Near-field Imaging of Surface-enhanced Raman Active Sites in Aggregated Gold Nanoparticles

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We observed near-field images of aggregates of gold nanospheres, by detecting TPI-PL from gold and Raman scattering from Rhodamine 6G adsorbed on the nanoparticles. The results were analyzed in relation to the localized Raman active site (hot spot) of surface-enhanced Raman scattering.

Although chemical specificity of Raman spectra is expected to be useful in various fields of science, small cross section of Raman scattering sometimes causes difficulties in practical applications. To extend the applicability of Raman spectroscopy to wider purposes, it is essential to enhance the scattering cross section. In surface-enhanced Raman scattering (SERS),[1] the Raman signal is so drastically enhanced that it would give an effective solution to the difficulties. Even single-molecule level Raman spectroscopy has been reported recently by using the SERS scheme.[2] In the mechanism of SERS, it is considered that enhancement of the electric field by plasmon in noble metal nanoparticles plays a crucial role. This mechanism of SERS is called electromagnetic (EM) enhancement.[3] In addition to the EM mechanism, chemical effects are also considered to have some contribution to the SERS enhancement. To understand and control the SERS process, knowledge about spatial structures and other characteristics of plasmons is indispensable.

In single-molecule level SERS, spatially localized plasmon resonance, called "hot spot," is believed to be essential for the Raman enhancement.[3] Understanding of the physical properties of hot spots and imaging of them are hence important. From electromagnetic calculations on dimers of noble metal spherical nanoparticles, it has recently been revealed that the radiation field is strongly enhanced in the interstitial space between the particles (sometimes called as "junction").[3] Such a structure may be regarded as a model system for the hot spot, but up to now direct microscopic observation of the dimeric structures and radiation field distribution has not been reported.

The present authors recently reported that the plasmonic modes are visualized using near-field two-photon induced photoluminescence (TPI-PL).[4] Applying this method to the aggregates of metal nanoparticles, distribution of the electric field can be imaged. By monitoring Raman signals, direct visualization of hot spot distribution is also possible. In this letter, we report imaging of hot spots on gold nanosphere aggregates by near-field TPI-PL and Raman imaging. We consider that such direct optical imaging with high spatial resolution is essential to understand structures of hot spots and the electromagnetic effects of junctions in SERS process.

Gold nanosphere (diameter 100 nm) solution was purchased from BB International. Gold dimers were prepared by aggregating the gold nanospheres on a cover-slip treated with trimethoxy[3-(methylamino)propyl]silane. The cover-slip was then spin-coated by a methanol/water solution of Rhodamine 6G (R6G) molecules. The area density of R6G molecules was estimated to be less than 15 molecules per $100 \times 100\,\text{nm}^2$, if we assume homogeneous dispersion of the molecules on the substrate. Morphology of the sample was verified by topography measurements by the scanning near-field optical microscope (SNOM) and/or by an atomic force microscope. The experimental setup has been described previously.[4] Briefly, a SNOM equipped with an apertured optical fiber probe (aperture diameter 50–100 nm) was used under ambient condition. A Ti:sapphire laser ($\lambda = 780\,\text{nm}$, $<100\,\text{fs}$) and He–Ne laser ($\lambda = 632.8\,\text{nm}$) were used to excite TPI-PL and Raman scattering, respectively. Laser power coupled to the other end of the near-field fiber probe was less than 2 mW. Emitted PL or Raman scattered radiation was collected by an objective and detected by an avalanche photodiode or by a polychromator-CCD, respectively. Near-field Raman spectra were measured at 30 nm steps across the scan area.

Figure 1a shows the topography of the sample surface. Dimeric aggregates as well as isolated nanospheres are seen in the figure. It is well known that the interparticle distance is important factor for electromagnetic field enhancement. From the topography measurements, interparticle distances are found to be less than 10 nm, while it is difficult to obtain the exact values because of limitation of the spatial resolution. Figures 1b and 1c show TPI-PL images of single gold particles and aggregates. It is to be noted that the aggregates (dimers) exhibit stronger TPI-PL than those from the isolated single particles, and the excitation probability is highly localized at the interstitial site of a pair of the particles. These observations are well correlated to the calculated electromagnetic field distribution,[3] and can be ascribed to the spatial distribution of the electric field enhanced by the plasmon mode excited. It is also to be noted that excitation probability of the PL from the dimer depends strongly on the incident polarization direction. This observation is explained as follows. In the dimeric aggregates, the coupling between the two spheres is anisotropic, and hence the field enhancement is strongly dependent on the incident polarization angle, in contrast to the single sphere case. The electric field at the interstitial site is most enhanced when the incident polarization is parallel to the dimeric axis, whereas it gives the minimum electric field when the incident polarization is perpendicular to the axis. This point is also in good correspondence with the electromagnetic calculations and proves the strong field enhancement at the interstitial sites.

TPI-PL spectrum of the single aggregate shows two peaks, ca. 550 and 660 nm. These band positions are approximately the same as those for the nanorods. Thus, the PL mechanism for the aggregates is considered to be essentially the same as that for the nanorods.[4] The PL bands are attributed to the recombination of electrons near the Fermi surface with holes in the d band.

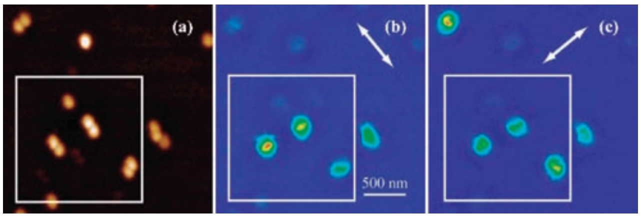

Figure 1. (a) Topography of dimeric aggregates and isolated gold nanoparticles. (b and c) TPI-PL images taken at different incident polarization directions (arrows). White frames show the area of Figure 2.

The two bands can be assigned to the transitions near the *L* and *X* symmetry points of the Brillouin zone.

In Figure 2a typical Raman spectrum of R6G observed at the single dimeric site (A) is shown. Observed Raman shifts are in good agreement with the reported values.[2,5] Intensity pattern in SERS spectra is, on the other hand, substantially different from that of the bulk system.[5] Although the origin of this spectral change is not clear yet, it may be partly due to the orientation of molecule at the surface of the particles with respect to the electromagnetic field at the active site. Another possible reason is vibrational-mode dependence of resonance enhancement for the chromophore molecule at the surface.

Near-field images monitored at the Raman bands at 1340 and 1580 cm^{-1} are shown in Figures 2b and 2c, respectively. The Raman band intensity was estimated by a fitting analysis assuming Lorentzian Raman band shapes for the two bands. The two images give nearly identical results. Neither flat portions (without nanoparticles) nor the single-particle sites show any detectable Raman signal. This clearly demonstrates that the aggregated structures of the nanoparticles (A–C) are essential for strong Raman enhancement. Though it is hard to estimate the enhancement factor in the present experiment, we may conclude that the enhancement is very high considering the very low density of R6G molecules on the sample substrate. The SERS signal detected for the dimer (A) is enhanced especially at the interstitial site of the particles. In this respect, the feature is similar to that obtained in TPI-PL (Figures 1b and 1c) and it again shows the importance of the hot spot at the interstitial site in SERS. The detailed features are different, however: in TPI-PL the signal is most intense at the center of the dimer, while in Raman images the positions giving most intense signal are deviated from the dimer axis to both sides. Possible reasons for the difference between TPI-PL and Raman images are as follows. One is concerning the difference in the optical processes. The TPI-PL is a nonlinear process and thus it may be more sensitive to the electromagnetic enhancement compared to Raman scattering. Another factor is the experimental configuration. In the present experimental setup (transmission-mode detection), the Raman signal is detected in the opposite side of the sample from the near-field excitation. Then the sizable fraction of the Raman scattered radiation might be back-scattered by the nanoparticles and not detected, especially for the center of the interstitial site, if the gap is very narrow. The detected signal at the center of the dimer may thus be not very strong. In TPI-PL, on the other hand, detection of PL is less obscured since the PL is emitted from the gold particles themselves.

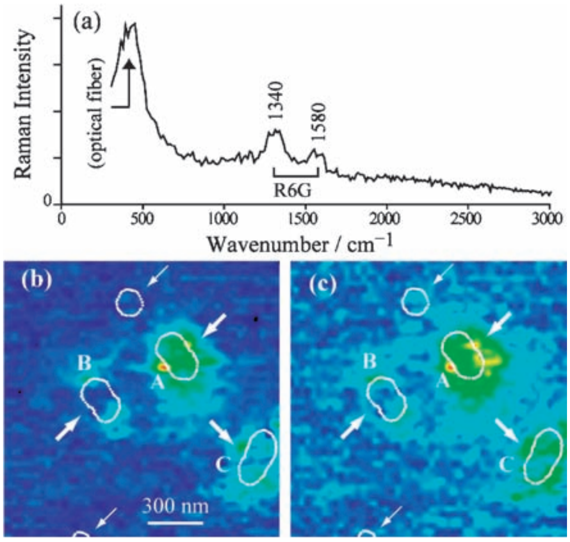

Figure 2. (a) SERS spectrum of R6G measured at dimeric site (A). (b and c) Near-field Raman image obtained for bands at 1340 and 1580 cm^{-1}, respectively. White lines indicate the approximate shapes of the gold particles obtained by the topography measurement. Thick and thin arrows indicate dimeric aggregates and isolated particles, respectively. Incident and detected polarizations are not controlled.

It is also to be noted that the dimer (B) give the SERS signals at the both ends of the dimer. The observation might be ascribed to the lightning rod effect, which is pronounced in general at sharp edges and/or corners.[6] Although the origin of the difference among dimers A, B, and C is not clear yet, it might be due to difference in plasmon resonance frequencies arising from microscopic structure differences undetectable by the topography measurements, such as fine structures of the individual particles or the gap between the particles.

In summary, we have succeeded in near-field imaging of hot spots on dimeric aggregates of gold nanospheres, by detecting TPI-PL and Raman scattering, combined with topographic measurements.

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