RESEARCH ACTIVITIES
Center for Mesoscopic Sciences

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

Nano-Optical Imaging and Chiral Light-Matter Interaction in Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

OKAMOTO, Hiromi
Professor
[aho@ims.ac.jp]

Education
1983 B.S. The University of Tokyo
1991 Ph.D. The University of Tokyo

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

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

Member
Research Assistant Professor
YAMANISHI, Junsuke
CHENG, An-Chieh
Project Assistant Professor (NINS)
AHN, Hyo-Yong
Technical Support Staff
ISHIKAWA, Akiko
Secretary
ITO, Atsuko

Keywords Nano Optics, Plasmons, Chirality

Studies of local optical properties of molecular assemblies and materials are the keys to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Optical microscopic methods, in particular nano-optical methods, such as scanning near-field optical microscopy (SNOM) which enables resolution beyond the diffraction limit of light, reveals essential characteristics of the materials and develop novel properties of them. Combination of microscopic techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of polarization dependence and nonlinear/time-resolved measurements. The developed apparatuses achieved nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies, plasmon wave packet propagation dynamics, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials is also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

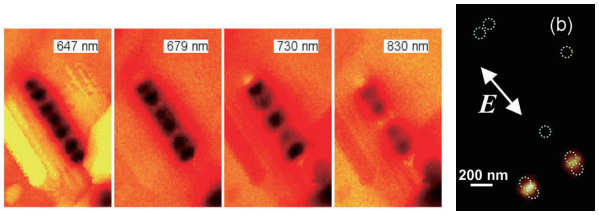

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

1. Local Chiro-Optical Effects in Gold Nanostructures Investigated by Chiral Photoinduced Force Microscopy

Photoinduced force microscopy (PiFM) is an optical near-field imaging technique based on the technique of atomic force microscopy (AFM). By irradiating light on a system consisting of a sample and a probe tip, and detecting the force arising from interactions between the light-induced polarizations of the sample and the probe, PiFM enables the visualization of local optical near-fields with nanometer-scale resolution. By employing left-handed and right-handed circularly polarized light as the excitation source, the differential force signal measured between the two polarization states (referred to as chiral PiFM) is expected to reflect chiro-optical effects in the near field. We previously demonstrated the feasibility of this approach through experimental measurements using pseudo two-dimensional chiral metallic nanostructures.[1)]

In the present study, we extend this methodology to investigate the general applicability of chiral PiFM and to gain deeper insights into its measurement principles. To this end, we perform chiral PiFM measurements and analyses on a variety of gold nanostructures with different geometries. In the case of three-dimensional chiral gold nanoparticles, near-field signals that correlate with the handedness of the particles were observed. For achiral assembled particle systems, local chiro-optical responses were observed in the peripheral areas, exhibiting spatially oscillatory patterns with alternating positive and negative signals. In spherical nanoparticles, where no chiro-optical effect is theoretically expected under circularly polarized illumination, weak signals were still observed in the chiral PiFM measurements. The result suggests that such signals may arise from symmetry-breaking effects involving the probe tip itself, and further analysis is ongoing to elucidate the underlying mechanisms.

2. Development of Far-Field Circular Dichroism Microscopy

Circular dichroism (CD) spectroscopy is a powerful technique widely employed for the detection and characterization of materials chirality. However, in anisotropic samples, signals arising from linear dichroism and other polarization-dependent effects often interfere with CD measurements. Consequently, the application of conventional CD measurement techniques to microscopic imaging has faced significant challenges to ensure signal accuracy and precision. Only very few reports on CD-based microscopic imaging have been published. In a previous study, we developed a high-precision far-field CD microscope based on a novel circular polarization modulation method, which enabled CD microscopic imaging with sufficiently suppressed interference from linear polarization effects.[2)]

To apply CD imaging to a wider range of research, diagnostics, and so forth, it is desirable to reduce measurement time and to simplify the optical alignment procedures. The previously developed system required a certain level of expertise for optical alignment and typical measurement times on the order of several minutes per image, indicating a need for further development. In the present work, we propose a new approach to CD microscopy aimed at substantially reducing imaging time and improving ease of operation. As a result of one such attempt, we have succeeded in acquiring CD images at several frames per second, with a slight compromise in signal accuracy compared to the earlier system configuration. This improvement represents a significant step toward the realization of real-time or live CD imaging, which is expected to broaden the applicability of CD microscopy in both fundamental and applied research.

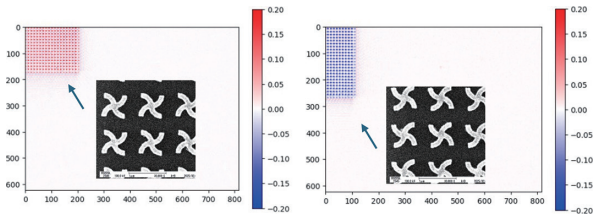

Figure 2. Examples of CD images of pinwheel-shaped gold nanostructure arrays. Red and blue parts indicate positive and negative CD signals.

3. Toward the Observation of Chirality-Induced Dynamics

In recent years, it has been reported that the irradiation of achiral plasmonic materials with circularly polarized light can induce the formation of chiral nanostructures through photochemical reactions. This process is believed to involve several key steps: The excitation of chiral plasmonic resonances on achiral structures under irradiation of circularly polarized light; generation of chiral local electromagnetic fields; the spatial arrangement and orientation of reactant molecules in response to these fields; and, finally, the photoexcitation (or thermal excitation) of the reactants followed by chemical reactions to form chiral nanostructures. To understand the mechanisms of the processes, we have constructed an experimental apparatus for time-resolved measurements of chiral optical responses. Using this setup, we are currently investigating the dynamics of chirality-induced optical responses in plasmonic materials.

References

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2) T. Narushima and H. Okamoto, *Sci. Rep.* **6**, 35731 (2016).

Awards

YAMANISHI, Junsuke; 56th Excellent Presentation Award from Japan Society of Applied Physics (2024).
YAMANISHI, Junsuke; Nagoya University Ishida Prize (2025).
AHN, Hyo-Yong; Award for Promotion of the Most Excellent Young Researcher from Plasmonic Chemistry Research Group (2025).

Nano- and Atomic-Scale Spectroscopy

Center for Mesoscopic Sciences
Division of Broadband Multiscale Analysis

KUMAGAI, Takashi
Associate Professor
[kuma@ims.ac.jp]

Education
2006 B.S. Ritsumeikan University
2008 M.S. Kyoto University
2011 Ph.D. Kyoto University

Professional Employment
2008 JSPS Research Fellow, Kyoto University
2011 JSPS Research Fellow, Fritz-Haber Institute
2013 Group Leader, Fritz-Haber Institute
2021 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2020 Guest Professor, Hokkaido University
2022 Guest Professor, Kyoto University

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

Member
Assistant Professor
NISHIDA, Jun
Visiting Scientist
LEE, Lu-Hsin*
Graduate Student
FUKUTOMI, Minoru
KAMADA, Kazuki†
Secretary
ITO, Atsuko

Keywords Tip-Enhanced Near-Field Spectroscopy, Atomic-Scale Light–Matter Interactions, Nanomaterials Characterization

A detailed understanding of atomic-scale structures, properties, and dynamics is fundamentally important for the design of next-generation devices and optimization of material and energy conversion processes, including optoelectronics, solar cells, and catalysis. The rapid advancement of nanotechnology requires measurement techniques capable of directly observing phenomena with simultaneous high spatial and temporal resolution at the (sub)nanometer scale. Optical spectroscopy is a powerful and versatile tool for characterizing materials, but its spatial resolution is fundamentally limited by diffraction, restricting its ability to directly observe nanoscale systems. Near-field optics overcomes this limitation and enables optical characterization beyond the diffraction limit.

Our group has focused on developing and applying cutting-edge tip-enhanced near-field techniques in combination with laser spectroscopy, including nonlinear and ultrafast time-resolved techniques, to investigate photophysical and photochemical phenomena. Recently, we have demonstrated atomic-level sensitivity and spatial resolution using tip-enhanced Raman spectroscopy (TERS) and scanning near-field optical microscopy (SNOM) based on low-temperature scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Furthermore, by integrating ultrashort pulsed lasers, we have shown that ultrafast coherent dynamics can be probed with atomic-scale resolution.

We are currently pushing the boundaries of atomic-scale spectroscopy with three key objectives: (1) extending its capabilities from the visible to the infrared region to investigate a broader range of materials and phenomena; (2) advancing nonlinear and time-resolved spectroscopic techniques; and (3) applying these methods to diverse low-dimensional systems to explore their unique optical properties.

Selected Publications

- B. Cirera *et al.*, "Joule Heating in Single-Molecule Point Contacts Studied by Tip-Enhanced Raman Spectroscopy," *ACS Nano* **16**, 16443 (2022).
- S. Liu *et al.*, "Nanoscale Coherent Phonon Spectroscopy," *Sci. Adv.* **8**, eabq5682 (2022).
- S. Liu *et al.*, "Inelastic Light Scattering in the Vicinity of a Single-Atom Quantum Point Contact in a Plasmonic Picocavity," *ACS Nano* **17**, 10172 (2023).
- J. Nishida *et al.*, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24**, 836 (2024).
- Y. Wang *et al.*, "Ultrafast Nano-Imaging of Spatially Modulated Many-Body Dynamics in CVD-Grown Monolayer WS_2," *ACS Photonics* **12**, 207 (2024).
- A. Shiotari *et al.*, "Picocavity-Enhanced Raman Spectroscopy of Physisorbed H_2 and D_2 Molecules," *Phys. Rev. Lett.* **134**, 206901 (2025).
- A. Shiotari *et al.*, "Scattering Near-Field Optical Microscopy at 1-nm Resolution Using Ultralow Tip Oscillation Amplitudes," *Sci. Adv.* **11**, eadu1415 (2025).
- J. Nishida *et al.*, "Ultrafast Infrared Nano-Imaging of Local Electron–Hole Dynamics in CVD-Grown Single-Walled Carbon Nanotubes," *Sci. Adv.* **11**, eadv9584 (2025).

1. Atomic-Scale Optical Spectroscopy

Atomic-scale light–matter interactions are a frontier of optical nanoscience, providing opportunities not only for ultra-sensitive and ultra-high-resolution spectroscopy, but also for establishing picoscale optics and photonics. Recent studies have shown that extreme confinement of near fields occurs at atomic-scale protrusions on metal nanostructures, referred to as 'picocavity,' leading to unique optical phenomena. Using TERS, we demonstrated atomic-scale vibrational spectroscopy and revealed how picoscale structural changes affect Raman scattering.[1)]

While TERS has been applied to the study of organic molecules and atomically thin films, it has not yet been used to investigate small molecules such as hydrogen, oxygen, and water. Recently, we reported on TERS of H_2 and D_2 molecules physisorbed within a plasmonic picocavity at 10 K.[2)] The intense Raman peaks resulting from the rotational and vibrational transitions are observed at picoscale gap distances of the junction formed by an Ag tip and an Ag(111) surface, where a picocavity-enhanced field plays a crucial role. A significant redshift of the H–H stretch frequency is observed as the gap distance decreases, while the D–D stretch frequency is unaffected. Density functional theory, path-integral molecular dynamics, and quantum anharmonic vibrational energy calculations suggest that this non-trivial isotope effect is explained by a different molecular density between H_2 and D_2 on the surface. The capability to measure such small molecules holds great promise as a method for probing local structures and reactions that are involved in the elementary processes of heterogeneous catalysis.

In addition, single-molecule TERS has generally been limited to measurements on plasmonic substrates such as Au, Ag, or Cu surfaces. Recently, we have demonstrated that single-molecule TERS measurements are also feasible on a bulk silicon surface.[3)] This represents an important step toward expanding the applicability of TERS-based chemical analysis to a broader range of material systems and holds promise as a method for investigating atomic-scale structures in nanodevices.

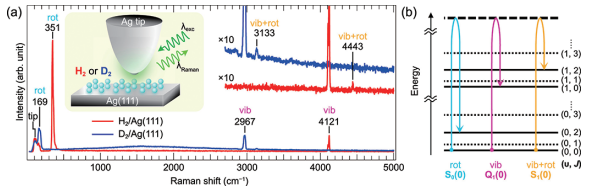

Figure 1. (a) TERS spectra of H_2 and D_2 confined within a picocavity. Raman peaks corresponding to rotational (rot), vibrational (vib), and combined vibrational–rotational (vib + rot) modes are clearly observed in each spectrum. (b) Schematic illustration of the rotational and vibrational energy level transitions of a hydrogen molecule, corresponding to the Raman peaks observed in (a).

2. Ultrafast Nano-Spectroscopy of Atomically-Confined Materials

Atomically confined materials, such as transition metal dichalcogenides (TMDs) and carbon nanotubes (CNTs), exhibit unique optoelectronic properties due to strong quantum confinement effects and are regarded as promising candidates for next-generation semiconductor materials. However, their properties are highly sensitive to local structures, such as defects, and interactions with the surrounding environment, owing to their extremely large surface-to-volume ratio. Recently, there has been growing interest in controlling their properties by stacking atomically thin layers to create moiré superlattices—nanoscale structural modulations that offer new degrees of freedom. These developments highlight the increasing importance of experimental techniques capable of simultaneously probing local structures and optical properties.

We have recently developed a highly sensitive ultrafast infrared SNOM, enabling real-time and real-space visualization of photoinduced dynamics in TMDs and CNTs.[4,5)] Figure 2 shows an example of photoexcited carrier dynamics in monolayer WS_2 grown by chemical vapor deposition (CVD) on a sapphire substrate. The near-field signal is stronger at the edges of the triangular domains, reflecting local variations in defect density within the WS_2. We also applied ultrafast nano-spectroscopy to directly observe exciton dynamics in CNTs grown on a sapphire substrate, capturing the generation and relaxation of electron–hole pairs confined within the one-dimensional structure at the nanoscale. These results demonstrate the capability of our technique to directly visualize spatial heterogeneity in ultrafast dynamics, arising from underlying local structures, which would otherwise be obscured in conventional, spatially averaged spectroscopic measurements. We are currently investigating ultrafast electron–phonon interactions in heterostructures composed of TMDs and hexagonal boron nitride, where ultrafast modulation of the photo-carrier and phonon polariton is observed.

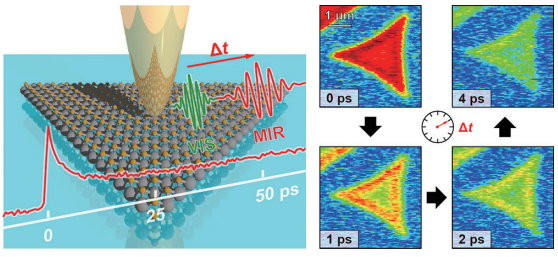

Figure 2. Ultrafast IR-SNOM imaging that visualizes spatially modulated photo-carrier dynamics within monolayer WS_2.

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