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
HORIMOTO, Noriko	IMS Fellow*
JIANG, Yuqiang	Post-Doctoral Fellow
WU, Huijun	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 nanoparticles 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. 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 theory. Such a localized strong optical field in the nanoparticle assembly is called as 'hot spot' and is considered as the major origin of the huge Raman enhancement in single-molecule level surface-enhanced Raman scattering. However, since the conventional optical microscopy is unable to resolve nanometric structures, there has been no information on the detailed structure of hot spots given by spectroscopic measurements.

In this study, we applied the near-field two-photon induced emission measurement to obtain spatial distribution of the optical fields in the vicinity of metal nanoparticle assemblies. As a result, we succeeded in clear visualization of localized intense optical fields in the assemblies of gold nanoparticles.[1)] Figure 1 shows typical topographic and near-field two-photon

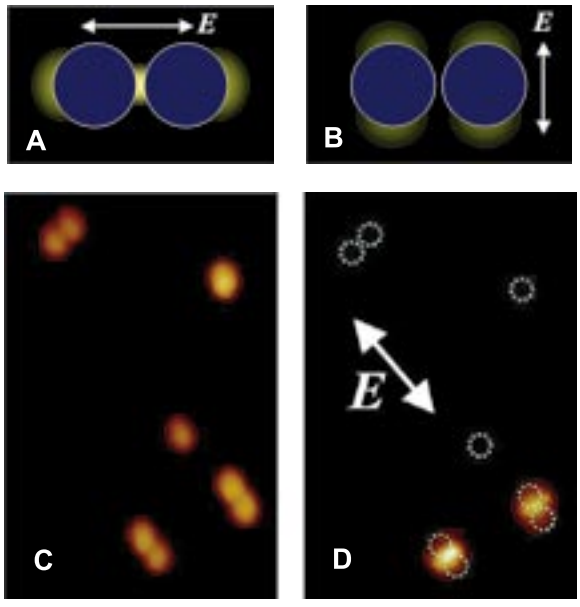

Figure 1. (A,B) Schematic view (theoretical prediction) of optical field strength in the vicinity of dimeric assemblies of metal nanospheres. The field strength is shown by the brightness. (C) Observed topography and (D) near-field two-photon excitation images of gold nanosphere (diameter 100 nm) assemblies. The dotted circles indicate positions of the nanospheres, deduced from the topography.

excitation probability images for dimeric gold nanospheres (diameter 100 nm). The two-photon image shows that the optical fields are confined at interstitial sites in the aggregates, when the incident polarization is parallel to the interparticle axes. This result agrees well with the theoretical expectations. We also performed near-field Raman imaging experiments and found that the Raman excitation is also strongly enhanced at the interstitial gaps.[1] The result gives a clear experimental proof to the hot-spot mechanism of surface-enhanced Raman scattering. In a similar way, we are examining fluorescence enhancements in the neighbor of gold nanoparticles of various shapes and their aggregates.

The methodology of visualizing the local optical field can be extensively applied to design metal nanostructures for the purpose of obtaining unique optical characteristics and/or optical fields strongly interacting with the nearby molecules. Studies in this line are under way.

2. Visualization of Plasmon Wavefunctions Induced in Various Metal Nanoparticles

We have reported that wavefunctions of localized plasmon resonances of metal nanoparticles can be visualized by using near-field transmission or two-photon excitation measurements.[2] The plasmons we visualized for chemically synthesized nanoparticles include the longitudinal modes in gold and silver nanorods and in-plane modes in gold triangular nanoplates. Figure 2 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 have reported that the images show excellent agreement with calculated images of local density of electromagnetic states which correspond to the square modulus of the resonant plasmon wavefunction.

We are extending the study to nanoparticles of other shapes and/or sizes, as well as the metal nanostructures manufactured by the electron-beam lithography technique, as a collaboration with the researchers outside of IMS. We have already obtained preliminary results for some metal nanostructures and have found peculiar plasmon waves in some cases. Such a study is also essential to design nanostructures of unique characteristics.

3. Ultrafast Transient Images of Gold Nanoparticles

We previously investigated ultrafast near-field transient transmission (space and time resolutions were *ca*. 50 nm and 100 fs) of single gold nanorods to reveal dynamic behavior of the material.[3] We used a near-infrared pulse to excite longitudinal plasmon resonance of the rod and detect transient transmission change after that. The transient image of a nanorod at *ca*. 1 ps shows characteristic features: the sign of the transient transmission change (induced or bleached) depends on the position, and the transient image contrast is sometimes reversed depending on the size of the rod.

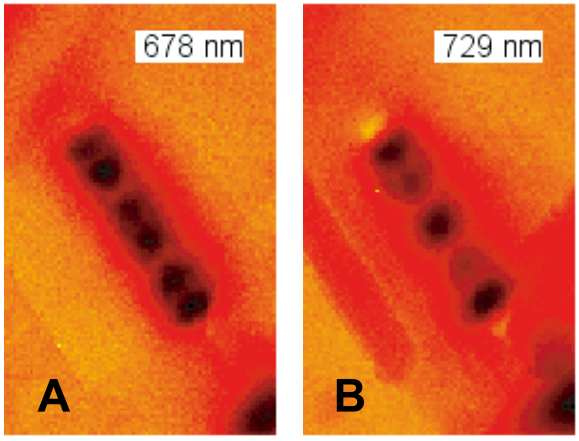

Figure 2. Near-field transmission images of a gold nanorod (diameter 20 nm, length 510 nm), observed at 678 nm (A) and 729 nm (B).

To understand the observed features, we simulated position-dependent transient transmission change based on electromagnetic density of states calculation. We have found that feature is qualitatively reproduced if we assume that the photoexcitation induces a homogeneous electronic temperature rise in the nanorod.

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

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Awards

IMURA, Kohei; The Chemical Society of Japan Award for Young Chemists.
IMURA, Kohei; Spectroscopical Society of Japan Award for Encouragement of Young Scientists.
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* Present Address; Tohoku University, Sendai 980-8578