Laser-Induced Size Reduction of Noble Metal Particles

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Irradiation of a pulsed Nd:YAG laser at 532 nm to gold particles of less than 50 nm in aqueous solution was found to cause the shape change and size reduction of the particles. Typically, the nonspherical gold particles between 20 and 50 nm in diameter disappeared, whereas the number of gold particles of spherical shape less than 10 nm increased. The size reduction ceased after 5 min irradiation. The maximum diameter in the size distribution decreased to ca. 10 nm when the laser fluence was increased up to nearly 800 mJ cm^{-2}. The temperature of the gold particles was estimated from the absorbed laser energy by the particles and was found to rise as high as the boiling point of gold; these results were supported by the measurements of the blackbody radiation from the particles. The shape change and size reduction are considered to occur through melting and vaporization of the gold particles. The high temperature, which causes melting and vaporization, is a result of the strong absorption of the laser energy by the particles and the low heat transfer to the surrounding water.

Introduction

Small metal and semiconductor particles are used in many different fields including catalysts, microelectrodes, and nonlinear materials because they exhibit different electronic and/or optical properties from the bulk counterparts owing to their nanometer-order size.[1] It is, therefore, very important to control their size distribution in host materials. However, once the particles are formed, it is very difficult to change their size with present technologies. If the irradiation of the laser beam to the particles can change their size (which is called the laser-induced size reduction in the present paper), it may provide a novel way to alter and possibly control the size of the particles. Indeed, we showed for the first time that irradiation of a pulsed laser can change the size of the silver and gold particles.[2,3] To apply the laser-induced size reduction to the size control of particles, investigation of its mechanism in terms of the interaction between the particles and the laser light is still required.

It is well known that gold particles of several decade nanometers show distinct absorption peaked at around 520 nm, as a result of the plasmon excitation,[1] and much work has been carried out to investigate the interaction between light and gold particles. Eckstein and Kreibig[4] reported that irradiation of 514 nm laser light using a continuous wave (cw) Ar^+ ion laser accelerated the aggregation of 10 nm gold particles in aqueous solution. Photoinduced coagulation of gold nanoparticles of less than 30 nm in organic liquids was reported by Satoh et al. using a high-pressure mercury lamp.[5] Takeuchi et al. recently studied the effect of irradiation of a cw Ar^+ ion laser where both coagulation and dispersion of gold particles in organic solvents were observed.[6] Relaxation processes of photoexcited plasmon in gold particles were also extensively studied by the transient absorption method with femto- and picosecond time resolutions.[7−9]

The interaction between pulsed laser light and noble metal particles was also investigated by us, and the laser-induced size reduction of nanometer-size silver and gold particles in aqueous solution was found to occur by irradiation of a pulsed Nd:YAG laser which was tuned to the wavelength corresponding to the plasmon absorption region.[2,3] There are a few similar observations related to the interaction between pulsed laser light and noble metal particles, and several plausible mechanisms were proposed.[10,11] For example, Kamat et al. recently observed the fragmentation of silver particles in aqueous solution by irradiation of a pulsed laser.[11] They claimed that accumulation of photoejected electrons at or near the surface of the silver particle caused disintegration of the parent particles into smaller particles because of the charging. The laser-induced size reduction is a novel phenomenon caused by the interaction between pulsed laser light and the silver and gold particles, and its mechanism is not fully explored yet, although the heating effect was suggested to be the cause in the case of the gold particles in the previous publication.[3]

In this paper, we show that the laser-induced size reduction of gold particles is caused by the heating of the particles by measuring the dependence of the maximum diameter of the gold particles on the laser fluence. The shape change and size reduction will be quantitatively discussed on the basis of the temperature estimation of the gold particles.

Experimental Section

Solutions of gold particles were produced from aqueous hydrogen tetrachloroaurate by chemical reduction. Typically, 5 mg of hydrogen tetrachloroaurate(III) tetrahydrate (Wako Chemical) was dissolved in 100 cm^3 water and heated. An aqueous solution of citric acid (5 cm^3, 0.15 g dm^{-3}; in some cases, tannic acid, Wako Chemical) was added at the stage of boiling, and the solution was agitated. A wine-red-colored solution of gold particles was soon obtained. The size distribution of the gold particles ranged from 5 to 50 nm, which was determined from transmission electron microscope (TEM) photographs. These solutions were stable for more than 1 month, when kept at 10 °C.

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For the laser irradiation experiment, 2 cm^3 of the solution was introduced in a rectangular quartz cell of $1 \times 1 \times 4$ cm^3. The solution was irradiated under agitation using a magnetic stirrer with the second harmonic of a Nd:YAG laser (Spectra-Physics DCR-11, 10 Hz, pulse length nominally 7 ns) at 532 nm. The laser beam cross section was determined by the burned pattern printed on a thermal recording paper, and was typically 0.38 cm^2. The laser pulse energy was measured by a power meter (Coherent, 200+). The energy was measured in front of and behind the cell, from which the absorbed laser energy by the gold particle solution was calculated.

The extinction spectra of the sample were measured by a UV−vis spectrometer (model U4000, Hitachi). The size distribution of the gold particles was obtained from the TEM (model H-7000, Hitach) photographs; the sample was prepared by the following procedure. A drop of the gold particle solution was placed on a copper grid, which was covered by a collodion film, and was dried in a desiccator. The particle size is defined as the average of the longest and shortest diameter of the particle. The minimum size of the gold particle measurable by TEM photographs is about 1 nm.

The emission from the gold particles in aqueous solution under the laser irradiation was measured with a photon counting system (model PMA-100, Hamamatsu). Two lenses were placed at right angle to the irradiation laser beam to collect the emission. A filter to cut the laser scattering light of 532 nm was placed between two lenses. A charge coupled device (CCD) detector was attached to a 50 cm monochromator. To minimize the effect of the jitter of the laser pulse, a photodiode was used to trigger a pulse generator, which controlled the delay and the gate width of the CCD detector. Emission was recorded for the wavelength region shorter than 800 nm because the sensitivity of the CCD detector decreased above 800 nm. The whole emission measurement system was calibrated by a calibrated lamp (model 7027B8H, Philips).

Results

A typical result of the pulsed-laser irradiation to the gold particles is first presented. A sample of the gold particles in aqueous solution was irradiated with a fluence of 210 mJ cm^{-2} for 10 min at 532 nm, and TEM photographs of the gold particles were taken before and after the irradiation, as shown in Figure 1. Comparing Figure 1(a) with (b), we can clearly observe the size reduction and shape change of the gold particles. Before the irradiation, the particle shape is not spherical, whereas after the irradiation, it is spherical, although relatively smaller particles in Figure 1(b) are connected to each other. To compare the particle size quantitatively, the size distribution was obtained from the TEM photographs. As shown in Figure 2, before the irradiation, the size is distributed between 19 and 47 nm, whereas after the irradiation, it is between 5 and 21 nm. The particles larger than 21 nm completely disappear and the number of the particles smaller than 20 nm increases. The peak of the distribution in Figure 2 is about 11 nm. These observations clearly show that the size reduction of the gold particles occurs by the irradiation of the pulsed laser.

According to Mie theory, the peak shift is expected to be observed in an extinction spectrum when the size distribution of the particles changes. Extinction spectra of the same samples as those used for Figure 1 were taken, and the peak shift from 531.5 to 517.0 nm was observed along with the irradiation, as shown in Figure 3. This qualitatively corresponds to the size reduction of gold particles observed in the TEM photographs. However, because the size reduction cannot be estimated quantitatively by applying Mie theory to the extinction spectra, the size distribution obtained from the TEM photographs is used for the following discussion.

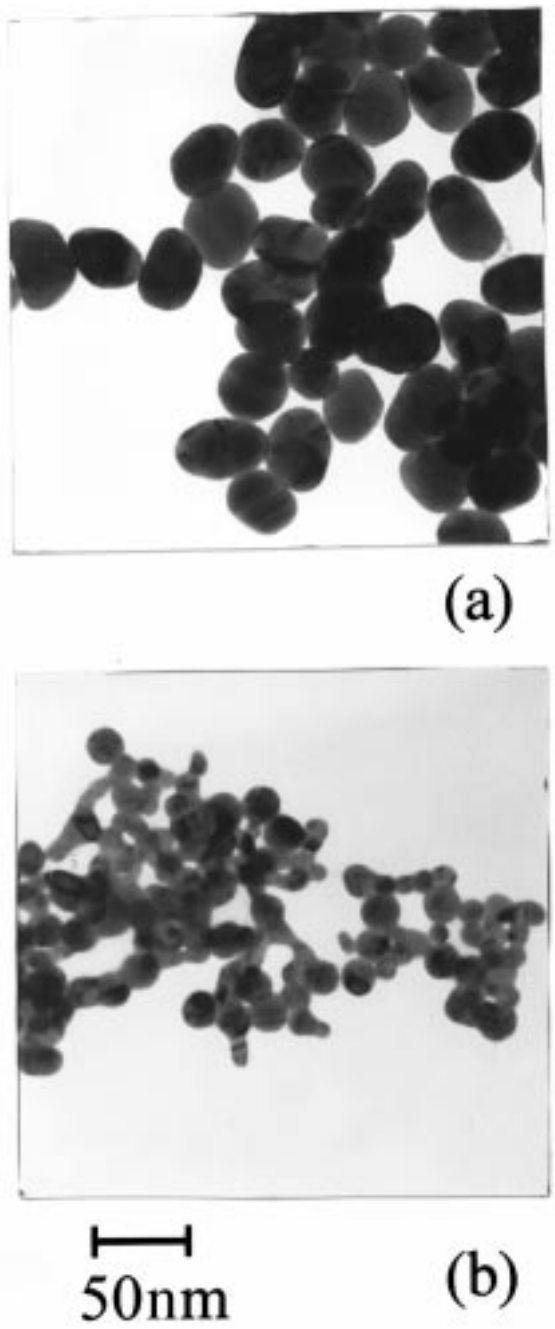

Figure 1. TEM photographs of the gold particles recorded with a magnification of 150 000: (a) before irradiation and (b) after irradiation with 210 mJ cm^{-2} and 10 Hz for 10 min.

As an extension of our previous research, dependence of the size reduction on the irradiation time and on the laser fluence was investigated in detail and will be discussed.

Effect of the Irradiation Time. To investigate the effect of the irradiation time on the size distribution, a sample of the gold particles was irradiated from 0 to 120 min with a laser fluence of 140 mJ cm^{-2}. The size distributions are shown in Figure 4. Features of the irradiation time dependence are as follows. The change of the size distribution is remarkable after 1 min irradiation, as shown in Figure 4(b). The number of particles around 5−10 nm in diameter increases drastically, whereas the particles larger than ca. 30 nm completely disappear.

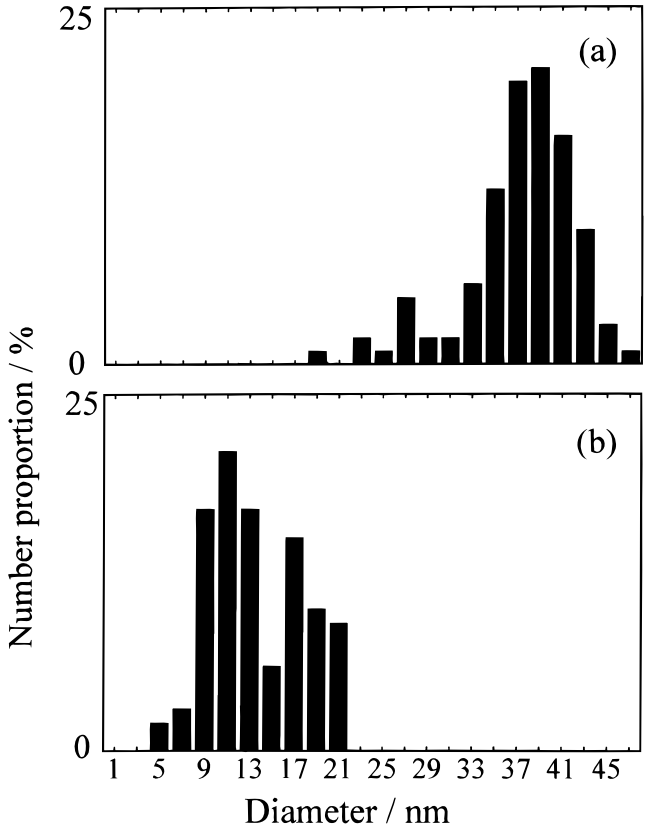

Figure 2. Size distributions of the gold particles obtained from TEM photographs: (a) before irradiation and (b) after irradiation with 210 mJ cm^{-2} and 10 Hz for 10 min.

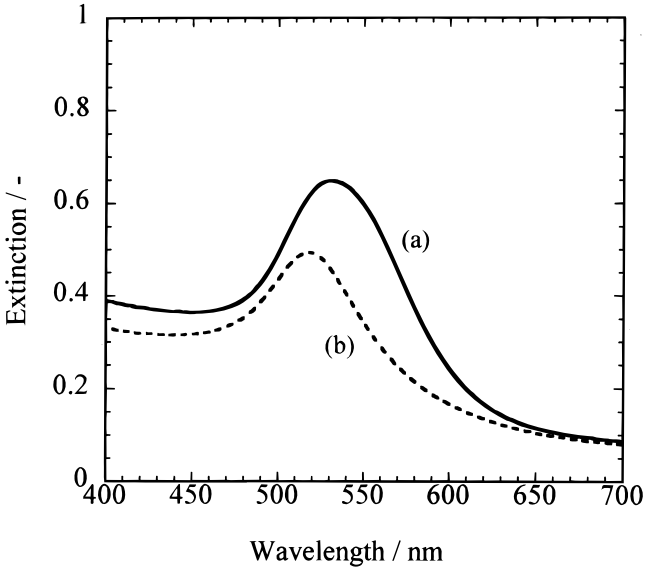

Figure 3. Extinction spectra of the gold particles recorded by a UV−vis spectrometer: (a) before irradiation (solid line) and (b) after irradiation with 210 mJ cm^{-2} and 10 Hz for 10 min (dashed line).

The size reduction seems to continue up to 5 min and the particles larger than ca. 22 nm disappear by 5 min. Longer irradiation than 5 min alters the size distribution very little. Comparison between Figures 4(c) and (d) shows that the size distribution after 120 min irradiation is similar to that for 5 min irradiation. In addition, the maximum diameter in the size distribution does not change for the long period of irradiation at this laser fluence. The maximum diameters are 22 nm in both Figures 4(c) and (d). In other words, the maximum diameter can be regarded as a threshold diameter for the laser-induced

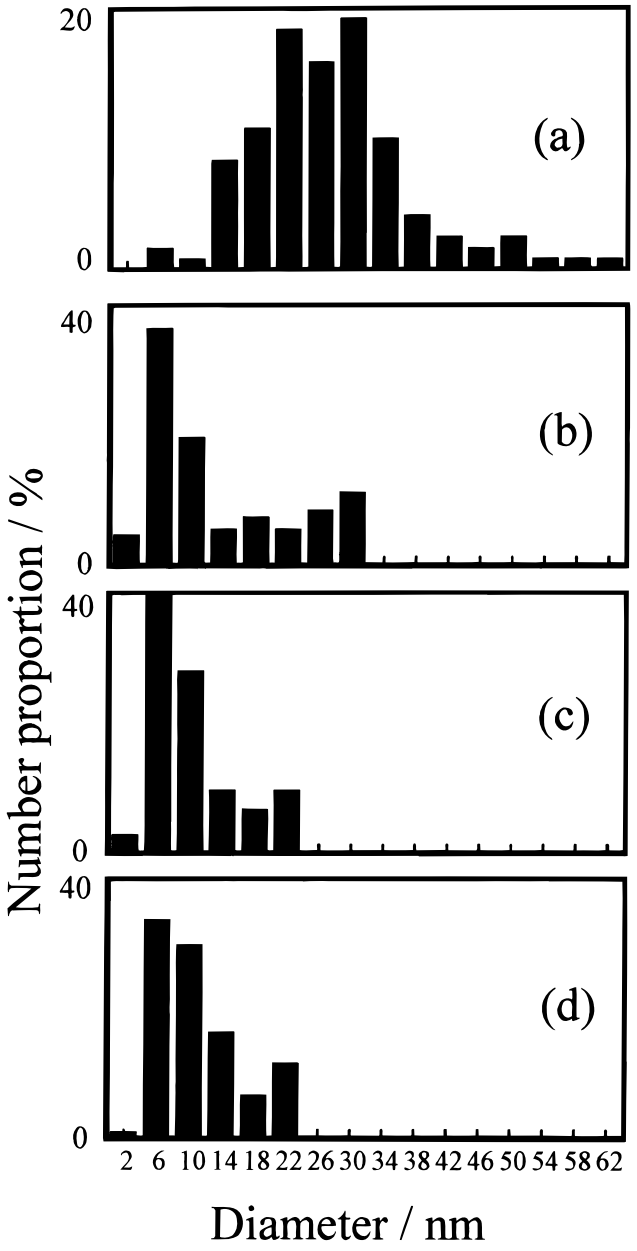

Figure 4. Size distributions of the gold particle obtained from TEM photographs: (a) before irradiation and (b), (c), and (d) after irradiation with 140 mJ cm^{-2} and 10 Hz for 1, 5, 120 min, respectively.

size reduction at a particular laser fluence. Hereafter, the maximum diameter is considered to be the threshold diameter for the laser-induced size reduction.

Effect of the Laser Fluence. To investigate the effect of the laser fluence, a sample of the gold particles was irradiated for 10−15 min with a varying laser fluence. Because the size distribution changes very little after 5 min irradiation, a period of 10−15 min irradiation is considered to be enough to investigate the dependence of the laser fluence. The initial size distribution ranged from 11 to 45 nm for the present investigation of the effect of the laser fluence. With the fluence of 14 mJ cm^{-2}, neither the size nor the shape changed. This is recognized by comparison between Figure 1(a) and Figure 5(a). The particles in Figure 5(a) remain nonspherical with a maximum diameter of 45 nm. With the fluence of 28 mJ cm^{-2}, only the shape of the particle changed, which is seen by comparison between Figure 1(a) and Figure 5(b). For our typical conditions, the shape change occurred at a fluence of 16 mJ cm^{-2}. The shape of the particles in Figure 5(b) is spherical,

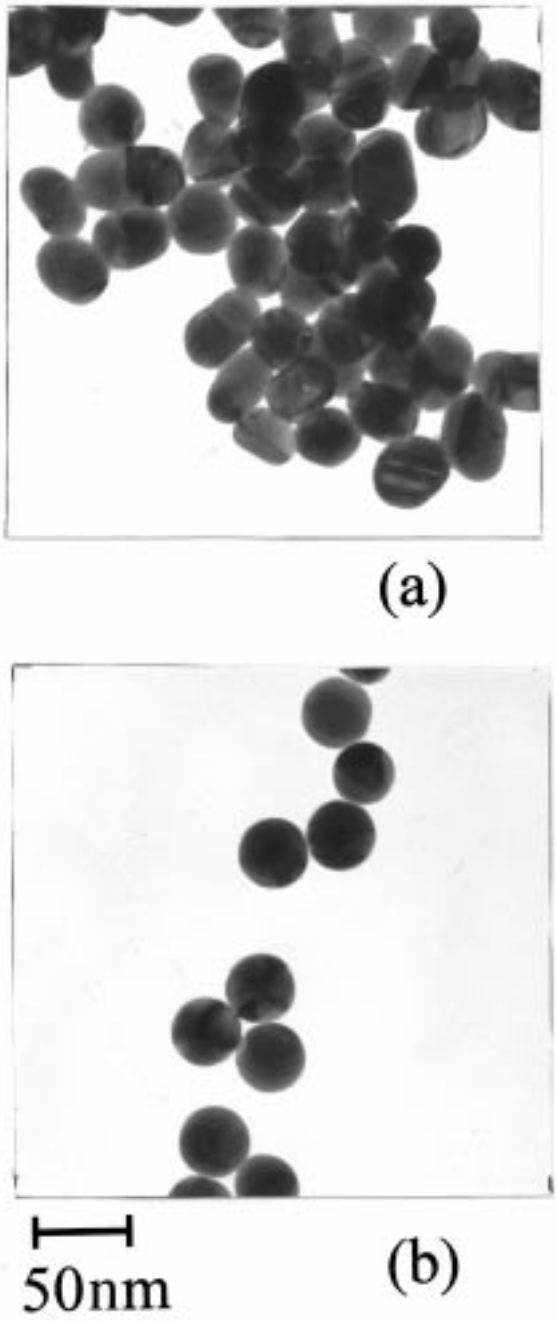

Figure 5. TEM photographs of the gold particles recorded with a magnification of 150 000: irradiation with 10 Hz for 10 min (a) with 14 mJ cm^{-2}, and (b) with 28 mJ cm^{-2}.

although the maximum diameter of the particles is 45 nm. When the fluence was increased, both the shape and the size changed and the maximum diameter of the gold particles gradually decreased. In Figure 6, the maximum diameters obtained from the TEM photographs are plotted as a function of the laser fluence. As shown in Figure 6, the maximum diameter seems to be determined by the laser fluence. For the fluence region lower than about 30 mJ cm^{-2}, the maximum diameter does not change. For the middle fluence region between 30 and 500 mJ cm^{-2}, the maximum diameter decreases as the laser fluence increases. For the laser fluence greater than 500 mJ cm^{-2}, the maximum diameter appears to be constant at ca.10 nm. When the sample that was diluted three times was used, the phenomena were the same as above, and the 10 nm particles were also observed with a fluence of about 800 mJ cm^{-2}.

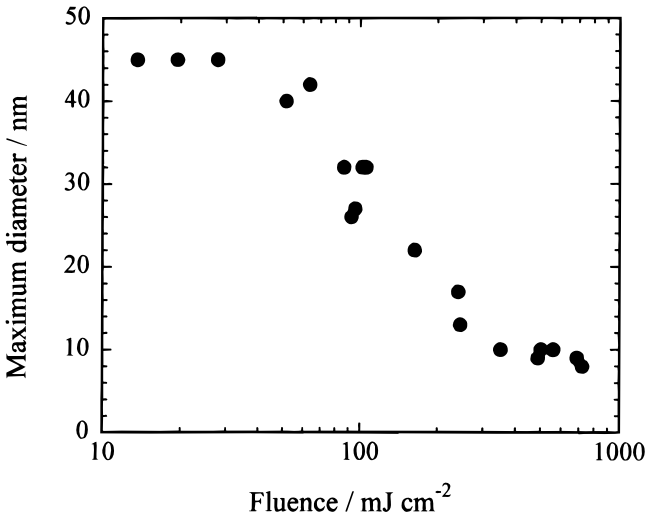

Figure 6. Dependence of the maximum diameter on the laser fluence.

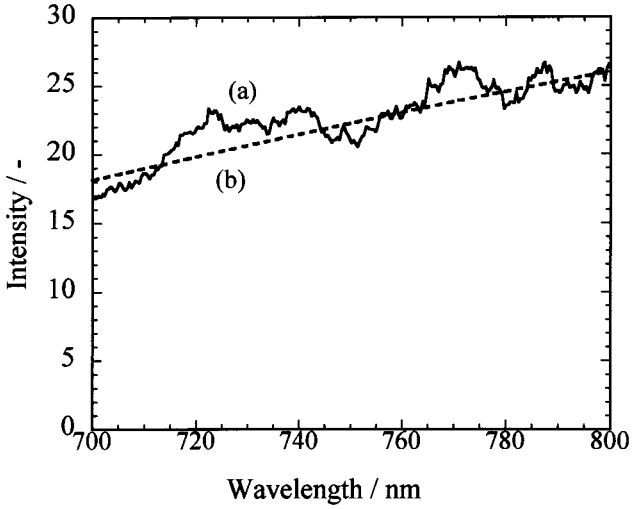

Figure 7. Emission spectra of the gold particles recorded with the photon counting system: (a) experimental spectrum (solid line) and (b) simulated spectrum (dashed line).

Blackbody Radiation from the Irradiated Particles. As we proposed in the previous paper,[3] the laser-induced size reduction is considered to be caused by the high temperature of the gold particles. If this is true, a blackbody radiation from the gold particles might be observed. The emission spectra of gold particles were taken with a photon counting system. A typical spectrum shown in Figure 7 was taken after 0.2 μs from the laser irradiation pulse with a gate width of 1.0 μs. The temperature was obtained from the spectrum by applying the Stefan−Boltzmann law, assuming that the emissivity is independent of the observed wavelength. The simulated intensity was normalized to the experimental intensity at 700 nm. The temperature obtained from the emission spectra is 2500 ± 100 K with $\pm 1.65\sigma$. The emission signal was not detectable after 100 μs from the laser irradiation, which indicates that the temperature of gold particles considerably cooled by 100 μs.

Discussion

Temperature of the Gold Particles. To determine whether the laser-induced size reduction of the gold particles is caused by the heating of the particles because of the absorption of the pulsed laser light, it is very important to estimate the temperature of the gold particles quantitatively. In this section, the temper-

ature of the gold particles is estimated directly from the measured absorbed laser energy by the gold particles. At first, the absorbed laser energy by the gold particles per unit mass of gold atom and per one pulse, Q (J g^{-1} pulse^{-1}), is calculated by

$$Q = \frac{E}{RCV} \tag{1}$$

where E is the laser energy absorbed by the solution of the gold particle per unit time (J s^{-1}) measured by the power meter, R is the repetition rate of the pulsed laser (10 Hz), C is the mass concentration of gold (g m^{-3}), and V is the irradiated volume of the solution (m^3).

Heat loss should be considered next. One of the heat loss processes is the conductive/convective heat loss to the surrounding water. In the present case, the boiling heat transfer is considered to be obeyed because the temperature of the gold particles is much higher than that of the surrounding water. The boiling heat transfer flux q from the ordinary material in water is at most 10^6 J m^{-2} s^{-1} when the temperature difference between the material and water is 10^3 degrees.[13] The second heat loss process is the radiative heat transfer whose flux from a blackbody is δT^4, where δ is the Stefan−Boltzmann constant, assuming that the emissivity is unity. The heat loss processes are calculated with the 45 nm particle at the boiling point of the gold. The conductive/convective heat loss from the 45 nm particles to water is estimated to be 4.5×10^{-17} J per particle per 7 ns, which is the nominal pulse duration of the laser. The radiative loss from the particles at the boiling point is estimated to be 2.3×10^{-16} J per particle per 7 ns. On the other hand, the minimum absorbed laser energy per one gold particle to cause the size reduction is 4.0×10^{-13} J for a 45 nm particle. The ratio of the sum of the two heat loss processes to the minimum absorbed laser energy is 6.9×10^{-4}. The same calculation is carried out for the particle of 25 and 10 nm in diameter, and the ratios are 1.2×10^{-3} and 3.1×10^{-3}, respectively. Thus, the heat loss processes within 7 ns are considered to be negligible compared to the absorbed laser energy.

The temperature, T (K), of the gold particles can be estimated on the basis of the absorbed laser energy by eqs 2 and 3 for higher temperature than the boiling point and the melting point, respectively, using bulk physical constants. The initial temperatures were considered to be room temperature (293 K).

$$T = \frac{Q - \Delta H_{\mathrm{melt}} - \Delta H_{\mathrm{vap}}}{C_{\mathrm{p}}} + 293 \tag{2}$$

$$T = \frac{Q - \Delta H_{\mathrm{melt}}}{C_{\mathrm{p}}} + 293 \tag{3}$$

where ΔH_{melt} is heat of melting (6.28×10^1 J g^{-1}), ΔH_{vap} is heat of vaporization (1.87×10^3 J g^{-1}), and C_{p} is the specific heat (0.131 J g^{-1} K^{-1}, independent of the phase). The heat loss is omitted because it is negligible within the laser pulse duration, as already mentioned. When eq 4 is true, the temperature is considered to be at the boiling point, and when eq 5 is true, temperature is at the melting point.

$$0 \le Q - (\Delta H_{\mathrm{melt}} + C_{\mathrm{p}} \times \Delta T_{\mathrm{b}}) \le \Delta H_{\mathrm{vap}} \tag{4}$$

$$0 \le Q - (C_{\mathrm{p}} \times \Delta T_{\mathrm{m}}) \le \Delta H_{\mathrm{melt}} \tag{5}$$

where ΔT_{b} and ΔT_{m} are difference between the boiling point and room temperature and between the melting point and room temperature, respectively. Estimation of temperature with bulk physical constants may be justified by the fact that the melting point of the gold particles decreases drastically only when the particle size is less than 5 nm.[14,15] Because the initial diameter of the gold particle in this experiment is larger than 5 nm, we consider that the physical constants of the metal gold may be applied as a first approximation for our analysis.

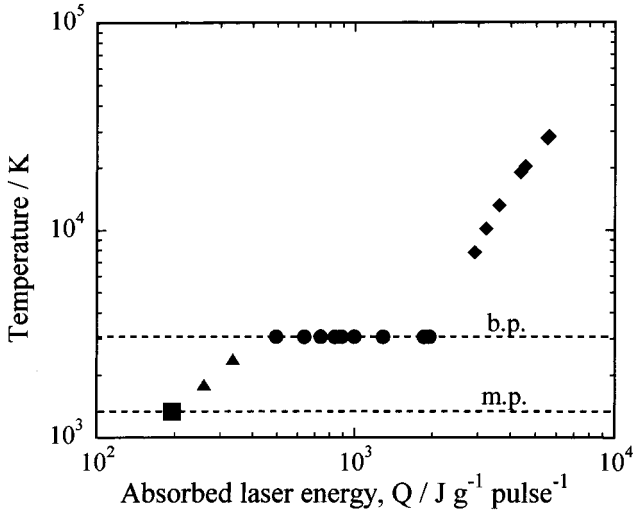

Figure 8. Dependence of the estimated temperature of the gold particles on the absorbed laser energy, Q. The meaning of the symbols is as follows: (■) neither shape nor size change is observed; (▲) only shape change is observed; (●) both shape and size change are observed and the maximum diameter is dependent on the absorbed laser energy, Q; (◆) both shape and size change are observed, and the maximum diameter is independent of the absorbed laser energy, Q, and is constant at ca.10 nm.

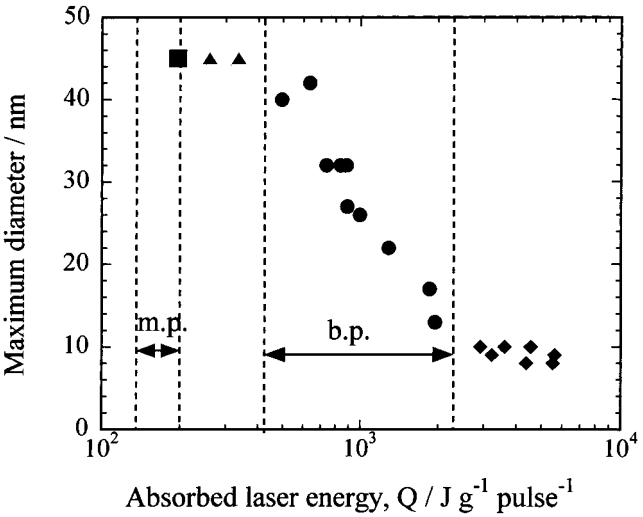

Figure 9. Dependence of the maximum diameter on the absorbed laser energy, Q. Symbols are same as those in Figure 8.

The temperature and the maximum diameter of the gold particles are plotted as a function of absorbed laser energy, Q, as shown in Figures 8 and 9, respectively. By comparing Figure 6 with Figure 9, one can recognize that the absorbed laser energy is almost linearly related to the fluence. Figure 8 clearly shows that the temperature of the gold particle can rise to the high temperature with an increase in the absorbed laser energy. The reason for the high temperature is considered to be because of the relatively large absorption of the pulsed laser energy by the gold particles, the plasmon absorption of which is large at 532 nm, compared with the heat transfer to the surrounding water, which is negligible. From Figures 5, 8, and 9, the following

features are elucidated. If the temperature is lower than the melting point, neither the shape nor the size change is observed, as indicated by filled squares (■). If the temperature is between the melting point and the boiling point, only the shape change is observed, as indicated by filled triangles (▲). If the temperature is at the boiling point, both the shape and the size changes, and the maximum diameter depends on the absorbed laser energy, as indicated by filled circles (●). If the temperature is higher than the boiling point, the maximum diameter is constant at ca. 10 nm, as indicated by filled rhombi (◆). The meaning of the temperature higher than the boiling point should be interpreted such that the absorbed laser energy is enough to completely vaporize the gold particle into atoms and/or small particles. Thus, the change of shape and size quantitatively relates to the temperature. Therefore, we conclude that the laser-induced size reduction of the gold particles is caused by the heating of the particles as a result of the absorption of the pulsed laser light.

As was mentioned, the temperature of the gold particles measured by the photon counting system is 2500 ± 100 K in Figure 7. The temperature estimated using eq 3 for the same condition is 2700 K. Using the fourth-order Runge−Kutta method, we estimate the temperature decrease of the gold particle with the conductive/convective heat transfer, q, of 10^6 J m^{-2} s^{-1} and the radiative heat transfer, δT^4, where δ is the Stefan−Boltzmann constant. When the emissivity is assumed to be unity, the estimated temperature is about 2480 K at 0.2 μs, which is considered to be high enough to detect the blackbody radiation. The estimated temperature reaches as low as room temperature by 70 μs, assuming that the emmissivity is 0.02.[13] It is understandable why the emission was not observed at 100 μs. Because the pulse-to-pulse interval is 100 ms, the particle completely cools to room temperature when the next laser pulse irradiates the particle.

Mechanism of the Laser-Induced Size Reduction. A mechanism of the laser-induced size reduction is proposed and the experimental results are explained. When the laser irradiates to the gold particles, plasmon in the gold particle absorbs photons and the electrons are excited. The relaxation from plasmon to lattice is very rapid and the lattice phonon mode is excited.[7,8] The temperature of the gold particles can be considered to be uniform because the root-mean-square distance of thermal diffusion of gold is about 1.5 μm for 10 ns, which is much larger than the diameter of the gold particle used in this experiment. The macroscopic heat loss from the gold particle is very small in 7 ns compared with the absorbed laser energy by the gold particle per pulse. Thus, the temperature of the gold particle is elevated. The shape change takes place because of the melting of the gold particle. Above the melting point, the gold particle melts and becomes liquid. Because the liquid droplet is considered to be spherical, the nonspherical shape is lost and the gold particle becomes spherical. As shown in Figure 8, the shape change occurs when the temperature is higher than the melting point. The size reduction takes place because of the vaporization of the gold particle. When the temperature of the gold particle rises to the boiling point, atoms and/or small particles are ejected through vaporization. As a result, the particle size is reduced. The amount of the ejected atoms and/or small particles depends on the absorbed laser energy, Q, as is clearly shown in Figure 9. The maximum diameter is determined through the balance between the ejection of atoms and/or small particles through vaporization and the deposition of ejected atoms and/or small particles on the particle. Because the ejected atoms and/or small particles are very unstable in aqueous solution, they tend to agglomerate and/or deposit on the gold particles remaining in the solution. As a preliminary experiment, the gold particles were irradiated in gelatin. Only 1−3 nm particles were detected and no particle larger than 10 nm was present. This indicates that the surrounding medium affects the particle size after irradiation. In aqueous solution, we consider that even the 10 nm particle is vaporized and the balance of the vaporization and the deposition of atoms and/or small particles determines the particle size.

The cross section of the quartz cell for the gold particle solution, where the laser beam irradiated, is about five times larger than the laser beam cross section. It takes about 30 s for 99% of the solution to be irradiated by more than one pulse, assuming that it takes 1 s for the solution in the cell to be uniform by agitation. The laser-induced size reduction is considered to be completed within one pulse of the laser. However, the change of the size distribution continues longer than 30 s, possibly up to 5 min as shown in Figure 4. This may be explained by the effect of deposition of ejected atoms and/or small particles onto the particle, which makes the particle larger and retards the size reduction.

The accumulation of photoejected electrons from a silver particle by two photon absorption with 355 nm irradiation at or near the surface of the particles supposedly leads to disintegration of the silver particles.[11] Because the work function of silver is about 4.3 eV, two photon absorption of 355 nm irradiation can eject photoelectrons. However, the work function of bulk gold is 5.1 eV, which is larger than two photon absorption of 532 nm (4.7 eV). Thus, the same mechanism as applied to the disintegration of the silver particle cannot be obeyed in the laser-induced size reduction of the gold particle, although occurrence and minor contribution of multiphoton absorption cannot be completely excluded.

The present laser-induced size reduction may be a seed for very useful technologies. For example, gold particles are known to be a good material with a high third-order susceptibility and have been used for the nonlinear material in aqueous solution.[16,17] To obtain the large third-order nonlinear optical response, volume fraction of the gold particles in the host materials should be increased. On the other hand, if the number density of the gold particles is too high in host materials, low optical response results because of the large absorption. In this case, the laser-induced size reduction may be used to control both size and volume fraction of the gold particles directly by the vaporization of the gold particle in the host materials.

In the present model for the size reduction, we have not taken into account the possibility that the absorption coefficient of the particles does not scale with their volume or that the plasmon absorption shifts with the size reduction. It is expected that these features might also play some role in the determination of the size distribution. With the analysis of these effects more precisely in future, the sophisticated technology of the nanoparticle size control is expected to be realized.

Conclusion

Irradiation of a pulsed Nd:YAG laser at 532 nm to the gold particles in aqueous solution causes the shape change and laser-induced size reduction. The maximum diameter after the laser irradiation depends on the absorbed laser energy by the gold particles. The shape change is due to the melting and the size reduction is due to the vaporization of the gold particles. The melting and vaporization of the gold particles are due to the high temperature built up inside the particles. The high temperature is caused by the large absorption of pulsed laser

energy by the gold particles and the low heat transfer to the surrounding water.

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