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 Laser Research Center for Molecular Science and the UVSOR, closely collaborate with the Department.

The core topics of the Department include ultrahigh-precision 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.

Development of Advanced Near-Field Spectroscopic Imaging and Application to Nanomaterials

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Division of Photo-Molecular Science I

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Education
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Professional Employment
1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
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2000 Professor, Institute for Molecular Science
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Keywords Near-Field Optical Microscopy, Plasmons, Excited States of Nanomaterials

There is much demand for the studies of local optical properties of molecular assemblies and materials, to understand nanoscale physical and chemical phenomena and/or to construct nanoscale optoelectronic devices. Scanning near-field optical microscopy (SNOM) is an imaging method that enables spatial resolution beyond the diffraction limit of light. Combination of this technique with various advanced spectroscopic methods may provide direct methods to probe dynamics in nanomaterials and nanoscale functionalities. It may yield essential and basic knowledge to analyze origins of characteristic features of the nanomaterial systems. We have constructed apparatuses of near-field spectroscopy and microscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable near-field measurements of two-photon induced emission, femtosecond time-resolved signals, and circular dichroism, in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatiotemporal 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, and so forth.

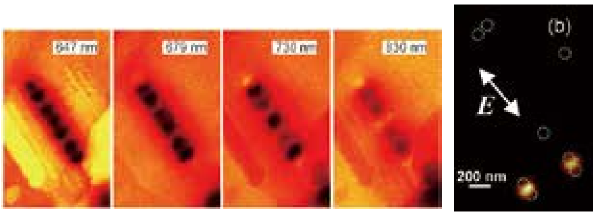

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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, 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).
- H. Okamoto and K. Imura, "Near-Field Optical Imaging of Enhanced Electric Fields and Plasmon Waves in Metal Nanostructures," *Prog. Surf. Sci.* **84**, 199–229 (2009).

1. Observation of Plasmon Wave Packet Motions via Femtosecond Time-Resolved Near-Field Imaging Techniques[1,2]

The generation and dynamics of plasmon wave packets in single gold nanorods were observed at a spatiotemporal scale of 100 nm and 10 fs via time-resolved near-field optical microscopy. Because an ultrashort pulse has a broad spectral width, one can excite more than two resonant modes of materials if their frequency range is covered with the pulse spectrum. In this study, dynamics after excitation of single plasmon mode (for a relatively low aspect ratio rod) and that after multi-mode excitation (for a relatively high aspect ratio rod) were compared.

When a single plasmon mode was excited, time-resolved signals showed single-exponential decay profiles reflecting the dephasing of the mode, and time-resolved near-field image feature was essentially independent of time. In contrast, if two plasmon modes of a nanorod were excited coherently with an ultrashort near-field pulse, a decay and revival feature of the time-resolved signal was obtained, which reflected the reciprocating motion of the wave packet. The time-resolved near-field images were also indicative of the wave packet motion. At some period of time after the excitation, the spatial features of the two modes appeared alternately (Figure 2(a)), showing motion of plasmonic wave crests along the rod. The wave packet propagation was clearly demonstrated from this observation with the aid of a simulation model (Figure 2(b,c)). The present experimental scheme opens the door to coherent control of plasmon-induced optical fields in a nanometer spatial scale and femtosecond temporal scale.

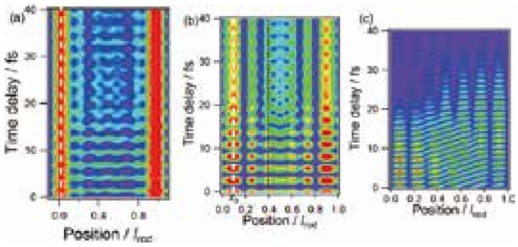

Figure 2. (a) Time variation (ordinate) of line profiles of transient near-field images of a gold nanorod along the rod axis (abscissa). At ~20 fs, two different features of plasmon modes appear alternately with a period of ~3 fs. (b) Model simulation of a position-time profile of excitation probability that corresponds to the near-field observation in panel (a), which qualitatively reproduced the characteristic feature observed at ~20 fs. (c) Simulated time evolution of the plasmon wave packet after local excitation with a single ultrashort pulse at a position x_0 in panel (b). Propagation of the wave packet from left to right (0–15 fs), reflection at the right end, and back propagation to left (20–40 fs) are observed.[2)]

2. Optical Activity Governed by Local Chiral Structures in Two-Dimensional Curved Metallic Nanostructures[3)]

Chiral nanostructures show macroscopic optical activity. Local optical activity and its handedness are not uniform in the nanostructure, and are spatially distributed depending on the shape of the nanostructure. In this study we fabricated curved chain nanostructures made of gold by connecting two or more arc structures in a two-dimensional plane. Spatial features of local optical activity in the chain structures were evaluated with near-field circular dichroism (CD) imaging. The electromagnetic simulation predicted that local optical activity appears at inflection points where arc structures are connected, and the handedness of the local optical activity was dependent on the handedness of the local chirality at the inflection point. In the near-field CD images of fabricated chain nanostructures, the local optical activity was found to be determined by the handedness of the inflection point, for the fabricated chain structures having two or more inflection points, consistent with the simulation. The local optical activity was thus governed primarily by the local chirality of the inflection points for the gold chain structures.

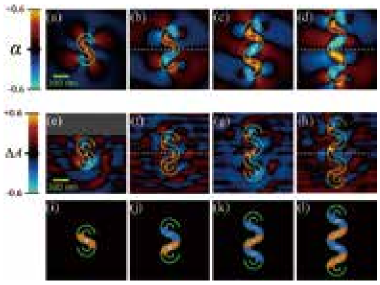

Figure 3. (a–d) Spatial distribution of theoretically calculated electric field intensity difference (α) for curved chain structures. (e–h) Spatial distribution of local CD signal (Δ*A*) observed with a near-field CD microscope for chain structures. (i–l) Schematic representations of the measured CD signal distribution in panels (e–h). The wavelength of observation was 785 nm for both the calculation and the imaging experiment. The inflection points gave local CD signals whose signs were determined by the handednesses (chirality) of the local structures, except for the minimal chain ("S" structure).[3)]

References

1) Y. Nishiyama, K. Imaeda, K. Imura and H. Okamoto, *J. Phys. Chem. C* **119**, 16215–16222 (2015).
2) Y. Nishiyama, K. Imura and H. Okamoto, *Nano Lett.* **15**, 7657–7665 (2015).
3) T. Narushima, S. Hashiyada and H. Okamoto, *Chirality* **28**, 540–544 (2016).

Awards

HASHIYADA, Shun; Excellent poster award 2015, Japan Society for Molecular Science.
NISHIYAMA, Yoshio; The OMC outstanding award, Optical Manipulation Conference 2016.

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Exploring Quantum-Classical Boundary

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Professional Employment

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2003	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2004	Visiting Professor, Tohoku University (–2005)
2007	Visiting Professor, Tokyo Institute of Technology (–2008)
2009	Visiting Professor, The University of Tokyo (–2011)
2012	Visiting Professor, University of Heidelberg
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Awards

1998	Award by Research Foundation for Opto-Science and Technology
2007	JSPS Prize
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  GOTO(SHIKANO), Haruka
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  TIRUMALASETTY PANDURANGA, Mahesh*
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Keywords Quantum-Classical Boundary, Coherent Control, Attosecond

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 a bulk solid composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as "collapse" in quantum mechanics, is often accepted as a discontinuous event, but a basic question arises: When and how the delocalized wave function becomes localized? Our dream is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this dream in mind, we have developed coherent control with precisions on the picometer spatial and attosecond temporal scales. Now we apply this ultrafast and ultrahigh-precision coherent control to delocalized wave functions of macroscopic many-particle systems such as an ensemble of ultracold Rydberg atoms and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

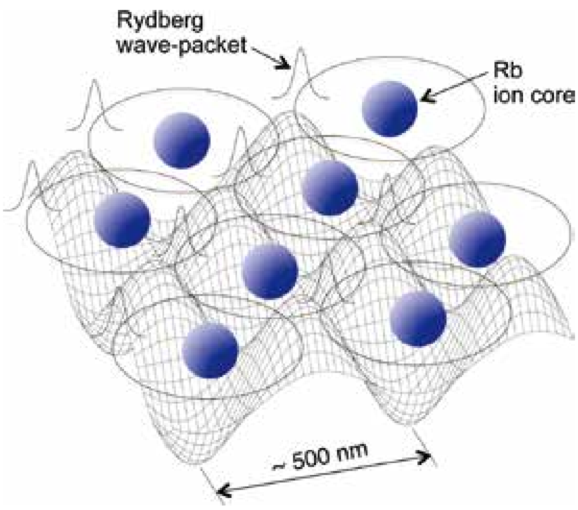

Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.2)

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 a Strongly-Correlated Ultracold Rydberg Gas," *arXiv:1504.03635* (2015).

1. Time Domain Ramsey Interferometry with Interacting Rydberg Atoms[3)]

We theoretically investigate the dynamics of a gas of strongly interacting Rydberg atoms subject to a time domain Ramsey interferometry protocol. The many-body dynamics is governed by an Ising-type Hamiltonian with long range interactions of tunable strength. We analyze and model the contrast degradation and phase accumulation of the Ramsey signal and identify scaling laws for varying interrogation times, ensemble densities and ensemble dimensionalities.

References

1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) C. Sommer *et al.*, *arXiv:1604.02314* (2016).

Awards

TAKEDA, Shuntaro; Young Scientist Award of the Physical Society of Japan (2016).
TAKEDA, Shuntaro; Inoue Research Award for Young Scientists (2016).

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Local Chemical State Analysis Using Soft X-Rays: Experiment and Theory

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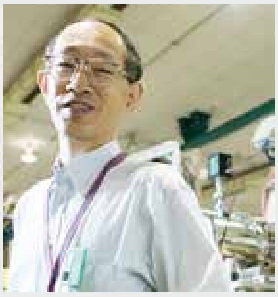

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Education

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Professional Employment

1981	JSPS Postdoctoral Fellow
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1988	Lecturer, The University of Tokyo
1989	Associate Professor, Kyoto University
1993	Professor, Institute for Molecular Science
1993	Professor, The Graduate University for Advanced Studies
1996	Visiting Professor, McMaster University, Canada
2008	Visiting Professor, Université P&M Curie - Paris VI, France
2011	Visiting Professor, Université Paris-Sud - Paris XI, France
2013	Visiting Professor, Freie Universität Berlin, Germany

Awards

2015	The 68th Chemical Society of Japan (CSJ) Award

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YAMANE, Hiroyuki
JSPS Post-Dctoral Fellow
YUZAWA, Hayato
Secretary
NAKANE, Junko
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Keywords X-Ray Spectroscopy, Local Chemical State Analysis, Quantum Chemistry

This research group has strong international network in the field of soft X-ray molecular sciences using world-leading advanced synchrotron radiation facilities for more than 20 years.

Soft X-rays cannot pass through air or bulk water due to photoabsorption of N_2, O_2, and H_2O molecules. Such strong photoabsorption can be used in highly sensitive chemical state analysis of thin or dilute samples, because soft X-rays with photon energies of 100–700 eV excite 1s inner-shell (K-shell) electrons of chemically important light elements such as C, N, and O selectively to unoccupied states of molecules. The 1s electron is localized and bound by an atom in the system but is slightly affected by surrounding atoms and chemical bonds. Therefore, we can select a 1s electron in each atom in molecules by choosing different X-ray energies with 10–100 meV accuracy, and know each atomic component and chemical environment in the unoccupied state.

In order to realize *in situ* and *in operando* chemical state analysis revealing local electronic structures and weak intermolecular interactions in molecular systems such as organic solids, liquids, aqueous solutions, and molecular clusters, we are developing and improving several kinds of thin sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). We are also using resonant and non-resonant X-ray emission spectroscopy (XES) and angle-resolved photoelectron spectroscopy (ARPES).

Sample thickness should be optimized below 1 μm to get optimal absorbance in XAS. For inhomogeneous samples, the 10 nm-scale spatial resolution is necessary. It is also important to reduce the radiation damage of samples due to strong light-matter interaction in the soft X-ray region.

Highly brilliant soft X-rays for the chemical state analysis are available on our UVSOR-III Synchrotron in IMS. In addition to quite unique experimental and instrumental developments at UVSOR-III BL3U, BL4U and BL6U, we are developing an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

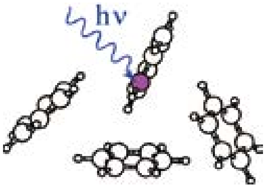

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

Selected Publications

- M. Nagasaka, H. Yuzawa, T. Horigome, A. P. Hitchcock and N. Kosugi, "Electrochemical Reaction of Aqueous Iron Sulfate Solutions Studied by Fe L-Edge Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. C* **117**, 16343–16348 (2013).
- M. Nagasaka, K. Mochizuki, V. Leloup and N. Kosugi, "Local Structures of Methanol-Water Binary Solutions Studied by Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. B* **118**, 4388–4396 (2014).
- H. Yamane and N. Kosugi, "Substituent-Induced Intermolecular Interaction in Organic Crystals Revealed by Precise Band Dispersion Mesurements," *Phys. Rev. Lett.* **111**, 086602 (5 pages) (2013).

1. Local Structures of Liquid Benzene Studied by C K-Edge Soft X-Ray Absorption Spectroscopy at Different Temperatures

Recently, we reported C K-edge X-ray absorption spectroscopy (XAS) of benzene in gas, cluster and solid phases.[1,2] Although solid benzene mainly shows T-shaped structures, liquid benzene shows both T-shaped and parallel structures. In this work, we have measured C K-edge XAS of liquid benzene at different temperatures by using a transmission-type liquid flow cell,[3] and studied the temperature effect of the molecular interaction.

Figure 2(a) shows C K-edge XAS of liquid benzene at different temperatures. The C 1s → π* peak shows adiabatic (0, 0) transition and vibrational fine structures at the higher photon energy. Figure 2(b) shows the energy shifts of (0, 0) transition peaks of liquid benzene from gas as a function of temperature. The π* peak shows a shift to the lower photon energy by increasing the temperature. The energy shift of liquid benzene relative to the gas phase is 29.4 meV at 25.3 °C. This shift is smaller than in solid benzene and clusters, which is 55 meV[2] and 70 meV,[1] respectively.

The lower energy shift of the π* peak is caused by induced polarization with surrounding molecules. Because the molecular distance in solid phase is smaller than that in liquid phase, the π* peak in solid phase shows lower photon energy shifts than that in liquid phase. We have performed molecular dynamics simulations of liquid benzene at different temperatures. The molecular distance in the T-shaped structure shows longer distances at higher temperatures. On the other hand, we found that the molecules in the parallel structure are getting close to each other by increasing the temperature. The lower energy shifts of the π* peak at higher temperatures would be derived from this parallel structure. In the near future, we will discuss the molecular interaction in liquid benzene by correlating C K-edge XAS results with infrared spectroscopy and molecular dynamics simulations.

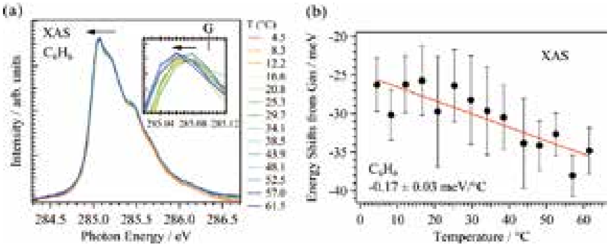

Figure 2. (a) C K-edge XAS of liquid benzene at different temperatures. The inset shows the maximum of the C 1s → π* transition in greater detail. (b) Energy shifts of C 1s → π* (0, 0) transition peak of liquid benzene relative to gaseous benzene as a function of temperature.

2. Site-Specific Organic/Metal Interaction Revealed from Shockley-Type Interface State

The Shockley state is a well-known surface state associated with the breakdown of the bulk-crystal periodicity at the surface, and can be observed by using angle-resolved photoemission spectroscopy (ARPES). In the present work, we have applied the Shockley-state measurement to the well-ordered monolayer of Co phthalocyanine (CoPc) on Au(111), in order to study the site-specific organic/metal interfacial interaction quantitatively.

The Shockley state of CoPc/Au(111) is compared with that of H_2Pc/Au(111) and that of the clean Au(111) at 23 K in Figure 3. The observed Shockley state of both CoPc/Au(111) and H_2Pc/Au(111), labeled S', shows the energy shift of about 120 meV towards the Fermi level (E_F) from that of the clean Au(111) surface. The observed upshift of the Shockley state upon adsorption originates from the exchange interaction of surface electron systems by CoPc. Furthermore, one more dispersive band just below E_F is observed for CoPc/Au(111), labeled X, which is not observable for H_2Pc/Au(111).

We found from the temperature dependence of ARPES for CoPc/Au(111) that peaks S' and X can be ascribed to the Shockley state modified by the site-specific interfacial interaction at the Pc-ligand site and the central-metal Co site in the molecule, respectively. Using the relation of $E_a = 0.106\ \Delta E_{SS}$, where E_a and ΔE_{SS} are the adsorption energy and the shift in the Shockley state, respectively,[4] we determined the site-specific interfacial bonding strength in CoPc/Au(111) at 23 K as E_a = 13.0 meV/Å^2 at the Pc-ligand site and E_a = 45.9 meV/Å^2 at the central-metal Co site.

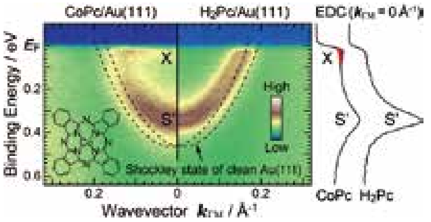

Figure 3. The *E*–***k*** map around the Shockley state for CoPc/Au(111) and H_2Pc/Au(111) at 23 K, together with the best-fit curve of the Shockley state for the clean Au(111) at 23 K (black dashed curve).

References

1) I. L. Bradeanu *et al.*, *Phys. Chem. Chem. Phys.* **8**, 1906 (2006).
2) R. Flesch *et al.*, *Phys. Chem. Chem. Phys.* **14**, 9397 (2012).
3) M. Nagasaka *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **200**, 293 (2015).
4) J. Ziroff *et al.*, *Surf. Sci.* **603**, 354 (2009).

Awards

KOSUGI, Nobuhiro; The 68th Chemical Society of Japan (CSJ) Award (2015).
NAGASAKA, Masanari; MORINO Foundation for Molecular Science 2016.

Electronic Property of Functional Organic Materials

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Education

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2003	Postdoctoral Fellow, Wuerzburg University
2004	Assistant Professor, Chiba University
2007	Associate Professor, Chiba University
2009	Visiting Associate Professor, Institute for Molecular Science
2013	Adjunct Lecturer, The Open University of Japan
2013	Visiting Associate Professor, Soochow University
2014	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting Professor, Chiba University

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SHIMIZU, Atsuko

Keywords Photoelectron Spectroscopy, Molecular Film, 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 its origin of various device characteristics are still under debate. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule for solid phases due to van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the impacts of weak interaction on the electronic structure would be appeared as small intensity modulation of photoelectron-emission fine features depending on adsorption and aggregation on the surface. By recent development in the instrumental we can assess hidden fine structures in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small gap-state DOS, weak band dispersion and dynamic electronic polarization. To elucidate what really happens for the FOM at the interface upon weak interaction, an evaluation on the wave-function spread of the electronic states would be very important because the interface states for the physisorbed systems are described to be a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Seeing a modification of electron wave function upon weak electronic coupling as well as strong electron–phonon coupling is central issue on our agenda.

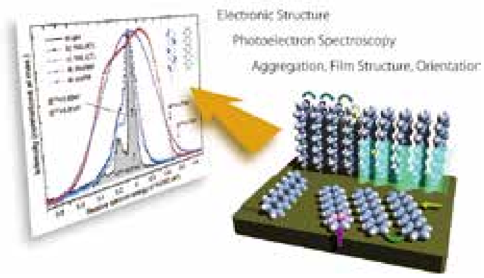

Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- F. Bussolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, "Gap States in Pentacene Thin Film Induced by Inert Gas Exposure," *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).
- S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno and S. Kera, "Charge Reorganization Energy and Small Polaron Binding Energy of Rubrene Thin Films by Ultraviolet Photoelectron Spectroscopy," *Adv. Mater.* **24**, 901–905 (2012).
- S. Kera, H. Yamane and N. Ueno, "First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films," *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Charge Transfer States Appear in the π-Conjugated Pure Hydrocarbon Molecule on Cu(111)[1)]

Understanding the metal and adsorbed molecule interaction is required to discuss the mechanism of charge transfer in functional molecular solids. We report on the results of experimental and theoretical studies on the electronic structure of gas-phase diindenoperylene (DIP) and DIP-monolayer(ML) on Cu(111). Vapor-phase ultraviolet photoelectron spectroscopy (UPS) was realized for 11.3 mg of DIP, giving reference orbital energies of isolated DIP, and UPS and inverse photoemission spectroscopy of DIP-ML/graphite were performed to obtain DIP-ML electronic states at a weak interfacial interaction. Furthermore, first-principles calculation clearly demonstrates the interfacial rearrangement. These results provide evidence that the rearrangement of orbital energies, which is realized in HOMO–LUMO and HOMO–HOMO-1 gaps, brings partially occupied LUMO through the surface-induced aromatic stabilization (SIAS) of DIP, a pure hydrocarbon molecule, on Cu(111) surface. It has been considered in SIAS, that a site-specific interaction between the heteroatoms in adsorbate molecules and the substrate plays a key role, while the present results demonstrated that the heteroatoms are not necessarily required for the formation of the charge transfer states through SIAS. In passing, it was reported that no charge transfer states are formed at the interface of perylene on Ag(111) and Cu(111), suggesting that the perylene core alone does not play a role in the CT state formation. We therefore conclude that a combination of a specific chemical structure and functional groups leading to the flexibility of the molecular skeleton is a key requirement of SIAS on metal substrates, even if the functional groups do not involve heteroatoms such as indeno-groups in DIP.

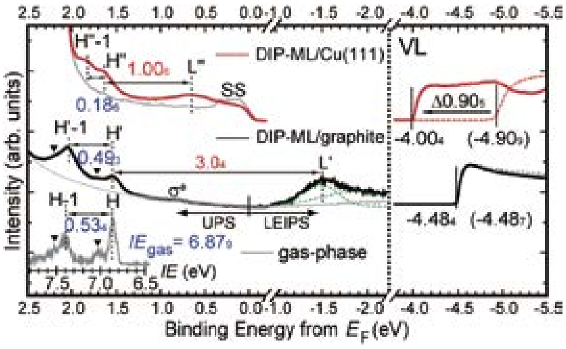

Figure 2. Comparison of He I UPS of DIP-ML on Cu(111) (red), Xe I UPS and LEIPS of DIP-ML on graphite (black), and gas-phase UPS (gray). The right panel shows vacuum levels before (dashed curves) and after (solid curves) DIP deposition. Spectra of clean surfaces of Cu(111) and graphite are also shown (pale gray). SS indicates the surface states of clean Cu(111). The gas-phase spectrum is shown in ionization energy for comparison with DIP MLs. Vibration satellites in the gas phase and DIP-ML-graphite spectra are indicated by inverted triangles. Weak features marked by σ* in UPSs of DIP-ML-graphite and the graphite substrate are the conduction band features of graphite.

2. Mechanism for Doping Induced p Type C_{60} Using Thermally Evaporated Molybdenum Trioxide (MoO_3) as a Dopant[2)]

Thermally evaporated molybdenum trioxide (MoO_3) doped C_{60} films, which could change n type features of pristine C_{60} to form a p type mixed C_{60} layer, are investigated by x-ray and ultraviolet photoelectron spectroscopy. It is found that C_{60} HOMO progressively shifts closer to the Fermi level after increased MoO_3 doping concentration, and final onset of C_{60} HOMO is pinned at binding energy of 0.20 eV, indicating the formation of p type C_{60} films. It is proposed that in charge transfer induced p type C_{60} formation, due to large electron affinity of MoO_3 (6.37 eV), electrons from HOMO of C_{60} could easily transfer to MoO_3 to form cations and therefore increase hole concentration, which could gradually push C_{60} HOMO to the Fermi level and finally form p type C_{60} films. Moreover, clear different types of C_{60} species have been confirmed from UPS spectra in highly doped films.

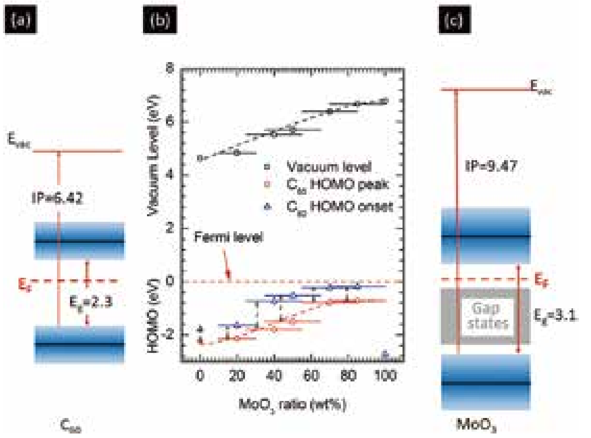

Figure 3. Evolution of energy level of MoO_3-doped C_{60} film with MoO_3 ratios. (a) and (c) Energy level diagram for pristine C_{60} and MoO_3 films respectively; (b) summarized HOMO peak of C_{60}, HOMO onset of C_{60} and vacuum level as a function of different MoO_3 doping ratios are shown according to the Fermi level position.

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Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Beam Physics, Astrobiology

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz wave to soft X-rays. Although it was constructed about 30 years ago, its performance is still in the world top level. This is the result of the continuous effort on improving the machine. Our research group has been developing accelerator technologies toward producing bright and stable synchrotron light, such as high brightness electron beam optics, novel insertion devices or state-of-the-art beam injection technique. We have been also developing novel light source technologies toward producing photons with excellent properties, such as free electron laser, coherent synchrotron radiation and laser Compton gamma-rays. We are also investigating beam physics which would be the basis of the novel light source technologies. We are exploring a future plan for the facility, such as a diffraction-limited storage ring or a free electron laser facility.

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

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- 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).
- E. Roussel, C. Evain, C. Szwaj, S. Bielawski, J. Raasch, P. Thoma, A. Scheuring, M. Hofherr, K. Ilin, S. Wünsch, M. Siegel, M. Hosaka, N. Yamamoto, Y. Takashima, H. Zen, T. Konomi, M. Adachi, S. Kimura and M. Katoh, "Microbunching Instability in Relativistic Electron Bunches: Direct Observations of the Microstructures Using Ultrafast YBCO Detectors," *Phys. Rev. Lett.* **113**, 094801 (2014).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have developed novel light source technologies using UVSOR-III electron storage ring and a dedicated experimental station BL1U which was constructed under the support of Quantum Beam Technology Program of JST/MEXT, for developing 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 beam-line. The generation of coherent synchrotron radiation based on our original method was successfully demonstrated in collaboration with Lille Univ. and Nagoya Univ. Its application is under preparation, in collaborating with Osaka Univ. Optical vortex beam from undulators are intensively investigated in collaboration with Hiroshima Univ., Nagoya Univ., AIST and so on.

Laser Compton scattering is a method to produce monochromatic and energy-tunable gamma-ray pulses. Laser pulses are injected to the storage ring and are scattered by the relativistic electrons circulating in the ring. We developed a unique method to produce ultra-short gamma-ray pulses in pico- and femtosecond range for the first time and demonstrated its potential as a powerful tool for material sciences by a photon-induced positron annihilation lifetime spectroscopy experiment, in collaboration with AIST. We have started developing an imaging technology for isotopes based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and JAEA. We have started reconstructing the resonator free electron laser on UVSOR-III, which will be used to produce intense gamma-rays through intra-cavity inverse Compton scattering.

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

2. Accelerator Technology Developments for Synchrotron Light Source and Free Electron Laser

We proposed several upgrade plans and have carried out all of them successfully. We designed a special electron beam optics intended to higher brightness. We designed necessary accelerator components, remodeled the machine and commissioned. We have designed six undulators and have successfully installed and commissioned all of them. We have succeeded in introducing a novel operation mode called Top-up operation, in which the electron beam intensity is kept quasi-constant at a high beam current, 300 mA. As the result of all these efforts, now, the machine is the brightest synchrotron light sources among the low energy machines below 1 GeV in the world.

We continue the efforts to improve the machine performance by introducing new technologies such as pulsed sextupole injection scheme. We are planning to replace some of the undulators to fit the changes of the users' requirements. Also, we are designing new accelerators for future project of the facility, such as linear accelerator based free electron laser or diffraction limited storage ring light source.

We are collaborating with Nagoya University Synchrotron Radiation Research Center (NUSR) for the accelerator developments at Aichi-SR. Accelerator magnets based on permanent magnets are being developed. Various electron sources are being developed and tested. New beam diagnostic technologies are being tested. Several PhD students from the University are involved. We are also collaborating with Accelerator Research Laboratory at KEK for the compact Energy Recovery Linac (cERL) project.

Figure 3. Optical Cavity for Resonator Free Electron Laser is under reconstruction at UVSOR-III.

Award

YAMAGUCHI, Kenta; 2016 Annual Meeting Award of the Particle Accelerator Society of Japan.

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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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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), a powerful tool in studying the electronic structure of complex materials, based on synchrotron radiation.

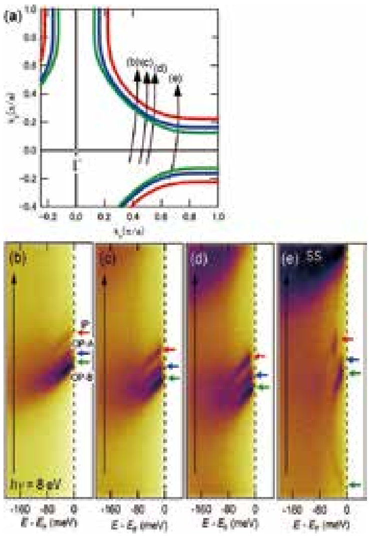

Figure 1. ARPES intensity plot of slightly-overdoped Bi2223 taken with $h\nu$ = 8 eV along FS.

Selected Publications

- K. Tanaka, T. Yoshida, A. Fujimori, D. H. Lu, Z.-X. Shen, X.-J. Zhou, H. Eisaki, Z. Hussain, S. Uchida, Y. Aiura, K. Ono, T. Sugaya, T. Mizuno and I. Terasaki, "Effects of Next-Nearest-Neighbor Hopping *t'* on the Electronic Structure of Cuprates," *Phys. Rev. B* **70**, 092503 (4 pages) (2004).
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- E. Uykur, K. Tanaka, T. Masui, S. Miyasaka and S. Tajima, "Coexistence of the Pseudogap and the Superconducting Gap Revealed by the *c*-Axis Optical Study of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$," *J. Phys. Soc. Jpn.* **82**, 033701 (4 pages) (2013).

1. Triple-Layer Splitting in Slightly-Overdoped $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ Observed by ARPES

It has been known that one of the most efficient ways to increase the critical temperature (T_c) of high-T_c cuprate superconductors (HTSCs) is to increase the number of neighboring CuO_2 planes (n). T_c generally increases from single-layer (n = 1), double-layer (n = 2), to tri-layer (n = 3) and then decreases for $n \geq 4$. Several mechanisms have been proposed to explain the n dependence of T_c. According to the tunneling mechanism of Cooper pairs between the CuO_2 planes, $T_{c,max}$ should increase with increasing n. However if one takes into account the charge imbalance between the planes and the existence of competing order, $T_{c,max}$ takes a maximum at n = 3 in agreement with experiment. Meanwhile, T_c shows tendency to increase with next-nearest-neighbor Cu–Cu hopping parameter t, which increases with the number of CuO_2 planes. Also, T_c increases with decreasing degree of out-of-plane disorder. So far, which governs the n dependence of $T_{c,max}$ has been unclear because of the lack of detailed knowledge about the electronic structure of the multi-layer cuprates.

In the case of Bi-based HTSCs, the optimum T_c ($T_{c,max}$) increases from the single-layer $Bi_2Sr_2CuO_{6+\delta}$ (Bi2201, $T_{c,max}$ = 35 K), the double-layer $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212, $T_{c,max}$ = 95 K) to the tri-layer $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223, $T_{c,max}$ = 110 K). Angle-resolved photoemission spectroscopy (ARPES) studies of double-layer Bi2212 and four-layer $Ba_2Ca_3Cu_4O_8F_2$ (F0234) have revealed the splitting of band dispersions and Fermi surfaces (FSs). In Bi2212, hybridization between the two CuO_2 planes causes splitting into the bonding and antibonding bands. The ARPES study on F0234 has indicated two energy bands due to the different hole concentrations of the outer CuO_2 planes and the inner CuO_2 planes, and correspondingly two FS sheets have been observed. In the previous ARPES results on the tri-layer Bi2223 have revealed only two FSs originated different hole concentrations of inner (IP) and outer (OP) CuO_2 planes and band splitting has not been observed. In the present study, we performed detailed low-photon-energy dependent ARPES study of slightly-overdoped Bi2223 in the superconducting states (T = 12 K) at UVSOR BL7U, and successfully observed the third band dispersion originated by the band splitting.

In Figures. 1(b)~(e), we plot ARPES intensity taken with $h\nu$ = 8 eV along FS, where the momentum positions in the k-space are shown in Figure 1(a). Three different band dispersions have been clearly observed as indicated by three arrows. By comparing the band positions in the momentum space to previous report, we have found that the band located in the center indicated by blue arrow is the newly observed band. Here, it should be noted that the intensity of each band strongly depended on the energy of incident photons and this results could not be obtained if the synchrotron light source was not used where the photon energy of the measurements is tunable.

In Figure 2, the symmetrized ARPES intensity against the Fermi level around k_x ~ 0.54 (Å^{-1}) is plotted. It clearly shows that three bands have different superconducting gaps.

The present results give us the following important messages. First, there is strong interaction between CuO_2 planes in Bi2223. Since this interaction has not been observed in four-layer F0234, it can be a critical factor to achieve the highest T_c. Second, it is not obvious why three bands show different superconducting gap size. To clarify the relationship between the interaction between CuO_2 planes and high-T_c superconductivity, it is necessary to perform temperature dependent measurements along the FS to define the Fermi arc region which should strongly contribute to the superconductivity.

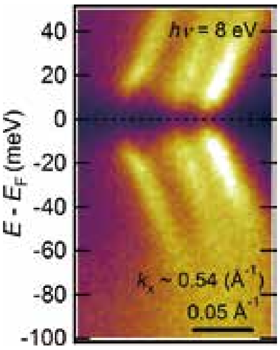

Figure 2. The symmetrized ARPES intensity against the Fermi level around k_x ~ 0.54 (Å^{-1}).

2. Development of New Spin-Resolved ARPES

UVSOR Facility in Institute for Molecular Science equipped two public undulator-beamlines for ARPES, one was BL5U in the photon energy $h\nu$ region of 20–200 eV and the other BL7U of $h\nu$ = 6–40 eV. Since the monochromator of BL5U was an old-style spherical grating type SGMTRAIN constructed in 1990s and the throughput intensity and energy resolution were poor, the whole beamline has been replaced to state-of-the-art monochromator and end station. The new beamline has been opened to users from FY2016. The newly developed electron lens system successfully achieved ~100 times better momentum resolution perpendicular to slit direction compared to the conventional ARPES. Together with the image-spin detection, which is under development, one should be able to obtain spin information of materials with much higher efficiency than the conventional spin-resolved ARPES.

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2) S. Ideta, K. Takashima, M. Hashimoto, T. Yoshida, A. Fujimori, H. Anzai, T. Fujita, Y. Nakashima, A. Ino, M. Arita, H. Namatame, M. Taniguchi, K. Ono, M. Kubota, D. H. Lu, Z.-X. Shen, K. M. Kojima and S. Uchida, *Phys. Rev. Lett.* **104**, 227001 (2010).

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Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

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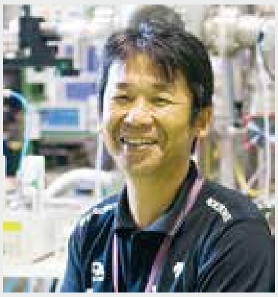

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Keywords Soft X-Ray Spectroscopy, Inner-Shell Excitation, Photodissociation Dynamics

The detailed comprehension of the electronic structure of molecules is an important step toward understanding the chemical and physical properties of matter, and also provides a link between atomic and solid-state physics. Information on photoexcitation, photoionization, and photodissociation processes derived from molecular spectroscopy is of fundamental importance, and also useful in various scientific disciplines, including astrophysics, planetary sciences, radiation chemistry, and biology.

Synchrotron radiation combined with a suitable monochromator is a powerful research tool for systematic investigations of outer- and inner-shell excitation and ionization processes in molecules, because the spectral range matches the binding energies of the valence and core electrons of the elements which form molecules of physical and chemical interest, namely low-Z molecules. In order to promote inner-shell electrons of low-Z molecules efficiently, it is indispensable to utilize monochromatized synchrotron radiation in the soft X-ray region.

Inner-shell excited states of low-Z molecules relax mainly through Auger decay, leading to the formation of highly excited singly or multiply charged molecular ions with outer-shell holes. These molecular ions are in general quite unstable, and immediately break apart into fragment ions and neutrals. The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

The major aim for investigating molecular inner-shell excitation is to determine what happens to molecules following the excitation and ionization of an inner-shell electron by using various spectroscopic techniques to define the initial photoexcitation process itself, and to characterize and correlate the electrons, ions, neutrals, and metastables that are produced as a result.

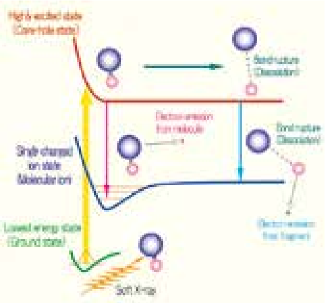

Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

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1. Site-Specific Production of H_3^+ Ions Following Core Ionization of CH_3Cl

Trihydrogen cation H_3^+ is one of the most interesting molecules in diverse fields from chemistry to astronomy because it is the simplest triatomic molecule and plays an important role in the interstellar. While the H_3^+ ions can be mainly generated from the proton transfer reactant ($H_2 + H_2^+ \rightarrow H_3^+ + H$), it was shown that unimolecular reactions of soft x-ray irradiated CH_3X molecules (X = Cl, OH, CN, *etc.*) also have a contribution of H_3^+ formation in the interstellar.[1)]

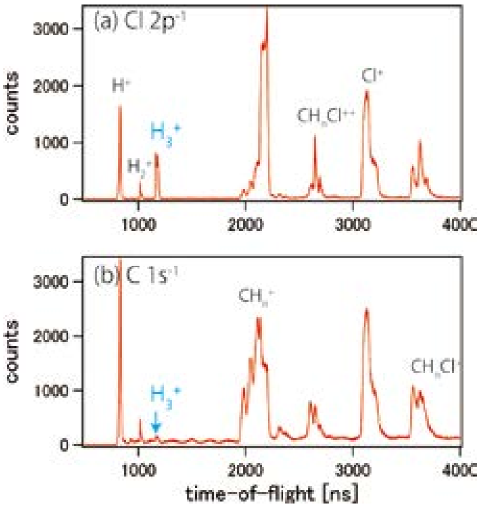

Figure 2. Time-of-flight spectra of ions taken in coincidence with (a) Cl 2p and (b) C 1s photoelectrons.

In this work, we investigate the H_3^+ production mechanism of soft x-ray irradiated CH_3Cl molecules with using an Auger-electron–ion coincidence technique, which allows us to correlate Auger final dicationic states with product ions. From coincidence Auger spectra, we reveal dicationic states which form the H_3^+ ions.

Figure 2 shows total ion TOF spectra following the Cl 2p and C 1s photoionization. Main fragment ions are H_n^+ (n = 1,2,3), CH_n^+ (n = 0–3), Cl^+ and CH_nCl^+ (n = 0,1,2). CH_3Cl^+ ions were not observed since the parent molecules following the Auger decay are doubly charged. Doubly charged ions such as Cl^{++} and CH_nCl^{++} (n = 0–3) were also observed. The most remarkable difference in fragmentation between the Cl 2p and C 1s photoionization is the relative abundance of H_3^+ ions. The relative intensity of H_3^+ ions for the Cl 2p photoionization is ten times larger than that for the C 1s photoionization. In order to correlate the production of H_n^+ (n = 1,2,3) ions with the Auger final states, we have measured the coincidence Auger spectra. It is clearly seen that the formation of the H_3^+ ions is related to only the lowest band around the binding energy of 32 eV for both the Cl 2p and C 1s photoionization. In order to understand the mechanism of such a site-specific production of the H_3^+ ions, theoretical calculations for the Auger final states of the CH_3Cl molecule are highly desired.

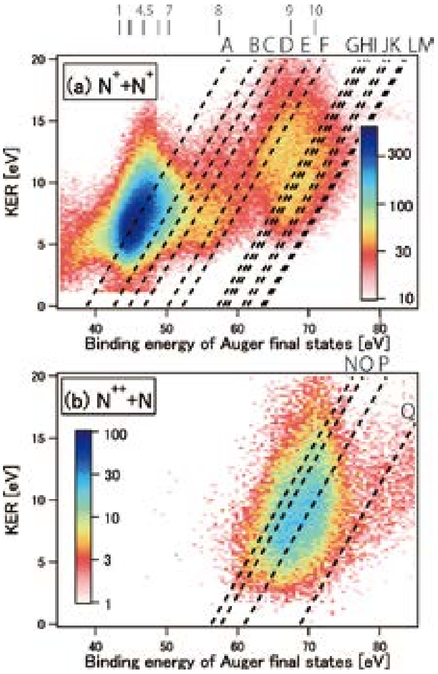

Figure 3. Two-dimensional Auger-electron–photoion coincidence maps for (a) $N_2^{++} \rightarrow N^+ + N^+$ and (b) $N^{++} + N$ dissociation pathways.

2. Photoionization of Helium Atoms by Higher Harmonic Radiation from a Helical Undulator

A core shell electron in a molecule can be promoted to unoccupied orbitals when a photon energy is tuned to resonances. For light elements ($Z < 26$), the Auger decay is the dominant process after the core excitation, and various ionic states are formed through the Auger electron emissions. The stability and dissociation dynamics of the Auger final states depend on their charge states and electronic states, which can be investigated by using an Auger-electron–photoion coincidence technique. In this work, we investigate the stability and dissociation dynamics of core excited N_2 molecules.[2)]

Two-dimensional Auger-electron–photoion coincidence maps are shown in Figure 3. The maps reveal diagonal structures, indicating correlations between Auger-electron binding energies and ion KERs. These correlations come from the fact that the KER is equal to the difference between the binding energy of the Auger final state and the dissociation limit energy. The dissociation limit energy corresponds to the binding energy at the dissociation asymptote, and depends on the electronic states of atomic fragments in addition to charge states. From the correlations in Figure 3, we have derived the dissociation limits of dissociative Auger final states. It is also found that the X $^1\Sigma_g^+$, A $^1\Pi_u$, and c $^3\Sigma_u^+$ states are associated with the formation of metastable dicationic states.

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2) H. Iwayama *et al.*, *J. Chem. Phys.* **145**, 034305 (2016).

Micro Solid-State Photonics

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2014	IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)

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- LIM, Hwanhong

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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, UV to THz wave generation. Moreover, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. The future may herald new photonics.

Giant pulse > 10 MW was obtained in 1064nm microchip lasers using micro-domain controlled materials. The world first laser ignited gasoline engine vehicle, giant-pulse UV (355 nm, 266 nm) and efficient VUV (118 nm) pulse generations have been successfully demonstrated. Also, few cycle mid-IR pulses for atto-second pulses are demonstrated by LA-PPMgLN. We have developed new theoretical models for the micro-domain control of anisotropic laser ceramics. These functional micro-domain based highly brightness/brightness-temperature compact lasers and nonlinear optics, so to speak "Giant Micro-photonics," are promising. Moreover, the new generation of micro and/or microchip lasers by using orientation-controlled advanced ceramics can provide extreme high performances in photonics.

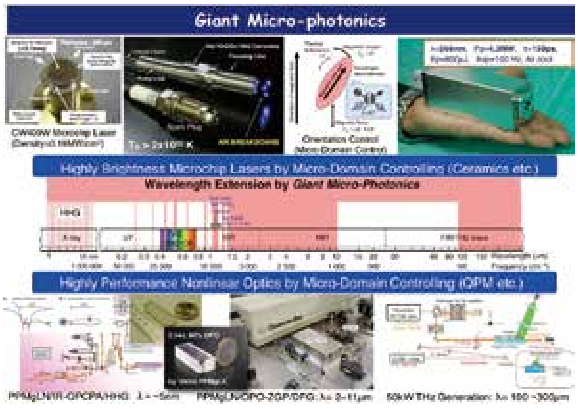

Figure 1. Giant micro-photonics.

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1. Giant-Pulse Nd:YVO$_4$ Microchip Laser with MW-Level Peak Power by Emission Cross-Sectional Control

Giant-pulse generation laser realized by the emission cross-section control of a gain medium in a passively Q-switched Nd:YVO$_4$ microchip laser with a Cr^{4+}:YAG saturable absorber. Up to 1.17 MW peak power and 1.03 mJ pulse energy were obtained with a 100 Hz repetition rate. By combining the Nd:YVO$_4$ crystal with a Sapphire plate, lower temperature difference between a pump region in the gain crystal and a crystal holder was obtained which helped to keep the cavity in stability zone at elevated temperatures and allowed the achievement of the high peak power for this laser system.

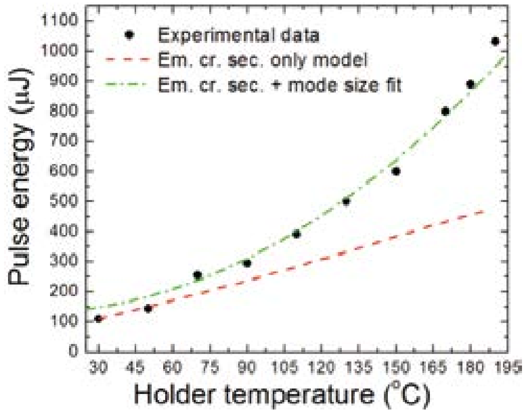

Figure 2. Experimental results of giant-pulse Sapphire/Nd:YVO$_4$ micro-laser.

2. Optical Gain in the Anisotropic Yb:FAP Laser Ceramics

Currently well-aligned anisotropic laser ceramics can be produced by only the orientation control by slip-casting under the magnetic field, therefore our methods should be the solution for appreciating advantages of anisotropic laser gain media and ceramic gain media, simultaneously. We fabricated Yb:FAP fluorapatite (FAP) ceramics by means of 1.4-T rotational magnetic field. If it can perform the optical amplification, it can be the best candidate of the gain medium for lasers with the extreme high brightness.

The experimental setup is shown in Figure 3. Uncoated *c*-cut Yb:FAP ceramic sample with the thickness of 0.6 mm was positioned with Brewster angle to the optical path. The fluorescence from the sample was detected by the spectrometer through the pump-cut filter (both of setup-a and -b) and the mirror-2 (only setup-b). As a result, fluorescence from anisotropic Yb:FAP laser ceramics was amplified to 2.8 times by constructing an optical resonator.

This amplification indicates that the laser-diode pumping formed the optical gain comparable to the optical loss in Yb:FAP ceramics. We are now expecting we can realize laser oscillation by use of the optical gain in Yb:FAP ceramics.

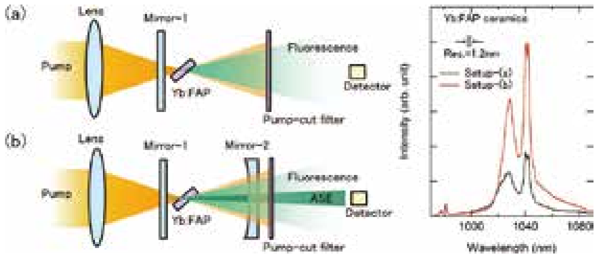

Figure 3. Experimental setup for the detection of fluorescence from Yb:FAP ceramics and their signals. (a) Without output coupler. (b) With output coupler.

3. Periodic Laminar Structured Quartz for Quasi-Phase Matched Wavelength Conversion

Crystal quartz, used in the first second harmonic generation (SHG) by Franken *et al.* in 1961, is one of major nonlinear material. Although its excellent optical properties, such as short absorption edge and high laser-damage threshold, its small birefringence has limited practical applications by conventional birefringent phase matching scheme.

Recent progress of laser-system development enabled to use intense short pulses with narrow spectra between ps and sub-ns pulse region, and periodic laminar structure (PLS) quartz pumped by the intense laser have became practical choice for next-generation wavelength-conversion device.

Figure 4(a) shows improvement of SHG-green output energy by PLS quartz. Resulting SHG by 48-plates stacking was increased 500 times higher than single-plate, non-phase matched SHG. Figure 4(b) shows SHG output on input pump energy of 48-plates PLS quartz. Maximum output energy of 8 μJ with 0.54 ns pulse duration could be obtained. Wavelength conversions such as third and forth harmonic generation by PLS quartz pumped by intense MCL can be also expected.

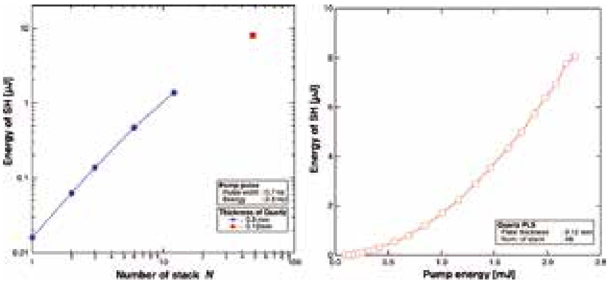

Figure 4. (a) Improvement of SHG output by PLS, (b) SHG output on input pump energy at 48-plates PLS.

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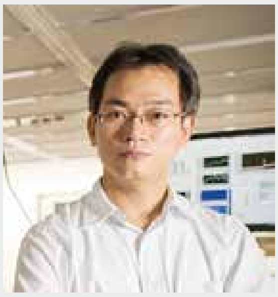
Ultrafast Laser Science

Laser Research Center for Molecular Science
Division of Advanced Laser Development



FUJI, Takao
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Education

1994	B.S. University of Tsukuba
1999	Ph.D. University of Tsukuba

Professional Employment

1999	Assistant Professor, The University of Tokyo
2002	JSPS Postdoctral Fellowship for Research Abroad, Vienna University of Technology (–2004)
2004	Guest Researcher, Max-Planck-Insitute of Quantum Optics
2006	Research Scientist, RIKEN
2008	Senior Scientist, RIKEN
2010	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

1999	Encouragement Award, The Optical Society of Japan
2008	Kondo Award, Osaka University
2015	Laser Research Development Award, the Laser Society of Japan

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Assistant Professor
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MALEVICH, Pavel

Secretary
MASUDA, Michiko

Keywords Ultrafast Science, Laser Physics, Nonlinear Optics

Light is very common in daily life, on the other hand, light has many interesting physical properties, for example, constancy of velocity, wave-particle duality, *etc*. The study of light is still important in modern physics.

Light is electro-magnetic field, same as radio wave, however, the measurement of the waveform of light is not easy task even in the 21st century. The difficulty comes from the extremely fast oscillation of the light wave. The oscillation frequency of light wave is the order of hundred terahertz (THz = 10^{12} Hz), in other words, the oscillation period of light wave is the order of femtosecond (fs = 10^{-15} s).

In 2013, we have developed a new method for the measurement of light wave. It is called FROG-CEP, frequency-resolved optical gating capable of carrier-envelope determination. Our method does not need attosecond pulses, even self-referencing is possible. The electric field oscillation of infrared light with the period of several femtoseconds were clearly measured with the method as is shown in Figure 1.

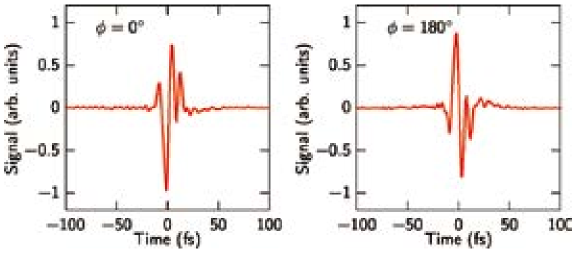

Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

Currently, amplitude modulation and phase modulation are common encoding techniques in optical communication. If we can encode information in the shape of the light wave itself, the communication speed becomes 3 orders of magnitude faster. We believe that our method, FROG-CEP, becomes very important to realize such communication technology.

Other than FROG-CEP, ultrabroadband mid-infrared continuum generation through filamentation and single-shot detection of ultrabroadband mid-infrared spectra has been realized in our laboratory. We are developing such cutting edge technologies for ultrafast laser science.

Selected Publications

- T. Fuji and Y. Nomura, "Generation of Phase-Stable Sub-Cycle Mid-Infrared Pulses from Filamentation in Nitrogen," *Appl. Sci.* **3**, 122–138 (2013).
- Y. Nomura, H. Shirai and T. Fuji, "Frequency-Resolved Optical Gating Capable of Carrier-Envelope Phase Determination," *Nat. Commun.* **4**, 2820 (11 pages) (2013).
- Y. Nomura M. Nishio, S. Kawato and T. Fuji, "Development of Ultrafast Laser Oscillators Based on Thulium-Doped ZBLAN Fibers," *IEEE J. Sel. Top. Quantum Electron.* **21**, 0900107 (7 pages) (2015).
- Y. Nomura, Y.-T. Wang, A. Yabushita, C.-W. Luo and T. Fuji, "Controlling the Carrier-Envelope Phase of Single-Cycle Mid-Infrared Pulses with Two-Color Filamentation," *Opt. Lett.* **40**, 423–426 (2015).
- T. Fuji, Y. Nomura and H. Shirai, "Generation and Characterization of Phase-Stable Sub-Single-Cycle Pulses at 3000 cm^{-1}," *IEEE J. Sel. Top. Quantum Electron.* **21**, 8700612 (12 pages) (2015).
- T. Fuji, H. Shirai and Y. Nomura, "Ultrabroadband Mid-Infrared Spectroscopy with Four-Wave Difference Frequency Generation," *J. Opt.* **17**, 094004 (9 pages) (2015).

Ultrafast lasers working in the 2 µm region have been attracting a lot of attention owing to a number of possible applications in various scientific and industrial fields. Thulium (Tm)-doped fiber or solid-state lasers are one of the most promising candidates to generate ultrashort pulses in this wavelength region because of their broad emission spectra. We have developed an oscillator based on a Tm-doped ZBLAN (ZrF_4-BaF_2-LaF_3-AlF_3-NaF) fiber which delivers 41 fs pulses at 2 µm.[1,2] Here we report the development of the amplifier for the oscillator output.

1. Chirped-Pulse Amplifier Based on Thulium-Doped ZBLAN Fibers

ZBLAN (ZrF_4-BaF_2-LaF_3-AlF_3-NaF) is fluoride glass known for high transmittance in the mid-infrared region. This suggests the ZBLAN glass has low material dispersion, which fact would be suitable for ultrafast amplifier system.

Here we demonstrate a chirped-pulse amplifier (CPA) system based on ZBLAN fibers. The experimental setup consists of an oscillator, a stretcher, an amplifier, and a compressor. The pulses from the oscillator are stretched with a normal-dispersion ZBLAN fiber with the core diameter of 5 µm (group velocity dispersion ~+30 fs^2/mm). After propagating through the 15-m-long ZBLAN fiber, the pulses are stretched to ~25 ps with ~50% transmission efficiency. After all the optics, the average power of the stretched pulses is 12 mW.

The stretched pulses are sent into the core of a 3.8-m-long, Tm-doped, large-mode-area double-clad ZBLAN fiber. The core of the fiber has a diameter of 32 µm and NA of 0.08, whereas the first clad has a diameter of 200 µm and NA of 0.5. The concentration of Tm ion in the core is 2 mol%.

The fiber is pumped in the counter-propagating direction, *i.e.*, from the side of the non-doped fiber, with a laser diode (LD) operating around 793 nm. When the output power of the LD is increased to 20 W, the maximum output power of 4.5 W is obtained. The slope efficiency is ~29% if we assume the pump coupling efficiency to be 90%.

Figure 1(a) shows the spectrum of the amplifier output, extending over more than 100 nm. This value is much less compared to the oscillator spectral width of 350 nm, which could be explained by gain narrowing effect and strong absorption of Tm ion in the short wavelength region.

The amplified pulses are compressed with a compressor comprised of a pair of transmission grating with grooves of 560 mm^{-1}. The average power after the compressor is 2.5 W. The compressed pulses are characterized with a home-built frequency-resolved optical gating (FROG) device designed for pulses around 2 µm region. A typical FROG trace and the pulse retrieved from it are shown in Figure 1(b) and (c). From this result, the duration of the compressed pulse is determined as 150 fs.

2. Ring Cavity Diode-Pumped Tm:YAP Regenerative Amplifier

To obtain higher pulse energy, we have developed an amplifier based on a solid-state laser, namely, diode pumped Tm:YAP regenerative amplifier.

The CPA system consists of a Tm:ZBLAN fiber oscillator, grating stretcher, ring-cavity regenerative amplifier and grating compressor. The Regenerative amplifier is based on Brewster- cut 4% doped 12 mm long 6.5 °C water cooled Tm:YAP crystal end-pumped by 794 nm InGaAs diodes, being reimaged into 400 µm spot on the crystal. The CPA system is seeded by 90 fs 52 MHz 4 nJ Tm:ZBLAN fiber oscillator. The seed pulses are sent to the Martinez type stretcher based on a 550 gr/mm transmissive grating and concave mirror with the group delay dispersion of 16 ps^2, which is necessary to avoid damage and non-linear effects while operating at high energies. The regenerative amplifier generates >0.9 mJ pulses at 1 kHz repetition rate, or, by decreasing repetition rate to 250 Hz, it is possible to extract up to 2.0 mJ pulses.

Even though the cavity is nitrogen purged (to 9% residual humidity level), the high water vapor absorption leads to generation of strongly modulated spectrum. Measured spectrum supports 0.46 ps duration, but recompression with 560 gr/mm gratings Treacy compressor results in autocorrelation of 1 ps spike with strong 10^s ps long pedestal, which can be cleaned out by stronger dehumidifying.

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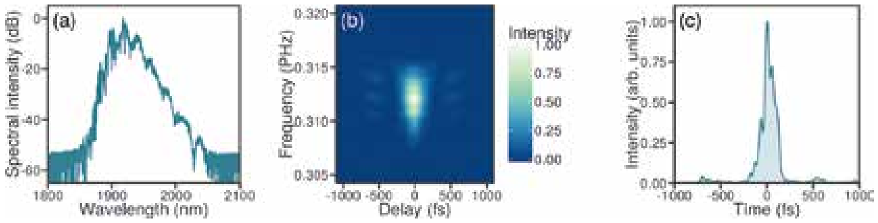

Figure 2. Output after amplification. (a) An output spectrum after the amplifier. (b) A FROG trace measured after compression. (c) The pulse shape retrieved from the FROG trace shown in (b).

Award

NOMURA, Yutaka; The 5th Young Scientist Award of National Institutes of Natural Sciences (2016).

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* IMS International Internship Program

Photoelectron Spectroscopy of Ionic Liquids and Thin Films Made of Fullerenes and Their Application to Photoelectrochemistry

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

KATAYANAGI, Hideki
Assistant Professor

Electrodes made of fullerenes and their derivatives and electrolytes containing ionic liquids (ILs) are used in the photovoltaic devices such as dye-sensitized solar cells (DSSCs) to make a breakthrough in the field of renewable energy sources. Both electronic structures and mesoscopic mixing schemes of the materials are key issues which affect their efficiency and lifetime. These structures can be investigated using a combined study of spectroscopic and thermodynamic measurements.

1. Fabrication of LB Film Electrodes of Sulfonated Fullerenes and Evaluation of Their Feasibility for the DSSCs

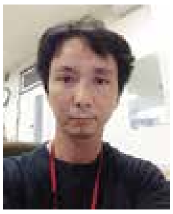
In the DSSCs, counter electrodes consist of Pt. The Pt electrode has some disadvantages such as cost and stability. Electrodes made of fullerenes and carbon nanotubes are candidates of substitutes for the Pt electrodes. To produce the carbon electrodes, we utilize the Langmuir-Blodgett (LB) technique which has low burden on the environment. Additionally, the LB technique has ability to make ordered structure. We have fabricated the LB films using fullerenes and their amphiphilic derivatives. We succeeded in producing homogeneous films on ITO glass substrates. The produced LB film electrodes were diagnosed by electrochemical methods. We are now trying to apply photoelectron spectroscopy to understand the electronic structures of the films which is essential to the efficiency of photovoltaic devices.

2. Combined Study of Photoelectron Spectroscopy and Thermodynamic Measurements of ILs and Their Mixtures

We have just started a research subject to apply the combined study of spectroscopic and thermodynamic measurements to the ILs. This combined study will allow us to understand the extraordinary characteristics of the ILs and their mixtures.

3-Dimensional Spectro-Microscopy

UVSOR Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

Scanning transmission X-ray microscopy (STXM) can realize nanoscale 2-dimensional (2D) chemical state analysis without any destructive process, in combination of soft X-ray absorption spectroscopy with nano-focused X-ray beams obtained by using a Fresnel zone plate (FZP). This STXM technique can be extended to nanoscale 3D analysis based on a computed tomography (CT) method; however, the short working distance (typically, less than 0.5 mm) problem inherent in the FZP applied to the soft X-ray region has to be solved.

We designed a special compact sample cell for CT by using a two-phase stepping motor (shown in Figure 1(a)). As a feasibility test of this method, polystyrene spheres of diameter of 5 μm were used as a standard sample, though 5 μm is a little thicker than the focal depth of the present nano-focused beam. STXM images were successfully obtained with rotating the sample by 3.6° each, and 50 STXM images were acquired in total, where the photon energy was 280 eV and the dwell time was 3 ms per a pixel. A reconstructed 3-dimensional volume image was obtained as shown in Figure 2. We will plan to apply this technique to μm-scale samples with heterogeneous chemical components.

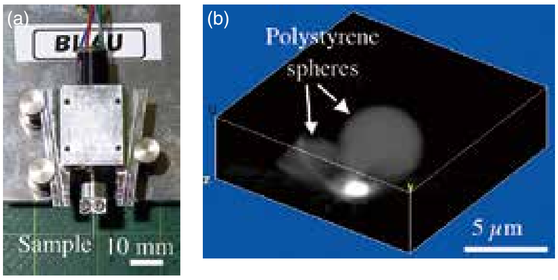


Figure 1. (a) A sample cell for computed tomography and (b) 3-dimensional volume image of polystyrene spheres.

Reference

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Visiting Professors

Visiting Professor

IMURA, Kohei *(from Waseda University)*

Development of Advanced Super-Resolution Microscopy and Their Application to Nanomaterials

Elementary excitations in nanomaterials generate amplified optical fields in the vicinity of the materials. Near-field interactions of molecules with the localized fields provide new frameworks in optical excitations. In order to utilize the novel optical excitation schemes for various applications, understanding of the near-field light-matter interaction is crucial. Near-field optical microcopy, which achieves a super-resolution, is promising for this purpose. Spectroscopic methods in the near-field optical microscope, however, have not been well developed. We have been extending the near-field optical microscope to linear- and non-linear spectroscopic imaging methods. Recently, we have developed reflection and ultrafast near-field imaging methods, and applied them to study optical properties of nanomaterials. We found that giant nonlinearity is effectively induced at the localized fields in the nanomaterials. We are currently extending these studies to controlling linear and non-linear optical properties of nanomaterials in space and time resolved manner. The study will open the door to coherent control of elementary excitations and photochemical reactions.

Visiting Associate Professor

YAMADA, Toyo Kazu *(from Chiba University)*

Dimensional Dependence of Organic Molecular Electronic States

Scanning tunneling microscopy (STM) has been used to visualize material topology with an atomic scale. For 2000–2016, I have developed spin-polarized STM setups to visualize not only atomic structures of materials but also electronic, spin, and quantum structures combined with spectroscopy techniques. 1-nm-size nano-materials, such as nano-magnets, single atoms, single molecules, and graphene nano-ribbons have been studied for realizing new nano-electronic devices with low cost, low power consumption, and high performance. In 2016, we have developed a new low-temperature STM setup and now try to fabricate two-dimensional molecular networks on an atomically-flat noble metal substrate. Subsequently, a magnetic metal will be deposited on the network, and try to make a new two-dimensional magnetic nano-dot array.

Visiting Associate Professor

HIRAHARA, Toru *(from Tokyo Institute of Technology)*

Spin-Split States at the Surface/Interface of Nonmagnetic Ultrathin Films

Recently there has been growing interest in utilizing the spin degree of freedom in electronic devices, the so-called *spintronics*. The conventional way is to use magnetic materials and manipulate the spin using a magnetic field. However, it is sometimes troublesome to apply a magnetic field to nano-scale materials and it is much easier to control the spin properties of materials using an electric field. By making use of the Rashba effect in which electrons become spin polarized in k-space due to spin–orbit coupling effects at the surface, such manipulation of electron spin with an electric field becomes possible, *i.e.*, a spin field effect transistor can be realized in such materials. We are developing a high-resolution spin- and angle- resolved photoemission spectroscopy measurement system equipped with *in situ* surface sample preparation facilities at BL-5U and characterize the novel spin property at the Rashba-split surface/interface states of nonmagnetic ultrathin films. We will also try to grow thin films of novel topological materials such as Dirac/Weyl/line-nodal semimetals.

Visiting Associate Professor

KISHIMOTO, Tetsuo *(from University of Electro-Communications)*

Development towards Continuous Production of Bose-Einstein Condensates

Our goal is to realize continuous production of Bose-Einstein Condensates (BEC) based on all-optical techniques. By using sympathetic cooling techniques, this can further extend the possibility of realizing CW BECs for many other different atomic species or even molecules that are not eligible for direct evaporative cooling. Currently we are exploring different laser cooling transitions in the fine structure of the 6P levels in 87-Rubidium atoms to obtain higher phase space density. As a separate project from this, we have also started to seek for a new method to manipulate quantum gas with high spatial resolution, using special wavelengths. With these special wavelengths, AC Stark effect from the irradiated laser light will be cancelled out on one of the hyperfine ground sublevels of the atoms, while there will be AC Stark effects on all the other sublevels. So far we are searching for such special wavelengths by spectroscopic measurements, using thermal vapor gas of rubidium.