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 nanomaterials. 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 nanomaterials, 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 shows typical near-field transmission images of longitudinal plasmon modes on a Au nanorod, which correspond to the square moduli of the plasmon wavefunctions. We also visualized optical fields in Au nanoparticle assemblies by the near-field two-photon excitation imaging method.[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.

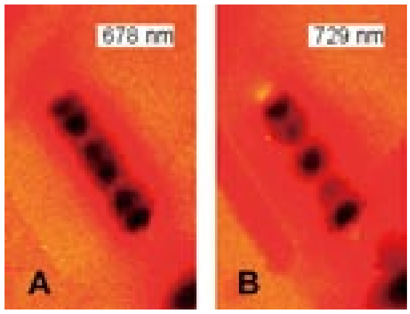

Figure 1. Near-field transmission images of a Au nanorod (diameter 20 nm, length 510 nm), observed at 678 nm (A) and 729 nm (B).

We are now extending the studies to metal nanostructures manufactured by the electron-beam lithography technique, in collaboration with researchers of other institution. Peculiar nano-optical characteristics and characteristic plasmon waves have been found for some metal nanostructures. Near-field properties of nano-void structures opened on thin gold metallic films on substrates have been also characterized, and the field distributions in the vicinities of the voids have been visualized. The detailed analyses of the characteristic optical fields are now under way. 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.

2. Properties of Two-Photon Induced Photoluminescence from Au and Ag Nanoparticles

We investigated properties of photoluminescence from Au and Ag nanorods induced by near-field two-photon excitation. For Au nanorods,[4] photoluminescence spectrum showed two peaks around 550 and 650 nm regardless of the rod dimensions, whereas the intensity ratio of the two spectral components varies from rod to rod. The observed spectral features were discussed based on electromagnetic calculations. We found that the spectral components were attributable to the interband transition of gold, and the intensity variation was explainable in terms of local field enhancement in the vicinity of the nanorod due to plasmon-mode excitation.

We also discussed the mechanism of the luminescence from Ag nanowires.[5)] The luminescence was most probably attributed to emission from the oxidized surface layer of the nanowires, which was enhanced in resonance with plasmons on the wires. In a similar way to the Au case, we succeeded in visualization of enhanced electric fields and plasmon modes for Ag nanowires (Figure 2) by the near-field two-photon excitation imaging, by detecting the luminescence from silver.

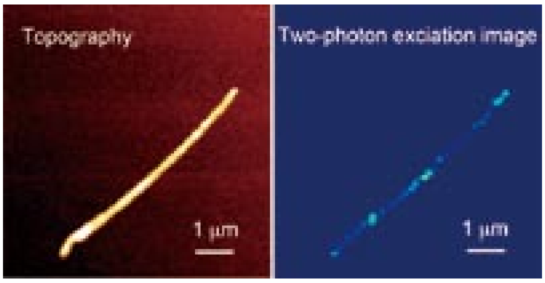

Figure 2. Topography (left) and near-field two-photon excitation (right) images of a silver nanowire (diameter 25 nm, length 6 µm).[5)] © 2009 Royal Society of Chemistry.

3. Bioimaging with Two-Photon-Induced Luminescence from Triangular Nanoplates and Nanoparticle Aggregates of Gold

Two-photon laser scanning microscopy (TPLSM) has been widely used recently in the field of biological imaging because of its merit in *z*-axis resolution and in effective avoidance of photodamage. Since it is difficult to completely eliminate the photobleaching for ordinary fluorophores, ideal optical imaging agents for TPLSM still have to be found. Recently, our group and some others found that two-photon-induced photoluminescence (TPIPL) from Au nanoparticles in the visible region shows quite high efficiency upon femtosecond near-infrared excitation. Based on detailed experimental and theoretical studies on the luminescence characteristics, we found that TPIPL from triangular Au nanoplates is especially efficient. Chemically stable (and as a consequence nontoxic) nature of Au is also beneficial in practical applications. Au nanoplates thus have the potential to be ideal agents for biosensing for microanlysis or bioimaging with TPIPL by TPLSM. In the present study we have demonstrated that Au nanoplate could be indeed a promising material for bioimaging studies by TPLSM.[6)]

Images of yeast cells conjugated to nanoplates were recorded by (far-field) TPLSM for biological use (Figure 3). We found that dried yeast as well as living cells in water can be clearly imaged by this method. We also found that cells

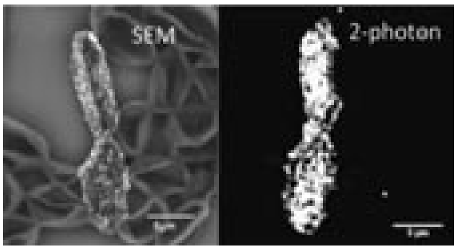

Figure 3. SEM (left) and far-field TPIPL (right) images of dried yeast cells conjugated to triangular Au nanoplates (base length ~300 nm) and some naked dried yeast cells.[6)] Scale bar: 5 µm. © 2009 Wiley-VCH Verlag.

conjugated with aggregated Au nanospheres give bright TPIPL, while isolated nanospheres were TPIPL-inactive.

4. 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.[2,7)] 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.

5. 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.

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