3P040 Synthesis of Silver Nanorods and Observation of Spatially-Resolved Surface Plasmon Absorption by Near-Field Microscopy

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【**Introduction**】Recently, experiments on optical properties of single clusters or individual nanoparticles become possible. We have previously studied optical and dynamic properties of gold nanorod systems by using scanning near-field optical microscopy (SNOM) combined with a time-resolved technique [1, 2]. Nanorod can be regarded as a kind of large cluster where atoms are aggregated with an order along the long axis of the rod. The purpose of the present study is to measure near-field images of silver nanorods, and to compare the results with those for gold. We report here observation of the local excitation density distribution of surface plasmon resonance (SPR) on individual silver nanorods.

【**Experiment**】**(1) Synthesis of silver nanorods.** Silver nanorods were prepared by reducing silver nitrate in the water solvent containing reducing agent (tri-sodium citrate) and surfactant (sodium dodecylsulfonate). By changing the concentration of reductant, the length of silver nanorods could be controlled from a few hundreds nanometers to a few micrometers. The pristine sample was a mixture of nanorods and nanospheres. The nanorod sample was purified by centrifugation. The typical condition of centrifugation was 4000 rpm, 30 min, and the supernatant was again centrifuged. This process was repeated until the color of supernatant disappeared (5 or 6 times).
(2) Observation of surface plasmon mode by SNOM. The samples for SNOM measurements were prepared on cover glasses. The solution of nanorods was dropped onto a rotating cover glass in a spin coater. While the cover glass was rotating, the dropped sample was blown by air to evaporate rapidly the solvent (water) so as to prevent aggregation. By this method, we could prepare well-dispersed nanorod samples on cover glasses, which was suitable for observing optical properties of each nanorod by SNOM. We used a home-made SNOM system equipped with a commercial near-field fiber probe (JASCO Corporation). The light source was a Xe discharge lamp, and the radiation incident on the sample was randomly polarized.

【**Results**】Figure 1 shows a SEM image of the synthesized silver nanorods. The relative density of nanorods against nanospheres was approximately 40% in number. The length of nanorods is distributed from a few hundreds nanometers to a few micrometers. The typical rod length is about a few hundred nanometers, which is expected to be suitable for observing the SPRs by visible light. Figure 2 shows extinction spectra of a low density solution (solution A, dotted curve) and a high density solution (solution B, solid curve) of nanorods. (The high-density sample is identical to that for Figure 1.) Compared with solution A, solution B shows relatively enhanced extinction in longer wavelength region from 600 nm to 900 nm. As the aspect ratio increases, the longitudinal SPR band is

expected to be red-shifted significantly. Since solution B contains more nanorods with higher aspect ratio, the enhanced extinction in the longer wavelength region is attributed to the red-shifted longitudinal SPR band.

We have tried to observe near-field images of SPR for some nanorods. A representative example for a silver nanorod of 900 nm in length and 35 nm in height is shown in Figure 3. Figure 3(a) shows the topography of the nanorod and Figure 3(b) and (c) are the simultaneously obtained near-field absorption images, at probing wavelength of 792 ~ 846 nm for (b) and 640 ~ 670 nm for (c), respectively. By changing the wavelength of light, different spatial profiles of SPR are obtained, as seen in the Figures. On the poster, we will analyze the observed images of silver nanorod and compare the results with the gold case.

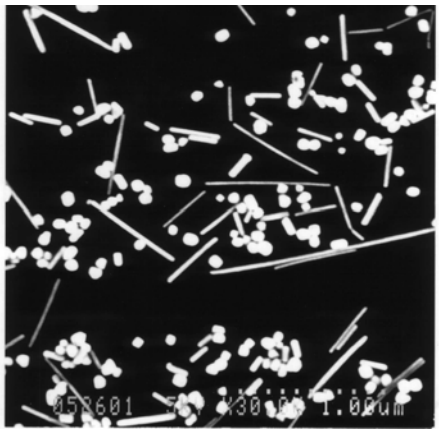

Figure 1. SEM image of silver nanorods. Image size: 3 μm × 3 μm.

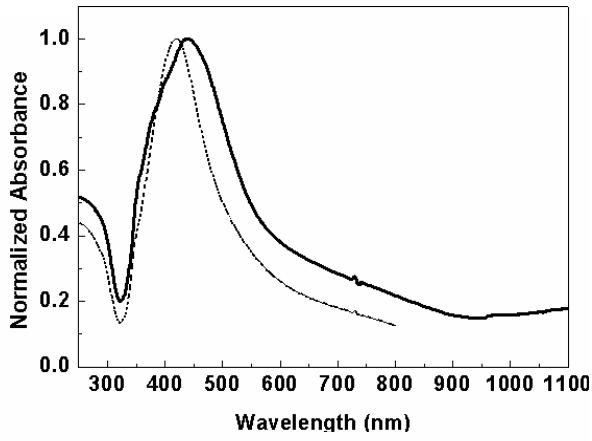

Figure 2. Absorption spectra of low density (dotted curve) and high density (solid curve) solutions of nanorods

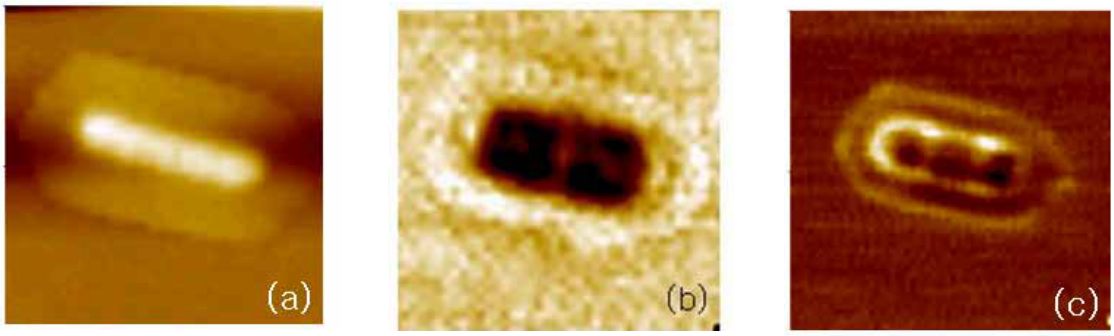

Figure 3. (a) The topography and (b, c) near-field scanning absorption images of a silver nanorod. Probe wavelength are 792 ~ 846 nm for (b) and 635 ~ 695 nm for (c), respectively. Image sizes: 1.5 μm × 1.5 μm.

[1] K. IMURA, T. NAGAHARA, H. OKAMOTO, *J. Phys. Chem. B* in press.

[2] K. IMURA *et al.,* This Conference, 4C06; 4P086.