disordered Mesophase at Topmost 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).
- H. Sato *et al.*, "Critical Impacts of Interfacial Water on C–H Activation in Photocatalytic Methane Conversion," *Commun. Chem.* **6**, 8 (2023).
- H. Sato *et al.*, "Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water," *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
- S. Takahashi *et al.*, "Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity," *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).

1. Positive and Negative Impacts of Interfacial Hydrogen Bonds on Photocatalytic Hydrogen Evolution(1)

Hydrogen production via photocatalytic water splitting is a sustainable solution for next-generation energy by utilizing light energy at room temperature. However, the design of innovative photocatalysts remains a challenge due to a limited molecular-level understanding of interfacial water molecules and their hydrogen bond networks. Unveiling the physicochemical properties of these interfacial water molecules is critical to optimizing photocatalytic efficiency and achieving breakthroughs in sustainable hydrogen production.(2)

We have comprehensively investigated the impact of interfacial H-bond networks using various TiO_2 photocatalysts and uncovered a crucial role of interfacial H-bond structure/dynamics and optimal interfacial water environment for H_2 evolution. We controlled the thickness of adsorbed water from sub-monolayer to multilayers by precisely adjusting water vapor pressure. With this approach, we succeeded in directly demonstrating the correlation between H_2 formation rate and the microscopic structure of H-bond networks using real-time mass spectrometry and infrared absorption spectroscopy. Regardless of the crystalline structure of the TiO_2 photocatalyst, we observed a linear increase in H_2 formation rate with water adsorption up to three layers, indicating that reactive water molecules are present not only in the first adsorbed layer but also in several overlying layers (Figure 1). However, the H_2 formation rate turned to decrease dramatically when more than three layers of water covered the TiO_2 surface (Figure 1). In this situation, infrared spectra clearly indicated two distinct types of adsorbed water on the TiO_2 surface: Interfacial water and liquid-like water. Due to many-body interactions among adsorbed water molecules, the liquid-like water adsorbed in more than three layers led to strengthening of interfacial H-bond, which hinder interfacial proton-coupled hole transfer and drastically decreased the H_2 formation rate. Based on these microscopic insights, their study suggests that depositing three water layers in a water vapor environment is optimal for photocatalytic hydrogen evolution. These findings open new avenues for the molecular-level design and engineering of interfacial water toward the development of more innovative photocatalytic systems for next-generation renewable energy production.

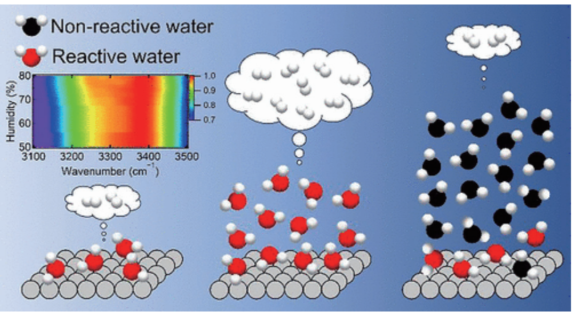

Figure 2. Identifying the reaction conditions that maximize catalytic activity in photocatalytic hydrogen evolution under water vapor atmospheres.

2. Direct Operando Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides(3)

Understanding of reactive electron species and active reaction sites on photocatalytic reduction reaction are vital for designing and manufacturing innovative catalysts with improved evolution activity of hydrogen as sustainable energy carrier.

We succeeded in significantly suppressing the signals derived from thermally excited electrons and observing the reactive photogenerated electrons contributing to the photocatalytic hydrogen evolution. Such innovation was achieved by a new method based on synchronization of the millisecond periodic excitations of photocatalysts with a Michelson interferometer used for FT–IR spectroscopy.(4) This demonstration was achieved for metal-loaded oxide photocatalysts under steam methane reforming and water splitting conditions. Although it has long been conventionally believed that loaded metal cocatalysts function as sinks for reactive photogenerated electrons and active sites for reduction reactions, we found that the free electron species in the metal cocatalysts were not directly involved in the photocatalytic reduction reaction. Alternatively, the electrons shallowly trapped in the in-gap states of oxides contributed to enhancing the hydrogen evolution rate upon the loading of metal cocatalysts. The electron abundance in the in-gap states, especially metal-induced semiconductor surface states, was clearly correlated to the reaction activity, suggesting that such metal-induced semiconductor surface states formed in the periphery of the metal cocatalyst play key roles in the photocatalytic hydrogen evolution. These microscopic insights shift a paradigm on the traditionally believed role of metal cocatalysts in photocatalysis and provide a fundamental basis for rational design of the metal/oxide complex interfaces.

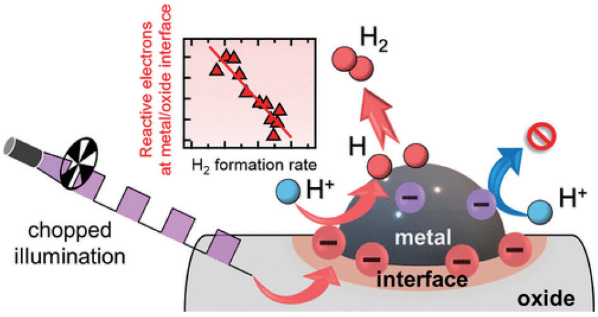

Figure 3. Unveiling actual role of metal cocatalysts. Electrons in cocatalyst periphery drive photocatalytic hydrogen evolution.

References

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2) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
3) H. Sato and T. Sugimoto, *J. Am. Chem. Soc.* **146**, 24800 (2024).
4) H. Sato and T. Sugimoto, *Vac. Surf. Sci.* **66**, 580 (2020).

Solid-State NMR for Molecular Science

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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 characterizations of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

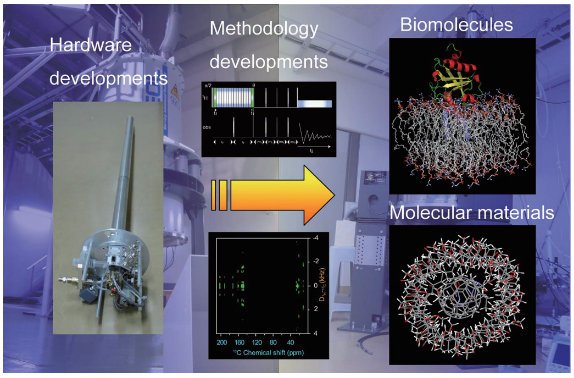


Figure 1. Outline of our studies.

Selected Publications

- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- T. Asakura, T. Ohata, S. Kametani, K. Okushita, K. Yazawa, Y. Nishiyama, K. Nishimura, A. Aoki, F. Suzuki, H. Kaji, A. Ulrich and M. Williamson, "Intermolecular Packing in B. Mori Silk Fibroin: Multinuclear NMR Study of the Model Peptide (Ala-Gly)15 Defines a Heterogeneous Antiparallel Antipolar Mode of Assembly in the Silk II Form," *Macromolecules* **48**, 28–36 (2015).
- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Huang, L. Zhai, D. E. Coupry, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine and D. Jiang, "Multi-Component Covalent Organic Frameworks," *Nat. Comm.* **7**, 12325 (12 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).
- M. Yagi-Utsumi, S. G. Itoh, H. Okumura, K. Yanagisawa, K. Kato and K. Nishimura, "The Double-Layered Structure of Amyloid-β Assemblage on GM1-Containing Membranes Catalytically Promotes Fibrillization," *ACS Chem. Neurosci.* **14**, 2648–2657 (2023).

1. Developments of Solid-State-NMR Techniques

Unlike solution NMR, it is not easy to achieve high resolution ^{1}H NMR spectra in solid-state NMR, since ^{1}H homonuclear dipolar couplings broaden the signals in rigid organic solids. In order to achieve ^{1}H high resolution spectra, ^{1}H homonuclear dipolar couplings must be removed by application of either sufficiently high magic angle spinning (MAS) or combination of MAS at moderate speed with multiple pulse (MP). Recent developments of fast MAS techniques enabled to remove ^{1}H homonuclear dipolar couplings efficiently with expense of sensitivity reduction. In the conventional latter approach, the MP average spin part of ^{1}H homonuclear dipolar coupling Hamiltonian at time scale shorter than MAS period. Using a high power radio frequency field, it is possible to achieve short cycle time for MP and enable combination of fast MAS without interferences between spin and spatial parts.

We have developed new MP sequences enabling us to achieve efficient ^{1}H homonuclear dipolar decoupling by removing high order correction terms. Those performances are theoretically evaluated and partly tested experimentally. The project is on the way.

In addition, we have developed new spectral editing pulse sequences which enable the selection of ^{13}C signals depending on the number of directly attached ^{1}H. The techniques are evaluated theoretically. This project is also on the way.

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

We have been working on developments of totally original solid-state NMR probes for a couple of years. The probe had been successfully built using originally designed parts except for a spinning module for 400MHz NMR. Then, we have been working on developments of original sample spinning modules for MAS solid-state NMR probes which are fully compatible with Bruker spectrometers and commercial sample tubes. We started the design of a spinning module for a standard 4.0 mm sample tube for Bruker. After 3 times of version up, our original spinning module exceeded the spinning performance of the commercial one from Bruker.

In order to achieve further improvements for our original spinning module, further developments are currently underway together with the development of original sample tubes. The spinning module is under designed in order to realize installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.

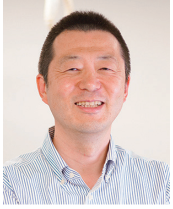
We have also started the development of the original spinning module for a 2.5 mm sample tube.

3. Characterization of Synthetic Molecules by Solid-State NMR

Solid-state NMR is one of the efficient techniques to characterize amorphous samples such as synthetic molecules. We are working on the characterization of new synthetic molecules categorized to covalent organic frameworks (COFs) which are designed by Associate Prof. Segawa group in IMS. Tentative ^{13}C solid-state NMR signal assignments had been successfully achieved. The obtained results sufficiently prove the achievement of the aimed molecular form of COFs for the sample. This project is also on the way.

Development of New Methods for Analyzing Surfaces and Interfaces Using Scanning Probe Microscopy

Instrument Center



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Analytical methods based on surface and interface sciences provide crucial information for understanding physical properties and reaction mechanisms with high precision. Scanning probe microscopy (SPM) enables the analysis of geometric structures, mechanical properties, electronic properties, magnetic properties, and reaction mechanisms at surfaces and interfaces with extremely high resolution and sensitivity. We have applied SPM to energy conversion systems, such as rechargeable batteries.[1,2]

In applying SPM to analyze surface and interface phenomena, it is essential to extract meaningful information from the data. However, the characteristics of SPM data can often be challenging to interpret. To address this, we have developed a new method to recognize specific structures and extract positional correlations in local structures from experimentally obtained SPM data. We have demonstrated that this method is applicable to mirror structures (Figure 1) and molecules adsorbed on metal surfaces, revealing specific characteristics in the positional correlations of molecular adsorption.[3]

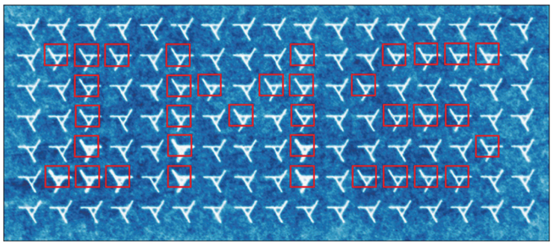

Figure 1. Recognition results for mirror structures in the scanning probe microscopy image. The red squares indicate the locations where specific structures were identified.[3] © 2024, *Appl. Phys. Express*, CC By 4.0.

We have also developed methods to analyze new physical properties of water. The wetting phenomenon of solid surfaces by water is common in everyday life, yet its detailed mechanisms remain not fully understood. Previous research suggested that as humidity increases, water molecules adsorb uniformly, leading to the formation of a water film. However, the latest studies using nonlinear spectroscopy have shown that water adsorption at low humidity is non-uniform. We have developed an experimental system that directly observes the microscopic wetting behavior on glass surfaces under different humidity levels. By using atomic force microscopy, we achieved the clarification of the change of adhesive force in nano-droplet of water.[4]

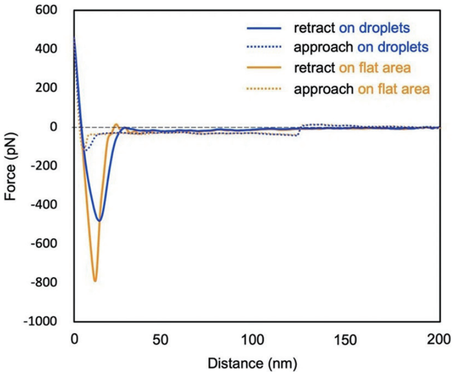

Figure 2. Force curves obtained from peak force tapping measurements at 80% humidity. The average of 10 force curves was acquired on nanometer-sized water droplets (blue) and on flat areas (orange), respectively. The dotted curves represent the approach curves, while the solid curves represent the retract curves.[4] © 2024, *Sci. Rep.*, CC By 4.0.

Additionally, we have developed an experimental system to study the physical properties of ice in liquid. While detailed studies of ice surfaces under ultra-high vacuum conditions have been reported, their true nature in liquid has not been fully clarified. We successfully observed atomically flat ice surfaces in alcohol and demonstrated changes in surface structure due to reactions with the alcohols.[5]

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3) S. Tsubokura, S. Kawano, Y. Imai, T. Ueda, K.-i. Nakamoto, H. Noma, H. Hioki and T. Minato, *Appl. Phys. Express* **17**, 035003 (2024).
4) Y. Araki, T. Minato and T. Arai, *Sci. Rep.* **14**, 10693 (2024).
5) R. Yanagisawa, T. Ueda, K.-i. Nakamoto, Z. Lu, H. Onishi and T. Minato, *J. Chem. Phys.* **161**, 024702 (2024).

Visiting Professors

Visiting Professor

TANAKA, Koichiro *(from Kyoto University)*

Ultrafast Laser Spectroscopy and Terahertz Optical Sciences

In recent years, the technology of ultra-short lasers and terahertz light has made remarkable progress, revealing unprecedented ultra-non-equilibrium physics and order formation of solid materials under high-intensity light irradiation. We make full use of such state-of-the-art optical technology to study the excited state dynamics of semiconductors, single-layer materials, photonic crystals, and metamaterials, as well as "non-equilibrium physics under high-intensity light fields." We are also looking for ways to bring out new physical properties by utilizing the interaction between light and matter. Specific research topics include (1) elucidation of non-equilibrium physical properties of solids in high-intensity light fields, (2) research on ultrafast nonlinear phenomena using ultrashort pulse lasers, and (3) new spectroscopy using terahertz light, (4) optical properties of monoatomic layer materials, (5) research on exciter quantum effects in semiconductors, *etc*.

Visiting Professor

OSAKA, Itaru *(from Hiroshima University)*

π-Conjugated Polymers for High-Efficiency Organic Photovoltaics

Organic photovoltaics (OPVs) have been attracting much attention due to lightweight, flexible, low-cost and low-energy solution-processability. Improving the power conversion efficiency is one of the important issues in OPVs. We designed and synthesized a series of π-conjugated polymers based on an extended fused ring, named dithienonaphthobisthiadiazole. The polymers had rigid and coplanar backbone structure, which resulted in high-crystalline structure in the thin film. The efficiency of the photovoltaic cells was as high as 12% when one of the polymers was combined with a fullerene acceptor, which was among the highest values for polymer/fullerene cells. Importantly, extremely high fill factors of over 0.8 were obtained, which was likely ascribed to the high charge carrier mobility. In addition, when another dithienonaphtobisthiadiazole-based polymer was combined with a nonfullerene acceptor, it showed high efficiencies of over 18%. Moreover, the polymer showed high photocurrent generation even with very small driving force energy. These results would be important guidelines for the development of high-performance polymers.

Visiting Associate Professor

AKIMOTO, Ikuko *(from Wakayama University)*

Pulse EPR Study of Photo-Induced Paramagnetic Centers in Solid Electrolyte $BaZr_{1-x}M_xO_3$ (M = Sc, Y)

Barium zirconate $BaZrO_3$ doped with trivalent metal ions (M = Sc, Y) is a promising candidate for solid electrolytes for proton transport in fuel cells. The oxygen vacancy is noted to be a key structure for accepting hydroxyl groups and transferring protons via the Grotthus Mechanism. However, it has been challenging to investigate the local structure of oxygen vacancies using conventional methods in the ion transport field. We found that ultraviolet (UV) irradiation induces paramagnetic centers, so-called F-centers, *i.e.* electrons bound to oxygen vacancies. Then, we can apply well-established electron paramagnetic resonance (EPR) techniques to this system to elucidate the fine structure through the magnetic interactions. We performed time-domain EPR measurements under UV light irradiation at cryogenic temperatures and investigated the shape of EPR spectrum, the spin multiplicity of the signal, and the hyperfine structure buried in the broadened spectral width. Based on the results that depend on the doped ion species and hydroxyl contents, we clarify the local structure in conjunction with EPR simulations.