

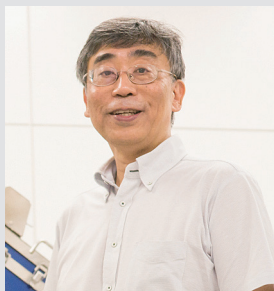
## RESEARCH ACTIVITIES

# 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

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Division of Electronic Structure



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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. Although photoelectron spectroscopic measurement is usually done under high vacuum, recent material science often requires ambient pressure measurements 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, more general chemical reactions on heterogeneous catalyst surfaces such as CO<sub>2</sub> hydrogenation using the AP-HAXPES system have been investigating on typical conditions of  $\sim 5 \times 10^4$  Pa and  $\sim 600$  K.

The third subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Moreover, conventional temperature dependent EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional materials as negative thermal expansion alloys.

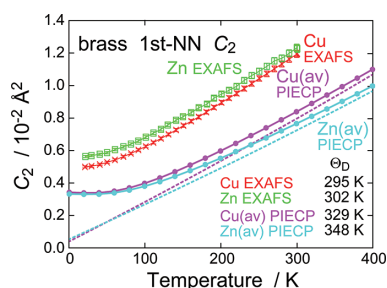
#### Selected Publications

- 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. Metallic Bonds and Thermal Vibration in Brass<sup>1)</sup>

Nature of the metallic bond and thermal vibration in brass alloy is investigated from the local structural and thermodynamical points of view by the temperature-dependent Cu and Zn K-edge EXAFS spectroscopy and the path-integral effective classical potential (PIECP) theoretical simulation. It is unexpectedly found that the thermal vibrational amplitude around Zn is a little but meaningfully smaller than that around Cu, although it is usually believed that Zn is a much softer metal than Cu in terms of various thermodynamical physical quantities of elemental metals. Moreover, it is found that the nearest neighbor distance around Zn is almost equivalent to that around Cu (only  $\sim 0.01$  Å difference), although the metallic radius of Zn commonly used is considerably larger than that of Cu ( $\sim 0.06$ – $0.09$  Å difference). These peculiar findings can be interpreted as a result of confinement of Zn atoms in a smaller space than usual and a significantly larger repulsive potential of Zn than Cu.

Figure 1 shows the mean square relative displacements  $C_2$  for the first-nearest neighbor (NN) shells obtained by the EXAFS experiment and the PIECP simulation. The EXAFS results show slightly smaller temperature dependence around Zn than around Cu, this yielding the Debye temperatures of  $\Theta_D(\text{Cu}) = 295$  K and  $\Theta_D(\text{Zn}) = 302$  K. The PIECP results agree with the EXAFS finding qualitatively [ $\Theta_D(\text{Cu}) = 329$  K and  $\Theta_D(\text{Zn}) = 348$  K]. This consequence is surprising since it seems to be essentially contradictory to the simple prediction based on the potential stiffness (Cu should be stiffer than Zn). The reason for a smaller thermal vibration and thus a larger force constant in Zn–Zn atom pair is probably ascribed to a steeper repulsive potential at a shorter distance side in the Zn–Zn pair. When the system is really diatomic, the Zn–Zn distance is hardly contracted due to the steep repulsive potential and is easily elongated, resulting in large anharmonic vibrational amplitude in the diatomic  $\text{Zn}_2$  molecule. On the contrary, in a closed packed solid like *fcc*, the Zn–Zn distance is hardly elongated due to the existence of other atoms at the opposite side, leading to confinement of the Zn atom. This indicates that the Zn atoms in brass are likely to be confined in a space that is a little too small for Zn and are hardly movable.

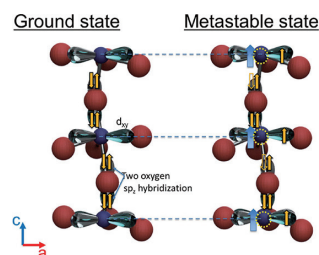


**Figure 1.** Mean square relative displacements  $C_2$  for the first-nearest neighbor pairs obtained by the EXAFS analysis (with error bars; Cu: Red; Zn: Green) and the PIECP simulations (average Cu: Magenta; average Zn: Light blue; solid line: Quantum; dashed line: Classical), respectively. The corresponding Debye temperatures are also given in the figure.

## 2. Metastable Structure of Photoexcited $\text{WO}_3$ Determined by the Pump–Probe EXAFS Spectroscopy<sup>2)</sup>

Photocatalysts have drawn much attention with respect to harvesting sunlight to split water into  $\text{H}_2$  and  $\text{O}_2$ . Usually, the process is understood using the energy band model. In the energy band model, the positions of Fermi level, minimum of the conduction band, and maximum of the valence band are important with respect to the reduction and oxidation potentials for  $\text{H}_2/\text{H}_2\text{O}$  and  $\text{O}_2/\text{H}_2\text{O}$ . The local structure and electronic state of the photoexcited state need to be elucidated to understand the photocatalysis of water splitting and to improve the performance of water-splitting photocatalysts. In this work, we report the PP-EXAFS results for the structure of the metastable (MS)  $\text{WO}_3$  state to clarify the local structure change and to attempt to explain the long formation time for the MS  $\text{WO}_3$ .

The  $\text{WO}_3$  aqueous solution jet was supplied to the cross point of the laser used for photoexcitation (mode-lock Ti-sapphire laser with a 1 ps pulse width, 945 Hz repetition rate, and 400 nm wavelength) and the X-ray beam emitted from the Photon Factory Advanced Ring (single bunch operation with pulse width of 100 ps, and pulse interval of 1.26  $\mu\text{s}$ ). The fluorescence X-rays were monitored using a scintillation counter with a Cu filter to attenuate the elastic X rays. The local structure of  $\text{WO}_3$  photocatalyst in the photoexcited MS state created 150 ps after laser irradiation as well as the ground state (GS) one has been determined by pump–probe EXAFS and constrained thorough search EXAFS analysis. As shown in Figure 2, a highly distorted octahedral local structure was found, especially one of the shortest W–O was further shortened. We have discussed some contradiction with theoretical calculation and propose a possible structure for the metastable state.



**Figure 2.** The local structure change in the ground state (GS)  $\text{WO}_3$  and the metastable (MS)  $\text{WO}_3$ . Large red and small blue circles represent O and W atoms, respectively. Yellow broken circles indicate the position of W in GS. Thick blue arrows show the movement of W atoms in the MS  $\text{WO}_3$ . W atoms along the *c*-axis move in the direction corresponding to  $\text{W}=\text{O}$  contraction. Orange filled and empty arrows in the orbitals correspond to electrons with spin and holes, respectively. Grey filled circles indicate holes. The unpaired electron spins are all parallel in the polaron cluster.

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- 1) T. Yokoyama, *Phys. Chem. Chem. Phys.* **25**, 3413–3419 (2023).
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# Exotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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#### Professional Employment

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2019 JST-PRESTO Researcher [Innovative optics and photonics]  
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#### Awards

2014 Young Scientist Award, 33<sup>rd</sup> Annual Meeting of the SSSJ  
2014 39<sup>th</sup> 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 12<sup>th</sup> Young Scientist Awards of the Japan Society for Molecular Science  
2019 The 14<sup>th</sup> Young Scientist Award of the Physical Society of Japan

#### Member

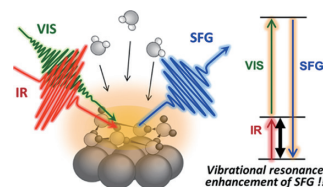
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Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down 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 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.*, “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).
- 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. Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity<sup>1)</sup>

Squeezing light beyond the diffraction limit and controlling the optical processes caused by the nano-confined light are central issues of nanophotonics. In particular, localized and enhanced light at the plasmonic nanogaps in scanning probe microscopes provides us unique platform for obtaining site-specific optical information at the molecular/atomic scale. Very recently, not only linear but also nonlinear optics have been applied to such tip-enhanced nanoscopy to gain higher sensitivity and spatial resolution. In this context, understanding the intrinsic nonlinear optical properties of plasmonic nanocavities is of growing importance to control the nanosized nonlinear optics more precisely. Recently, we have directly tackled this issue by focusing on second harmonics of wide range of infrared light enhanced in the tip-substrate plasmonic nanogaps. Combining a wavelength-tunable femtosecond pulse laser system with a scanning tunnelling microscope, we for the first time report unexpectedly broad tip-enhanced nonlinear optical response in a plasmonic nanocavity.

We demonstrated that the strong tip-enhancement of second harmonic generation (SHG) is maintained over the visible to infrared wavelength range. The prominent geometrical effects of plasmonic tips dominating this broadband enhancement ability were also verified; while the micrometer-scale tip shafts extend the spectral range of the field enhancement to the near- and mid-infrared region, the nanometer-scale tip apexes mainly contribute to boosting the visible/near-infrared light. This indicates that the nanometer-scale tip apexes and micrometer-scale tip shafts jointly enable the simultaneous enhancement of both infrared excitation and visible/infrared radiation processes, realizing the strongly enhanced SHG over the visible to infrared broadband region. Indeed, we have also succeeded in demonstrating both experimentally and theoretically that the broadband tip-enhanced SHG properties can be significantly altered in response to the micro- and macro-scale tip structures.

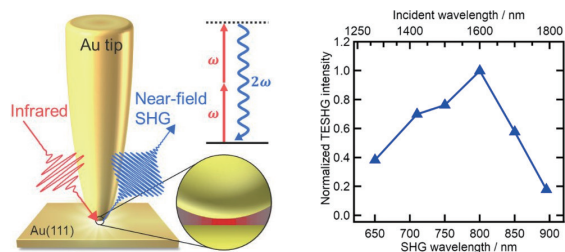


Figure 2. Tip-enhanced second harmonic generation.

## 2. Critical Impacts of Interfacial Water on the Photocatalytic C–H Conversion of Methane<sup>2,3)</sup>

On-site and on-demand photocatalytic methane conversion under ambient conditions is one of the urgent global challenges for the sustainable use of ubiquitous methane resources. However, the lack of microscopic knowledge on its reaction

mechanism prevents the development of engineering strategies for methane photocatalysis. Combining real-time mass spectrometry and *operando* infrared absorption spectroscopy with *ab initio* molecular dynamics simulations, here we report key molecular-level insights into photocatalytic green utilization of methane. Activation of the robust C–H bond of methane is hardly induced by the direct interaction with photogenerated holes trapped at the surface of photocatalyst; instead, the C–H activation is significantly promoted by the photoactivated interfacial water species. The interfacial water hydrates and properly stabilizes hydrocarbon radical intermediates, thereby suppressing their overstabilization. Owing to these water-assisted effects, the photocatalytic conversion rates of methane under wet conditions are dramatically improved by typically more than 30 times at ambient temperatures ( $\sim 300$  K) and pressures ( $\sim 1$  atm) in comparison to those under dry conditions. This study sheds new light on the role of interfacial water and provides a firm basis for design strategies for non-thermal heterogeneous catalysis of methane under ambient conditions.

## 3. Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water<sup>4)</sup>

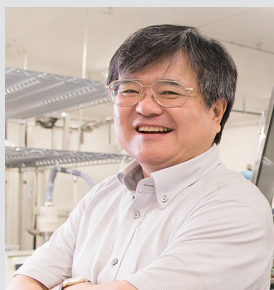
Environmentally sustainable and selective conversion of methane to valuable chemicals under ambient conditions is pivotal for the development of next-generation photocatalytic technology. However, due to the lack of microscopic knowledge about the non-thermal methane conversion, controlling and modulating photocatalytic oxidation processes driven by photogenerated holes remain a challenge. Here, we report novel function of metal cocatalysts to accept photogenerated holes and dominate the oxidation selectivity of methane, which is clearly beyond the conventional concept in photocatalysis that the metal cocatalysts loaded on the surfaces of semiconductor photocatalysts mostly capture photogenerated electrons and dominate reduction reactions exclusively. The novel photocatalytic role of metal cocatalysts was verified by *operando* molecular spectroscopy combined with real-time mass spectrometry for metal-loaded  $\text{Ga}_2\text{O}_3$  model photocatalysts under methane gas and water vapor at ambient temperature and pressure. Our concept of metal cocatalysts that modulate photocatalytic oxidation as well as reduction opens a new avenue for controlling photocatalytic redox reactions by metal-cocatalyst engineering.

### References

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- 2) H. Sato, A. Ishikawa, H. Saito, T. Higashi, K. Takeyasu and T. Sugimoto, *Commun. Chem.* **6**, 8 (2023).
- 3) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).
- 4) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).



## Organic Solar Cells

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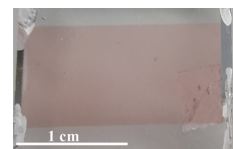
**Keywords**

Organic Semiconductors, Up-Conversion, Lateral Junction

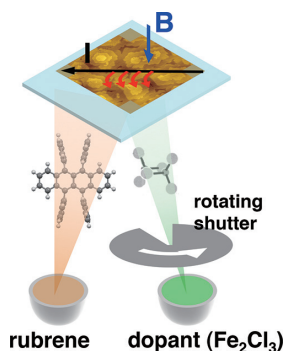
Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc.* Followings are our recent results. (1) Photon up-conversion (UC) from near infrared (NIR) to visible yellow (Figure 1) by utilizing charge transfer (CT) states at donor/acceptor (D/A) interface of organic solar cells. (2) A novel concept of the structure of organic solar cell, namely, a lateral junction in which the photogenerated holes and electrons are laterally transported and extracted to the respective electrodes. Even 1.8 cm-length lateral cells (Figure 2) showed clear photovoltaic behavior. (3) The reduction of open-circuit voltage ( $V_{oc}$ ) loss due to non-radiative recombination in organic solar cells by using high-mobility organic semiconductors. The  $V_{oc}$  reaching to thermodynamic (Shockley-Queisser) limit was observed. (4) 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, and the ppm-level doping effects using an ultra-slow deposition technique reaching  $10^{-9}$  nm  $s^{-1}$  (Figure 3) in organic rubrene single crystals measured by the Hall effect, which shows a doping efficiency of 82% comparable to the B in Si. These results can be regarded as a foundation for the construction of highly efficient organic solar cells.



**Figure 1.** Up-converted (UC) yellow emission by star-shaped near infrared irradiation.



**Figure 2.** Picture of a 1.8 cm-length lateral cell.



**Figure 3.** Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

**Selected Publications**

- 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).
- S. Izawa and M. Hiramoto, “Efficient Solid-State Photon Upconversion by Spin Inversion at Organic Semiconductor Interface,” *Nat. Photonics* **15**, 895–900 (2021).
- J. P. Ithikkal, A. Girault, M. Kikuchi, Y. Yabara, S. Izawa and M.

Hiramoto, “Photovoltaic Behavior of Centimeter-Long Lateral Organic Junctions,” *Appl. Phys Express* **14**, 094001 (2021).

- *Organic Solar Cells—Energetic and Nanostructural Design*, M. Hiramoto and S. Izawa, Eds., Springer Nature Singapore Pte Ltd. (2021).
- M. Hiramoto, “Organic Photocurrent Multiplication,” in *the Series of Electronic Materials: Science & Technology*, Springer Nature Singapore Pte Ltd. (2023).

## 1. Blue Organic Light-Emitting Diode with a Turn-On Voltage at 1.47 V<sup>1)</sup>

Blue light is vital for light-emitting devices, lighting applications, as well as smartphone screens and large screen displays. However, it is challenging to develop efficient blue organic light-emitting diodes (OLEDs) owing to the high applied voltage required for their function. Conventional blue OLEDs typically require around 4 V for a luminance of 100 cd/m<sup>2</sup>; this is higher than the industrial target of 3.7 V—the voltage of lithium-ion batteries commonly used in smartphones. Therefore, there is an urgent need to develop novel blue OLEDs that can operate at lower voltages.

We reported a novel OLED device with a remarkable ultralow turn-on voltage of 1.47 V for blue emission and a peak wavelength at 462 nm (2.68 eV) (Figure 4).<sup>1)</sup> This OLED operates via a mechanism called upconversion (UC). Herein, holes and electrons are injected into donor (emitter) and acceptor (electron transport) layers, respectively. They recombine at the donor/acceptor (D/A) interface to form a charge transfer (CT) state. Subsequently, the energy of the CT state is selectively transferred to the low-energy first triplet excited states of the emitter, which results in blue light emission through the formation of a high-energy first singlet excited state by triplet–triplet annihilation (TTA). As the energy of the CT state is much lower than the emitter's bandgap energy, the UC mechanism with TTA significantly decreases the applied voltage required for exciting the emitter. As a result, this UC-OLED reaches a luminance of 100 cd/m<sup>2</sup>, equivalent to that of a commercial display, at just 1.97 V.

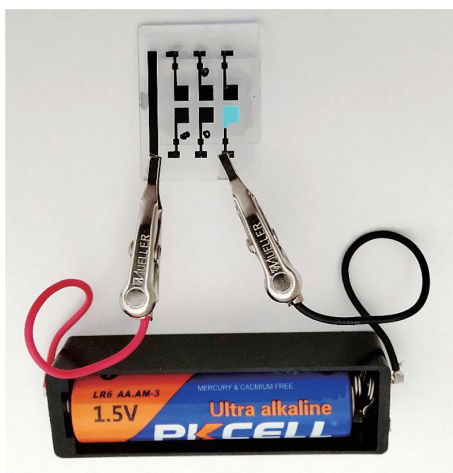


Figure 4. Lighting up a blue organic LED with a single 1.5 V battery.

## 2. Exciton-Free Carrier Generation in Doped Rubrene Single Crystals<sup>2)</sup>

We combined the rubrene organic single crystal growth technique with our original ultra-slow deposition technique of 10<sup>-9</sup> nm s<sup>-1</sup> and have succeeded in producing the 1 ppm doped organic single crystal and in detecting the Hall effect signal (Figure 3).

Doping efficiencies of 82 and 60% for hole creation were observed for the rubrene single crystal by doping with the organic acceptors F4-TCNQ and HAT-CN, respectively. Corresponding activation energies ( $\Delta E_A$ ) are 9 and 26 meV (Figure 5), which are smaller than the thermal energy of room temperature. So, the organic acceptor doping can be regarded as exciton-free carrier generation. The organic dopants also observed a slight decrease in Hall mobility. An interstitial doping model is proposed to avoid hole scattering and disturbance of hole delocalization. On the other hand, less efficient doping efficiencies of 37 and 8% by doping inorganic acceptors of Mo<sub>3</sub>O<sub>9</sub> and Fe<sub>2</sub>Cl<sub>6</sub> were observed. Corresponding  $\Delta E_A$  are 51 and 144 meV (Figure 5). This can be regarded as carrier generation through the Wannier excitons. A significant decrease in Hall mobility was observed for the inorganic dopants. A substitutional doping model that considers both hole scattering and the disturbance of hole delocalization is proposed.

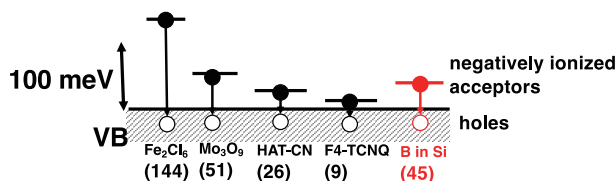


Figure 5. Energetic diagram of acceptor levels for Mo<sub>3</sub>O<sub>9</sub>, Fe<sub>2</sub>Cl<sub>6</sub>, F4-TCNQ, and HAT-CN in rubrene single crystal. That for B in Si is also shown for comparison. Numericals in the parentheses are activation energies in meV.

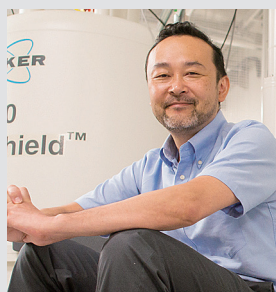
### References

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- 2) M. Hiramoto, “Carrier generation in high-mobility organic semiconductors,” Keynote lecture in 13th International Conference on Nano-Molecular Electronics, Tokyo Institute of Technology, Japan, 13, Dec. 2022.

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# Solid-State NMR for Molecular Science

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2006 Associate Professor, Institute for Molecular Science  
Associate Professor, The Graduate University for Advanced Studies

### Award

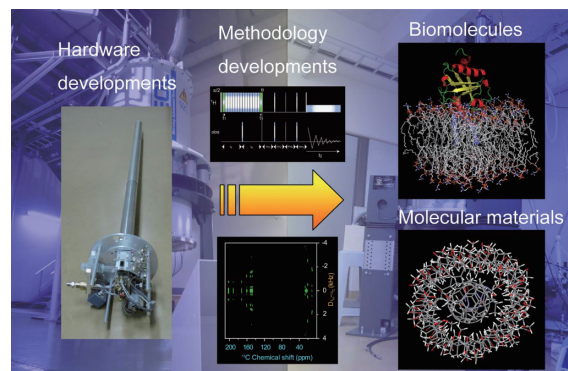
2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

Member  
Secretary  
YOKOTA, Mitsuyo

**Keywords** Solid State NMR, Biomolecules, Developments

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

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



**Figure 1.** Outline of our studies.

### Selected Publications

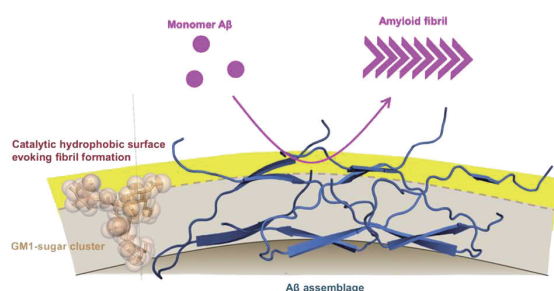
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## 1. Structural Determination of Amyloid- $\beta$ Protein Oligomer Promoted on Model Neuronal Cell Membranes Using State NMR<sup>1)</sup>

Amyloid  $\beta$  ( $A\beta$ ) 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  $A\beta$  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  $A\beta(1-40)$  induced on DMPC bilayers based on solid-state NMR.<sup>2)</sup> We have been collaborated with Prof. Kato group and Prof. Okumura group for those  $A\beta$  studies.

In the current study, the molecular structure of  $A\beta(1-40)$  oligomer induced on model neuronal cell membranes consisting of GM1 and DMPC have been determined together with their intermolecular packing using solid-state NMR. Based on information of intra- and intermolecular distances and torsion angles of backbone obtained from solid-state NMR analyses, precise molecular structure of  $A\beta$  oligomer was determined from restrained molecular dynamics simulations. In addition, the location of C-terminal segment of  $A\beta(1-40)$  on the lipid bilayers has been clarified by solid-state NMR experiment in addition to biochemical experiments.



**Figure 2.** Schematic drawing of  $A\beta$  assemblage on GM1-containing membrane which catalytically promotes amyloid fibrillization.

The determined  $A\beta$  structure conforms disordered N-terminus followed by center and C-terminus  $\beta$ -sheets.  $A\beta$  takes intermolecular configuration of antiparallel  $\beta$ -sheet among adjacent molecules, in which different from  $A\beta$  fibrils prepared in solution and also  $A\beta$  oligomer induced on DMPC bilayers.<sup>2)</sup> Those suggest specific roles of GM1 for the formation of  $A\beta$  oligomers. Based on those experimental evidences, finally we have proposed the model process that  $A\beta$  assemblage on GM1-containing membrane catalytically promotes amyloid fibrillization as shown in Figure 1. We expect the significant contribution of our determined  $A\beta$  oligomer structure to reveal the molecular mechanism of  $A\beta$  fibrils on neuronal cell membranes, and thus understanding of Alzheimer's disease.

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

We have been working on developments of totally original solid-state NMR probes during a couple of years. The probe has been built using originally designed parts except for spinning module. Then, we have been working on developments of original sample spinning modules for magic angle spinning (MAS) solid-state NMR probes which are fully compatible with currently using Bruker spectrometer and commercial sample tubes. We started the design of a spinning module for standard 4.0 mm sample tube for Bruker. After 3 times of version up, our original spinning module over the spinning performance of commercial one from Bruker. In order to improve spinning performance further for our original spinning module, the development of original sample tube may be essential due to the lack of strength of commercial sample tube.

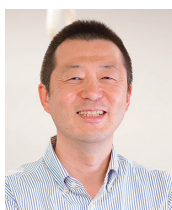
Currently, final version of the spinning module is under development in order to realize installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.

### References

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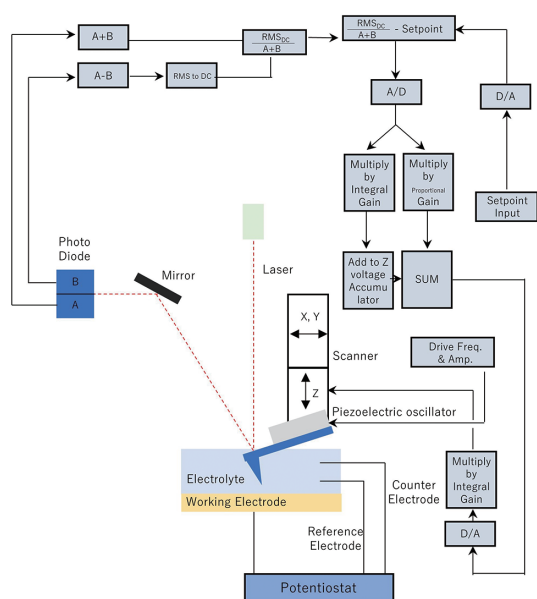
# Clarification of Physical Properties and Reaction Mechanisms at Surfaces and Interfaces by Scanning Probe Microscopy

## Instrument Center



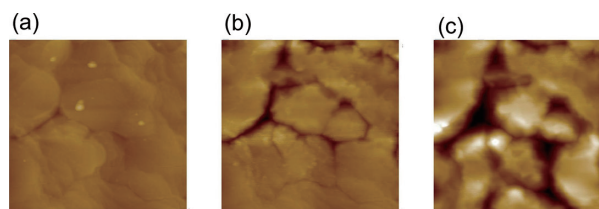
MINATO, Taketoshi  
Senior Researcher

Surfaces and interfaces are fascinating fields for physical, chemical and biological phenomena. While these phenomena are well known, the mechanisms underlying them remain poorly understood in many cases. Scanning probe microscopy (SPM) is a superior method for analyzing the mechanism. We have established the advanced system to clarify these mechanisms at surface and interface in nano/atomic scales (Figure 1).



**Figure 1.** SPM system used in the analysis of physical properties and reaction mechanism at the surface and interface.

Recently, our focus has been on analyzing the electrode/electrolyte interface in electrochemical reactions.<sup>1,2</sup> Figure 2 shows the changes of the surface structure of gold electrode during the electrochemical dissolution in aqueous electrolyte. This dissolution reaction proceeds through the reactions of halogen ions with gold atoms. However, the elemental process driving this reaction remain unsolved. Through high resolved image and mechanical properties analysis of the surface by SPM, we have found the reactions are triggered by the distortion of the surface structure.



**Figure 2.** SPM images ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) of the dissolution of gold surface obtained in aqueous electrolyte after (a) 0 min, (b) 5 min and (c) 9 min from starting dissolution.

In addition to above analysis, we reported several significant achievements in understanding the physical properties and reaction mechanisms by SPM. It is reported that when the electron transfers within chiral molecules, the conductivities exhibit spin-selectivity. By employing molecules capable of undergoing chiral transformations through photon and thermal excitation, stable switching of the spin selectivity within a molecule was demonstrated.<sup>3</sup> Also, it was reported that the spin-selectivity are not limited to only micro-scale chirality but can be applied to macro-scale chirality.<sup>4</sup> These reports are based on the collaborative works with the research group of Prof. Hiroshi Yamamoto at IMS. Further, we reported on investigations into the wettability and surface tension of ionic liquids with pentyl, ethoxyethyl, and ethylthioethyl groups.<sup>5</sup> This achievement is a collaborative work with the research group of Prof. Hideaki Shirota at Chiba University. These studies demonstrated that SPM can unravel the mechanism underlying surfaces and interfaces.

## References

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## 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*)

### $\pi$ -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  $\pi$ -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 dithienonaphthobisthiadiazole-based polymer was combined with a nonfullerene acceptor, it showed high efficiencies of over 16%. 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*)

### Time-Resolved Cyclotron Resonance of Optically Injected Free Carriers in Semiconductor Crystals

Momentum and spin are degrees of freedom for free carriers other than charge, which have recently attracted attention as valleytronics and spintronics. Silicon, a semiconductor commonly used in electronics, is also a strong candidate for valleytronics due to the multi-valley structures in its conduction band. Maintaining and transporting valley polarization is key to device design. Time-resolved cyclotron resonance (TRCR) can measure valley polarization by distinguishing electrons with different effective masses under a magnetic field. We performed TRCR measurements of optically injected electrons in a highly pure silicon crystal at cryogenic temperatures using a time-resolved electron spin resonator by applying an additional DC-electric field. Analysis of the evolution of the TRCR spectra after a laser pulse elucidates how the optically induced valley polarization is dispersed by intra-valley and inter-valley electron scattering under an operando DC-electric field. The results provide basic physical parameters for designing future devices.