Development of Advanced Near-Field Spectroscopy 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 J apan (CSJ) Award for Creative Work

Member
Assistant Professor
NARUSHIMA, Tetsuya
IMS Research Assistant Professor
NISHIYAMA, Yoshio
Post-Doctoral Fellow
KOWAKA, Yasuyuki
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 probing methods for 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 given 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.

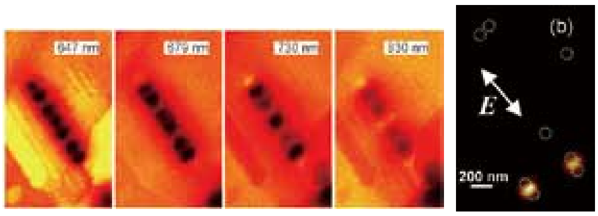

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).
- H. Okamoto, "Nanooptical Studies on Physical and Chemical Characteristics of Noble Metal Nanostructures," *Bull. Chem. Soc. Jpn.* **86**, 397–413 (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. Plasmon-Mode Analysis of Gold Nanodisks[1)]

Spatial and spectral properties of plasmons in noble metal nanoparticles are strongly influenced by the geometry of the particles. We previously demonstrated that standing wave functions of plasmon modes of gold nanorods (1-dimensional system) could be visualized by near-field microscopy. In the present study we visualized plasmon-modes for gold nanodisks (2-dimensional system) fabricated by the electron-beam lithography lift-off method. Near-field transmission spectrum of a single nanodisk exhibited multiple plasmon resonances in the visible to near-infrared region. Near-field transmission images observed at these resonance wavelengths show wavy spatial features depending on the wavelength of observation, which are much more complicated than those of the 1-dimensional rods. Theoretical analysis is indispensable to clarify the origins of the spatial features of the modes. For this purpose, numerical simulations with a novel theoretical formalism based on spatial correlation between electromagnetic fundamental modes inside and outside of the disc were performed. Simulated images reproduced the observed spatial structures excited in the disc.

Compared with other electromagnetic simulation methods frequently used for the analysis of plasmons, such as finite-difference time-domain (FDTD) method, the present method is advantageous in its capability of mode-based analysis of the electromagnetic fields. Mode-analysis of the simulated images indicates that the spatial features observed in the transmission images originate mainly from a few fundamental modes of the disc. The relative phases of the collective oscillation of electrons in the lobes observed near-field images were also clarified by this analysis.

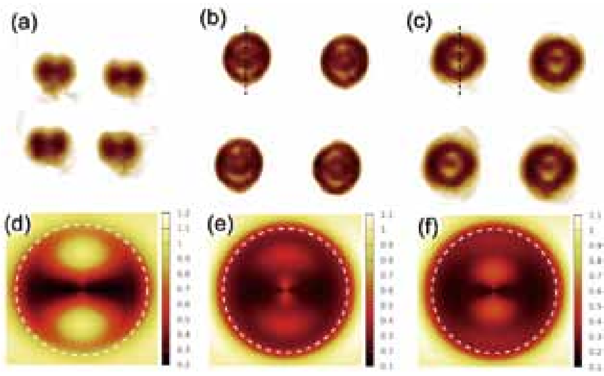

Figure 2. Observed (a–c) and simulated (d–f) near-field transmission images of gold nanodisks (thickness 35 nm).[1)] The diameters of the disks were 400 nm (a,d) and 800 nm (b,c,e,f). The wavelengths of observation and calculation were 780 nm (a,d), 710 nm (b), 790 nm (c), 705 nm (e), and 765 nm (f).

2. Strong Nanoscale Local Optical Activity in 2-D Chiral Metal Nanostructures

Nanostructures with chiral shapes show optical activity. Chiral metal nanostructures are expected to yield particularly strong optical activity arising from plasmon resonances. We recently developed a near-field circular dichroism (CD) imaging system with 100-nm-scale spatial resolution.

In the present work, we measured near-field CD images of S-shaped gold nanostructures and compared the results with the macroscopically obtained CD spectrum.[2)] Local CD signals of both handedness coexisted in the individual nanostructures, and the spatial distribution of the CD reflected the chiral symmetry of the nanostructure (Figure 3). When integrated over the entire nanostructure, the local CD signal was approximately 1% of the maximum of the local CD signal, which approximately coincided with the macroscopic CD signal. This indicates that there are possibly prominent nanoscale local CD signals even if only a tiny CD signal is observed macroscopically. We also studied developing optical activity with increasing chirality.[3)] We measured 2-D nanostructures composed of two symmetrically arranged C-shaped partial structures with various distances between them, which formed an "S" structure when the two partial structures were contacted. The chirality formed with the two partial structures caused an enhanced local optical activity when the partial structures were close enough to each other, even without a physical contact between them.

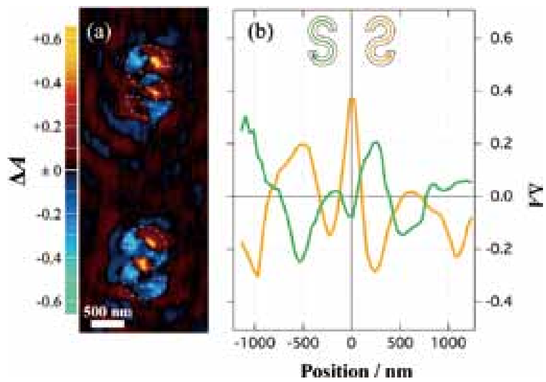

Figure 3. Near-field CD images of "S" shaped gold nanostructures (thickness 35 nm) observed at 785 nm (a) and the line profiles along the curves of the structures (b).[2)]

References

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2) T. Narushima and H. Okamoto, *J. Phys. Chem. C* **117**, 23964–23969 (2013).

3) T. Narushima, S. Hashiyada and H. Okamoto, *ACS Photonics* **1**, 732–738 (2014).

Awards

HASHIYADA, Shun; Optics & Photonics Japan Best Presentation Award (2013).
NISHIYAMA, Yoshio; Best Presentation Award, The Spectroscopical Society of Japan (2014).