Multipole Resonance Modes in Localized Surface Plasmon of Single Hexagonal/Triangular Gold Nanoplates

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We investigated the optical properties of the hexagonal/triangle gold nanoplates by single particle spectroscopy. By comparison with scanning electron microscope (SEM) observations, we successfully demonstrated that light scattering spectra of the hexagonal nanoplates with 360 ± 120-nm edge lengths and the triangular ones of 190 ± 60 nm exhibited two peaks in visible–near infrared region corresponding to quadrupole and higher multipole modes of localized surface plasmon resonance (LSPR).

Recently, extensive efforts have been paid for synthesis of gold nanoparticles with various shapes; i.e., nanorods,[1] triangular and hexagonal nanoplates,[2] nanocubes,[3] and nanorings,[4] because of their unique optical/spectroscopic properties, such as a strong optical anisotropy in LSPR spectrum depending on their shapes and an enormous enhancement effect of electromagnetic fields near the sharp edge of nanoparticles.[5] However, their optical properties have not been well characterized except for nanorods,[6] since the LSPR spectrum has been examined by measuring extinction spectra of colloidal dispersion with a conventional spectrometer. A colloidal solution of gold nanoplates, for example, exhibited two broad, unpronounced absorption peaks around 540 and 860 nm.[2b] This is owing to a large distribution of particle shape and size in a sample solution and to contribution of light scattering in absorption measurements. Therefore, to investigate the geometrical shape dependence of LSPR, it is important and indispensable to measure the optical properties of individual particles. In this study, we demonstrated LSPR spectra of single gold hexagonal/trianglar nanoplates by means of resonant Rayleigh light-scattering microspectroscopy using a dark-field setup.

A sample colloidal solution was prepared by the photoreduction method described in ref 2a. The conventional absorption spectrum of the sample colloid shows a single peak at 545 nm, corresponding to LSPR of spherical nanoparticles.[7] Figure 1 shows typical SEM images of the nanoparticles. From SEM observation, the solution consisting of a lot of small spherical nanoparticles with 80 ± 30 nm diameters, hexagonal nanoplates of 360 ± 120-nm edge lengths, and triangular ones of 190 ± 60 nm.[7] The number ratio of hexagonal and triangular nanoplates was about 3.9:1. The height of the nanoplates was confirmed as about 40 nm by AFM measurements.[7]

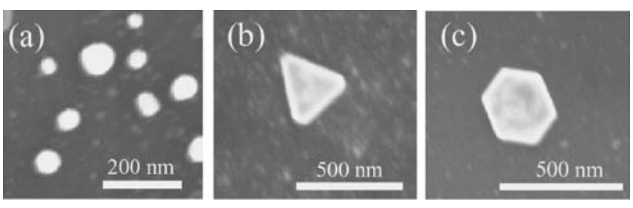

Figure 1. SEM images of gold nanoparticles contained in the prepared colloidal solution. (a) spherical nanoparticles, (b) a triangular nanoplate, and (c) a hexagonal nanoplate.

The gold nanoparticles were dispersed on a glass substrate by spin-coating a diluted colloidal sample. The substrate was covered with pure water, then light-scattering spectra of single gold nanoparticles were measured by resonant Rayleigh light scattering microspectroscopy using a dark-field setup.[7,8] We measured 65 particles and could classify 58 particles into three groups on the basis of the spectral shapes, intensities, and their polarization dependence. The typical light-scattering spectra of the each group particle are shown in Figure 2. Group I particles, which exhibit a weak scattering with a peak in 550–600 nm region (Figure 2a), can be assigned to small spherical particles. Thus, their spectral shapes are well reproduced with the calculated spectrum on the basis of Mie theory[9] for spherical gold nanoparticles with diameters of 60–90 nm. Also, their light scatterings show almost no polarization dependence. On the other hand, groups II and III particles presented strong optical anisotropy. Figures 2b and 2c represent the typical light-scattering spectra of the group II and III particles, respectively. The spectra of group II display a distinct peak around 650–700 nm, and that of group III particles show two peaks in visible varied from particle to particle. In Figures 2b and 2c, we also show the polarization light-scattering spectra for each particle. As changing the

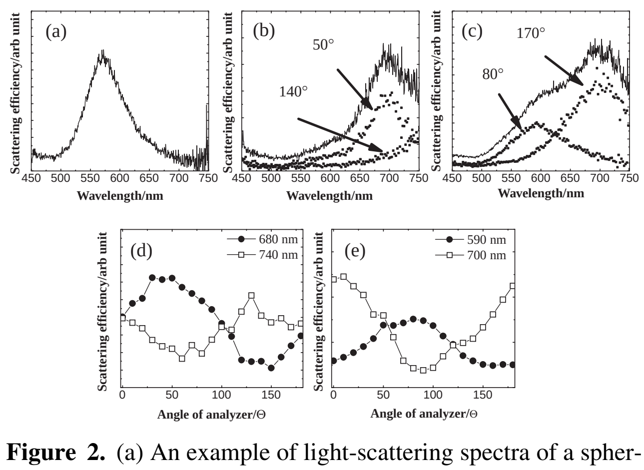

Figure 2. (a) An example of light-scattering spectra of a spherical nanoparticle. (b), (c) Unpolarized (solid lines) and polarized (dotted lines) light-scattering spectra of single particles, which are categorized in group II and III, respectively (see text). (d), (e) Polarization plots of scattering light intensities for each spectrum (b) and (c) at two fixed wavelength.

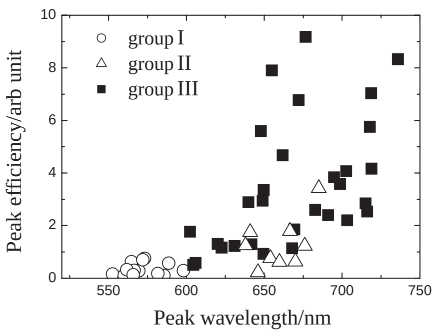

Figure 3. Relationship between peak scattering efficiency and peak wavelength of light-scattering spectra of single gold nanoparticles.

polarization detection angle, two bands in visible to near-infrared region grow and diminish alternately in the spectra. Thus, the optical anisotropy measurement indicates that the two peaks of light scattering spectra correspond to different resonance modes of LSPR. Shuford and co-workers have recently reported the calculated extinction spectra of gold triangular nanoplates with large edge lengths (50–200 nm) and nanoplates with snipped off edges.[10] The extinction spectrum of the nanoplates with a 150-nm edge length and a 5-nm height exhibited two peaks at 849 and 749 nm, which correspond to quadrupole and higherpole resonances modes and the dipole resonance mode at 1539 nm. Also, the snipped off triangular nanoplates, namely the nanoplates similar to hexagonal nanoplates also showed the peaks due to quadrupole and higherpole resonances modes with a slight shift compared to triangular nanoplates. Therefore, we can safely assign the two peaks in Figures 2b and 2c to the quadrupole and higherpole resonances modes.

In Figure 3, we summarize the relation between the peak efficiency and peak wavelength of light-scattering spectra of single gold nanoparticles. For both groups II and III, the scattering efficiency increases with the peak wavelength, which might be owing to increasing particle size. Group III particles show an average stronger light scattering when compared to group II ones. The ratio of particle number in groups II and III is about 1:3.1, which is rather close to that of triangular and hexagonal nanoplates estimated by SEM observation. These results strongly suggest that group II and III particles will correspond to triangular and hexagonal nanoplates, respectively.

Figures 2d and 2e show the polarization plots of the light-scattering intensity. It is noteworthy that the polarization dependence shows a 180 degrees rotational symmetry for both case, although 120 or 60 degrees symmetry is expected from the geometrical shape of the triangles or hexagons. This is in contrast to the optical anistropy of nanorods, in which two dipole modes can be categorized well into transverse and longitudinal modes along the short and long axes of nanorods, respectively.[6] This might be owing to the fact that in this experiment we observed quadrupole or higherpole resonances, not dipole resonance. The comparison with the dipole discrete approximation calculation is currently under investigation in order to clear the physical origin of the optical anisotropy.

In conclusion, we investigated hexagonal/triangular nanoplates by single particle spectroscopy and demonstrated that the light-scattering spectra of the nanoplates show two peaks due to quadrupole and higherpole resonances modes of LSPR in visible–near-infrared region. Resonant Rayleigh light-scattering microspectroscopy using a dark-field setup is powerful and useful to reveal the optical properties of single nanoparticles. The multipole resonance modes of the hexagonal/triangular nanoplates can be accessible to sensing and spectroscopy applications such as surface enhanced Raman scattering.

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