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.

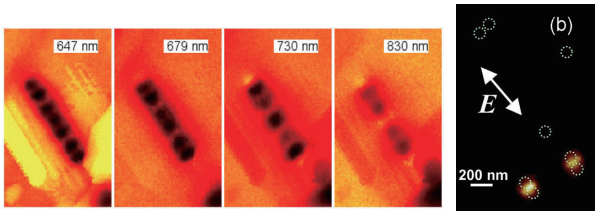

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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. Highly Chiral Light Emission Using Plasmonic Helicoid Nanoparticles[1)]

Materials generating circularly polarized luminescence (CPL) have received increasing interest due to their potential applications in bioimaging, sensing, etc. A chiral plasmonic nanostructure is one candidate for generating strong and highly dissymmetric CPL by coupling with the surrounding luminescent material. In this study, the generation of circularly polarized two-photon-induced photoluminescence (TPI-PL) from chiral gold nanostructures is demonstrated. Measurements of TPI-PL show that it has a strong dissymmetry factor of ≈0.7 for a single chiral Au nanoparticle. It is believed that this work provides a new route for novel CPL-generating materials with strong dissymmetry and holds promise for various applications using CPL technology.

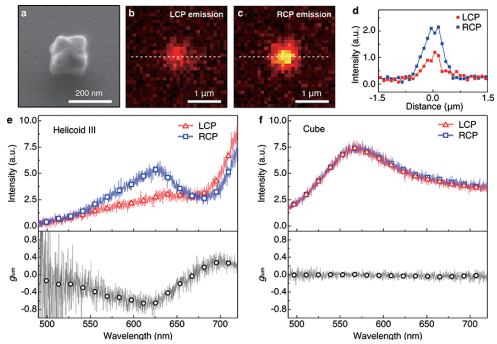

Figure 2. (a) SEM image and TPI-PL images for (b) left and (c) right circularly polarized emission of a single Au helicoid nanoparticle (NP). (d) Line profiles of the TPI-PL intensity along the dashed lines in (b) and (c). TPI-PL spectra (upper) and corresponding luminescence dissymmetry g_{lum} (lower) of (e) the Au helicoid NP and (f) the cubic NP. CC-BY-NC

2. Creation of a Photopolymerized Double Spiral Structure by Interference of Plasmonic Scattering and Circularly Polarized Light[2)]

Chiro-optical effects of materials enable many intriguing optical phenomena in the subwavelength regime and are expanding their application in broad areas. Recently, the possibility of producing strong chiro-optical effects using achiral plasmonic nanostructures has been intensively studied. The interaction of achiral nanostructures with circularly polarized light can break the mirror symmetry. In this study, we present a method to create a novel chiral structure by using achiral plasmonic nanoparticles and circularly polarized light. The interference between the circularly polarized incident field and the plasmonic scattering field produced a double spiral pattern of the electro-magnetic fields, which was replicated via the photopolymerization reaction and resulted in chiral surface relief patterns of the polymer layer.

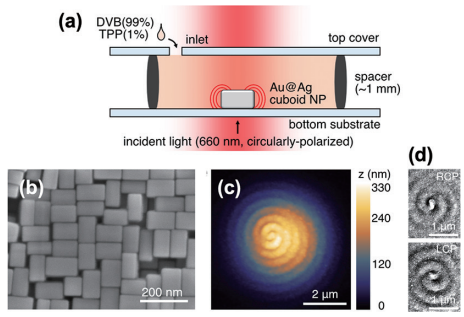

Figure 3. (a) Schematic illustration of the cell for the photopolymerization process. (b) SEM image of as-synthesized Au@Ag cuboid nanoparticles. (c) AFM images of the double spiral structures created by the irradiation of RCP light. (d) SEM images observed around the centers of the RCP and LCP light-exposed areas. CC-BY-NC-ND

3. Circular Dichroism of Pseudo-2-Dimensional Metal Nanostructures: Rotational Symmetry and Reciprocity[3)]

Circular dichroism (CD) spectra for pseudo-two-dimensional chiral nanomaterials were systematically investigated and analyzed in relation to the rotational symmetry of the nanomaterials. For pseudo-two-dimensional chiral gold nanostructures fabricated on glass substrates using electron beam lithography, a matter with 4-fold rotational symmetry is found to be CD active, contrary to the theoretical expectation for the ideal two-dimensional case to exhibit no CD. The CD signal measured from the back side is found to be the same as that measured from the front side. The observed chiro-optical behavior arises from three-dimensional chiral characteristics of the material. For a matter that is 2- or 1-fold rotationally symmetric, the CD signal measured from the back side is not coincident with that from the front side. The observed CD spectral behavior is considered to be determined by a balance between the in-plane isotropic and anisotropic components of the chiral permittivity.

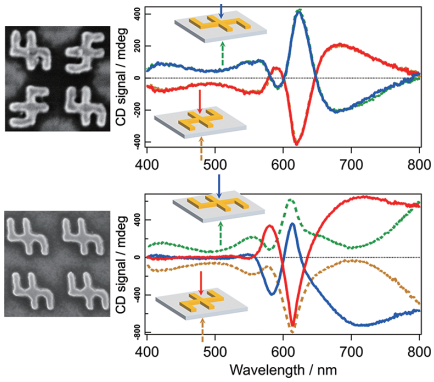

Figure 4. CD spectra obtained for (top) 4-fold rotational symmetry arrays and (bottom) translational arrays of italic f-shaped gold nanostructures. CC-BY

References

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2) H.-Y. Ahn, T. Narushima and H. Okamoto, *J. Phys. Chem. C* **128**, 7159 (2024).
3) K. Endo, S. Hashiyada, T. Narushima, Y. Togawa and H. Okamoto, *J. Chem. Phys.* **159**, 234706 (2023).

Nano- and Atomic-Scale Spectroscopy

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

An in-depth understanding of the structure and dynamics of matter at the atomic scale is crucial for designing next-generation devices and optimizing material/energy conversion processes, such as optoelectronics, solar cells, and catalysis. The rapid advancement of nanotechnology requires sophisticated measurement techniques capable of capturing phenomena with simultaneous spatiotemporal resolution at the (sub)nanometer length and pico/femtosecond time scale. Optical spectroscopy serves as a versatile tool for studying the microscopic structures, properties, and dynamics of a wide variety of materials. However, its spatial resolution is inherently limited by the diffraction limit, which restricts the ability to directly characterize nanoscale objects. Nano-spectroscopy using near-field optics offers a unique approach to overcome this physical limitation, enabling the investigation of materials at the nanoscale.

Our group has focused on the development and application of cutting-edge scanning near-field optical microscopy (SNOM) combined with various advanced spectroscopic methods, including nonlinear and ultrafast time-resolved measurements. In particular, we explore atomic-scale light–matter interactions to achieve nano-spectroscopy at the unprecedented spatiotemporal resolution. Recently, we have demonstrated the atomic-level sensitivity and spatial resolution using tip-enhanced Raman spectroscopy (TERS) based on low-temperature scanning tunneling microscopy (STM), providing novel insights into the intricate phenomena in nanoscale systems. Furthermore, by integrating ultrashort pulsed lasers, we have opened new avenues for directly observing the coherent dynamics of electrons and lattices within the STM junction. This capability is a critical step towards realizing atomic-scale ultrafast nano-spectroscopy, allowing us to probe dynamic processes that were previously inaccessible.

We are currently further pushing the boundary of nano-spectroscopy techniques with three key objectives: (1) extending the capabilities of atomic-scale spectroscopy from the visible to the infrared region to explore a broader range of materials and phenomena, (2) developing manifold nonlinear nano-spectroscopy techniques to investigate complex quantum interactions, and (3) applying these advanced methods to diverse materials, including low-dimensional materials, quantum dots, and biological molecules. These advancements will provide profound insights into the fundamental quantum properties and interactions of materials, potentially leading to the discovery of novel functionalities and the creation of innovative nanoscale devices.

Selected Publications

- 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).
- J. Nishida *et al.*, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24**, 836 (2024).

1. Atomic-Scale Optical Spectroscopy

Understanding and controlling of atomic-scale confinement of optical fields is a highly active area of research in light–matter interactions and their applications such as ultrasensitive spectroscopy and nano-optoelectronics. Recent studies have demonstrated that extreme confinement of near fields occurs in the presence of atomic-scale protrusions on metallic nanostructures, often referred to as "picocavity," formed by features as small as single atoms, resulting in unique optical phenomena. Yet, the underlying mechanisms remain to be elucidated, requiring highly precise experiments using atomically well-defined model systems. To address this, we investigated Raman scattering of a single Ag atom adsorbed onto the Ag(111) surface using low-temperature TERS,[1] as shown in Figure 1. The experiment demonstrated that the vibration localized at the adatom is distinctly observable in the TERS spectrum. We further explored the relationship between the gap-distance dependence and Raman scattering in the different electron transport regimes of the picocavity, specifically comparing the tunneling and quantum point contact (QPC) regimes. Notably, the TERS spectra exhibited significant changes upon the formation of the QPC. These findings highlight that atomic-level structural changes can significantly influence the plasmonic properties of the system, offering new insights into how atomic-scale features modulate optical responses.

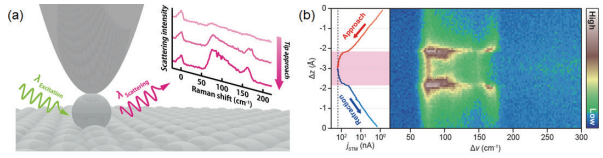

Figure 1. Inelastic light scattering spectroscopy for a single Ag adatom on the Ag(111) surface. (a) Schematic of the experiment. (b) Raman spectra measured as a function of the tip–adatom distance.

2. Nanoscale Coherent Phonon Spectroscopy

Coherent phonon spectroscopy is a valuable technique for gaining microscopic insights into ultrafast lattice dynamics, especially under nonequilibrium conditions. Understanding these dynamics is crucial for advancing our knowledge of fundamental material properties and for the development of ultrafast electronic and photonic devices. However, the conventional method cannot directly observe phonon dynamics at the nanoscale. To overcome these limitations, recently we have successfully demonstrated nanoscale coherent phonon spectroscopy using an ultrafast laser-induced STM within a plasmonic junction, as shown in Figure 2.[2] This approach uniquely leverages the highly confined plasmonic field to locally excite coherent phonons in ultrathin zinc oxide films, which are then probed via the photoinduced tunneling current through an electronic resonance of the zinc oxide film. Unlike the Raman spectra, the phonon dynamics detected in coherent phonon spectroscopy display pronounced nanoscale spatial variations that correlate with the distribution of the electronic local density of states. We plan to further extend this technique to investigate various low-dimensional systems.

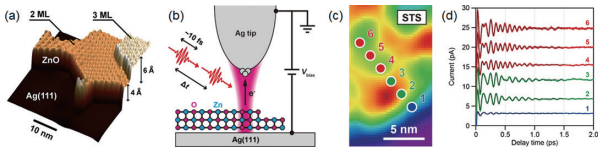

Figure 2. Nanoscale coherent phonon spectroscopy. (a) STM image of the ZnO ultrathin film grown on the Ag(111) surface. (b) Schematic of the experiment. (c) STS map of the ZnO ultrathin film. (d) Interferometric autocorrelation of the tunneling current recorded over the ZnO ultrathin film.

3. Nanoscale Infrared Nano-Spectroscopy of Nanomaterials

We have developed an advanced SNOM system based on atomic force microscopy (AFM), equipped with a wavelength-tunable pulsed laser that spans from the visible to the mid-infrared (MIR) region. This system allows us to perform nanoscale infrared (nano-IR) spectroscopy with exceptional sensitivity and resolution. The sensitivity of our nano-IR spectroscopy was demonstrated by successfully measuring the MIR response of a single protein molecule isolated on a gold (Au) surface, as shown in Figure 3.[3] By implementing a unique detection scheme that extracts highly localized near-field MIR scattering down to a spatial resolution of just a few nanometers, we have achieved world-record sensitivity.

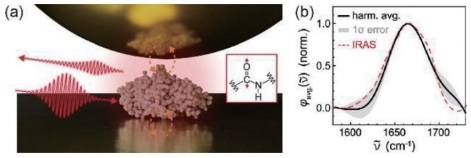

Figure 3. MIR vibrational spectroscopy of a single protein. (a) Schematic of the experiment. (b) MIR spectrum around the vibrational resonance of the amid group.

Figure 4 illustrates the application of the ultrafast visible-pump–MIR-probe nano-spectroscopy to visualize the spatially modulated many-body photo-carrier dynamics within a monolayer WS_2. By capturing these dynamics, we can directly observe how photo-carriers behave and interact in response to optical excitation, revealing intricate details of the material's electronic properties.

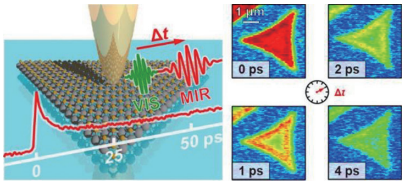

Figure 4. Ultrafast nano-imaging of spatially modulated many-body dynamics in monolayer WS_2.

References

1) S. Liu *et al.*, *ACS Nano* **17**, 10172 (2023).
2) S. Liu *et al.*, *Sci. Adv.* **8**, eabq5682 (2022).
3) J. Nishida *et al.*, *Nano Lett.* **24**, 836 (2024).