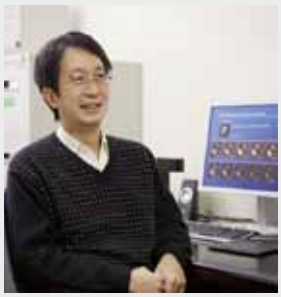
Development of Advanced Near-Field Spectroscopy/Imaging and Application to Nanomaterials

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



OKAMOTO, Hiromi
Professor

NARUSHIMA, Tetsuya
Assistant Professor

NISHIYAMA, Yoshio
IMS Research Assistant Professor

KOWAKA, Yasuyuki	Post-Doctoral Fellow	ISHIKAWA, Akiko	Technical Fellow
HASHIYADA, Shun	Graduate Student	NOMURA, Emiko	Secretary
WU, Huijun	Technical Fellow	YAMASAKI, Yumi	Secretary

There is much demand for the study 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.

1. Visualization of Localized Optical Fields and Plasmon Wavefunctions in Metal Nanostructures

We reported that wavefunctions of localized plasmon resonances of chemically synthesized metal (Au and Ag) nanoparticles are visualized by near-field transmission or two-photon excitation measurements.[1,2] The same methods were also applied to Au nanoparticle assemblies to visualize confined optical fields.[1,2]

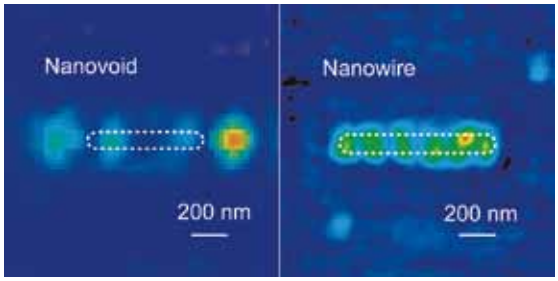


Figure 1. Near-field two-photon excitation images of an elongated rectangular nanoaperture on Au film (630 nm^l × 90 nm^w × 30 nm^t) observed at 810 nm (left) and a nanowire (860 nm^l × 100 nm^w × 30 nm^t) observed at 800 nm (right).

We have extended the studies to a variety of metal nanostructures including those manufactured by the electron-beam lithography technique, in part as collaboration with researchers of other institutions. For elongated rectangular apertures opened on thin Au film, we observed spatially oscillating features in the apertures that are arising from localized surface plasmon resonance of the nanostructures (Figure 1).[3] The elongated rectangular aperture corresponds to an inverted structure of a nanorod, and the oscillating structure observed may have a similar origin to that for nanorods.

For one-dimensional linear array of spherical Au nanoparticles, we revealed that enhanced fields (observed at ~800 nm) tend to localize near the ends of the arrays, when the number of particles exceeds 5 (Figure 2).[4] This observation is interpreted as a result of plasmon propagation among the particles and existence of localized modes near the boundaries

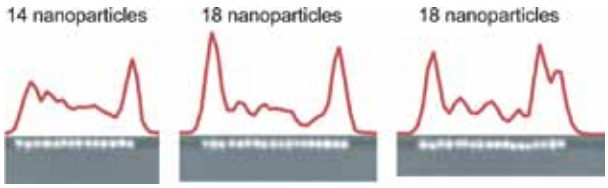


Figure 2. Plots of near-field two-photon excitation signals for the linear arrays of spherical Au nanoparticles (diameters ~100 nm) along the chain axis, observed at 785 nm. Images below the plot are corresponding scanning electron micrographs.

of the arrays.

We also tried to observe enhanced field characteristics for assemblies of particles with different shapes, specifically Ag nanowires joined with Ag nanospheres.[5] We have found that enhanced fields at the interstitial sites, polarized *perpendicular* to the long axis of the wire, are excited when the incident photons are polarized *along* the long axis of the wire. Such studies are essential as bases for designing unique optical properties and functions of metal nanostructures.

2. Near-Field Circular Dichroism Microscopy of Nanomaterials

Circular dichroism (CD) spectroscopy is widely used in the studies of chiral materials and magnetism. Some of nanomaterials composed of achiral molecules are reported to show CD activities arising from the nanoscale chirality. Two-dimensionally chiral metal nanostructures also show CD activities. Investigation of nanoscale local CD may provide valuable information on the origins of CD activities of such materials. For this purpose, we are developing an apparatus for near-field CD microscopy based on polarization modulation technique with a photoelastic modulator, and measuring CD images of nanoscale chiral materials.

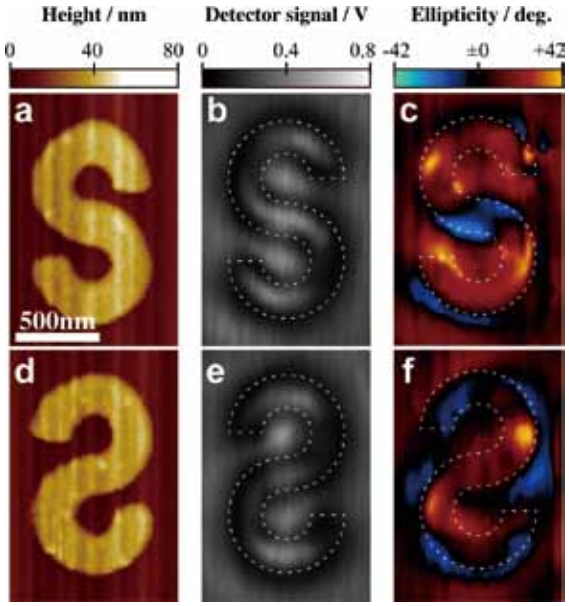


Figure 3. Topography (a, d), near-field transmission (b, e), and near-field CD (c, f) images of an S-shaped Au nanostructure (a, b, c) and its mirror-imaged structure (d, e, f) observed at 633 nm.

Here we report on a nanoscale CD imaging for a two-dimensional chiral pair of Au nanostructures to elucidate the relationship between nanoscale chirality and CD activity.[6] We adopted a two-dimensional "S"-shaped nanostructure (1200 nm × 700 nm, Au film thickness 40 nm) prepared with electron-beam lithography technique and its mirrored structure as the samples. The chiral pair exhibited very high local ellipticity at the center of the S-structure, and signals of both handedness coexisted in one nanostructure (Figure 3).

Based upon a model analysis for rotating dipole induced by the circular polarized light, we propose a mechanism of the strong CD signal at the center of the S-structure as mentioned in the following. If the rotational velocity of the induced polarization, in addition to the magnitude, changes reflecting the asymmetric structure of the sample, it produces perceivable difference between the optical response to the left-handed circular polarized light and that to the right-handed one, which yields a strong CD signal. This result indicates that it yields strong chiral field at the center of the structure, which may be potentially utilized for analysis of chiral molecules, chiral reaction fields, and so forth.

3. Construction of Apparatuses for Sub-20-fs Ultrafast Near-Field Spectroscopy

Surface plasmons of noble metal nanoparticles have very short lifetimes in the range of ~2-20 fs. To achieve a SNOM observation of such fast dynamics in the individual nanoparticles, we have to overcome serious dispersion effects arising from the optical components involved, especially from the optical fiber of the SNOM probe. We achieved that by combining the conventional dispersion compensation devices composed of prism and grating pairs with adaptive pulse shaping technique, and succeeded in delivering sub-20-fs pulses to the near-field aperture with a spatial resolution of ~100 nm.[1] At present we have obtained pulses of less than 15 fs FWHM at the near-field aperture. We are conducting position-dependence measurements for the dephasing time of localized plasmons for single gold nanorods.

References

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