

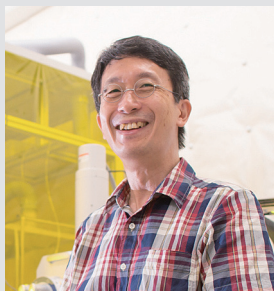
# RESEARCH ACTIVITIES

## Center for Mesoscopic Sciences

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

# Nano-Optical Imaging and Application to Nanomaterials

## Center for Mesoscopic Sciences Division of Supersensitive Measurements



**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

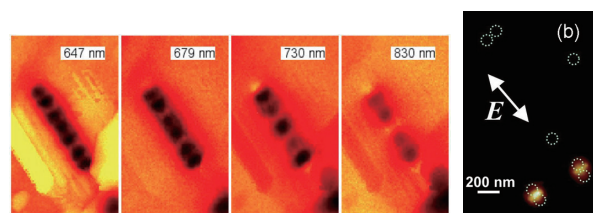
### Member

Assistant Professor  
NARUSHIMA, Tetsuya  
YOSHIZAWA, Daichi  
Project Assistant Professor (NINS)  
AHN, Hyo-Yong  
Post-Doctoral Fellow  
YAMANISHI, Junsuke  
Technical Fellow  
ISHIKAWA, Akiko  
Secretary  
NOMURA, Emiko

**Keywords** Nano Optics, Plasmons, Chirality

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

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



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

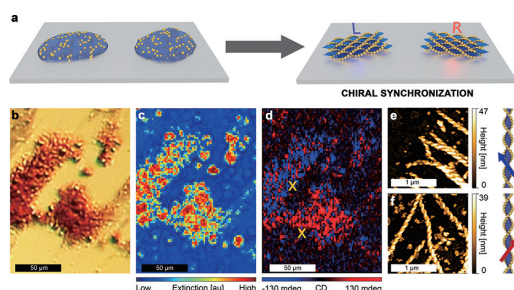
### Selected Publications

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

- Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

## 1. Supramolecular Chirality Synchronization in Thin Films of Plasmonic Nanocomposites<sup>1)</sup>

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

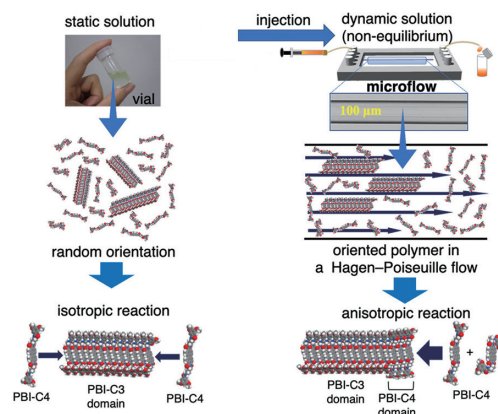


**Figure 2.** Micrometer-scale circular dichroism measurements of the helical Au nanoparticle assemblies.<sup>1)</sup> (a) Graphical representation of the chiral synchronization process. (b) Optical micrograph, (c) extinction intensity map at 550 nm, and (d) CD map at 550 nm from the same region of the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

## 2. Directional Supramolecular Polymerization to Form Nanofibers in a Microflow Reaction System<sup>2,3)</sup>

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

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



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

## 3. Optical Trapping of Chiral Metal Nanoparticles

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

### References

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

# Atomic-Scale Optical Spectroscopy

## Center for Mesoscopic Sciences Division of Broadband Multiscale Analysis



**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

### 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

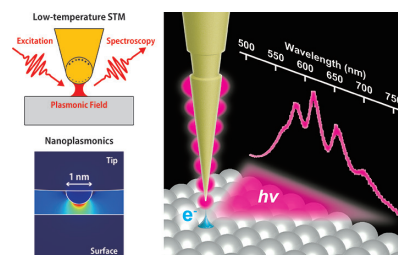
Assistant Professor  
NISHIDA, Jun  
Secretary  
ITO, Atsuko

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

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

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

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



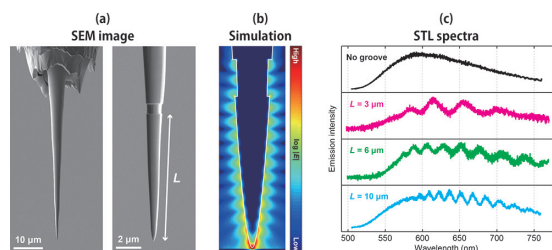
**Figure 1.** Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

### Selected Publications

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

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

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

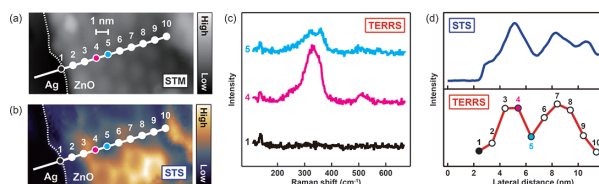


**Figure 2.** Nanofabrication of plasmonic tip with focused ion beam milling. (a) Scanning electron micrograph of a nanoscopically sharpened gold tip. (b) Simulation of plasmonic Fabry–Pérot tip. (c) Scanning tunneling luminescence spectra of the plasmonic Fabry–Pérot tip.

## 2. Ultrasensitive and Ultrahigh Resolution Tip-Enhanced Raman Spectroscopy

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

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



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

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

### References

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

### Awards

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

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

# Center for Mesoscopic Sciences as an Interdepartmental Facility

|                    |                     |
|--------------------|---------------------|
| OKAMOTO, Hiromi    | Director, Professor |
| OHMORI, Kenji      | Professor           |
| IINO, Ryota        | Professor           |
| EHARA, Masahiro    | Professor           |
| SUGIMOTO, Toshiki  | Associate Professor |
| MINAMITANI, Emi    | Associate Professor |
| KUMAGAI, Takashi   | Associate Professor |
| NARUSHIMA, Tetsuya | Assistant Professor |
| YOSHIZAWA, Daichi  | Assistant Professor |
| NISHIDA, Jun       | Assistant Professor |
| OKANO, Yasuaki     | Technical Associate |
| NOMURA, Emiko      | Secretary           |

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

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

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

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