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

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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.

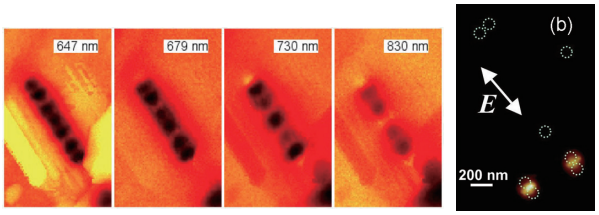

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right)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

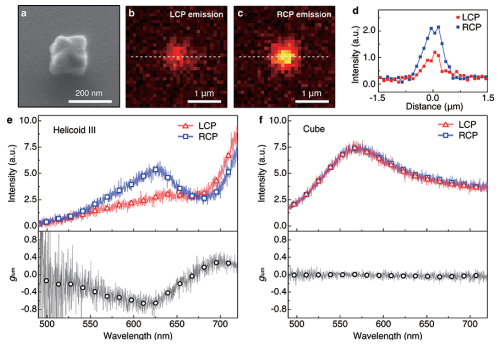

Figure 2. (a) SEM image and TPI-PL images for (b) left and (c) right circularly polarized emission of a single Au helicoid nanoparticle (NP). (d) Line profiles of the TPI-PL intensity along the dashed lines in (b) and (c). TPI-PL spectra (upper) and corresponding luminescence dissymmetry g_{lum} (lower)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

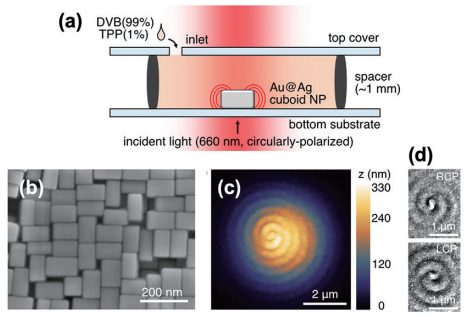

Figure 3. (a) Schematic illustration of the cell for the photopolymerization process. (b) SEM image of as-synthesized Au@Ag cuboid nanoparticles. (c) AFM images of the double spiral structures created by the irradiation of RCP light. (d) SEM images observed around the centers of the RCP and LCP light-exposed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

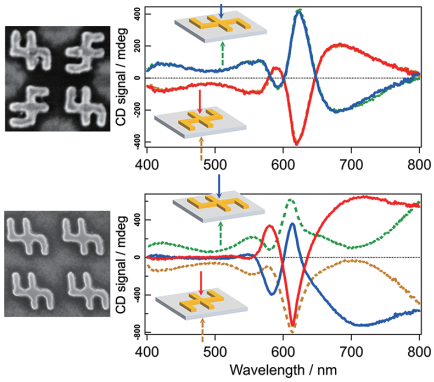

Figure 4. CD spectra obtained for (top) 4-fold rotational symmetry arrays and (bottom) translational arrays of italic f-shaped gold nanostructures. CC-BY

References

1) H.-Y. Ahn, K. Q. Le, T. Narushima, J. Yamanishi, R. M. Kim, K. T. Nam and H. Okamoto, *Adv. Opt. Mater.* **12**, 2400699 (2024).
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).