

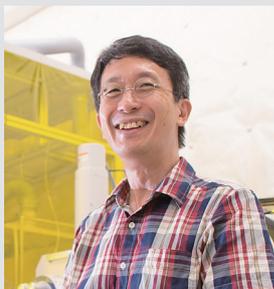
RESEARCH ACTIVITIES

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



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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. 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.

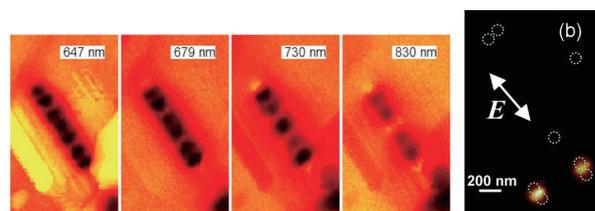


Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20 \text{ nm}^D \times 510 \text{ nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spherical 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. Optical Trapping of Chiral Metal Nanoparticles¹⁾

Micro- to nano-scale particle can be trapped by tightly focused laser beam at the focal point of the beam. This is due to the interaction between the incident optical field and induced polarization on the particle. The force exerted on the particle is in the direction of the gradient of the optical intensity (gradient force), and the particle is stabilized at the most intense position, *i.e.*, the focal point, of the optical beam. The strength of the gradient force has been considered to be determined by the real part of the refractive index of the particle.

When a chiral nanoparticle is optically trapped using a circularly polarized laser beam, a circular polarization (CP)-dependent gradient force can be induced on the particle. We investigated the CP-dependent gradient force exerted on three-dimensional chiral nanoparticles.²⁾ The experimental results showed that the gradient force depended on the handedness of the CP of the trapping light as well as the particle chirality. The analysis revealed that the spectral features of the CP-handedness-dependent gradient force are not simply influenced by the real part of the refractive index but also by the electromagnetic field perturbed by the chiral particle resonant with the incident light. This is in sharp contrast to the well-known behavior of the gradient force, which is governed by the real part of the refractive index. The extended aspect of the chiral optical force obtained here can provide novel methodologies on chirality sensing, manipulation, separation, enantio-selective biological reactions, and other fields.

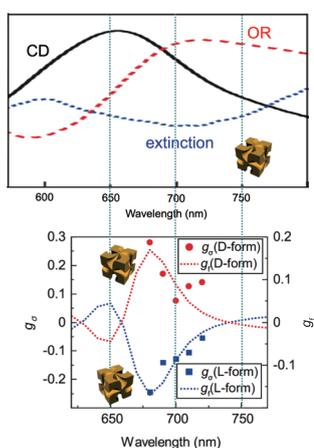


Figure 2. (Top panel) Circular dichroism (CD), optical rotation (OR), and extinction spectra of the colloidal solution of chiral gold nanoparticles. (Bottom panel) Dissymmetry factors (g -values: $|g| \leq 2$) of the gradient forces exerted on the chiral nanoparticles by circularly polarized light, experimentally observed (dots) and simulated (dashed curves). The dissymmetry factor follows the CD spectrum of the colloidal solution of the particle rather than OR. This observation gives a new insight into the mechanism of chirality-dependent gradient forces.

2. Development of High-Precision Circular Dichroism Microscopy³⁾

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.⁴⁾ 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 of rare-earth complexes and chiral assemblies of molecules. In contrast, chiral plasmons have potentials to provide highly circularly polarized luminescence. Based on this idea, we previously reported generation of circularly polarized luminescence from the chiral plasmonic material combined with achiral fluorescent molecules. We are now pursuing the possibility to further improve the characteristics of the circularly polarized luminescence.

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.

References

- 1) J. Yamanishi, H.-Y. Ahn, H. Yamane, S. Hashiyada, H. Ishihara, K. T. Nam and H. Okamoto, *Sci. Adv.* **8**, eqbq2604 (2022).
- 2) H.-E. Lee, H.-Y. Ahn, J. Mun, Y. Y. Lee, M. Kim, N. H. Cho, K. Chang, W. S. Kim, J. Rho and K. T. Nam, *Nature* **556**, 360 (2018).
- 3) H. Okamoto and T. Narushima, PAT. P. (PCT).
- 4) T. Narushima and H. Okamoto, *Sci. Rep.* **6**, 35731 (2016).

Atomic-Scale Optical Spectroscopy

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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.

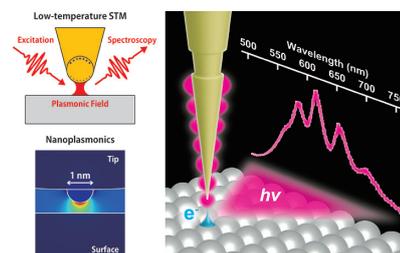


Figure 1. Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

Selected Publications

- 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.*, “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).

1. Inelastic Light Scattering by a Plasmonic Nanogap

Light scattering from plasmonic nanojunctions is routinely used to assess their optical properties. However, the microscopic mechanism remains imperfectly understood, and an accurate description requires the experiment in a well-defined environment with a highly precise control of the nanojunction. We investigated inelastic light scattering (ILS) in a plasmonic STM junction at cryogenic temperature and found that a broad continuum occurs in the anti-Stokes regime when the bias voltage is applied (Figure 2).¹⁾ The underlying mechanism was examined by recording the ILS spectra concurrently with STM luminescence. We proposed that electronic Raman scattering is dominant when the excitation wavelength matches the gap-mode plasmon, whereas photoluminescence mainly contributes under off-resonance conditions. The results provide an in-depth understanding of ILS by electrically biased plasmonic nanojunctions and demonstrate nonthermal origin of the anti-Stokes scattering.

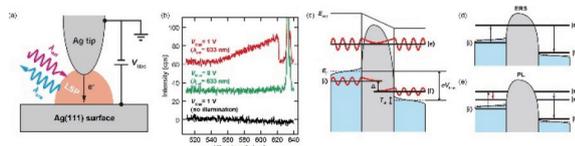


Figure 2. (a) Schematic of the experiment. (b) ILS spectra in the anti-Stokes regime measured for the Ag tip–vacuum–Ag(111) junction at a different bias voltage and in the presence/absence of the illumination. (c–e) Anti-Stokes scattering mechanism in an electrically-biased STM junction. (d) Electronic Raman scattering. (e) Photoluminescence.

2. Atomic-Point Contact Raman Spectroscopy

Tip-enhanced Raman spectroscopy (TERS) is a powerful tool for ultrasensitive chemical analysis at surfaces. Although the enhancement mechanism underlying TERS has been intensively studied, it remains to be elucidated, particularly in sub-nanometer plasmonic gaps. We investigated TERS at atomic-point contacts (APCs) in plasmonic STM junctions and found that large enhancement can be obtained when APCs are formed. Figure 3 shows an example of APC-TERS for an ultrathin ZnO film epitaxially grown on the Ag(111) surface.²⁾ The

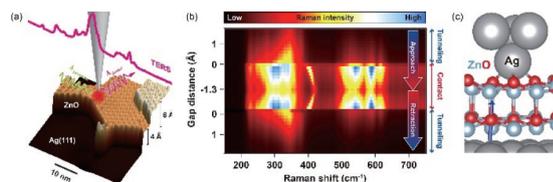


Figure 3. (a) Schematic of the experiment. (b) Waterfall plot of the gap-distance-dependent TER spectra recorded over 2-ML ZnO. The tip approaches and retracts toward and backward from the ZnO from the tunneling to the APC regime. (c) Structure at the APC determined by the DFT calculation.

TERS spectra are recorded as a function of the tip–surface distance including two distinct regimes, namely the tunneling and APC regimes. The remarkable enhancement can be observed at the distance of the APC formation. We suggest that the enhancement is explained by chemical effects resulting from hybridization between the tip apex and surface atoms of the ZnO film.

3. Nanoscale Heating of an Ultrathin Oxide Film

Heating is one of the most basic physical processes. Rapid advances of nanofabrication techniques raise a fundamental issue regarding thermal management at nanoscale. TERS thermometry provides a unique opportunity to study local heating. We investigated the nanoscale heating mechanism of an ultrathin ZnO film using TERS (Figure 4).³⁾ The exceptional sensitivity of TERS allowed to observe Stokes and anti-Stokes scattering of the ZnO film and to perform nanoscale thermometry. It was revealed that the local heating originates mainly from inelastic electron tunneling through the electronic resonance when the bias voltage exceeds the conduction band edge of the 2-monolayer (ML) ZnO. When the bias voltage is lower than the conduction band edge, the local heating arises from two different contributions, namely direct optical excitation between the interface state and the conduction band of 2-ML ZnO or injection of photoexcited electrons from an Ag tip into the conduction band. Simultaneous mapping of tip-enhanced Raman spectroscopy and scanning tunneling spectroscopy for 2-ML ZnO including an atomic-scale defect demonstrates visualizing a correlation between the heating efficiency and the local density of states, which further allows us to analyze the local electron-phonon coupling strength with ~ 2 nm spatial resolution.

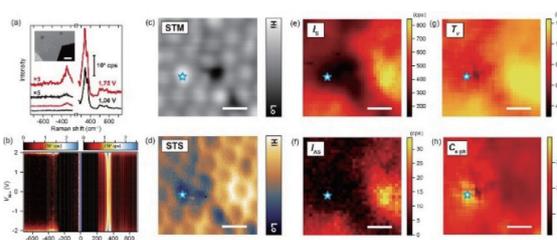


Figure 4. (a) TERS spectra of 2-monolayer ZnO/Ag(111) including the Stokes and anti-Stokes regimes. (b) Waterfall TERS plot as a function of the applied bias voltage. (c) and (d) STS image of 2-monolayer ZnO film including an atomic-scale defect and the corresponding STS mapping. (e–g) Mapping of the Stokes and anti-Stokes intensity and the effective temperature recorded in the same area with (c–d). (f) Mapping of the relative electron–phonon coupling strength.

References

- 1) S. Liu *et al.*, *ACS Photonics* **8**, 2610–2617 (2021).
- 2) S. Liu *et al.*, *Nano Lett.* **20**, 5879–5884 (2020).
- 3) S. Liu *et al.*, *Phys. Rev. Lett.* **128**, 206803 (2022).