Enormous Size Growth of Thiol-passivated Gold Nanoparticles Induced by Near-IR Laser Light

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Irradiation of pulsed 1064-nm laser light to dodecanethiol-passivated gold nanoparticles in cyclohexane resulted in enormous growth of the particles. The size increased up to ~ 200 nanometers.

Control of particle size is one of the important keys to successful applications of metal nanoparticles because of their potentials in technological applications such as catalysts and nonlinear optical materials.[1,2] Photochemical processes are convenient and have the potential to change the size of the nanoparticles. Previous studies showed that the size of gold[3-6] and silver[7] nanoparticles in colloidal solutions were reduced by pulsed laser photofragmentation. Quite recently, somewhat size growth of gold nanoparticles using pulsed 532-nm laser light was reported; but the size was at most less than 100 nm, due to the subsequent photofragmentation.[7] In this study, we used pulsed 1064-nm laser light which was off-resonant from the plasmon bands of gold nanoparticles, and found the formation of enormously large spherical gold particles.

Cyclohexane solutions of dodecanethiol (DT)-passivated gold nanoparticles were prepared according to the previous method.[8] Hydrogen tetrachloroaurate was chemically reduced by sodium borohydride in toluene, in the presence of an appropriate amount of DT at the Au : S molar ratio of 3.5 : 1. After removing the solvents and free DT, the DT-passivated gold nanoparticles were collected, and then dispersed again in cyclohexane.

Fundamental light (1064 nm) from a Nd-YAG laser (Continuum Powerlite 8000, 6~8 ns, 350 mJ/pulse, 10 Hz) was used without focusing (cross section ~0.4 cm^2). Laser irradiation of DT-passivated gold nanoparticles in cyclohexane (3 ml, 0.25 mg/ml) was carried out in a quartz cell (1 × 1 × 4 cm) at a controlled temperature (20 °C). The colloidal solution was stirred by a magnetic stirrer. Transmission electron micrograph (TEM) observations were performed on a JEOL JEM-200CX (200 kV) electron microscope. The TEM sample was prepared by evaporating a drop of the sample solution on a copper mesh coated with a carbon film. Absorption spectra were recorded on a JASCO V-570 spectrophotometer.

Figure 1 shows absorption spectral changes of the sample colloidal solution with proceeding laser irradiation. Before irradiation, the solution showed a weak plasmon band at around 520 nm, as was reported previously for thiol-passivated gold nanoparticles.[9] This plasmon band increased very slowly in less than 20 minutes of irradiation, but subsequent irradiation accelerated the increase in the band intensity without appreciable peak shift or broadening until ~40 minutes. After 40 minutes, the spectrum was somewhat broadened in longer wavelength regions lasting as long as > 1100 nm. The plasmon band

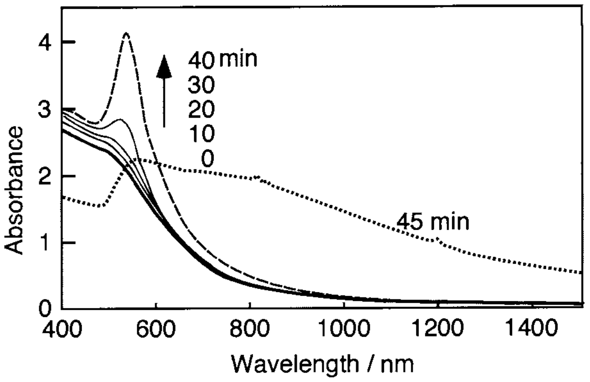

Figure 1. Absorption spectra of DT-passivated gold nanoparticles in cyclohexane (0.25 mg/ml) before (0 min: thick solid line) and after (10-45 min) irradiation by the 1064-nm laser light (350 mJ/pulse, 5-7 ns, 10 Hz).

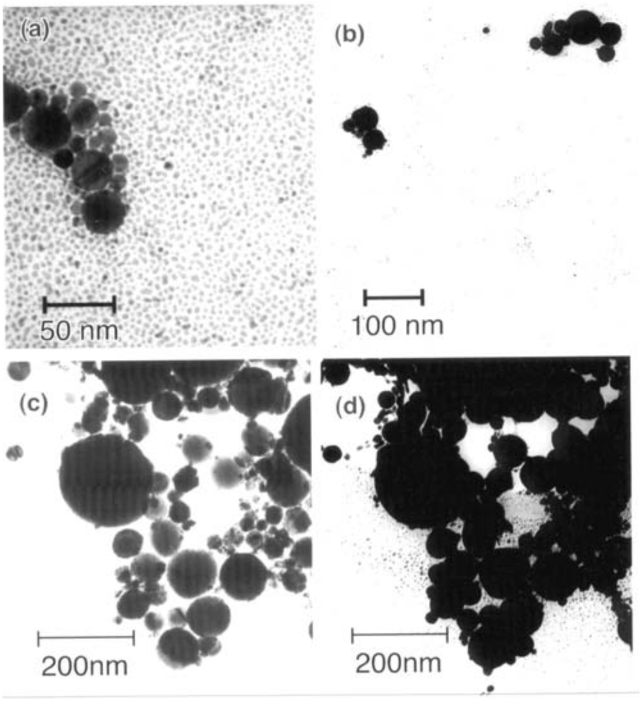

Figure 2. TEM photographs of gold colloid solution after irradiation for 20 (a), 40 (b), and 45 min (c) and (d). (350 mJ/pulse) The brightness of (c) is changed to clarify the presence of small particles as (d).

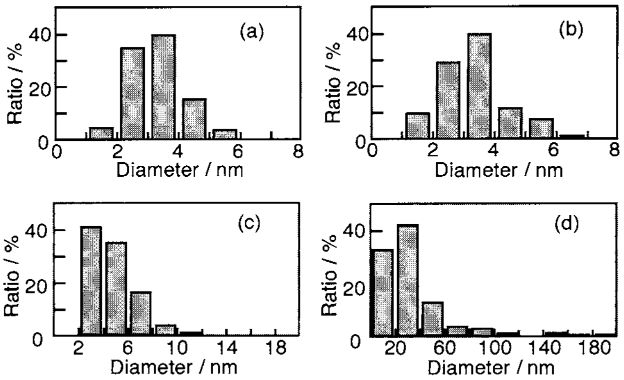

Figure 3. Size distributions of gold nanoparticles obtained by TEM photographs: (a) before irradiation, (b), (c), and (d) after irradiation for 20, 40, 45 min, respectively (350 mJ/pulse).

became very broad above 500-nm by further irradiation, indicating aggregation of the gold particle. At the same time, black precipitates formed.

In order to investigate the change of the particle size, TEM observations were carried out at some selected irradiation times, as typically shown in Figure 2. Size distribution of the gold particles were determined by counting 300 ~ 1,800 particles from the TEM photographs (Figure 3). Before irradiation, the mean diameter is 3.2 ± 0.92 nm (Figure 3(a)). After 20 minutes, some of larger particles are seen (Figure 2(a)), and the size distribution slightly shifted to larger diameters (Figure 3(b)). The size distribution of a large number of residual small particles is almost unchanged.

Considerable increase in the particle size (diameter ~ 100 nm) was seen at 40 minutes (Figure 2(b) and 3(c)). Subsequent irradiation for 5 minutes gave huge particles of as large as ~ 200-nm diameters (Figures 2(c) and 3(d)). In all cases, large particles were roughly spherical. Note that smaller particles of less than ~10 nm still coexist with the large ones. Thus, the fusion (melting) of the particles proceeds exclusively while the photofragmentation is unlikely even for the larger particles. When the 1064-nm irradiation was carried out for larger particles (~ 7.5 ± 5.0 nm) as the starting sample, huge and spherical particles were also formed within ~ 20 minutes under the identical experimental condition as Figure 1. Since the larger particles have higher absorptivities in the longer wavelength region, the absorption probability for 1064-nm photons becomes higher.

Colloidal stability of the generated huge particles was poor and black precipitates appeared slowly in the sample cell after the irradiation of longer than 40 minutes. In the presence of excess DT (0.1 mol dm^{-3}), absorption spectral changes were very small even for 40 minutes of irradiation. In addition the particle size distribution did not change appreciably. Thus, removal (and/or possible photodecomposition) of the adsorbed DT molecules at least some extent from the particle seems to be indispensable to the fusion of the particles.

In the previous reports,[3-6] nanosecond 532-nm laser excitation of gold nanoparticles resulted only in the size reduction due to combination of photofragmentation, melting, and vaporization. Somewhat increase in the particle size (< ~ 100 nm) was observed in the picosecond 532-nm laser excitation of thionicotinamide-passivated gold nanoparticles.[7] In that case, however, subsequent laser irradiation also resulted in the size reduction due to photofragmentation. Thus, experimental condition might be very critical, if any, in the case of the direct irradiation of the plasmon band.

From Figure 1, it is clear that before irradiation the particles cannot absorb 1064-nm photons effectively. Thus, the size growth, in other words, fusion by melting proceeds very slowly. When the particles becomes so large as to be able to absorb 1064-nm photons effectively, size growth will be accelerated by enhanced absorption of the photons, though the number of larger particles are still very low. On the other hand, the 1064-nm excitation must retard fragmentation of larger particles due to their lower absorptivities at 1064 nm as compared with the plasmon bands. The effect of laser power was also investigated. However, transmittance (T) of the 1064-nm laser light did not change appreciably (T = 0.80 - 0.72 for 12 - 360 mJ/pulse), suffering from unavoidable scattering and very small absorptivity (if any). Accordingly, 1064-nm excitation in cyclohexane has been successful for the size growth.

In conclusion, the use of off-resonant 1064-nm laser excitation was successful for preparing enormously large spherical gold particles, using DT-passivated gold nanoparticles in cyclohexane.

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