Nano-Optical Imaging and Application to 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. 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 succeeded 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.

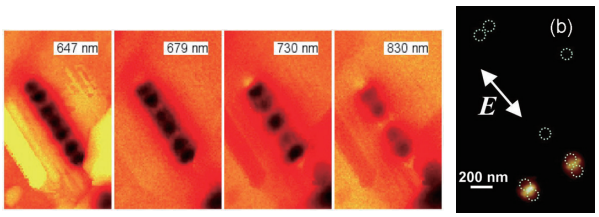

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right)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

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.

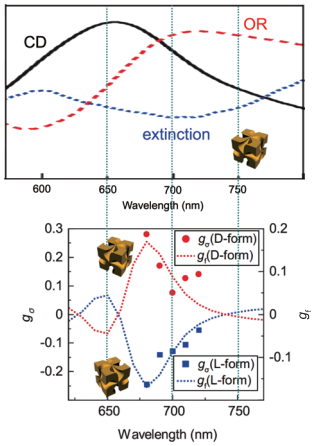

Figure 2. (Top panel) Circular dichroism (CD), optical rotation (OR), and extinction spectra of the colloidal solution of chiral gold nanoparticles. (Bottom panel) Dissymmetry factors (*g*-values: $|g| \leq 2$) of the gradient forces exerted on the chiral nanoparticles by circularly polarized light, 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 Microscopy[3)]

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

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