RESEARCH ACTIVITIES II
Department of Molecular Structure

II-A Development of Dynamic Near-Field Spectroscopy and Application to Nanometric Systems

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), which enables spatial resolution beyond the diffraction limit of light, showed remarkable progress in technology in the past decade. Combination of this advanced optical technology with ultrafast/nonlinear spectroscopic methods may offer a direct probe of molecular dynamical processes in mesoscopic systems. It may bring essential and basic knowledge for analyzing origins of characteristic features and functionalities of mesoscopic systems. We have constructed apparatuses for near-field dynamic spectroscopy with the femtosecond temporal resolution and the nanometer spatial resolution. Using the apparatuses developed, we are observing the characteristic spatiotemporal behavior of various organic molecular systems and metal nanoparticles, for the purpose of understanding spatial coherence and dissipation of excitations, and their dynamics. We also investigate experimentally the basic characteristics of near-field microscopic measurements. Outlines of the experimental results obtained are summarized here.

II-A-1 Photoluminescence from Gold Nanoplates Induced by Near-Field Two-Photon Absorption

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

[*Appl. Phys. Lett.* **88**, 023104 (2006)]

We have investigated two-photon-induced photoluminescence (TPI-PL) properties of single gold nanoplates by using an apertured scanning near-field optical microscope. We found the remarkably large cross sections of TPI-PL from the gold nanoplates. It is one or two orders of magnitudes larger than those observed from the gold nanorods. The near-field PL images show characteristic spatial features. These PL images are in good agreement with the calculated spatial distribution of the electric fields adjacent to the particles at the excitation wavelength. We attribute the observed images to spatial characteristics of plasmon-mode wavefunctions. The TPI-PL images of the gold triangles are strongly dependent on the incident polarization and wavelength. We also found that the plasmon-mode excitation is the primary factor for enhancing the TPI-PL process. The result suggests that it would be possible to further improve the efficiency of TPI-PL by synthesizing the nanoparticles of controlled size and shape.

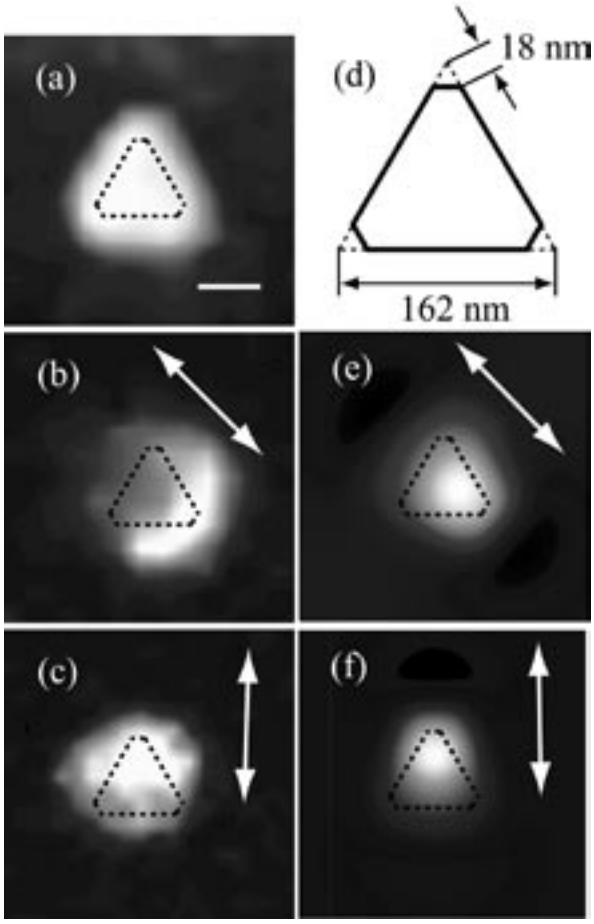

Figure 1. (a) Topography of a single gold triangle. (b), (c) Observed incident-polarization dependent TPI-PL images of the single gold triangle. (d) Schematic drawing of a snipped triangle used for calculations (e), (f). (e), (f) Calculated polarization-dependent electric field distributions near the snipped triangle. Arrows indicate the direction of the incident polarization. Dashed lines indicate approximate shape of the triangle. Scale bar: 100 nm.

II-A-2 Near-Field Imaging of SERS-Active Hot Spots on Metal-Nanoparticle Aggregates

IMURA, Kohei; OKAMOTO, Hiromi; HOSSAIN, Mohammad K.[1]; KITAJIMA, Masahiro[2]
([1]Univ. Tsukuba and NIMS; [2]NIMS, Univ. Tsukuba and IMS)

[*Chem. Lett.* **35**, 78–79 (2006)]

It is of fundamental importance to reveal the origin of the huge Raman enhancement in single-molecular level surface-enhanced Raman scattering. The major factor of the enhancement is considered to be an electromagnetic mechanism, *i.e.*, electric field enhancement induced by a plasmon resonance. For aggregated nanoparticles, strong electric field is expected in interstitial gaps between the nanoparticles ("hot spot"). Up to now, however, Raman enhancement on the hot spot site has not been directly shown by experiment. In this study, we succeeded in imaging of spatial distributions of electric-field enhancement and Raman-excitation probability for aggregates of gold nanospheres, using a scanning near-field optical microscope. To observe electric field enhancement, we used two-photon excitation probability imaging.[1)] The Raman excitation images were obtained by monitoring Raman band intensities while exciting the samples by cw lasers through the near-field fiber probe.

Figure 1 shows topographic, near-field two-photon excitation probability, and near-field Raman excitation probability (for dilutely doped dye molecule R6G) images, for aggregated gold nanospheres (diameter 100 nm). The two-photon image reflects spatial distribution of plasmon-induced electric field enhancement. The image shows that the aggregates, especially the gaps in the dimers, show strong electric field enhancements. Strong enhancements for the dimeric aggregates are also found in the Raman image. In contrast, the enhancements are not prominent in isolated particles. The present result gives a clear experimental proof to the theoretical prediction of hot spots.

Reference

1) K. Imura, T. Nagahara and H. Okamoto, *J. Phys. Chem. B* **109**, 13214 (2005).

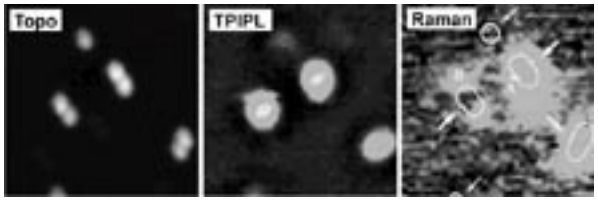

Figure 1. Topograph (left), near-field two-photon excitation (center), and near-field Raman excitation (right) images of gold nanospheres doped with R6G molecules. The Raman image was obtained for the R6G band at 1340 cm^{-1}. Image size: 1.5 μm × 1.5 μm.

II-A-3 Reciprocity in Scanning Near-Field Optical Microscopy: Illumination and Collection Modes of Transmission Measurements

IMURA, Kohei; OKAMOTO, Hiromi

[*Opt. Lett.* **31**, 1474–1476 (2006)]

There are two operational modes of near-field transmission experimental setup, *i.e.*, illumination (I) and collection (C) modes. In I-mode the object is illuminated through the near-field aperture probe, and the transmitted light is detected in the far field. In C-mode the object is illuminated by the far-field radiation, and the transmitted light is collected by the near-field probe. The configurations of I- and C-modes are optically reciprocal to each other. However, in the near-field experiment the reciprocity is not apparent or trivial.

We experimentally investigated the reciprocity of near-field measurements between I- and C-modes. Near-field transmission images of single gold spheres and nanorods observed by the two modes are found to be equivalent to each other in the region from visible to near infrared. This result shows that reciprocity holds for the near-field scattering problems. We found that the conventional optical selection rule for far-field excitations does not apply not only under I-mode but also with C-mode arrangements. The possible origin of this observation might be the near-field probe. The existence of the near-field probe tip close to the nanorod may perturb the electric field distribution near the gold nanorods. The local electric field generated in the presence of the near-field probe would allow SP-mode excitation at the tip position.

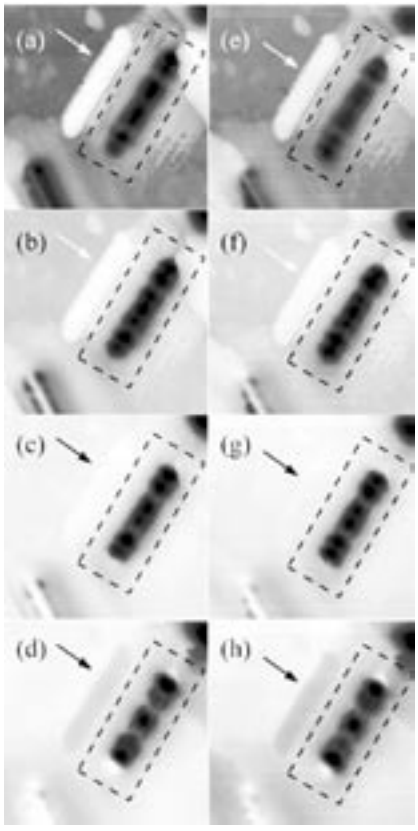

Figure 1. Transmission near-field optical images of a single gold nanorod (diameter 22±3 nm, length 510±30 nm): (a-d) I-mode, (e-h) C-mode. The scan area is 1 μm × 1 μm. Observed spectral region: (a,e) 607–627 nm, (b,f) 647–666 nm, (c,g) 666–686 nm, (d,h) 705–725 nm. Arrows indicate *z*-motion artifacts.

II-A-4 Near-Field Raman Study on the Close-Packed 2D Nanostructures of Gold Nanoparticles

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([1]NIMS and Univ. Tsukuba; [2]NIMS; [3]NIMS, Univ. Tsukuba and IMS)

Metallic nanostructure, particularly gold nanostructure is an indispensable candidate for future nanoscale science and technology for its unique properties. We have studied electromagnetic field enhancement with surface-enhanced Raman scattering (SERS) and near-field spectroscopy for well-ordered two-dimensional (2D) nanostructures of gold nanoparticles. 2D nanostructures of gold nanoparticles (diameter 100 nm) were fabricated from gold colloids without using capping reagent or surfactant on glass substrate. The individual gold nanoparticles of the 2D structure were not in contact. The over all 2D structure area ranged from several 100 μm^2 to mm^2. Crystal violet (CV) or rhodamine 6G (R6G) molecules were dispersed on this 2D structure by spin-coating method.

The microscopic SERS spectrum of the adsorbed molecules on this Au 2D surface were measured. Several distinguishing peaks confirmed that such substrate was indeed SERS-active. The enhancement was highest at the edge of the 2D nanostructure.[1)] To exploit the spatial distributions of electromagnetic enhancement, scanning near-field optical measurement was performed for this 2D nanostructure. The Raman signal was enhanced at the 2D nanostructure of gold nanoparticles, especially along the edge of the 2D structure.

Reference

1) M. K. Hossain, K. Shibamoto, K. Ishioka, M. Kitajima, T. Mitani and S. Nakashima, *J. Lumin.* **122-123**, 792 (2006).

II-A-5 Enhancement and Quenching of Fluorescence from Dye Molecules by Single Gold Nanoparticles

HORIMOTO, Noriko N.; IMURA, Kohei; OKAMOTO, Hiromi

We investigated the enhancement and quenching of fluorescence from dye molecules by single gold nanoparticles, and their dependence on particle shape and size, using an aperture-type scanning near-field optical microscope. Gold nanoplates (thickness ~ 20 nm) showed large enhancements, and gold nanospheres (diameter ~ 30–100 nm) showed a moderate enhancement. On the other hand, gold nanorods (diameter ~ 20–40 nm, length ~ 100–500 nm) showed quenching. The enhancement and quenching mechanism is discussed based on electromagnetic effects.

II-A-6 Near-Field Two-Photon-Induced Photoluminescence from Single Gold Nanorods

IMURA, Kohei; OKAMOTO, Hiromi

We investigated photoluminescence (PL) properties of single gold nanorods (diameter 20–32 nm, length 190–630 nm) by using a near-field two-photon microscope. A PL spectrum of a single gold nanorod shows two peak wavelengths. The peaks are always observed near 550 nm and 650 nm, regardless the rod dimensions and plasmon modes excited. The intensity ratio (I_{650nm}/I_{550nm}) of the two spectral components varies with the rod dimension, and becomes nearly zero in the spherical particle limit. The results indicate that the PL appeared in the longer wavelength (~650 nm) gains the intensity in resonance with the longitudinal plasmon mode. The spectral features as well as polarization characters of the PL indicate that the emission process is dominantly occurred though a radiative recombination of an electron-hole pair generated by the two-photon excitation.

II-A-7 Ultrafast Near-Field Transient Imaging of Single Gold Nanorods

IMURA, Kohei; OKAMOTO, Hiromi

We investigated ultrafast transient behaviors in single nanorods (diameter 30 nm, length 300–330 nm) after an optical excitation with a 50-nm spatial resolution and a 100-fs time resolution. We used a near-infrared pulse to excite longitudinal plasmon resonances of the nanorod. Spatial patterns of transient images of the single nanorods observed at 1 ps delay time were similar to those of plasmon wavefunctions found in the steady-state transmission measurements (Figure 1).[1)] However, depending on the rod dimension, the image shows either induced absorptions or absorption bleaches at end edges of the nanorod.

To get a deeper understanding for the observed features of the transient transmission images, we simulated position-dependent transient transmission change by assuming that the photoexcitation induces a homogeneous electronic temperature rise in the nanorod. In the simulation, the transient transmission change at a position was considered to be proportional to the change of the electromagnetic local density-of-states (LDOS) due to the elevation of electronic temperature. The change of LDOS was evaluated by taking the temperature dependency of the dielectric constants of the gold into account. Simulated transient images qualitatively reproduced the observations. The observed transient images were thus assignable to the change of the LDOS due to the electronic temperature rise.

Reference

1) K. Imura, T. Nagahara and H. Okamoto, *J. Phys. Chem. B* **108**, 16344 (2004).

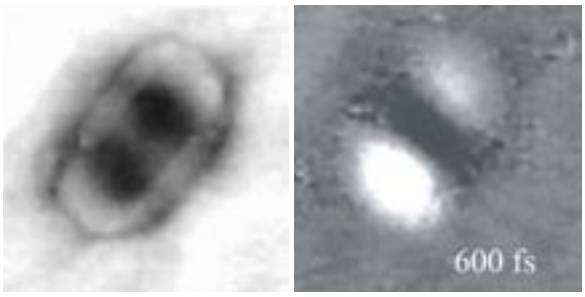

Figure 1. Typical near-field static transmission (left) and transient transmission change (right) images of gold nanorod (diameter 30 nm, length 300 nm). In the right panel, bleached and induced extinctions are indicated, respectively, in black and white.

II-A-8 Scanning Near-Field Optical Microscopic Study of Porphyrin Nanowire

NAGAHARA, Tetsuhiko; IMURA, Kohei; OKAMOTO, Hiromi; OZAWA, Hiroaki; OGAWA, Takuji

We studied optical properties of molecular nanowires of coupled zinc porphyrins with bulky dendric groups, by means of scanning near-field optical microscopy and spectroscopy. The topographic images and the near-field-excited fluorescence images gave string-like structures, and correlated well to each other. We also performed polarization dependence measurements. From the result of the analysis, it has been suggested that the photoexcitation is spatially propagated along the chain for appreciably long distance.