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 mesoscopic phenomena and/or to construct optoelectronic devices in the nanometric scale. 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 of dynamical processes in nano-materials. It may provide essential and basic knowledge for analyzing origins of characteristic features and functionalities of the nanometric systems. We have constructed apparatuses of near-field spectroscopy for excited-state studies of nano-materials, with the feasibilities of nonlinear and time-resolved measurements. They enable near-field measurements of two-photon induced emission and femtosecond transient transmission, 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 Plasmon Wavefunctions and Enhanced Optical Fields Induced in Metal Nanoparticles

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.[1,2] Figure 1(a) shows a typical near-field two-photon excitation image of the longitudinal plasmon mode on a Au nanorod, which correspond to the square modulus of the plasmon wavefunction. We also visualized optical fields in Au nanoparticle assemblies by the near-field two-photon excitation imaging method, as shown in Figure 1(b).[1,3] It was revealed for the 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.

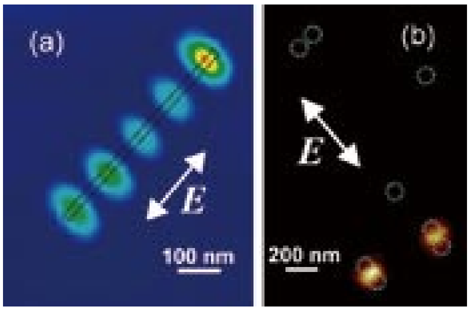

Figure 1. Near-field two-photon excitation images of (a) a Au nanorod (diameter 20 nm, length 540 nm), at 780 nm and (b) assembled Au spherical nanoparticles (diameter 100 nm).

We are now extending the studies to metal nanostructures manufactured by the electron-beam lithography technique, in collaboration with researchers of other institution, or other top-down fabrication techniques. Unique nano-optical characteristics, such as anomalous transmission enhancement through metal nanodisks, were found, and characteristic plasmon waves were observed for some metal nanostructures. Near-field properties of nano-void structures, opened on thin gold metallic films on glass substrates, have also been characterized, and the field distributions in the vicinities of the voids have been visualized. In circular void chain structures, we found that confined optical fields were generated in the interstitial sites between voids. The field distributions were analyzed based on the electromagnetic theories and calculations. Special attention has been paid for comparison of field distributions of complementary nanostructures, nanoparticle assembly and nano-void assembly, for instance, in relation to Babinet's principle in optics. Such a study is essential as a basis for designing unique optical properties and functions of metal nanostructures, and their applications to highly sensitive spectroscopic methods and exotic photochemical fields, as well as to nanoscale optical waveguids.

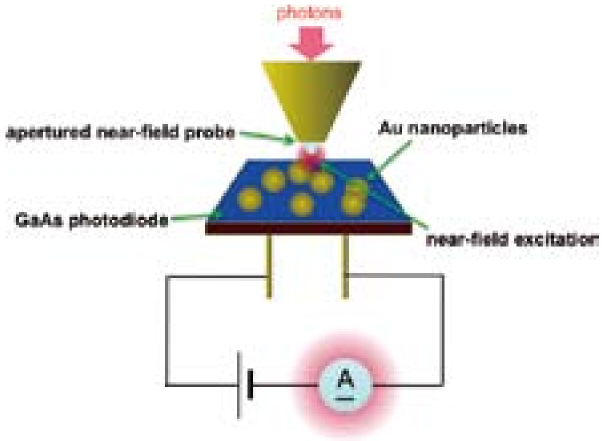

Figure 2. Schematic diagram of near-field photocurrent imaging measurement.

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

It has been known that metal nanoparticles and their assemblies collect photon energies to give confined and enhanced optical fields in the vicinities of the particles due to plasmon resonances, under suitably arranged conditions. Recently, it has been reported by a number of researchers that efficiencies of photoenergy conversion systems 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 photoenergy conversion process and design more efficient conversion systems, studies of detailed nanostructures and site-dependence of photoirradiation effects are essential.

We applied SNOM to clarify effects of surface plasmon resonance on photo-current conversion in inorganic semiconductor photovoltaic cells modified with metal nanoparticles, where the photocurrent is reported to be enhanced compared with unmodified cells based on macroscopic measurements. The spatial characteristics of photocurrent for GaAs photodiodes with gold nanoparticles (nanospheres and nanorods) dispersed on the active surfaces were investigated by photocurrent imaging using a SNOM (Figure 2). In the case of gold nanospheres (diameter 100 nm), near-infrared light irradiation (785 nm) gave rise to the enhancement of photocurrent, resulted from re-radiation of photons *via* plasmon resonance on the gold nanosphere into the photovoltaic area, while photons in shorter wavelengths did not show enhanced photocurrent. In the case of gold nanorod, characteristic spatial oscillation of photocurrent caused by the longitudinal plasmon mode of the rod was observed. We are now analyzing the results obtained based on the near-field optical characteristics of the metal nanoparticles.

3. Construction of Apparatuses for Nonlinear and Ultrafast Near-Field Spectroscopy

In previous studies we achieved ultrafast near-field imaging with a time resolution of ~100 fs.[2,4] To further extend the dynamical studies of plasmons, we are now developing basic technologies to achieve near-field time-resolved measurements with <20 fs time resolution. We are also constructing an apparatus for near-field/far-field microscopic nonlinear optical measurements based on the technique of atomic-force microscope.

4. Near-Field Imaging of Organic Molecular Assemblies and Hybrid Systems

We are studying nanometric structures and optical properties of organic molecular assemblies such as carbon nanotubes embedded in sugar polymer chains, LB films of functional conjugated molecules, and hybrid systems consist of metal nanoparticles and organic functional materials, mainly as collaborations with other research groups.

5. Nonlinear Effects in Optical Trapping

The optical trapping technique has been widely used in various areas to manipulate particles, cells, and so forth. The principle of trapping is based on the interaction between optical electric fields and induced linear polarizations. In the course of the studies on behavior of gold nanoparticles under pulsed laser fields, we have found a novel phenomenon of optical trapping of spherical gold nanoparticles arising from nonlinear polarization when we trap the nanoparticles by ultrashort near-infrared laser pulses. That is, the stable trap site (usually appears in the center of the focused beam) is split into two equivalent positions, and the split trap positions are aligned along the direction of the incident laser polarization. The split distance depends on the trapping-laser power and wavelength. We have found that the results were successfully interpreted in terms of the nonlinear polarization caused by the femtosecond pulses.

References

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Award

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