Aggregation of Gold Nanorods by Synchrotron X-Ray Irradiation

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Introduction

Rod-like gold nanoparticles (gold nanorods: NRs) show unique optical properties depending on the size and the aspect ratio. The unique optical properties have materialized extended applications of the NRs to sensors and nonlinear optical materials. Pulsed laser excitation on the NRs in aqueous solutions induces some morphological changes such as fusion and/or fragmentation, and transformation of the NRs to nanoparticles. In this study, we examined the changes of NRs induced by the irradiation of X-ray, since it can provide much larger energy than that of the pulsed-laser irradiation.

Experimental

Gold NRs were prepared by the electrochemical method [1]. The NR solution was centrifuged three times to remove the excess amount of hexadecyltrimethylammonium bromide that was essential to the preparation of NRs. Then, the NR solution was filled in a thin plastic cell made of polymethymethacrylate, and irradiated by White X-ray and monochromated X-rays (5–20 keV). The beam spot size of the X-ray irradiation was 1.15 × 6.15 mm. The monitor light from a halogen lamp passed through the cell perpendicular to the direction of X-ray irradiation. Optical path length for the monitor light and the X-ray irradiation were 10 mm and about 3 mm, respectively. The spectral changes of the NR solution were monitored by a multi-channel spectrophotometer (Ocean Optics, SD-1024DWX).

Results and Discussion

Figure 1 shows the absorption spectra of the NR solution before (a) and after (b) the centrifugation. A couple of absorption peaks of NRs are the surface plasmon (SP) bands of NRs. One SP band corresponding to the transverse mode locates in the visible region at around 520 nm, while the other to the longitudinal mode in the near-infrared (near-IR) region. Since the centrifuged NR solution shows much broader longitudinal SP bands (b) than that of the initial NRs (a), the centrifuged NRs probably contain agglomerates in the solution.

Spectral changes of the NR solution irradiated by 17.5-keV of X-ray are recorded as difference spectra (Figure 2). Continuous irradiation reduced the peak intensities of the SP bands, while absorbance at around 600 nm increased. Those are typical changes for coagulation of gold NRs.

In order to clarify the dependence of the coagulation of NRs on X-ray photon energy, decreases of absorbance at the peak position of the longitudinal SP band (~700 nm) were plotted against the X-ray photon energy (Figure 3). The absorbance decrease was normalized by the photon flux of X-ray and the absorption coefficient of gold. This plot shows that the spectral change (coagulation of gold NRs) is induced when the photon energy is larger than 13 keV. Thus, photochemical processes to induce the coagulation of NRs require larger photon energy than that of the L3-edge of gold (11.9 keV).

References

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Figure 1. Absorption spectra of NR solution before (a) and after the centrifugation (b).

Figure 2. Spectral changes of gold NR solution induced by 17.5 keV of X-ray irradiation. Irradiation time: (a), 10; (b), 20; (c), 30 min.

Figure 3. Decrease of absorbance after 30 min of X-ray irradiation at the longitudinal SP band of gold NRs. The decreases were normalized by the photon flux and absorption coefficient of gold.