Controlling the Pulsed-Laser-Induced Size Reduction of Au and Ag Nanoparticles via Changes in the External Pressure, Laser Intensity, and Excitation Wavelength

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ABSTRACT: The laser-induced size reduction of aqueous noble metal nanoparticles has been the subject of intensive research, because of the mechanistic interest in the light–nanoparticle interactions and its potential application to size control. The photothermal evaporation hypothesis has gained solid support. However, the polydispersity of the final products is considered as an inherent drawback of the method. It is likely that the polydispersity arises from the uncontrolled heat dissipation caused by vapor bubble formation in the ambient atmosphere. To overcome this problem, we applied high pressures of 30−100 MPa. The particle size was regulated by adjusting three parameters: the pressure, laser intensity, and excitation wavelength. For example, starting from a colloidal solution of 100 nm diameter gold nanoparticles, highly monodisperse (±3−5%) spheres with various diameters ranging from 90 to 30 nm were fabricated by tuning the laser intensity at 100 MPa, using an excitation wavelength of 532 nm. Further size reduction of the diameter to 20 nm was achieved by reducing the pressure and switching the excitation wavelength to 355 nm. It was found that the application of high pressures led to the heat loss-controlled size-reduction of the gold nanoparticles. More complicated results were obtained for 100 nm silver nanoparticles, possibly because of the different size-dependent light-absorbing nature of these particles. Based on our extensive experimental studies, a detailed picture was developed for the nanosecond laser-induced fabrication of gold and silver nanoparticles, leading to unprecedented size control.

INTRODUCTION

The interactions of noble metal nanoparticles (NPs) with pulsed lasers have been the subject of intensive research for more than a decade, with the aim of improving the basic understanding of light–nanomaterial interactions. Ultrafast excitation with a femtosecond laser revealed the generation and instantaneous relaxation of hot electrons (electron−electron relaxation), lattice heating by thermalized electrons (electron−lattice relaxation), and heat transfer to the surrounding medium (lattice−lattice relaxation).1−4 Picosecond and nanosecond laser excitation of the localized surface plasmon resonance (LSPR) band resulted in the melting and size-reduction of NPs in solution. This laser-induced size reduction of noble metal NPs has attracted a great deal of attention because of the melting of the particle (mp: 1337 K); the size-reduction was assumed to take place via evaporation from particles heated above their boiling point (bp: ≈3100 K) when the particles are subjected to high-intensity nanosecond pulses.6 This photothermal model for the morphological changes in NPs was supported by the results of rigorous calculations for the time profile of a particle temperature as a function of the laser intensity.6 Despite these promising theoretical results, however, typical photothermal size reduction experiments show the formation of polydisperse particles and interconnected structures.6,8−11 The polydispersity may arise as a consequence of vapor bubble formation around the particles as they reduce in size. It has been shown that photothermal vapor bubble formation takes place during the pulsed-laser excitation of Au NPs dispersed in water, when laser fluences that are likely to cause size reduction are used.12−15 It has also been demonstrated that NPs are formed inside the cavitation bubbles that form during the laser ablation of Ti, Au, and Ag targets.16,17

The size reduction depends on both the exposure period and the laser fluence, as shown in Scheme 1. It has been shown that the average particle size reduces with increasing irradiation time when growth processes such as fusion are absent (Scheme 1a).6 In the photothermal process, insufficient cooling of the laser-heated NPs inside the bubbles (which act as a thermal shield) could be one reason for the efficient vaporization from the particles. This would suggest that poor management of the laser-generated local heating could cause uncontrollable size...
pressure and excitation wavelength. Specifically, Au sphere diameters ranging from 90 to 20 nm and narrow size distributions were achieved, by adjusting the laser fluence and pressure, and by choosing the excitation wavelength. Moreover, by incorporating a heat loss-controlled reaction protocol, we made progress in the interpretation of the data.

**RESULTS AND DISCUSSION**

**Size Reduction of 100 nm Au NPs.** Aqueous colloidal Au NPs with an average diameter of 100 nm (100 ± 8 nm) were subjected to excitation with a 532 nm nanosecond pulsed laser, under a hydrostatic pressure of 100 MPa. Irradiation was carried out with different laser energy densities (fluences: mJ cm$^{-2}$) for various numbers of laser pulses, and TEM images were acquired after irradiation. Figure 1 summarizes the results for 72 000–108 000 laser pulses, showing TEM images and the corresponding particle size distribution histograms (see Supporting Information, Figure S2 for extinction spectra). The inspection of Figure 1 reveals that remarkably spherical Au NPs were formed. The spheres were highly monodisperse (±3–5%) after irradiation with a sufficient number of laser pulses (as described above). Further irradiation did not reduce the particle size or improve the size distributions. We found that the final size distribution was determined by the pulse-to-pulse laser fluctuations. Most importantly, the diameters of the Au NPs thus prepared were laser fluence-dependent: the diameter progressively decreased with increases in the laser fluence. It should be noted that besides these very spherical particles, small Au particles with diameters below 10 nm were formed. These small particles can be seen in the background of the TEM images shown in Figure 1.

In a previous study, we investigated the size reduction of 58 nm Au NPs by applying high pressures ranging from 30 to 200 MPa. We employed a small cuvette volume of 0.4 mL (4.0 mm × 4.0 mm × 2.5 mm), and the solutions were not agitated. The small volume was used to maximize the volume of the solution that could be irradiated with a laser beam 4.2 mm in diameter; however, effective heat convection, the importance of which will be mentioned below, was not considered. Because of these technical deficiencies, monodisperse size distributions were not achieved in these experiments.

In the nanosecond laser excitation regime, size reduction is considered to occur via photothermal evaporation from Au NPs heated above their boiling temperature by laser heating. This model predicts the evaporation of atoms and clusters from the particle surface, leaving core particles. The model might explain the observations of Figure 1, but it is also possible that small evaporated clusters could coalesce to form particles 

**EXPERIMENTAL METHODS**

Au NPs were obtained from British Biocell International (EMGC100, diameter 100 ± 8 nm determined using TEM, see Supporting Information, Figure S1; 5.6 × 10$^{-3}$ mL$^{-1}$), and Ag NPs were purchased from Sigma-Aldrich (#730777, nominal diameter of 100 ± 7 nm, 3.6 × 10$^{-3}$ mL$^{-1}$). The laser irradiation of 2 mL aliquots of aqueous colloidal solutions contained in a quartz cuvette (optical path length 1.0 cm, width 1.0 cm, height 2.0 cm) was conducted using the second and third harmonics of an Nd:YAG laser (Continuum, Surelite I-10). The cuvette was placed in a hydrostatically pressurized container ($<$100 MPa) similar to the one described previously, but this container was modified to incorporate cuvettes with >2 mL volumes instead of 0.4 mL, and to allow the agitation of the solution. This change in the design permitted a forced-convective heat transfer. The NP solutions were agitated using a magnetic stirrer during the irradiation. The laser parameters were as follows: wavelength, 532 and 355 nm; repetition rate, 10 Hz; pulse width, 5–6 ns full width at half-maximum; beam area, (0.12 ± 0.01) cm$^2$. TEM photographs of the particles were recorded on a JEM-2100F microscope (JEOL) operated at 200 kV. The specimens for the TEM measurements were prepared by placing one drop of a sample solution on a support consisting of Cu mesh coated with an evaporated 13 nm thick carbon film. The support was dried under vacuum. The preparation of the TEM specimens was carried out on the same day as the laser irradiation. The software package Image J (http://rsbweb.nih.gov/ij/) was used to process the particle images.
A Au NPs. Laser pulses, (d) 90.2 mJ cm\(^{-2}\). Figure 2 summarizes the mean diameters of the generated spherical particles as a function of laser fluence at 30, 60, and 100 MPa. The mean diameter decreased nonlinearly with increases in the laser fluence. This observation showed that increasing laser fluences were required to form smaller core particles. The laser fluence-dependent size reduction was also found to be pressure-dependent (for example, see Supporting Information Figure S4 for the size distribution at 60 MPa). For increasing pressures (30 < 60 < 100 MPa), higher laser fluences were required to achieve similar particle diameters. This might have been partly due to the differences in the boiling points (bp) of the particles, because the boiling point of bulk gold is pressure-dependent. By applying the Clausius–Clapeyron equation, the bp was calculated as 5500 K at 30 MPa, 6200 K at 60 MPa, and 6800 K at 100 MPa. Additionally, the convective/conductive heat transfer in water is pressure-dependent, as will be described below. These results suggested that the pressure values, as well as the laser fluences, were decisive in controlling the final core particle diameter. At 100 MPa, we found it difficult to prepare monodisperse core particles with diameters ≤30 nm, because at laser fluences of ≥140 mJ cm\(^{-2}\) the size distribution suddenly became wide. In contrast, at 30 MPa, particles with a minimum core diameter of 20 nm were prepared with a size distribution of ±15%. These results suggested that the core particle sizes could be fine-tuned by adjusting either the laser fluence or the external pressure. Although the size distribution was very narrow at 100 MPa, a much wider distribution was observed at 30 MPa. To investigate the dependence of the size reduction on the excitation wavelength, laser irradiation was performed at 355 and 532 nm, at a pressure of 30 MPa. As shown in Figure 3, smaller core particles were formed at 355 nm than at 532 nm, with similar laser fluences. These results showed that the size reduction efficiency was higher under excitation at 355 nm. The effects of the excitation wavelength will be detailed and explained below.

Size Reduction of 100 nm Ag NPs. The generation of size-controlled, monodisperse core particles from initial 100 nm Au NPs via the adjustment of the laser fluence at high pressures prompted us to investigate the applicability of the method to other materials. We measured the laser fluence-dependent size reduction of ≈100 nm Ag NPs at 60 MPa, as shown in Figure 4 (for the changes in the extinction spectra, see Supporting Information Figure S5). The laser fluence-dependent core diameter curves for the Ag NPs were also excitation wavelength-dependent, but were noticeably different from those observed for the Au NPs. Under excitation at 355 nm, a sudden decrease in the core diameter was observed when the laser fluence was increased from 35 to 45 mJ cm\(^{-2}\); the average diameter dropped from 90 to 20 nm. In contrast, at an

Figure 1. Particle images (TEM photographs) and corresponding size distributions at 100 MPa after irradiation with 532 nm nanosecond laser pulses (10 Hz) at various laser fluences, for the original 100 nm Au NPs. Laser fluences and pulse numbers: (a) 43.1 mJ cm\(^{-2}\), 72 000 pulses, (b) 60.2 mJ cm\(^{-2}\), 72 000 pulses, (c) 78.0 mJ cm\(^{-2}\), 90 000 pulses, (d) 90.2 mJ cm\(^{-2}\), 108 000 pulses, (e) 106.5 mJ cm\(^{-2}\), 108 000 pulses, (f) 136.6 mJ cm\(^{-2}\), 108 000 pulses. The number of particles measured ranged from 700 to 1300. NPs with diameters bigger than 10 nm were counted. The 100 nm scale bar is applicable to all of the TEM images. Corresponding extinction spectra are given in Supporting Information Figure S2.

Figure 2. Mean diameter of Au NPs as a function of laser fluence at 30 MPa (red curve with closed green diamonds), 60 MPa (green curve with closed blue triangles), and 100 MPa (black curve with open circles), based on the measurement of the size distributions. The vertical error bars show the standard deviations of Gaussian distributions. The horizontal error bars represent the uncertainties in the laser beam diameter and the pulse energy fluctuations. The particle images and size distributions obtained at 60 MPa are given in Supporting Information Figure S4.

<10 nm; particles such as these were observed in the background of our TEM images. The laser fluence-dependent, controlled size reduction of core particles was only observed in water that was pressurized above the critical pressure (22.1 MPa). At an ambient pressure of 0.1 MPa, the laser-induced size reduction was uncontrollably rapid, and no mechanisms (as shown in Scheme 1a) operated to stop the size reduction. For instance, a complete size reduction from 100 nm to less than 10 nm occurred within 30 min under irradiation of 59.9 mJ cm\(^{-2}\) (Supporting Information, Figure S3), while only a 30% reduction in diameter was observed at 100 MPa. The observation that the size reduction stopped at a fixed size, even after repeated irradiations, is unusual; at ambient pressures, repeated irradiations of already-size-reduced Au NPs typically cause further size reductions, due to light absorption, until the absorption cross-section of the particles is negligible (<2 nm for excitation at 532 nm). To achieve a better understanding of the photothermal mechanism at high pressures, we performed laser irradiation at various pressures.

Figure 2 summarizes the mean diameters of the generated spheres as a function of the laser fluence at 30, 60, and 100 MPa. The mean diameter decreased nonlinearly with increases in the laser fluence. This observation showed that increasing laser fluences were required to form smaller core particles. The laser fluence-dependent size reduction was also found to be pressure-dependent (for example, see Supporting Information Figure S4 for the size distribution at 60 MPa). For increasing pressures (30 < 60 < 100 MPa), higher laser fluences were required to achieve similar particle diameters. This might have been partly due to the differences in the boiling points (bp) of the particles, because the boiling point of bulk gold is pressure-dependent. By applying the Clausius–Clapeyron equation, the bp was calculated as 5500 K at 30 MPa, 6200 K at 60 MPa, and 6800 K at 100 MPa. Additionally, the convective/conductive heat transfer in water is pressure-dependent, as will be described below. These results suggested that the pressure values, as well as the laser fluences, were decisive in controlling the final core particle diameter. At 100 MPa, we found it difficult to prepare monodisperse core particles with diameters ≤30 nm, because at laser fluences of ≥140 mJ cm\(^{-2}\) the size distribution suddenly became wide. In contrast, at 30 MPa, particles with a minimum core diameter of 20 nm were prepared with a size distribution of ±15%. These results suggested that the core particle sizes could be fine-tuned by adjusting either the laser fluence or the external pressure. Although the size distribution was very narrow at 100 MPa, a much wider distribution was observed at 30 MPa. To investigate the dependence of the size reduction on the excitation wavelength, laser irradiation was performed at 355 and 532 nm, at a pressure of 30 MPa. As shown in Figure 3, smaller core particles were formed at 355 nm than at 532 nm, with similar laser fluences. These results showed that the size reduction efficiency was higher under excitation at 355 nm. The effects of the excitation wavelength will be detailed and explained below.

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excitation wavelength of 355 nm and from 100 nm diameter particles. The accumulated laser pulse numbers are 108 000.

Figure 3. Mean diameters of Au NPs as a function of laser fluence at 30 MPa, after excitation at two wavelengths: 355 nm (red curve with closed rectangles) and 532 nm (black curve with open circles), starting from 100 nm diameter particles. The accumulated laser pulse numbers are 108 000.

excitation wavelength of 532 nm, the average diameter of the Ag NPs was useful in giving general insights into the size reduction occurring at much higher laser fluences (100–180 mJ cm\(^{-2}\)) (Figure 5). At these high laser fluences, an approximately bimodal size distribution—instead of a monodisperse distribution—was observed after the size reduction. Under atmospheric pressure, the threshold laser fluence for the size reduction of the 100 nm Ag NPs was \(\approx15\) mJ cm\(^{-2}\) at an excitation wavelength of 355 nm and \(\approx50\) mJ cm\(^{-2}\) at 532 nm. The retardation resulting from the pressurization of the water was remarkable for the Ag NPs, but the size reduction could not be controlled by changing the laser fluence, in contrast with the Au NPs. For the Ag NPs at 60 MPa, the slope of the particle diameter versus laser fluence curve in the range from 35 to 45 mJ cm\(^{-2}\) for excitation at 355 nm was too steep to allow control over the particle size; the curve measured at 532 nm was not steep enough, and this resulted in polydispersity, rather than the monodispersity observed for the Au NPs. In spite of the unsatisfactory size control results, the observations made for the Ag NPs were useful in giving general insights into the size reduction phenomena.

Mechanistic Aspects. Scheme 2 shows a schematic representation of the laser-induced size-reduction of an Au NP in water at pressures \(p \geq 22.1\) MPa. The absorption of the laser energy from a nanosecond pulse by the Au NP allows the instantaneous heating of the particle, and this is followed by heat transfer to the surrounding medium.\(^{3,5}\) Although it has been revealed that bubbles of water vapor are formed around particles heated to 400–674 K at ambient pressure \((0.1\) MPa),\(^{11,12,23}\) a supercritical water layer can form around the NP at temperatures above 647 K when the external pressure exceeds 22.1 MPa.\(^{7,24}\) In this case, it is likely that the slow evaporation observed at high pressures was mainly due to the efficient particle cooling caused by the greater heat dissipation to the medium in the supercritical water compared with that in the bubble. As the pressure increased, we observed that it was increasingly difficult for the Au NPs to undergo further size reduction as the particle size was reduced (see Figure 2). This can be explained by the increased convective/conductive heat transfer to the medium, which resulted from the fact that the core particles undergoing evaporation were smaller. Thus, Scheme 2 functions as follows:

The particle temperature \(T_p\) and the medium temperature \(T_m\) under nanosecond pulsed-laser-heating are defined by a set of differential equations:\(^{5}\)

\[
\begin{align*}
C_p \frac{dT_p}{dt} &= S - F \quad (1a) \\
C_m \frac{dT_m}{dt} &= \bar{V}(k_m \frac{dT_m}{dt}) + F \quad (1b)
\end{align*}
\]

where \(C_p\) (J m\(^{-3}\) K\(^{-1}\)) and \(C_m\) (J m\(^{-3}\) K\(^{-1}\)) represent the heat capacities of the particle and medium and \(k_m\) (W m\(^{-1}\) K\(^{-1}\)) represents the thermal conductivity of the medium. The absorbed laser energy term \(S\) that contributes to the temperature increase of the Au NPs and the heat transfer term \(F\) that contributes to the temperature decrease of the Au NPs are given by

\[
S = \frac{C_{ab} P}{V_p} \quad (2a)
\]

\[
F = \frac{h A_p}{V_p} (T_p - T_m) \quad (2b)
\]

where \(P\) (W m\(^{-2}\)) represents the laser power density, \(C_{ab}\) (m\(^3\)) is the temperature-dependent absorption cross section of a Au NP, \(V_p\) (m\(^3\)) is the particle volume, \(A_p\) (m\(^2\)) is the NP surface area, and \(h\) (W m\(^{-2}\) K\(^{-1}\)) is the heat transfer coefficient. Equation 2b predicts that the heat loss through the NP–water interface is proportional to the surface-to-volume ratio \(A_p/V_p\) and the heat transfer coefficient \(h\). The coefficient \(h\) is defined as \((k_m \text{Nu})/D_p\) where Nu denotes the Nusselt number\(^{27}\) and \(D_p\) is the particle diameter. When a constant temperature gradient \((T_p - T_m)\) is assumed (at constant external pressure), the heat transfer term \(F\) of a sphere with diameter \(D_p\) is given by

\[
F \propto \frac{6k_m \text{Nu}}{D_p^2} \equiv K
\]

Equation 3 predicts that the heat transfer is inversely proportional to the square of the diameter of the sphere \((F \propto 1/D_p^2)\). Note that the thermal conductivity of the fluid \(k_m(T, p)\) is a function of both temperature and pressure.\(^{28}\) Here, an increase in the pressure results in an increased thermal conductivity \(k_m\) giving rise to greater heat dissipation.

Figure 6 gives an approximate picture of \(K\) (W m\(^{-3}\) K\(^{-1}\), scale on the right), a measure of heat loss, calculated as a function of particle diameter. The rate of heat loss (or cooling) for a
particle is greater for smaller particles. For example, the rate of heat loss from a 70 nm Au NP is twice that of a 100 nm sphere, and the rate of heat loss for a 50 nm particle is four times as large as that of a 100 nm particle. This picture is consistent with previous experimental results from Hartland’s group.\(^1\) They determined a quadratic dependence of the cooling time constants \(\tau_{\text{cooling}}\) on the diameter of Au NPs (i.e., \(\tau_{\text{cooling}} \propto D_P^2\)) by applying femtosecond pump-probe spectroscopy. The cooling rate constant \(\tau_{\text{cooling}}^{-1}\) reproduced from their work is also included in Figure 6 (scale shown on the left). The experimental \(D_P\)-dependent cooling rate constants agreed qualitatively with those of our model. According to eq 1a, the minimum core diameter (which is reached via surface evaporation caused by increases in the temperature) is determined by the laser heating term \(S\) and the cooling term \(F\). At a given laser fluence \(P\), the laser-induced size reduction of an Au NP stops when the size at which the heat loss term exceeds the heating term is reached, leading to a particle temperature \(T_P\) that is below the evaporation threshold. A

\[T_P \approx T_{\text{evap}}\]

\(T_P\) is the particle temperature, and \(T_{\text{evap}}\) is the evaporation temperature for the AuNPs. The laser-induced heating of the particle to \(T_P \approx T_{\text{evap}}\) sets the particle evaporation in motion, and if the condition of \(T_P \geq T_{\text{evap}}\) is met, enhanced particle evaporation takes place. This enhanced evaporation causes considerable size reduction, which also brings about enhanced heat loss. As a result, the size reduction stops when the condition \(T_P < T_{\text{evap}}\) is met.

Figure 5. Histograms representing the particle size distributions of Ag NPs at higher laser intensities than those given in Figure 4 for 532 nm laser excitation at 60 MPa: 113 mJ cm\(^{-2}\) (a), 131 mJ cm\(^{-2}\) (b), 145 mJ cm\(^{-2}\) (c), and 179 mJ cm\(^{-2}\) (d). Extinction spectral changes are given in Supporting Information Figure S5. The laser pulse numbers are 108 000.

Scheme 2. Schematic Illustration Representing the Nanosecond Laser-Induced Size Reduction of an Aqueous Au NP at \(p > 22.1\) MPa\(^a\)

\[\text{High pressure container} \quad T_P \approx T_{\text{evap}} \quad T_P \geq T_{\text{evap}} \quad T_P < T_{\text{evap}}\]

\(a\) Extinction spectral changes are given in Supporting Information Figure S5.
larger laser power is therefore required to achieve further reductions in size. The cooling rate vs $D_P$ relation qualitatively explains the relationship between the core particle size and the laser fluence, as shown in Scheme 2. At ambient pressure, the heating term $S$ far exceeds the cooling term $F$, because $F \approx 0$ for Au NPs inside bubbles; this results in very rapid evaporation. The high-pressure results shown here represent a heat loss-controlled reaction; its nonequilibrium nature is quite unique. Note that the highly efficient cooling mechanism observed here at high pressures may not work under femtosecond laser excitations. Under such excitation conditions, the time scale for heating the particle to its maximum temperature is shorter than the cooling time constant of Au NPs (20 ps to 1 ns).\textsuperscript{5,7} Thus, particle evaporation can occur before the cooling of the particle sets in. In addition, the Coulomb explosion mechanism can operate instantaneously after femtosecond laser excitation, before the particle evaporation takes place.\textsuperscript{5,7,29}

We observed that the gradual, laser fluence-dependent core-size reduction did not occur for the Ag NPs. Here, the role of the laser heating term $S$ in eq 2a must be examined. This term is dependent on $C_{abs}/V_p$ at a given laser power density $P$, as shown in eq 2a. The absorption of light by the NPs initially takes place at ambient temperatures. However, the absorption of light causes both $T_p$ and $T_m$ to increase during the excitation pulse (FWHM: 5–6 ns), until the particle boiling temperature is reached. The temperature increase affects the $C_{abs}$ values, because the values are dependent on both $T_p$ and $T_m$. The effect of $T_m$ is much greater, as shown in Supporting Information Figure S6. During the size reduction, the temperature rise causes alterations in the $C_{abs}$ values as a result of the progressive reduction of the refractive index of water. The refractive index in supercritical water can be $\approx 1$ at pressures $> 60$ MPa and $T_m > 1000$ K. The water temperature at the NP interface is able to reach such high values because of the heat transfer.

Figure 7 shows the $C_{abs}/V_p$ values as a function of particle diameter, calculated for the Au and Ag NPs at excitation wavelengths of 532 and 355 nm. For the Au NPs at 532 nm (Figure 7a), the curve for $n \approx 1.0$ was nearly flat, with a slight decreasing trend with decreasing particle diameter from 80 to 30 nm. This could have been a foundation for the observed controlled size reduction phenomenon, because in this case the heating term $S$ gradually increases with increasing $P$, and the size reduction proceeds until the size-dependent cooling term $F$ becomes dominant. The $C_{abs}/V_p$ versus $D_P$ curve was also nearly flat for excitation at 355 nm (Figure 7b), but the values at $n \approx 1.0$ were 1.5 times greater than those observed with excitation at 532 nm. This could have been a reason for the slightly higher efficiency observed in Figure 3. The $C_{abs}/V_p$ versus $D_P$ curves for the Ag NPs were markedly different from those observed for the Au NPs, and the effects of the two excitation wavelengths on the $C_{abs}/V_p$ versus $D_P$ curve were remarkably different. Under excitation at 355 nm (Figure 7d), the $C_{abs}/V_p$ values increased significantly with decreasing $D_P$. This suggested that the contribution of the heating term increased monotonically with decreasing $D_P$ values, resulting in almost uncontrollable size reduction. This deduction is
consistent with the observations of the sudden size reduction that took place at 35–45 mJ cm⁻² for excitation at 355 nm (Figure 4). Under excitation at 532 nm, the C_{ext}/V_p values were an order of magnitude smaller (note the difference between the vertical scale in Figure 7c and that in Figure 7d). This showed that the excitation efficiency at this wavelength was very low, which likely led to the inefficient size reduction that was observed (Figures 4 and 5). Accordingly, the analysis based on eq 1 qualitatively explains the entire size reduction process for both the Au and Ag NPs. However, quantitative calculations might be necessary to obtain a full understanding.

From a practical point of view, the current work suggests that nanosecond pulsed lasers can be used efficiently for the size-controlled preparation of Au NPs. With eventual practical applications in mind, the additional processing step of separating the fragments expelled from the core particles was therefore carried out. We demonstrated the separation of monodisperse particles using centrifugation, as shown in Figure 8 and Supporting Information Figure S7. Such particles can be used as building blocks for plasmonic crystals, for which NPs with a polydispersity of less than 10% are required.³¹,³²

### CONCLUSION

We have achieved a technological advance in the pulsed laser-induced size-reduction of Au NPs in water by applying high pressures of 30–100 MPa. Below <400 MPa, the high pressure technique can be more easily implemented than ultrahigh vacuum and ultralow temperature techniques. We demonstrated that the combination of three parameters—high external pressures, the excitation laser intensity, and the excitation wavelength—is instrumental to the performance of photothermal layer-by-layer size reduction in a controlled manner. As a result, we successfully prepared highly monodisperse Au spheres with diameters in the 20–100 nm range, starting from ca. 100 nm diameter Au particles. Mechanistically, the management of the laser-generated heat through convective/conductive transfer is important, as demonstrated for the Au NPs. The success critically depended on the size-dependent light absorption behavior of the NPs at high temperatures. In this regard, the Ag NPs were not particularly suitable for achieving controlled size reduction. Overall, the introduction of an additional parameter—the high pressures—promoted the better understanding of the nature of liquid-phase laser processing of NPs.

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**Figure 8.** Particle images showing the effect of centrifugation on the sample shown in Figure 1d: (a) before, and (b) after the separation of the core particles from the expelled fragments. The solution was centrifuged at 2000 rpm for 60 min. The supernatant that contained the fragments was removed, and the core particles were dispersed again in distilled water. This process was repeated three times. The TEM picture in Figure 8b shows the Au NPs 2 weeks after fabrication. The inset gives the corresponding size distribution. The particles showed no size changes after the centrifugation treatment. To construct the histogram, 907 particles were measured. Additional TEM photographs of the Au NPs and extinction spectra, together with Mie fits for the Au NP solutions after the cleaning process, are given in Supporting Information Figure S6.

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**ASSOCIATED CONTENT**

5 Supporting Information

Particle images (TEM micrographs) and corresponding size distribution of 100 nm Au NPs, extinction spectra for 100 nm Au NPs after laser irradiation, particle images (TEM micrographs) and corresponding size distributions after laser irradiation at 0.1 MPa, particle images and corresponding histograms for Au NPs prepared at 60 MPa, changes in the extinction spectra for ≈100 nm diameter Ag NPs after laser irradiation at 60 MPa, particle images (TEM micrographs), absorption cross section spectra (C_{abs}) for Au NPs (d = 100, 80, 50 nm) in water, depending on the refractive index (n) of the medium and the particle temperature (n = 1.33), and particle images (TEM micrographs) and changes in the extinction spectra for Au NPs after centrifugation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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**ACKNOWLEDGMENTS**

This work was supported by KAKENHI (No. 23310065) from the Japan Society for the Promotion of Science (JSPS) and the Amada Foundation (AF-2011201). A JSPS fellowship to D.W. (No. 201107976) is also gratefully acknowledged. Mr. Tomoyuki Ueki, Mr. Satoshi Sugano, and Mr. Taka Fujimoto are acknowledged for TEM photograph acquisition. We thank Dr. Vasudevan P. Biju of AIST Shikoku Center for critical reading of the manuscript.

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