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
IMURA, Kohei	Assistant Professor
NARUSHIMA, Tetsuya	Assistant Professor
JIANG, Yuqiang	Post-Doctoral Fellow
HARADA, Yosuke	Post-Doctoral Fellow
WU, Huijun	Graduate Student
KIM, Su Il	Graduate Student*
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), which enables spatial resolution beyond the diffraction limit of light, has been remarkably progressed in technology in the past decade. Combination of this advanced optical technology with various nonlinear and ultrafast laser spectroscopic methods may offer a direct probe of molecular dynamical processes in mesoscopic materials systems. It may provide essential and basic knowledge for analyzing origins of characteristic features and functionalities of the mesoscopic systems. We have constructed apparatuses for near-field dynamic spectroscopy with the femtosecond time resolution and the nanometer spatial resolution. They are capable of measuring conventional near-field transmission, emission, and Raman-scattering, and unique near-field two-photon induced emission and ultrafast transient transmission as well. Based on these methods, we are observing the characteristic spatio-temporal behavior of various metal nanoparticle systems and molecular assemblies, for the purpose of understanding nano-optical characteristics, spatial coherence of excitations, dynamics, *etc*. We also investigate the basic characteristics of near-field microscopic measurements.

1. Visualization of Plasmon Wavefunctions Induced in Various Metal Nanoparticles

We recently reported that wavefunctions of localized plasmon resonances of metal nanoparticles can be visualized by near-field transmission or two-photon excitation measurements.[1)] The plasmons we visualized include the longitudinal modes of chemically synthesized gold and silver nanorods and in-plane modes of chemically synthesized gold triangular nanoplates. Figure 1 shows typical examples of near-field transmission images for longitudinal plasmon modes on a nanorod (the images correspond to the square moduli of the wavefunctions). We reported that the images show excellent agreement with calculated images of local density of electromagnetic states (LDOS) which correspond to the square moduli of the resonant plasmon wavefunctions.

We are extending the study to the metal nanostructures manufactured by the electron-beam lithography technique, in collaboration with researchers of other institution. We have obtained preliminary results for some metal nanostructures and have found characteristic plasmon waves. Such a study is essential as a basis to design unique optical properties and functions of metal nanostructures.

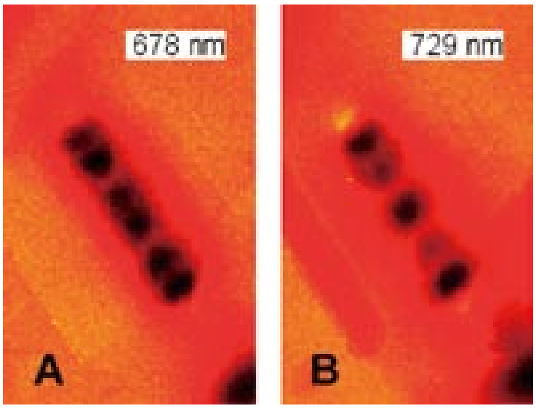

Figure 1. Near-field transmission images of a gold nanorod (diameter 20 nm, length 510 nm), observed at 678 nm (A) and 729 nm (B).

2. Ultrafast Transient Images of Gold Nanoparticles

We previously reported ultrafast near-field transient transmission (space/time resolution was *ca.* 50 nm/100 fs) of single gold nanorods to reveal dynamic behavior of the material.[2] We used a near-infrared pulse to excite longitudinal plasmon resonance of the rod and detect transient transmission change after that. Figure 2A shows the transient image of a nanorod at *ca.* 600 fs. Although the rod consists of uniform crystalline gold, the signal is strongly dependent on the position: bleached absorption is observed in the central part, while induced absorption is found in both ends.

To understand the observed features, we simulated in the present study position-dependent transient transmission change based on electromagnetic LDOS calculation.[3] Figure 2B shows a simulated image. The image reproduces well the observed features of the transient image in Figure 2A. From this analysis, it has been revealed that the LDOS change arises from variation in plasmon mode wavefunctions due to the photoinduced transient electronic temperature elevation in the nanorod. The present result suggests a potential for transient optical control of plasmon modes by photoexcitation of metal nanostructures.

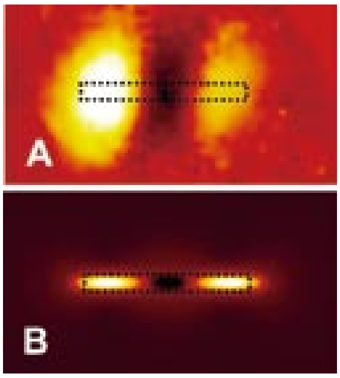

Figure 2. (A) Transient transmission image of a single gold nanorod (diameter 30 nm, length 300 nm) observed at a delay time of 600 fs. A dotted square indicates an approximate shape of the nanorod estimated from the topography measurement. Bright and dark parts indicate regions giving induced absorption and bleached absorption, respectively. (B) Simulated transient transmission (LDOS) change image for the nanorod. Bright and dark parts indicate regions giving enhanced and reduced LDOS, respectively.

3. Near-Field Imaging of Locally Enhanced Optical Fields in Metal Nanoparticle Assemblies

It is of fundamental importance to reveal spatial distribution of localized optical field in metal nanostructures. In aggregated noble metal nanoparticles, for example, strong electric field is expected in the interstitial gaps between the nanoparticles, according to the electromagnetic calculations. Such an enhanced optical field is considered as the major origin of the huge Raman enhancement in single-molecule level surface-enhanced Raman scattering (SERS). Recently,

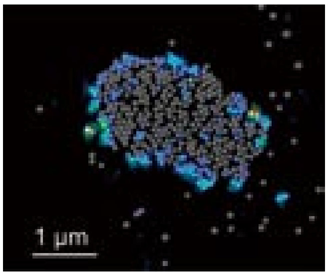

Figure 3. Two-photon excitation SNOM image of monolayer assembly of gold nanoparticles. The image is superimposed on the SEM image (displayed in black-white).

we visualized highly localized optical fields at interstitial sites in gold-nanoparticle dimers, by two-photon excitation imaging using SNOM.[4] For larger nanostructures, however, the correlation between the geometrical structure and the optical field distribution has been less understood.

In this study, we analyzed the correlation between the near-field optical properties and the particle configuration in monolayer assemblies of gold nanoparticles by a combination of SNOM and SEM images (Figure 3).[5] Two-photon excitation SNOM measurements show enhanced optical fields distributed over the whole area of assembly, and especially intensified at the rim of the assembly. The difference between the inner part and the rim may be related to delocalization of surface plasmon excitation in two-dimensional nanostructures. The non-uniform nature of the enhanced electric field in the assembly found here gives a new guideline for designing highly sensitive SERS substrate.

4. Near-Field Imaging of Organic Molecular Assemblies

We are studying mesoscopic structures and optical properties of organic molecular assemblies such as porphyrin wires, carbon nanotubes embedded in sugar molecule chains, Lagmuir-Blodgett films of functional conjugated molecules, mainly as collaborations with other research groups.

References

1) H. Okamoto and K. Imura, *Jpn. J. Appl. Phys.* **47**, 6055–6062 (2008).
2) K. Imura, T. Nagahara and H. Okamoto, *J. Phys. Chem. B* **108**, 16344–16347 (2004).
3) K. Imura and H. Okamoto, *Phys. Rev. B* **77**, 041401(R) (4 pages) (2008).
4) K. Imura, H. Okamoto, M. K. Hossain and M. Kitajima, *Nano Lett.* **6**, 2173–2176 (2006).
5) T. Shimada, K. Imura, M. K. Hossain, H. Okamoto and M. Kitajima, *J. Phys. Chem. C* **112**, 4033–4035 (2008).

* from KAIST, Korea