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

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Keywords Near-Field Optical Microscopy, Plasmons, Excited States of Nanomaterials

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.

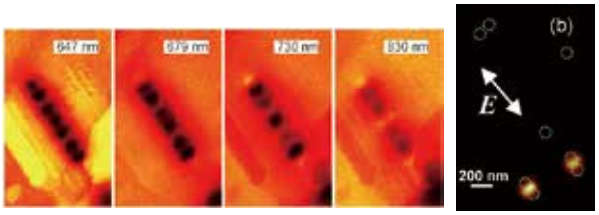

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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. Observation of Plasmon Wave Packet Motions via Femtosecond Time-Resolved Near-Field Imaging Techniques[1,2)]

The generation and dynamics of plasmon wave packets in single gold nanorods were observed at a spatiotemporal scale of 100 nm and 10 fs via time-resolved near-field optical microscopy. Because an ultrashort pulse has a broad spectral width, one can excite more than two resonant modes of materials if their frequency range is covered with the pulse spectrum. In this study, dynamics after excitation of single plasmon mode (for a relatively low aspect ratio rod) and that after multi-mode excitation (for a relatively high aspect ratio rod) were compared.

When a single plasmon mode was excited, time-resolved signals showed single-exponential decay profiles reflecting the dephasing of the mode, and time-resolved near-field image feature was essentially independent of time. In contrast, if two plasmon modes of a nanorod were excited coherently with an ultrashort near-field pulse, a decay and revival feature of the time-resolved signal was obtained, which reflected the reciprocating motion of the wave packet. The time-resolved near-field images were also indicative of the wave packet motion. At some period of time after the excitation, the spatial features of the two modes appeared alternately (Figure 2(a)), showing motion of plasmonic wave crests along the rod. The wave packet propagation was clearly demonstrated from this observation with the aid of a simulation model (Figure 2(b,c)). The present experimental scheme opens the door to coherent control of plasmon-induced optical fields in a nanometer spatial scale and femtosecond temporal scale.

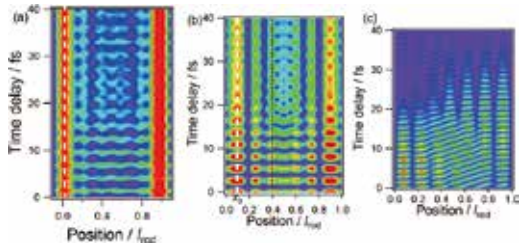

Figure 2. (a) Time variation (ordinate) of line profiles of transient near-field images of a gold nanorod along the rod axis (abscissa). At ~20 fs, two different features of plasmon modes appear alternately with a period of ~3 fs. (b) Model simulation of a position-time profile of excitation probability that corresponds to the near-field observation in panel (a), which qualitatively reproduced the characteristic feature observed at ~20 fs. (c) Simulated time evolution of the plasmon wave packet after local excitation with a single ultrashort pulse at a position x_0 in panel (b). Propagation of the wave packet from left to right (0–15 fs), reflection at the right end, and back propagation to left (20–40 fs) are observed.[2)]

2. Optical Activity Governed by Local Chiral Structures in Two-Dimensional Curved Metallic Nanostructures[3)]

Chiral nanostructures show macroscopic optical activity. Local optical activity and its handedness are not uniform in the nanostructure, and are spatially distributed depending on the shape of the nanostructure. In this study we fabricated curved chain nanostructures made of gold by connecting two or more arc structures in a two-dimensional plane. Spatial features of local optical activity in the chain structures were evaluated with near-field circular dichroism (CD) imaging. The electromagnetic simulation predicted that local optical activity appears at inflection points where arc structures are connected, and the handedness of the local optical activity was dependent on the handedness of the local chirality at the inflection point. In the near-field CD images of fabricated chain nanostructures, the local optical activity was found to be determined by the handedness of the inflection point, for the fabricated chain structures having two or more inflection points, consistent with the simulation. The local optical activity was thus governed primarily by the local chirality of the inflection points for the gold chain structures.

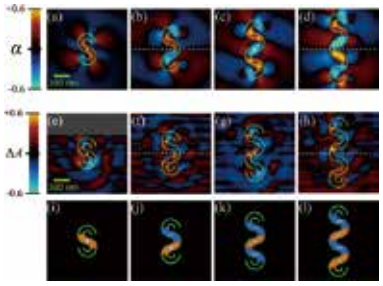

Figure 3. (a–d) Spatial distribution of theoretically calculated electric field intensity difference (α) for curved chain structures. (e–h) Spatial distribution of local CD signal (Δ*A*) observed with a near-field CD microscope for chain structures. (i–l) Schematic representations of the measured CD signal distribution in panels (e–h). The wavelength of observation was 785 nm for both the calculation and the imaging experiment. The inflection points gave local CD signals whose signs were determined by the handednesses (chirality) of the local structures, except for the minimal chain ("S" structure).[3)]

References

1) Y. Nishiyama, K. Imaeda, K. Imura and H. Okamoto, *J. Phys. Chem. C* **119**, 16215–16222 (2015).
2) Y. Nishiyama, K. Imura and H. Okamoto, *Nano Lett.* **15**, 7657–7665 (2015).
3) T. Narushima, S. Hashiyada and H. Okamoto, *Chirality* **28**, 540–544 (2016).

Awards

HASHIYADA, Shun; Excellent poster award 2015, Japan Society for Molecular Science.
NISHIYAMA, Yoshio; The OMC outstanding award, Optical Manipulation Conference 2016.

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