Development of Advanced 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 key 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 directly nanoscale functionalities and dynamics. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterials 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 recent few years, we have also 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.

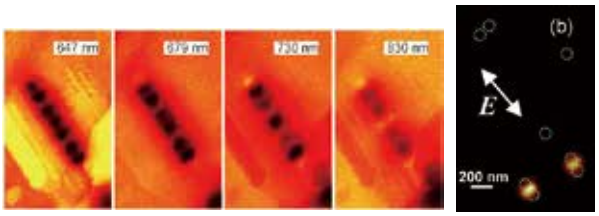

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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, 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).
- H. Okamoto and K. Imura, "Near-Field Optical Imaging of Enhanced Electric Fields and Plasmon Waves in Metal Nanostructures," *Prog. Surf. Sci.* **84**, 199–229 (2009).

1. Circular Dichroism Microscopy Free from Commingling Linear Dichroism via Discretely Modulated Circular Polarization[1)]

Circular dichroism (CD) is a representative method to detect chirality in materials spectroscopically. Microscopy based on CD signals provides unique and powerful technique for the studies of nanomaterials with chiro-optical and magneto-optical functions, biomolecular systems, *etc*. One of difficulty in CD microscopy is commingling of linear birefringence (LB) and linear dichroism (LD) signals, that arise from optical anisotropy of the samples. Because LB and LD signal levels are in general much larger than that of CD, slight imperfections of optical components and nonlinearity (in particular from polarization modulation devices) cause commingling LB and LD signals to CD.

In this work, we developed a far-field CD imaging microscope with a device to suppress the commingling of LB and LD signals. CD signals are, in principle, free from the commingling influence of LD and LB if the sample is illuminated with pure circularly polarized light, with no linear polarization contribution. Based on this idea, we here propose a novel circular polarization modulation method to suppress the contribution of linear polarization, which enables high-sensitivity CD detection (10^{-4} level in optical density unit or mdeg level in ellipticity) for microscopic imaging at a nearly diffraction limited spatial resolution (sub-μm level). The highly sensitive, diffraction-limited local CD detection will make direct analyses of chiral structures and spatial mappings of optical activity feasible for μm- to sub-μm-sized materials and may yield a number of applications as a unique optical imaging method.

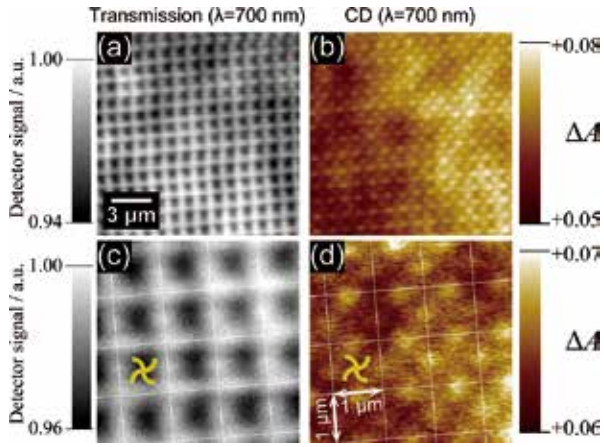

Figure 2. Transmission (a, c) and CD (b, d) images of the two-dimensional array of chiral (swirl-shaped) gold nanostructures. The wavelength of observation both for the transmission and CD images was 700 nm.[1)]

2. Near-Field Nonlinear CD Imaging of Single Gold Nanostructures[2)]

We demonstrated near-field nonlinear circular dichroism (CD) imaging of single rectangular (achiral) gold nanostructures using a two-photon excitation method. The gold rectangles were illuminated by pulses of circularly polarized light (CPL) to generate two-photon excitation images of the longitudinal plasmon modes. The observed images consisted of oval-shaped spatial features (corresponding to the antinodes of the plasmon modes) tilted from the long axis of the rectangles. The tilting direction depended on the handedness (left or right) of the CPL used for illumination, which led to the observation of a strong local dissymmetry of the two-photon excitation signals. The tilts of the oval features were not observed under linearly polarized pulse illumination with any polarization direction. The nonlinear CD images constructed from the differential two-photon excitation probability for left- and right-CPL pulses exhibited spatial features that were reasonably explained by the multipolar characters of the excited plasmon modes.

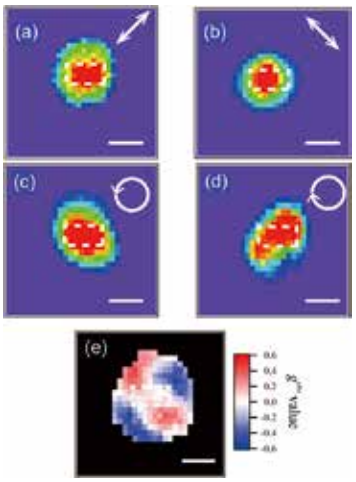

Figure 3. (a–d) Near-field two-photon excitation images of the rectangle at the excitation wavelength of 830 nm. Incident pulses are (a) linearly polarized, rotated by 45° from the long axis, (b) linearly polarized, rotated by −45° from the long axis, (c) left-circularly polarized, and (d) right-circularly polarized. (e) Near-field two-photon CD image evaluated from (c) and (d). The CD signals (g^{obs}) were not evaluated for the black areas outside the rectangular nanostructures because of low TPI-PL intensity. The dotted lines represent the approximate shape of the rectangle. Scale bars: 100 nm.[2)]

References

1) T. Narushima and H. Okamoto, *Sci. Rep.* **6**, 35731 (2016).
2) Y. Nishiyama and H. Okamoto, *J. Phys. Chem. C* **120**, 28157–28162 (2016).

Awards

HASHIYADA, Shun; The Best Poster Presentation Award, NFO-14 (2016).
HASHIYADA, Shun; OSJ-OSA Joint Symposia Student Award (2016).

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