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.

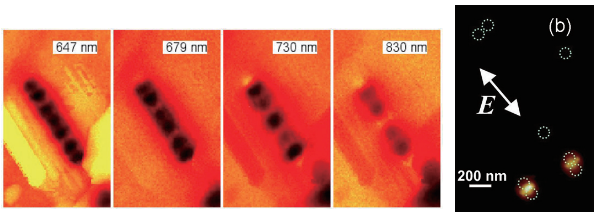

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right)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

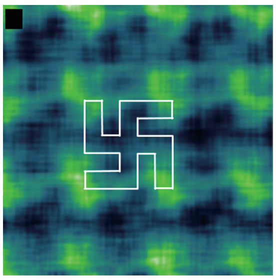

Figure 2. Chiro-optical force image of a gammadion-shaped gold nanostructure fabricated with electron beam lithography lift-off method. The base length of the gammadion is 460 nm.

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.

References

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