Resonant light scattering from individual Ag nanoparticles and particle pairs

Hiroharu Tamaru[a)]
Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo 153-8904, Japan and CREST, Japan Science and Technology Corporation (JST), Kawaguchi 332-0012, Japan

Hitoshi Kuwata
Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan

Hideki T. Miyazaki
PRESTO, Japan Science and Technology Corporation (JST) Kawaguchi 332-0012, Japan and Materials Engineering Laboratory, National Institute for Materials Science, Tsukuba 305-0047, Japan

Kenjiro Miyano
Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo 153-8904, Japan and CREST, Japan Science and Technology Corporation (JST), Kawaguchi 332-0012, Japan

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Light scattering by individual Ag nanoparticles and structures have been studied spectroscopically. Individual particles were selected and manipulated with a micromanipulator installed inside a scanning electron microscope (SEM). With typical particle dimensions of some 100 nm, the plasma resonances of particles and the coupled modes of particle pairs were observed in the visible region. The polarization dependence of the resonance frequencies strongly reflects the shape anisotropy; the effect that would be averaged out for experiments on ensembles. With a simple approximation to take the glass substrate into account, the results are in good agreement with the analytical calculations by Mie scattering, and with numerical calculations by the finite-difference time-domain method, both of which are performed with the morphological parameters obtained from the SEM observation for the corresponding particle or particle pair. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1461072]

Nanosized particles and structures are known to exhibit a strong interaction with light. This is the principle of operation in a scattering-type scanning near-field optical microscope[1] and it is believed to be the cause of the vast signal enhancement in surface-enhanced Raman spectroscopy[2–5] (SERS). It is widely discussed that the size, shape, and structure of these particles determine optical properties like resonant frequencies, field distributions, field enhancements, etc.[2–7] In particular, many calculations suggest that nanospaced particle pairs are responsible for the strong signal enhancement for SERS.[2–4] Thus, it should be of major interest to identify the morphologies of the individual particle/cluster/structure and to investigate the optical responses from them separately. In this work, we present the results of microspectrometry of light scattered from individual Ag particles or biparticles, structures of which were individually identified using a scanning electron microscope (SEM).

The samples are Ag particles on a cover glass. Commercially available Ag nanosized particles were suspended in water and centrifuged. A droplet from the fraction, corresponding to roughly 100 nm in diameter, was placed on an uncoated cover glass and let dry. SEM images were acquired in several progressive magnifications so that large features can serve as markers for optical microscope observation to locate each particle or particle pair (biparticle) identified under SEM. Some Ag particles and biparticles in desirable shape and arrangement had been selected and, with a micromanipulator installed inside the SEM,[8] surrounding excess particles were swept away *in situ*, so as not to interfere with the selected particles during the optical measurements that followed.

Our optical setup is based on an inverted microscope (Zeiss Axiovert 100) equipped with an infinity-corrected $\times 40$ (NA$=1.3$) oil immersion objective. The sample was illuminated by a 100 W halogen lamp from above. A beam block was placed at the Fourier plane of the objective to reject the directly transmitted light, which, in our case, arrives inside the ring corresponding to NA$=1$. Thus, only the scattered light in the range of NA between 1 and 1.3, the so-called forbidden light, was collected.[9] This scattered forbidden light was refocused onto a pinhole to select an area corresponding to a disk 3 μm in diameter in the sample plane, which was finally sent to a spectrometer equipped with a liquid-nitrogen-cooled charge-coupled-device camera. The incident light was linearly polarized, and no analyzer was used.

Figure 1 shows some typical results. In Fig. 1(a), a less-deformed sphere is shown which presents little anisotropy with respect to the incident polarization. On the other hand, for a spheroid as shown in Fig. 1(b), a strong anisotropy was observed. For particles with more distortion, the spectra often had multiple peaks in different polarizations. Figure 1(c) shows a bisphere case. Here, the coupled interaction modes

a)Electronic mail: tamaru@myn.rcast.u-tokyo.ac.jp

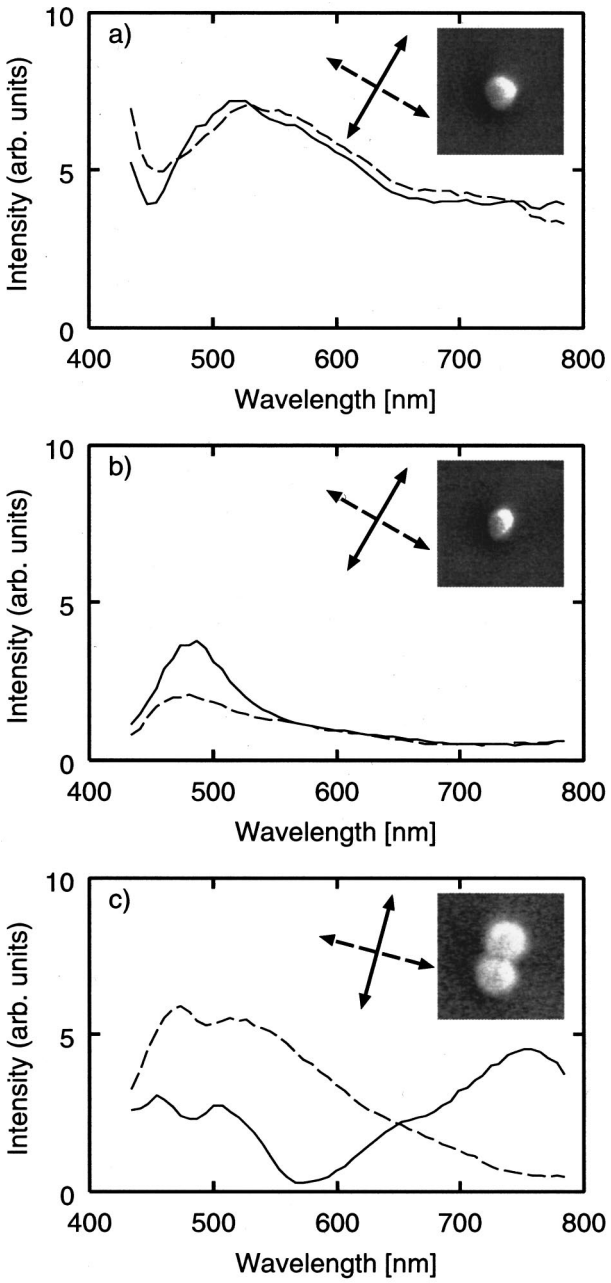

FIG. 1. Typical scattered-light spectra from Ag particles. Inset shows the SEM image (300 nm×300 nm) of each particle(s), arrows denote the polarization of the incident light; (a) spherical particle, (b) spheroidal particle, and (c) spherical biparticle.

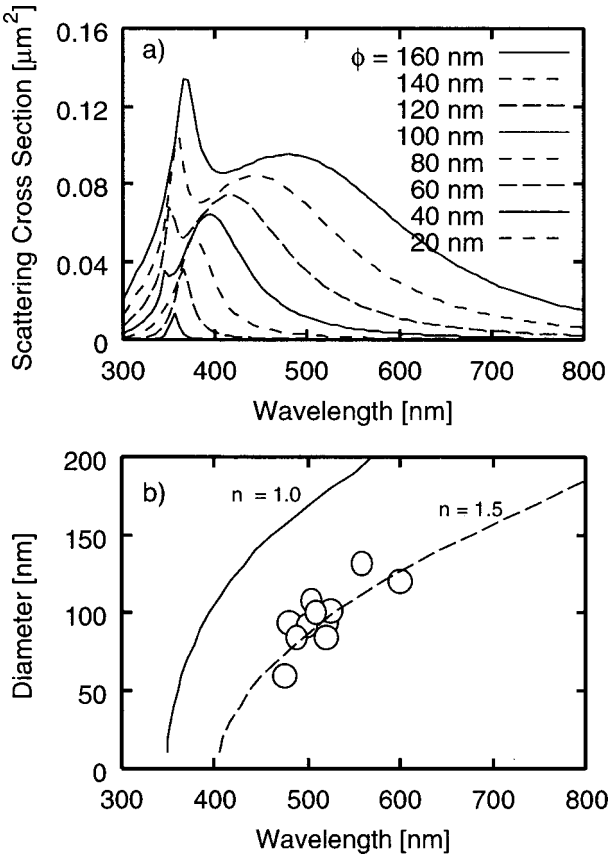

FIG. 2. (a) Integrated scattering cross section calculated according to Mie's theory. The first two modes with respect to the sphere diameters are shown. The dielectric constant of Ag was approximated by the Drude dispersion. (b) Solid line shows the resonance wavelengths of the first mode as in (a). Dashed line shows the same resonance with the index of refraction of the surrounding media taken at 1.5. Circles denote the experimental data.

are observed, showing a clear distinction between the two orthogonal polarizations.

To identify the resonances seen in each spectrum, a series of calculations were performed. For single particle cases, Mie's theory of scattering is employed.[10] Figure 2(a) shows the integrated scattering cross-section spectra from Ag spheres with various diameters. Here, only the first two modes $l=1$ and $l=2$ are taken into account, and the dielectric constant of Ag is represented by the Drude dispersion $\epsilon(\omega)=\epsilon_\infty-\omega_p^2/\{\omega(\omega+i\delta)\}$, in which $\omega_p=9.6$ eV, $\delta=0.0544$ eV, and $\epsilon_\infty=5.266$ were chosen to best fit the figures presented by Johnson and Christy.[11]

Since surface plasma resonances are in fact polaritons, it is very sensitive to the dielectric constant ϵ_m of the surrounding media. Thus, the effect of the glass substrate must be considered. Taking this interaction into account properly is not a trivial task. Instead of doing elaborate numerical calculations, we chose to examine an extreme case in which the Ag spheres are embedded in a medium of $\epsilon_m=1.5^2=2.25$. This is shown in Fig. 2(b) by the dashed line. In a real situation, where the Ag particles are sitting on the substrate, the results are expected to fall somewhere in between the solid and dashed lines.

Alternatively, since the lowest resonance of a sphere is a dipole-like oscillation, another simple approximation based on the image dipole method should also be reasonable.[12] Here, with a sphere geometry, and the dipole parallel to the glass substrate, the dipole moment μ is expected to be reduced by some factor of 0.64, which in turn would lower the oscillation energy by a factor of $\sqrt{0.64}=0.8$. The result turns out to be quite close to the dashed line in Fig. 2(b).

The experimentally observed dependence of the resonance wavelength on the particle diameter is shown in open circles in Fig. 2(b), and is in good agreement with the prediction.

For the biparticle case, a series of finite-difference time-domain (FDTD) calculations were performed. In this calculation, Ag spheres of specified size were placed in vacuum. The incident light was described as a linearly polarized plane wave. The FDTD parameters $\Delta x=\Delta y=\Delta z=1.1$ nm, and $\Delta t=0.0005$ fs were used. We integrated the far-zone radiation intensity scattered at right angles to the incident beam

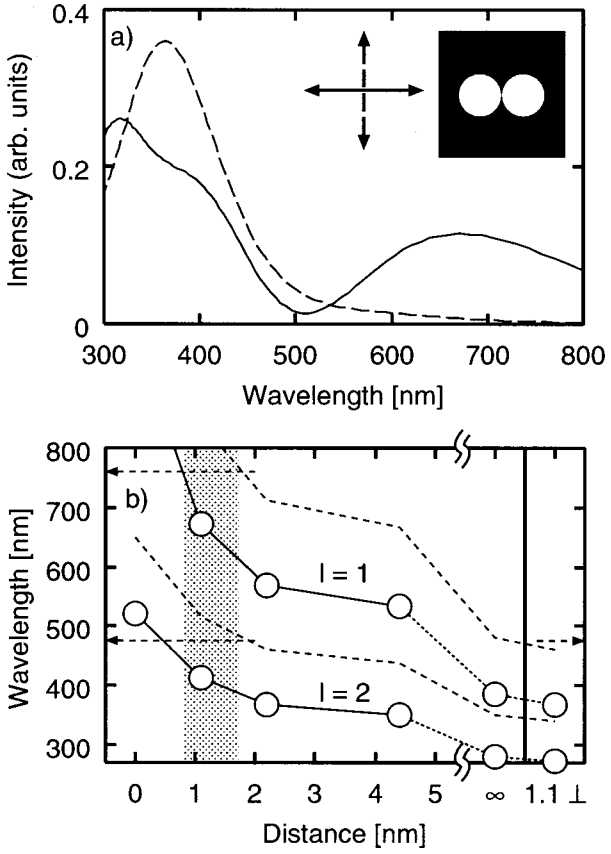

FIG. 3. FDTD calculation. (a) Far-field distributions of the scattered light from two 100-nm-diam Ag spheres placed 1.1 nm apart in vacuum. Inset shows the top view of the calculation model, and arrows denote the polarization of the incident light. (b) Resonance wavelengths of the 100-nm-diam bisphere system with respect to the distance between the spheres. Left panel is for the incident polarization parallel to the long axis [solid line in (a)], and right panel, perpendicular. Dotted lines represent the energy reduction to 80% of the solid lines. Arrows denote the experimentally observed resonance wavelengths.

over the full 2π rad angles, so as to simulate the collection scheme employed in our experiment: This corresponds to collecting the light scattered into the NA$=1$ ring. Choosing an angle slightly different from 90° to the incident wave vector did not affect the major characteristics of the results. The scattered-light spectra were calculated for several sphere diameters and sphere spacings. Figure 3 shows some of the results.

Figure 3(a) shows the case in which two 100 nm spheres were placed 1.1 nm apart. The scattering spectra for the two characteristic incident polarizations are shown in qualitative agreement with Fig. 1(c).

The lowest-energy mode of an isolated sphere $l=1$ splits into two odd ($m=0,1$), and two even ($m=0,1$) modes.[13] One of each are optically active ($m=0$ for the odd mode, and $m=1$ for the even mode). For $l=2$, the mode splits into six modes, in which one odd and one even modes are optically active. This can be seen in Fig. 3(b), where the resonance peak wavelengths obtained from a series of FDTD calculations are plotted. Using the same rationale as before, the effect of the substrate is taken into account by multiplying the resonance energy by 0.8, which is shown by the dotted lines. The experimentally observed resonance wavelengths are drawn by dotted arrows. The separation of the biparticle should be somewhere in the shaded region, corresponding to the distance of 1–2 nm. This is not inconsistent with the SEM observation [Fig. 1(c)], because the lateral resolution of our SEM is around 5 nm.

In conclusion, we have observed a one-to-one correspondence between the shape, size, and arrangement of an individual isolated Ag particle/cluster as imaged under SEM, and the optical scattering caused by this particle/cluster. The individual spectrum is strongly influenced by the morphology. The analytical and numerical calculations performed using a given set of parameters obtained by SEM well account for the observed spectra. It is clear that the characterization of the individual particle/cluster, instead of measurements of ensembles, is essential to bring out the strong near-field interactions.

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