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

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There is much demand for the study of local optical properties of molecular assemblies and materials, to understand nanoscale physical and chemical phenomena and/or to construct nanoscale optoelectronic devices. 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 for dynamics in nanomaterials and nanoscale functionalities. It may provide essential and basic knowledge to analyze origins of characteristic features of the nanomaterial systems. We have constructed apparatuses of near-field spectroscopy and microscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable near-field measurements of two-photon induced emission and femtosecond time-resolved signals, 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 Au nanoparticle 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. We also observed confined optical fields in gaps between circular apertures opened on thin gold films.

We are extending the studies to various two-dimensional metal nanostructures manufactured by the electron-beam lithography technique, in part as collaboration with researchers of other institution, with which structures that are difficult to obtain with the chemical methods can be available. The nanostructures now under study are circular Au nanodisks, assembled Au nanodisks with designed arrangements, elongated rectangular nanoapertures opened on Au thin films, and so forth. Such a study is essential as a basis for designing unique optical properties and functions of metal nanostructures.

2. Studies of Metal-Nanostructure Modified Photovoltaic Cells by Near-Field Excited Site-Specific Photocurrent Detection

Metal nanoparticles and their assemblies collect photon energies to yield confined and enhanced optical fields in the vicinities of the particles due to plasmon resonances. Recently, it has been reported that efficiencies of photoenergy conversion can be improved by the use of noble metal nanostructures. The photoenergy conversion system ranges from wet-type and solid-state photo-current conversion cells to photo-chemical conversion systems. To reveal the mechanism of the enhanced photoenergy conversion process, studies of detailed nanostructures and site-dependent photocurrent measurements are essential.

We applied SNOM to clarify effects of surface plasmon resonance on photo-current conversion in GaAs semiconductor cells modified with Au nanoparticles, by photocurrent imaging measurements with localized near-field photoirradiation (Figure 1).[2)] Isolated nanospheres caused local photocurrent sup-

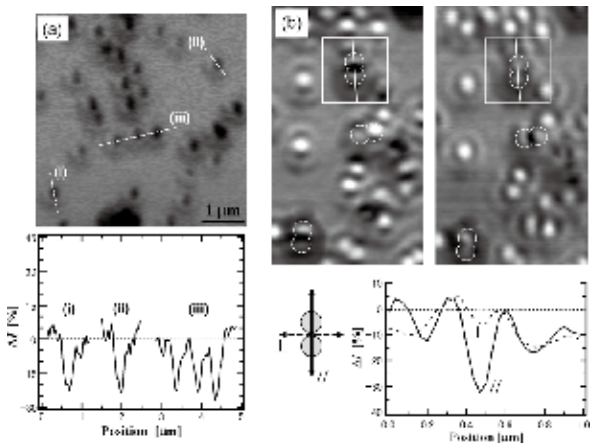

Figure 1. Near-field photocurrent images for GaAs photodiode modified with Au spherical nanoparticles. (a) Phorocurrent image at 532 nm for isolated particles (top) and line profiles along the dashed lines in the image (bottom). (b) Photocurrent images at 785 nm for dimeric particles (top; dimers are indicated with white circles; vertical and horizontal polarizations for left and right images, respectively) and line profiles along the white lines in the image for respective polarization directions (bottom).

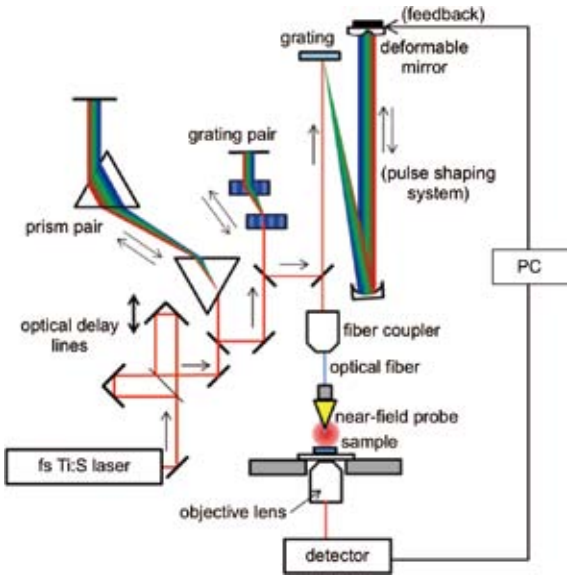

Figure 2. Experimental setup of sub-20-fs ultrafast near-field measurement.

pressions at the plasmon resonance wavelengths (~530 nm). In assemblies (dimers and trimers) of the spheres, a remarkable decrease of photocurrent at the gap site between the spheres was observed at ~800 nm near the dimer plasmon resonance, despite anticipated field enhancements in the gap sites. From the results, it is concluded that the enhanced optical fields induced by the plasmons do not improve the photovoltaic efficiency. The far-field forward scattering of photons by the gold nanoparticles may be more important than the enhanced field effects for the GaAs photovoltaic device studied.

3. Construction of Apparatuses for Sub-20-fs Ultrafast Near-Field Spectroscopy

Surface plasmons of noble metal nanoparticles have very short lifetimes in the range of ~2–20 fs. To achieve a SNOM observation of such fast dynamics in the individual nanoparticles, we have to overcome serious dispersion effects arising from the optical components involved, especially from the optical fiber. We achieved that by combining the conventional dispersion compensation devices composed of prism and grating pairs with adaptive pulse shaping technique, and succeeded in delivering 17-fs pulses to the the near-field aperture with a spatial resolution of ~100 nm.[3)]

The layout of the experimental setup is shown in Figure 2. A pair of transmission gratings and an SF14 prism pair were adopted to precompensate for the second- and third-order group velocity dispersion effects. The beam was then sent to adaptive pulse shaping system equipped with a deformable mirror, whose surface shape was adjusted to yield a shortest pulse duration at the probe tip using a genetic algorithm. The laser beam was then coupled to a 150-mm-long optical fiber to introduce the light into the apertured near-field probe tip. We used time-correlated two-photon-induced photoluminescence (TPI-PL) measurements to demonstrate the performance of the system. The light pulses were incident on a gold nanostructure sample through the near-field probe to excite the TPI-PL from Au, whose intensity was recorded as a function of the pump–probe delay time. With this setup we succeeded in measuring dephasing of ~10 fs in Au nanostructures. Position dependent dephasing measurements for Au nanostructures are now under way.

4. Near-Field Circular Dichroism Microscopy of Nanomaterials

Circular dichroism (CD) spectroscopy is widely used in the studies of chiral materials and magnetism. Some of nanomaterials composed of achiral molecules are reported to show CD activities arising from the nanoscale chirality. Two-dimensionally chiral metal nanostructures also show CD activities. Investigation of nanoscale local CD may provide valuable information on the origins of CD activities of such materials. For this purpose, we are developing an apparatus for near-field CD microscopy and measuring CD images of nanoscale chiral materials.

References

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