Development of Advanced Near-Field Spectroscopic Imaging and Application to Nanomaterials

Department of Photo-Molecular Science
Division of Photo-Molecular Science I

OKAMOTO, Hiromi
Professor
[aho@ims.ac.jp]

Education
1983 B.S. The University of Tokyo
1991 Ph.D. The University of Tokyo

Professional Employment
1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Award
2012 The Chemical Society of Japan (CSJ) Award for Creative Work

Member
Assistant Professor
NARUSHIMA, Tetsuya
IMS Research Assistant Professor
NISHIYAMA, Yoshio
Post-Doctoral Fellow
KOWAKA, Yasuyuki
Visiting Scientist
SAIN, Basudeb*
JACK, Calum†
Graduate Student
HASHIYADA, Shun
Technical Fellow
ISHIKAWA, Akiko
Secretary
NOMURA, Emiko

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There is much demand for the studies of local optical properties of molecular assemblies and materials, to understand nanoscale physical and chemical phenomena and/or to construct nanoscale optoelectronic devices. Scanning near-field optical microscopy (SNOM) is an imaging method that enables spatial resolution beyond the diffraction limit of light. Combination of this technique with various advanced spectroscopic methods may provide direct methods to probe dynamics in nanomaterials and nanoscale functionalities. It may yield essential and basic knowledge to analyze origins of characteristic features of the nanomaterial systems. We have constructed apparatuses of near-field spectroscopy and microscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable near-field measurements of two-photon induced emission, femtosecond time-resolved signals, and circular dichroism, in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatiotemporal 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, and so forth.

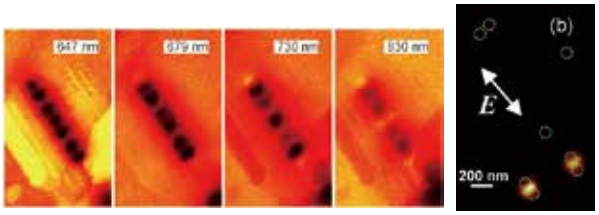

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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. Local Optical Activity in Achiral Two-Dimensional Gold Nanostructures[1,2)]

Since the discovery of molecular chirality, the geometrical chirality of a material, which means that the material has a non-superposable mirror image, has been considered the prerequisite for exhibiting optical activity of the structural origin. Circular dichroism (CD, defined as the differential absorption of left and right circularly polarized light) is a representative measurement method of optical activity. We recently developed a scanning near-field CD microscope, which is capable of optical imaging with CD of a specimen as the signal with a spatial resolution beyond the diffraction limit of light, and applied the method to local optical activity measurements of plasmonic chiral nanostructures. In the present study, we report an experimental demonstration of nanoscale local CD activities for highly symmetric achiral (non-chiral) rectangular gold nanostructures.[1)] Macroscopic CD spectral measurements of the nanostructure sample did not show any CD activity over the entire range of measured wavelengths, as expected from the achiral shape of the rectangle. In contrast, we found both locally positive and negative CD signals in a single rectangular nanostructure, whose spatial distribution was symmetric about the center of the rectangle, with strong CD signals at the corners (Figure 2(b)). The strong local CD signals in achiral material were also found in crescent (C-shaped) gold nanostructures.[2)] These results demonstrate that the established selection rule of optical activity is not valid for local microscopic measurements, and suggest that strongly chiral optical fields are generated in the vicinities of plasmonic materials even if the materials are achiral.

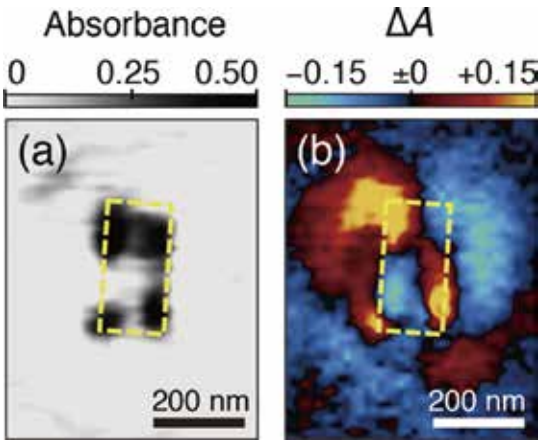

Figure 2. Near-field optical images (at 633 nm) of a rectangular gold nanostructure fabricated on a glass substrate via electron beam lithography and lift-off method.[1)] (a) Transmission image. (b) CD image. Dashed yellow lines represent approximate shape of the nanostructure.

2. Plasmon Dephasing in Single Gold Nanorods Observed by Ultrafast Near-Field Optical Imaging[3)]

We applied time-resolved near-field optical microscopic measurements with ultrashort light pulses of ~16 fs duration to observe plasmon dephasing processes in single gold nanorods. The correlation width of the time-resolved signal obtained at each position on the nanorod was broadened compared with the auto-correlation width of the pulse, because the plasmon dephasing was convolved on the system response function given by the pulse auto-correlation function. The correlation width maps of the rods (Figure 3) showed spatially oscillating patterns that look similar to the plasmon mode structures observed in the static near-field optical images (as typified with Figure 1). The spatial variation of the correlation widths was explained as arising from the position dependent contribution of the resonant plasmon excitation in the time-resolved signals relative to that of the non-resonant excitation. The dephasing times of the resonant plasmon modes were constant regardless of the excitation position, which is understood to be a consequence of the spatial coherence of the plasmon mode across the rod.

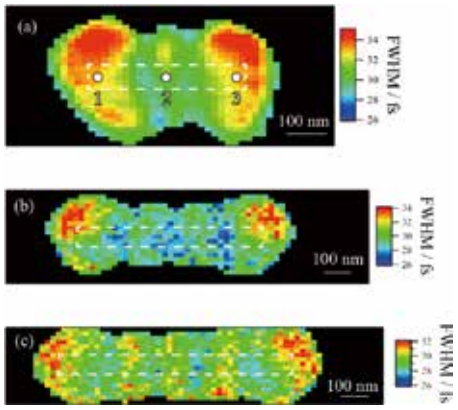

Figure 3. Correlation width maps obtained for time-resolved signals of gold nanorods with different dimensions.[3)] Dashed white lines represent approximate shapes of the nanorods. The black parts outside of the nanorods are the areas where the correlation widths were not evaluated because of low signal intensities.

References

1) S. Hashiyada, T. Narushima and H. Okamoto, *J. Phys. Chem. C* **118**, 22229–22233 (2014).
2) T. Narushima, S. Hashiyada and H. Okamoto, *ACS Photon.* **1**, 732–738 (2014).
3) Y. Nishiyama, K. Imaeda, K. Imura and H. Okamoto, *J. Phys. Chem. C* **119**, 16215–16222 (2015).

Award

HASHIYADA, Shun; Chemical Society of Japan Student Presentation Award 2015.

* IMS International Internship Program (Graduate Student from Indian Association for the Cultivation of Science)
† Graduate Student from University of Glasgow