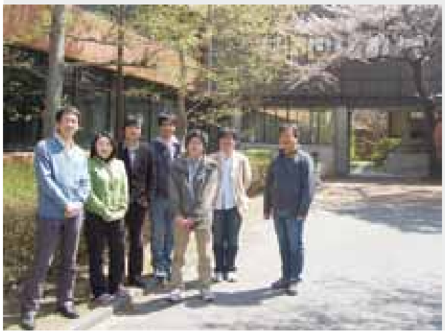
Development of Advanced Near-Field Spectroscopy and Application to Nanometric Systems

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



OKAMOTO, Hiromi	Professor
JEONG, Dae Hong	Visiting Associate Professor
NARUSHIMA, Tetsuya	Assistant Professor
NISHIYAMA, Yoshio	IMS Research Assistant Professor
HARADA, Yosuke	Post-Doctoral Fellow
LIM, Jong Kuk	Post-Doctoral Fellow
WU, Huijun	Graduate Student
OCHIAI, Takao	Graduate Student*
ISHIKAWA, Akiko	Technical Fellow
NOMURA, Emiko	Secretary

There is much demand for the study of local optical properties of molecular assemblies and materials, to understand mesoscopic phenomena and/or to construct optoelectronic devices in the nanometric scale. 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 offer a direct probe of dynamical processes in nanomaterials. It may provide essential and basic knowledge for analyzing origins of characteristic features and functionalities of the nanometric systems. We have constructed apparatuses of near-field spectroscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. They enable near-field measurements of two-photon induced emission and femtosecond transient transmission, in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatiotemporal behaviors of various metal-nanoparticle systems and molecular assemblies.

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

We recently 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] The same methods were also applied to Au nanoparticle assemblies to visualize confined optical fields.[1] It was revealed for the dimers that highly localized optical field is generated at the interstitial sites between the particles. In many-particle assemblies, the localized fields were especially intensified at the rim parts of the assemblies, and such a characteristic field distribution has been attributed to interaction between plasmon excitations induced on the particles.[2]

We have extended the studies to metal nanostructures

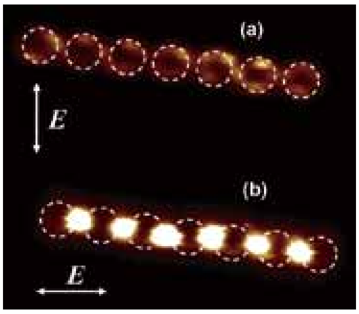


Figure 1. Near-field two-photon excitation images of a nanovoid chain opened on a Au film (thickness ~20 nm).[3] The diameter of the void was ~400 nm. The incident polarization was nearly perpendicular (a) and parallel (b) to the chain. Excitation: 785 nm.

manufactured by the electron-beam lithography technique, in collaboration with researchers of other institution, or other top-down fabrication techniques, with which structures that are difficult to obtain with the chemical methods can be available. As an example, near-field properties of nano-void structures, opened on thin gold metallic films on glass substrates, were characterized, and the field distributions in the vicinities of the voids were visualized.[3] In circular void chain structures, we found that confined optical fields were generated in the interstitial sites between voids under some circumstances (Figure 1). The field distributions were analyzed based on the electromagnetic theories and calculations. The observed and calculated field distribution was discussed in relation to Babinet's principle in optics, which gives general relation between electromagnetic field distributions for complementary nanostructures made of thin conductors, such as a nanoparticle assembly and a nano-void assembly.

Such a study is essential as a basis for designing unique optical properties and functions of metal nanostructures, and their applications to highly sensitive spectroscopic methods and exotic photochemical fields, as well as to nanoscale optical waveguids.

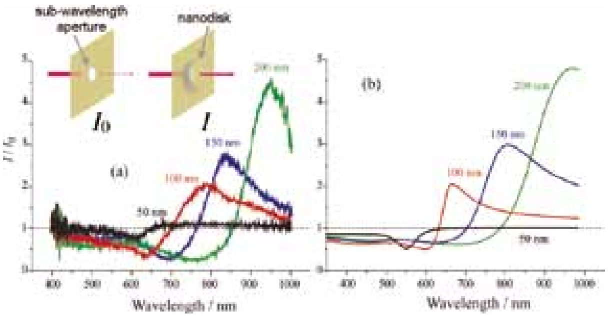


Figure 2. Transmittance spectra of capped nanoapertures, (a) experimental and (b) model calculation. The inset shows the schematic models of an uncapped and a capped nanoapertures.

Figure 3. Two gold nanoparticles trapped by ultrashort pulses. Two particles are trapped separately and aligned along the incident laser polarization (arrows).

2. Anomalous Light Transmission through Capped Nanoapertures

In the course of near-field studies on metal nanodisks fabricated on glass substrates by electron-beam lithography, we examined light intensity transmitted through a nanometer-scale aperture opened on an opaque metallic screen. When the aperture is obscured by an opaque metallic disk (cap) with a larger diameter than the aperture, the transmitted light was found to be, paradoxically, even stronger than that without the disk.[4)]

We investigated spectroscopic characteristics of light transmission through a nanoaperture on a gold film with a diameter of ~100 nm (Figure 2, inset, left; apertured near-field probe, in practice) and that capped with gold nanodisks (diameter 50–200 nm) at a distance of ~30 nm from the aperture (Figure 2, inset, right). The transmittance through the capped aperture is defined as the ratio between intensities for the capped aperture (I) and for the aperture without the disk (I_0) and is plotted in Figure 2(a). In the long wavelength region, the transmittance through the capped aperture exceeds 1, and surprisingly, the maximum transmittance becomes even higher for larger disks. We analyzed the spectra based upon a theoretical model, and it turned out that the phenomenon arise from the property of localized plasmon resonances: The anomalous transmission is due to highly efficient performance of the nanodisks for conversion between near-field and far-field radiations.

3. Nonlinear Effects in Optical Trapping

The optical trapping technique has been widely used in various areas to manipulate particles, cells, and so forth. The principle of trapping is based on the interaction between optical electric fields and induced linear polarizations. In the course of the studies on behavior of gold nanoparticles under pulsed laser fields, we have found a novel phenomenon of optical trapping of spherical gold nanoparticles arising from nonlinear polarization when we trap the nanoparticles by ultrashort near-infrared laser pulses.[5)] That is, the stable trap site (usually appears in the center of the focused beam) is split into two equivalent positions, and the split trap positions are aligned along the direction of the incident laser polarization. The split distance depends on the trapping-laser power and wavelength. We have found that the results were successfully interpreted in terms of the nonlinear polarization caused by the femtosecond pulses. This is the first report that treats the nonlinear effects in optical trapping.

4. Construction of Apparatuses for Nonlinear and Ultrafast Near-Field Spectroscopy

In previous studies we achieved ultrafast near-field imaging with a time resolution of ~100 fs.[1)] To further extend the dynamical studies of plasmons, we are now developing an apparatus that achieves near-field time-resolved measurements with < 20 fs time resolution. We have also constructed an apparatus for near-field/far-field microscopic nonlinear optical measurements based on the technique of atomic-force microscope.

5. Near-Field Imaging of Organic Molecular Assemblies and Hybrid Systems

We are studying nanometric structures and optical properties of organic molecular assemblies such as LB films of functional conjugated molecules, and hybrid systems consist of metal nanoparticles and organic functional materials, mainly as collaborations with other research groups.

References

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* carrying out graduate research on Cooperative Education Program of IMS with University of Tsukuba.