

## RESEARCH ACTIVITIES II

### Department of Molecular Structure

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

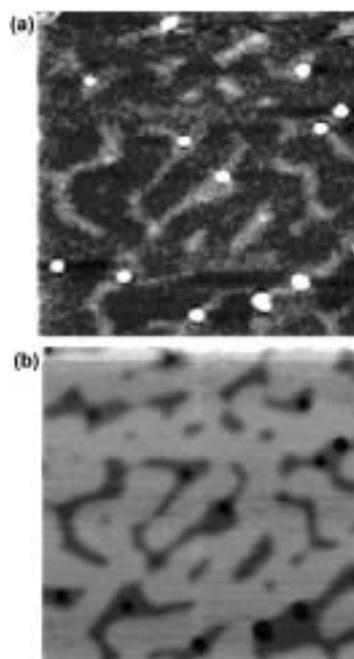
There is much demand for the study of local optical properties of molecular assemblies and materials, to understand mesoscopic phenomena and/or to construct optoelectronic devices in the nanometric scale. Scanning near-field optical microscopy (SNOM), which enables spatial resolution beyond the diffraction limit of light, shows remarkable progress in technology in these days. Combination of this advanced optical technology with ultrafast 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 are constructing apparatuses for near-field dynamic spectroscopy with the femtosecond temporal resolution and the nanometer spatial resolution. Using the apparatuses developed, we have observed 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. Outlines of the experimental results obtained are summarized here.

##### II-A-1 Morphological and Spectroscopic Properties of Thin Films of Self-Assembling Amphiphilic Porphyrins on Hydrophilic Surface as Revealed by Scanning Near-Field Optical Microscopy

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[*J. Phys. Chem. B* **109**, 19839–19844 (2005)]

We fabricated porphyrin thin films on mica surfaces from acidic aqueous solutions of the pre-organized H-aggregates of amphiphilic porphyrins (5,10,15,20-tetrakis(4-(4-(trimethylammonio)butoxy)phenyl)porphyrin bromide, TABPP, and the related compounds) by simple spin-coating method. The morphological and spectroscopic properties of the film formed on mica substrate were investigated by atomic force microscopy and scanning near-field optical microscopy. The surface topographic image and the near-field transmission image taken at the wavelength of the H-aggregate band (Figures 1a and b) are negatively correlated very well each other. That is, the optical transmission at the position of higher topographic height (the bright part in the topographic image) is lower than that at the lower-height position. This indicates that the film of ~3 nm height consists mainly of the H-aggregate. The results obtained demonstrate that the pre-organized H-aggregate structure in solution can be transferred as a thin film with a thickness of monolayer level without losing their substantial structure and photophysical properties.



**Figure 1.** (a) Surface topography of the thin-film sample of TABPP on mica (scan area:  $10\ \mu\text{m} \times 10\ \mu\text{m} \times 3\ \text{nm}$ ). Bright and dark parts correspond to high and low parts of the sample surface, respectively. (b) Transmission image of the sample obtained at 430 nm. Bright and dark parts correspond to high and low transmission intensities, respectively.

##### II-A-2 Scanning Near-Field Optical Microscopic Study of Porphyrin Nanowire

NAGAHARA, Tetsuhiko; IMURA, Kohei;  
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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. The analysis of the obtained data is now in progress.

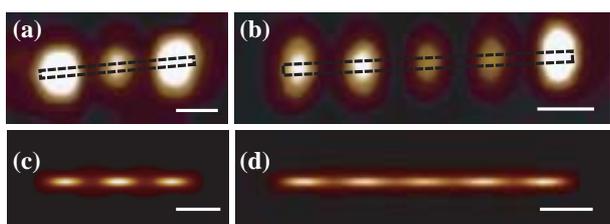
### II-A-3 Imaging of Plasmon Modes in Gold Nanorods

IMURA, Kohei; NAGAHARA, Tetsuhiko;  
OKAMOTO, Hiromi

[*J. Phys. Chem. B* **109**, 13214–13220 (2005)]

Surface plasmon resonances (SPRs) of noble metals have attracted much interest, since the SPR gives not only fundamental importance in science but also various applications in nanotechnology. Knowledge of the spatial characteristics of the surface plasmons, as well as the spectral and polarization characteristics, is essential for the control of electric field confinement in near-field and of plasmon properties. We investigate the spatial characteristics of plasmon-mode wavefunctions by a SNOM.

Gold nanorods were prepared in solutions using the seed-mediated methods. For SNOM measurements, gold nanorods were dispersed on cover-slips by spin-coating method. Figures 1(a,b) show two typical near-field two-photon induced photoluminescence (TPI-PL) images observed for single gold nanorods. The dotted squares indicate approximate shapes of the rods estimated from the topographic measurements. As can be seen in the figures, the PL intensities show characteristic spatial oscillations along the long axis. Figures 1(c,d) show calculated electromagnetic local density of states (LDOS) images for the corresponding nanorods. The good agreements between the observations and the calculated LDOS images indicate that oscillatory structures found in Figures 1(a,b) represent spatial characteristics of the plasmon modes of the nanorods at the excitation wavelength.



**Figure 1.** (a,b) TPI-PL images for single gold nanorods: (a)  $20 \pm 5$  nm  $\times$   $330 \pm 30$  nm, (b)  $20 \pm 5$  nm  $\times$   $540 \pm 40$  nm. (c,d) Calculated LDOS maps for the corresponding gold nanorods (a,b), respectively. Scale bars are 100 nm.

### II-A-4 Near-Field Two-Photon Induced Photoluminescence from Single Gold Nanorods

IMURA, Kohei; NAGAHARA, Tetsuhiko;  
OKAMOTO, Hiromi

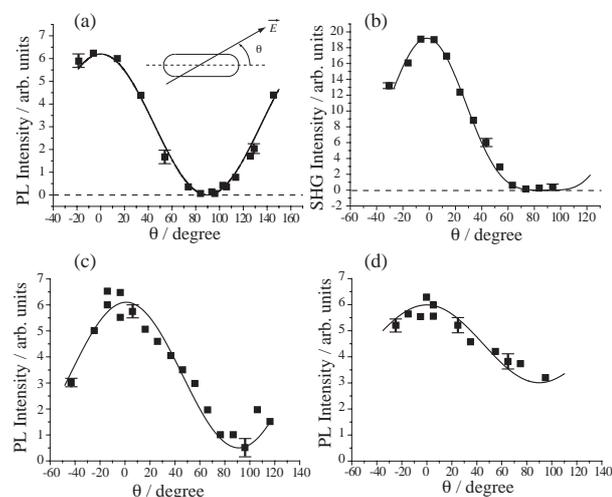
[*J. Phys. Chem. B* **109**, 13214–13220 (2005)]

Studies of photoluminescence (PL) from the metal nanoparticles were limited because of very low quantum efficiencies. A strong enhancement of PL from gold nanorods upon single photon excitation was reported.<sup>1)</sup> The enhancement was ascribed to the local field enhancement due to the SPR of the gold nanorods. Two-photon optical processes involve an additional field enhancement, and thus a greater enhancement of PL efficiency is expected. We investigate two-photon induced PL (TPI-PL) from single gold nanorods of variety of lengths and diameters using an apertured SNOM, in order to characterize the emission mechanism and the optical features of the TPI-PL process.

Dependencies of the PL intensity on the polarizations of both the excitation (incoming) and the emitted (outgoing) photons are shown in Figure 1. The dependence of the PL intensity on the incident electric-field polarization [Figure 1(a)] indicates that TPI-PL is excited by the sequential one-photon process. Figures 1(c) and 1(d) show polarization characteristics of the emitted photons from the X (645–655 nm) and L (450–550 nm) regions, respectively. The emission from the X region shows an almost perfect polarization along the long axis while that from the L region is only partially polarized. The polarization characteristics obtained can be reasonably understood on the basis of the crystalline structure and the band structure of the gold nanorods.

### Reference

1) M. B. Mohamed, V. Volkov, S. Link and M. A. El-Sayed, *Chem. Phys. Lett.* **317**, 517 (2000).



**Figure 1.** (a) Incident polarization dependence of the PL intensity. (b) Incident polarization dependence of the SHG intensity from the same nanorod. (c,d) Polarization characteristics of the detected photons in (c) the X region (645–655 nm) and (d) the L region (450–550 nm), respectively.

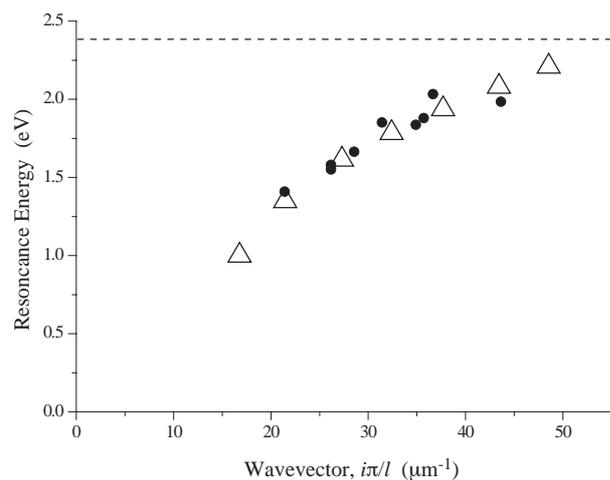
### II-A-5 Dispersion Relation of Plasmon Modes in the Gold Nanorods

IMURA, Kohei; NAGAHARA, Tetsuhiko;  
OKAMOTO, Hiromi

[*J. Chem. Phys.* **122**, 154701 (2005)]

Surface plasmon (SP) resonances of noble metal particles have recently attracted much interest, especially for their ability in local confinement of optical near-field. Imaging of electromagnetic local density of states (LDOS) inside single noble particles leads to direct optical observation of the SP modes. We study the optical-frequency dependent spatial characteristics of the LDOS inside the gold nanorods by the transmission-mode SNOM to obtain a dispersion relation of the SP modes.

By plotting the resonance frequencies of SP modes versus the wave vectors (which are directly obtained from the SP-mode images), the dispersion relation of the gold nanorod is obtained. The dispersion relation based on the DOS calculations for the rods is given in Figure 1 (triangles). The calculated points roughly follow a single dispersion curve, which is converging to the resonance frequency of the transverse SP mode at high wavenumber limit. We have also found that the near-field observations for various length nanorods with approximately the same diameter (closed circles) follow this curve. The results indicate that the resonance energies of multipolar SP modes in various rods of a given diameter can be estimated from the dispersion curve, even if the rod lengths are different.



**Figure 1.** SP dispersion relation for gold nanorods. Closed circles: Observations. Open triangles: Calculations. Dashed horizontal line indicates the transverse SP resonance energy.

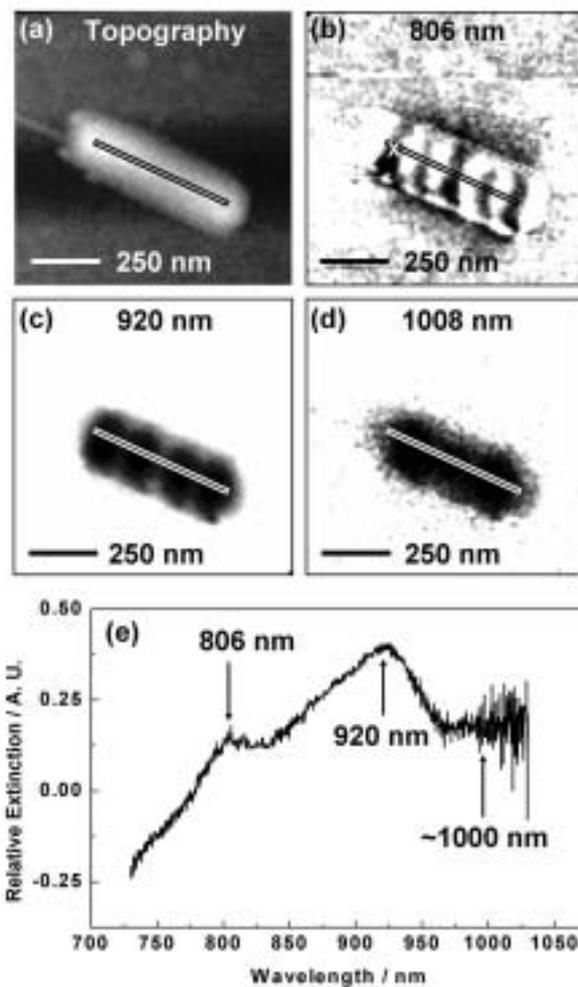
#### II-A-6 Imaging and Dispersion Relations of Surface Plasmon Modes in Silver Nanorods by Near-Field Spectroscopy

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[*Chem. Phys. Lett.* **412**, 41–45 (2005)]

Surface plasmons of silver nanorods were investigated by using scanning near-field optical microscopy. The silver nanorods were synthesized in water solution by reducing  $\text{AgNO}_3$  under existence of surfactant molecules. Near-field transmission images showed spatially oscillatory patterns in the silver nanorods. The oscillatory features of images are attributable to plasmon-

mode wavefunctions. As is similar to the gold nanorod cases, the spatial oscillation period depends on the wavelength of the observing light. From the near-field images and spectra, the wave vectors and the resonant frequencies of the plasmon modes observed were directly estimated. In this way the dispersion relations of the plasmon modes for various silver nanorods were obtained. It was found that dispersion relation of a nanorod is dependent on its diameter. The spectral features obtained are compared with those for gold nanorods.



**Figure 1.** Representative images of nanorods and their near-field spectrum. (a) Topography of silver nanorod, *ca.* 20 nm in diameter and *ca.* 530 nm in length. (b)–(d) Near-field transmission images probed with an unpolarized light at 806, 920, and 1008 nm, respectively. (e) Near-field spectrum taken at the position marked “X” in the near-field transmission (b).

#### II-A-7 Ultrafast Near-Field Imaging of Single Gold Nanorods and Nanoplates

IMURA, Kohei; OKAMOTO, Hiromi

It is of fundamental importance to know how the electron-electron and electron-phonon scattering processes after photoexcitation depend upon size and shape of nanoparticles and how they proceed inside the particle. Dynamic spectroscopy of a single particle with

high temporal and spatial resolution must be informative for this purpose. Previously we performed ultrafast near-field pump-probe imaging of relatively short gold nanorods, and revealed the position dependent electron-phonon relaxation. In the present study, we have extended the study to longer nanorods and nanoparticles of other shapes, and investigated the dynamic behavior after photoexcitation in a space- and time-resolved manner.

A Ti:sapphire laser ( $\lambda = 780$  nm,  $< 100$  fs, 80 MHz) was used for time-resolved pump-probe measurements. From the near-field pump-probe measurements of various single gold nanorods and nanoplates, we found that the energy dissipation processes are dependent upon its size and shape, as well as upon the internal position of the nanoparticle.

### **II-A-8 Near-Field Spectroscopy of Close-Packed Self-Assembled Monolayer Films of Gold Nanoparticles**

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Two-dimensional (2D) nanostructured materials of noble metal nanoparticles, in particular gold nanoparticles, have attracted much attention because of their unique optical properties. To characterize its optical properties as well as its potentiality in industry, we are studying the transmission, two-photon induced photoluminescence (TPI-PL), and surface enhanced Raman scattering (SERS) from the 2D structure by near-field spectroscopy and microscopy.

The 2D nanostructure of gold nanoparticles was fabricated by simply controlling the surface tension and the coverage area. The surface morphology of the fabricated 2D structure was examined by an atomic force microscope and a scanning electron microscope, and found to be a well-ordered close-packed monolayer, whose area is as large as several hundreds  $\mu\text{m}^2$  to  $\text{mm}^2$ .

In the near-field transmission spectra, it is found that the 2D structure exhibits several longitudinal surface plasmon resonances resulted from the localized plasmon coupling. In these regions, near-field TPI-PL and SERS intensities from the 2D structure are stronger than those from the isolated particles. These observations can be ascribed to the higher electric field enhancements in the ordered structure.