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

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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.

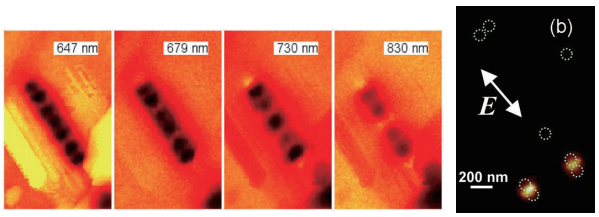

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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. Development of Nanoscopic Observation Method of Chiral Optical Fields by Optical Force Measurement[1)]

Nanoscopic observation of chiro-optical phenomena is essential in wide scientific areas but the measurement is sometimes not straightforward. To obtain a full understanding of the physics of chiro-optical systems and derive the full potentials, it is essential to perform in situ observation of the chiro-optical effect from the individual parts because the macroscopic chiro-optical effect cannot be translated directly into microscopic effects. One of the methods to overcome difficulties in direct access to nanoscopic chiro-optical characteristics is the use of near-field optical microscopy. In the present study, we develop an alternative method to access to near-field chiro-optical responses with optical force measurements. We achieved that at the nanoscale level by detecting the chiro-optical forces, which were generated by illumination of the material/probe system with left- and right-circularly polarized light. The induced optical force was dependent on the handedness of the incident circularly polarized light.

The measured differential image between left- and right-circularly polarized light illuminations was well correlated to the difference in the electric-field intensity near the nanostructure simulated with electromagnetic theory. Our results facilitate the clarification of chiro-optical phenomena at the nanoscale level and could innovate chiro-optical nanotechnologies. The present optical measurement method based on chiral photoinduced force microscopy is anticipated to be applied to chemical, biological, and pharmaceutical sciences, where the chirality of molecules plays an essential role.

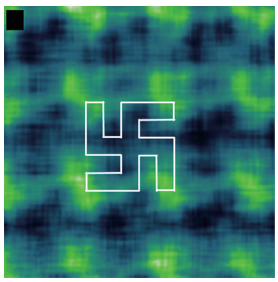

Figure 2. Chiro-optical force image of a gammadion-shaped gold nanostructure fabricated with electron beam lithography lift-off method. The base length of the gammadion is 460 nm.

2. Development of High-Precision Circular Dichroism Microscopy[2)]

Circular dichroism (CD) is a general and powerful method widely used to detect chirality of materials. However, signal is in general weak and difficult to detect, and interference from linear dichroism signal is sometimes serious for inhomogeneous anisotropic samples. For this reason, only very few microscopic measurements of CD have been reported until now. Some years ago, we developed a novel CD imaging method that is in principle free from linear dichroism and achieved high-precision CD imaging of micro- to nano-scale samples.[3)] Presently, we improved this method by introducing a new mechanism of detection, and achieved higher sensitivity and shorter measurement time compared to the previous apparatus. The detection sensitivity at the present stage is ≈0.06 mOD (≈2 mdeg in ellipticity) with a reasonable measurement time. We are now trying to achieve further rapid measurement time and extension of the wavelength range.

3. Circularly Polarized Luminescence from Chiral Plasmons

A number of studies to develop materials yielding circularly polarized luminescence have been reported. One of the ways to achieve the circularly polarized luminescence is synthesizing luminescent molecules with chiral structure. However, in most cases, the dissymmetry factor of the circular polarization (g-value: $|g| = 2$ for completely circularly polarized luminescence) was found to be small (typically of the order of 10^{-5} to 10^{-3}), with a few exceptions. In contrast, chiral plasmons have potentials to provide highly circularly polarized luminescence. We are now pursuing the possibility to obtain highly circularly polarized luminescence with chiral plasmonic systems.

4. Chiral Nanostructure Creation with Plasmonic Chemical Reaction Field

Chiral plasmons can be generated by illuminating metal nanostructure with circularly polarized light, even if the material is achiral. Chiral nanostructure formation is expected by chemical reactions induced by the chiral plasmonic excitations on achiral metal nanostructures. In this case, the handedness of the product is determined by that of the circularly polarized light. We have found a unique chiral structure formation based on this idea, and the detailed study on it is now under way.

5. Fundamental Characteristics of Chiro-Optical Properties of Pseudo Two-Dimensional Chiral Nanostructures

Based on the electromagnetic theory, it is expected that (ideal) two-dimensional chiral structures with 1- or 2-fold rotational symmetry exhibit chiro-optical effects, while those with 3-fold or higher rotational symmetry do not. However, for the pseudo two-dimensional gammadion-type metal nanostructures with 4-fold rotational symmetry in reality fabricated by electron beam lithography, they exhibit strong chiro-optical effects. In the present study, we experimentally confirmed that difference in rotational symmetry of the pseudo two-dimensional nanostructure gives totally different chiro-optical characteristics. We also obtain information on the origin of chiro-optical effects in pseudo two-dimensional 4-fold symmetry systems.

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

Nano- and Atomic-Scale Spectroscopy

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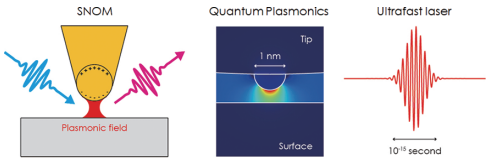
Keywords Atomic-Scale Optical Spectroscopy, Scanning Probe Microscopy, Nanoscale Science

Optical spectroscopy is a potent method to study material structures and properties through light–matter interactions. As nanoscience and nanotechnology have advanced, the significance of spectroscopy at the nanoscale, and even at the atomic scale, has grown immensely. Achieving optical imaging and spectroscopy at atomic resolution stands at the forefront of nanoscience and nanotechnology, allowing for the direct investigation of atomic-scale structures, properties and dynamics in real space and real time. Using near-field optics, electromagnetic fields can be confined at the nano- and atomic-scale. In particular, the localized surface plasmons of metallic nanostructures enable exceptionally sensitive optical spectroscopy due to their significant field enhancement. To achieve nano- and atomic-scale optical spectroscopy, we integrate advanced technologies such as low-temperature scanning tunneling microscopy (STM), laser spectroscopy, and quantum plasmonics. Specifically, the use of low-temperature STM allows us to directly observe atomic-level structures and to precisely manipulate individual atoms and molecules, whereas laser spectroscopy not only facilitates precise optical measurements but also traces ultrafast dynamics using ultrashort laser pulses. Consequently, the combination of these techniques offers a promising avenue for optical spectroscopy with ultrahigh spatiotemporal resolution.

In this review, I provide a concise summary of our recent advancements in nano- and atomic-scale spectroscopy.



Cutting-edge nanospectroscopy for nano-material research

Selected Publications

- 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," *ACS Photonics* **8**, 2610–2617 (2021).
- B. Cirera *et al.*, "Charge Transfer-Mediated Dramatic Enhancement of Raman Scattering upon Molecular Point Contact Formation," *Nano Lett.* **22**, 2170–2176 (2022).
- S. Liu *et al.*, "Nanoscale Heating of an Ultrathin Oxide Film Studied by Tip-Enhanced Raman Spectroscopy," *Phys. Rev. Lett.* **128**, 206803 (2022).
- 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).
- K. Nishikawa, J. Nishida *et al.*, "Metastability in the Insulator Metal Transition for Individual Vanadium Dioxide Nanoparticles," *J. Phys. Chem. C* **127**, 16485–16495 (2023).

1. Atomic-Scale Optical Spectroscopy

Recent studies have demonstrated that sub-nanometer confinement of near fields arises in the presence of atomic-scale protrusions on metallic nanostructures, and extremely strong light–matter interactions occur in "picocavity." However, the specific impact of atomic-level structures on plasmonic properties still remains to be elucidated. This requires precise experiments using atomically well-defined model systems. We investigated inelastic light scattering of a single Ag atom adsorbed onto the Ag(111) surface using low-temperature tip-enhanced Raman spectroscopy (TERS), as shown in Figure 1. We discovered that the vibration mode localized at the adatom can be observed in the TERS spectrum. Furthermore, we trace how the TERS spectrum evolves as a function of the gap distance. The exceptional stability provided by the low-temperature STM enabled us to clearly examine the different electron transport regimes of the picocavity, specifically in both the tunneling and quantum point contact (QPC) regimes. Our measurements highlight a distinct vibration mode localized at the adatom. Moreover, its TERS intensity undergoes a pronounced shift upon the QPC formation. This observation underscores that the atomic-level structure has a crucial impact on the plasmonic properties. To gain microscopic insights into the intricate of picocavity optomechanics, we meticulously analyzed the structure and plasmonic field within the STM junction, employing time-dependent density functional theory. These simulations unveiled that atomic-scale structural relaxations at the single-atom QPC lead to discernible variations in the plasmonic field's strength, volume, distribution, as well as the vibration mode localized at the individual atom.

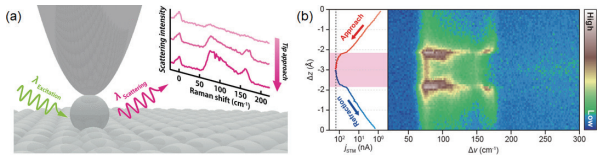


Figure 1. Inelastic light scattering spectroscopy for a single Ag adatom on the Ag(111) surface. (a) Schematic of the experiment. (b) ILS spectra measured as a function of the tip–adatom distance.

2. Nanoscale Coherent Phonon Spectroscopy

Coherent phonon spectroscopy offers microscopic insights into ultrafast lattice dynamics, especially when considering its interaction with other degrees of freedom in nonequilibrium conditions. While ultrafast optical spectroscopy is an established method for studying coherent phonons, the restrictions imposed by the diffraction limit have made direct observations of their nanoscale dynamics elusive. We successfully showcased nanoscale coherent phonon spectroscopy using an ultrafast laser-induced STM within a plasmonic junction (Figure 2). Coherent phonons are locally excited in ultrathin zinc oxide films by the highly confined plasmonic field and are probed via the photoinduced tunneling current through an electronic resonance of the zinc oxide film. Using concurrently performed TERS, we revealed the specific phonon modes involved. Unlike the Raman spectra, the phonon dynamics detected in coherent phonon spectroscopy display pronounced nanoscale spatial variations. These variations correlate with the distribution of the electronic local density of states, as discerned by scanning tunneling spectroscopy..

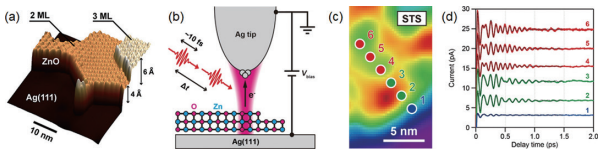


Figure 2. Nanoscale coherent phonon spectroscopy. (a) STM image of the ZnO ultrathin film expitaxially grown on the Ag(111) surface. (b) Schematic of the experiment. (c) Scanning tunneling spectroscopy image of the ZnO ultrathin film. (d) Interferometric autocorrelation of the tunneling current recorded over the ZnO ultrathin film.

3. Nanoscale Infrared Imaging of Nanomaterials

We have also developed advanced mid-infrared (MIR) spectroscopy and imaging techniques based on scattering-type scanning near-field optical microscopy (s-SNOM). We have successfully set up s-SNOM equipped with a MIR tunable broadband laser for investigation of nanomaterials. Figure 3 presents a direct observation of the insulator–metal transition in individual vanadium dioxide (VO_2) nanoparticles. Using temperature-dependent mid-IR nanoimaging, we were able to discern the phase transition of these individual VO_2 nanoparticles. Particles of smaller volumes generally transition to metal at elevated temperatures. This is attributed to fewer nucleation sites within each particle. Using mid-IR nanoimaging, we observed that the phase transition displays a stochastic behavior: The same particle shows varying transition temperatures across different heating cycles. Our findings suggest that the phase transition in VO_2 nanoparticles is prone to superheating and supercooling, and these transitions are limited by nucleation.

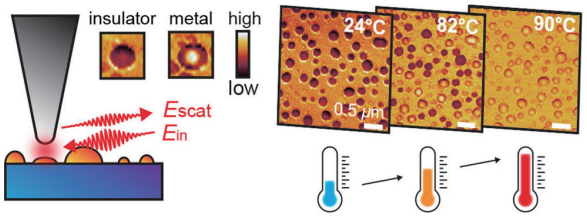


Figure 3. Nanoscale MIR imaging of VO_2 nanoparticles at different temperatures.

References

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2) S. Liu *et al.*, *Sci. Adv.* **8**, eabq5682 (2022).
3) K. Nishikawa, J. Nishida *et al.*, *J. Phys. Chem. C* **127**, 16485 (2023).