Mechanism of Laser-induced Size-reduction of Gold Nanoparticles as Studied by Nanosecond Transient Absorption Spectroscopy

Kunihiro Yamada,[†] **Yuki Tokumoto, Takashi Nagata, and Fumitaka Mafuné***

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan

Gold nanoparticles with an average diameter of ≈8 nm (Au ≈ 15 000) were irradiated with a tightly focused pulse laser at 355 nm in an aqueous solution of sodium dodecyl sulfate (SDS). Transient absorption spectra of the solution were measured at 25−100 ns after the laser irradiation. The observed transient absorption around 720 nm is assignable to the 2p ← 1s transition of solvated electrons produced via multiple ionization of the gold nanoparticles. The nascent charge state of the gold nanoparticles was estimated from the transient absorbance. The dependence of the charge state on the SDS concentration shows a gradual increase from ≈ +60 to ≈ +70 in the 2×10^{-4} to 3×10^{-4} M range and an abrupt increase up to ≈ +710 at the critical micelle concentration (CMC) of SDS, 8×10^{-3} M. TEM measurements after laser irradiation reveal that the gold nanoparticles fragment into $Au_{\approx 1000}$ at a SDS concentration of 3×10^{-4} M, whereas they are significantly dissociated into $Au_{\approx 100}$ above the CMC. The observed correlation between the nascent charge states and the extent of size reduction of the gold nanoparticles after the laser treatment indicates that the size reduction is caused by the Coulomb explosion of the highly charged gold nanoparticles. The mechanism of laser-induced size reduction is quantitatively discussed based on the liquid drop model.

1. Introduction

Gold nanoparticles have been attracting much attention because of their size-dependent physical and chemical properties.[1−7] Considerable effort has been directed toward preparing nanoparticles with a particular diameter.[8−12] More recently, there has been a growing interest in controlling the shape and size of the nanoparticles by laser irradiation.[13−16] For instance, surfactant-free gold nanoparticles in propanol were found to aggregate under the irradiation of a CW Ar ion laser to form networked structures.[17] Gold nanorods were reshaped into the spherical nanoparticles under the irradiation of a pulse Nd:YAG laser.[18] The aggregation and the reshaping of the gold nanoparticles are considered to be induced by photoexcitation followed by melting of the nanoparticles.

On the other hand, thiol-stabilized or surfactant-stabilized gold nanoparticles are known to be pulverized into the small particles by pulse-laser irradiation.[19−22] The mechanism of the size-reduction has been proposed by several groups: Kamat and co-workers concluded from picosecond photoabsorption spectroscopic measurements that Coulomb explosion of the photoionized metal nanoparticles was responsible for the fragmentation.[19] On the contrary, Koda and co-workers proposed a possible mechanism suggesting that fragmentation of the photoexcited gold nanoparticles proceeds through melting and vaporization caused by multiphoton absorption.[20] Recently, Plech et al. observed the structural changes of nanoparticles and the water molecules in the vicinity of the nanoparticles by time-resolved X-ray scattering.[21] They found that the particles undergo a melting transition within a time scale of 1 ns, and

hence, they are fragmented into small particles by the thermal process. Henglein et al. observed that silver ions together with solvated electrons were produced when an aqueous solution of nanoparticles were irradiated with a pulse laser.[23,24] The ions and electrons that were produced are then dissolved in the solution. This laser dissolution is possibly the cause of the size-reduction of gold nanoparticles. Although several mechanisms have been proposed, the mechanism of the size reduction is not yet well understood.

In a previous study, we have demonstrated that gold nanoparticles can be either aggregated or fragmented by photoexcitation in a controlled manner. The studies involved irradiation of gold nanoparticles in an aqueous SDS solution with a 532-nm or 355-nm laser: The results showed that in dilute solutions the nanoparticles were found to aggregate, whereas in the concentrated solutions they were found to be spherical and size-reduced.[25,26] The gold nanoparticles were even further size-reduced when the SDS solution was above its CMC. On the basis of these experimental findings, the issues addressed in the present study consist of (1) dynamics of photoexcited gold nanoparticles leading to fragmentation and (2) the role of SDS in the photoinduced aggregation/fragmentation processes. In this article, we observe solvated electrons formed by laser irradiation of gold nanoparticles in an aqueous solution of SDS by using nanosecond transient absorption spectroscopy. The abundance of the solvated electrons is measured as a function of the SDS concentration, and the correlation between the nascent charge state of the photoexcited gold nanoparticles and the size distribution of the nanoparticles after the laser treatment is examined.

2. Experimental Section

Gold nanoparticles were prepared by laser ablation of a gold metal plate in an aqueous solution.[27] Here, the gold metal plate

* To whom correspondence should be addressed. E-mail: mafune@cluster.c.u-tokyo.ac.jp.
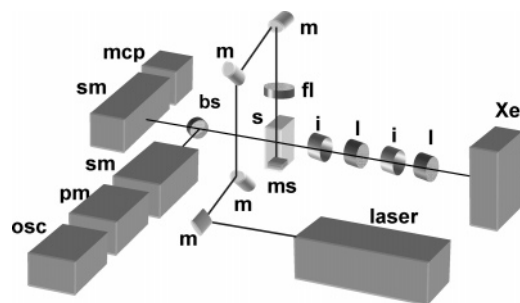† Permanent affiliation: Department of Applied Chemistry, Graduate School of Science and Engineering, Chuo University.

Figure 1. Schematic diagram of the apparatus for nanosecond transient absorption spectroscopy: (laser) Nd:YAG pulse laser, (Xe) Xe lamp, (pm) photomultiplier, (sm) spectrometer, (mcp) linear diode allay, (m) mirror, (l) lens, (i) iris, (fl) focusing lens, (bs) beam splitter, (ms) magnetic stirrer, (s) sample, and (osc) oscilloscope.

was placed on the bottom of a glass vessel filled with 10 mL of a 10^{-5} M SDS aqueous solution. The fundamental (1064 nm) of a Nd:YAG pulse laser operating at 10 Hz with a pulse energy of 90 mJ was focused by a 250-mm focal length lens onto the metal plate. The concentration of the gold atoms dispersed in the solution as gold nanoparticles was typically 1.2 mM after 36 000 laser shots. Hereafter, when the concentration of gold nanoparticles is given in this paper, it refers to the concentration of gold atoms dispersed as gold nanoparticles. The average size of the gold nanoparticles produced was determined to be ≈8 nm ($Au_{≈15000}$) with a standard deviation of 5 nm. The gold nanoparticles that are produced are negatively charged, because they are covered with DS^- and OH^-.[28]

In the transient absorption measurements, a 0.2-mM solution of gold nanoparticles in a 2×10^{-4} to 5×10^{-2} M SDS solution was used. As shown in Figure 1, the solution in an optical SiO_2 cell was irradiated with the output of the third harmonic (355 nm) of a Nd:YAG pulse laser (pulse energy, 50 mJ·pulse^{-1}; pulse width, 10 ns; repetition rate, 10 Hz). The pulse laser was focused by the lens onto the solution through the opening of the optical cell. The laser fluence was set to be 94.3 MW·cm^{-2} at the surface of the aqueous solution. A magnetic stirrer was used to keep the solution homogeneous during the measurements. Transient absorption spectra of the solution were obtained at 25 and 100 ns after the laser irradiation by using a Xe lamp as a probe light, which was introduced into the cell perpendicular to the laser pulse. The broad-band probe light was dispersed by a spectrometer (Hamamatsu C5094), and the light intensities at each wavelength were measured by a MOS linear image sensor equipped with an image intensifier having a <5-ns gate width (Hamamatsu C4562). Both triggers for the Q-switch of the 355-nm laser and the image intensifier were synchronized, and the delay time between the laser irradiation and the detection of the spectrum was controlled by a digital delay generator (Stanford Research, DG535).

As shown in the following section, the transient absorption spectrum exhibits a broad-band nature, having a $\lambda_{max} \sim 720$ nm, and the spectral feature scarcely changes with the delay time. To measure the time dependence of the spectral intensity, the transient absorbance at 700 ± 4.4 nm was monitored by a photomultiplier in combination with a 200-MHz digital storage scope.

3. Results

Figure 2 shows typical transient absorption spectra of the 2×10^{-2}-M SDS aqueous solution containing 0.2-mM gold nanoparticles measured at delay times of 25 and 100 ns after 355-nm laser irradiation. The transient absorption spectra were
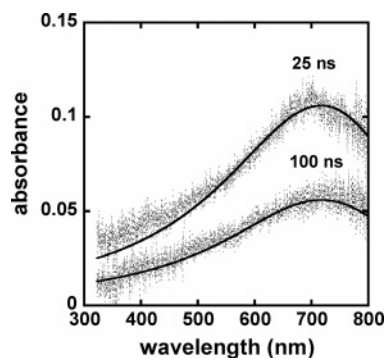

Figure 2. Transient absorption spectra of a 0.2-mM gold nanoparticle in a 0.02-M SDS aqueous solution at delay times of 25 and 100 ns after 355-nm laser irradiation with a pulse energy of 50 mJ/pulse. The solid lines are the Gaussian (low energy) and Lorentzian (high energy) fittings for the solvated-electron spectra in water (ref 30). The slight enhancement of the absorbance around 300−500 nm in the observed spectra arises from the change in the absorbance of the original solution by the 355-nm laser irradiation and should not be taken into consideration.
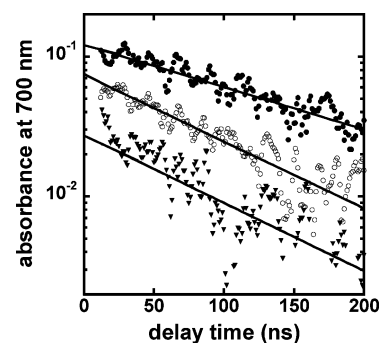

Figure 3. Decay of the absorbance at 700 nm after the 355-nm laser irradiation under the almost identical condition as Figure 2 at different SDS concentrations (2×10^{-2} M (●), 6×10^{-3} M (○), and 2×10^{-3} M (▼)).

obtained by taking a natural logarithm of the transmittance at each wavelength. Both spectra show a broad band around 720 nm. Although the spectral absorbance decreases with the delay time, spectral features remain almost unchanged within the delay time of 25−100 ns. On the basis of the observed spectral positions and band shapes, we have assigned the broad band as the 2p ← 1s transition of the solvated electrons formed by the 355-nm laser irradiation.[29] The solid lines in Figure 2 represent Gaussian (low energy) and Lorentzian (high energy) fits to the observed spectra.[30] The slight enhancement of the absorbance around 300−500 nm in the observed spectra arises from the change in the absorbance of the original solution by the 355-nm laser irradiation. The transient absorption spectra longer than 600 nm are exclusively attributed to the solvated electrons. The assignment is further supported by the fact that almost identical transient spectra were observed, when platinum nanoparticles were used instead of the gold nanoparticles or when PVP (poly-(vinylpyrrolidinone)) was used as a stabilizer instead of SDS: these findings indicate that neither the metal atoms nor the stabilizing reagents should be involved in the temporally formed species.

The decrease in the absorbance with the delay time in Figure 2 is due to the decay of the solvated electrons. Figure 3 shows the absorbance at 700 nm as a function of time after the laser irradiation at different SDS concentrations. The time dependence can be approximated by the following equation

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$$\log_e A = \log_e A_0 - \frac{t}{\tau} \qquad (1)$$

where A, A_0, and τ stand for the transient absorbance, the absorbance at $t = 0$, and the decay constant, respectively. The quantity A_0 is directly proportional to the abundance of solvated electrons existing in the solution right after the 10-ns laser irradiation. By definition, A_0 is free from the decay processes occurring in the nanosecond time scale. As seen in Figure 3, A_0 depends on the SDS concentration, indicating that the abundance of the nascent solvated electrons is also SDS-concentration dependent. As will be discussed in the next section, the absolute number density of the nascent solvated electrons is a key to the size-reduction mechanism of the photoexcited gold nanoparticles. Hence, from the observed values of A_0, we estimate the number density of the solvated electrons generated by the 10-ns laser irradiation. The absorbance A_0 is given by

$$A_0 = c_0 \sigma l \qquad (2)$$

according to Lambert−Beer's law. In eq 2, c_0, σ, and l represent the number density of the solvated electrons at $t = 0$, the absorption cross section of a solvated electron (8×10^{-17} cm^2 at 274 K[31]) and the optical length (0.26 cm), respectively. For example, A_0 is observed to be 0.12 for the 2×10^{-2}-M SDS aqueous solution containing 0.2 mM gold nanoparticles, from which c_0 is estimated to be 5.7×10^{15} cm^{-3}. Figure 4 shows the dependence of c_0 on the concentration of gold nanoparticles in a 2×10^{-2}-M SDS solution. The quantity c_0 increases almost linearly with the concentration of gold nanoparticles; therefore, the gold nanoparticles serve as the chromophore relevant to the production of solvated electrons by the laser irradiation. In Figure 5, c_0 is plotted as a function of the SDS concentration (nanoparticle concentration, 0.2 mM). Solvated electrons were hardly observed below 1×10^{-4} M with the detection sensitivity of our experimental setup. The c_0 value starts to increase at 2×10^{-4} M and shows a sharp increase around the critical micelle concentration (CMC) of SDS (8.1 mM at 298 K).

Figure 6 shows the electron micrographs together with the size distributions of gold nanoparticles after 355-nm laser irradiation in 5×10^{-2} and 5×10^{-3}-M SDS aqueous solutions. The size distributions are obtained by measuring more than 200 gold nanoparticles in sight of the electron micrographs. Average diameters of the gold nanoparticles are 1.4 ± 0.4 and 2.7 ± 0.4 nm in 5×10^{-2} and 5×10^{-3}-M SDS aqueous solution, respectively. Figure 7 depicts the average diameter of the gold nanoparticles after the laser irradiation as a function of the SDS concentration. The average diameter decreases drastically at CMC and levels off with an increase in the SDS concentration. Also shown for comparison is the charge state of gold nanoparticles, which is estimated from the quantity c_0 (see next section). The concentration dependence of the charge state is almost the mirror image of that of the average diameter of the gold nanoparticles.

4. Discussion

Formation of Multiply Charged Nanoparticles. The photoabsorption spectrum of gold nanoparticles exhibits a sharp peak at the 520-nm characteristic of the surface plasmon band on the broad interband absorption extending from the ultraviolet to the visible region.[32−35] As the 355-nm laser is resonant with the interband transition, the nanoparticles are readily excited to the electronically excited state. Through rapid relaxation processes, the gold nanoparticles are likely to decay to the
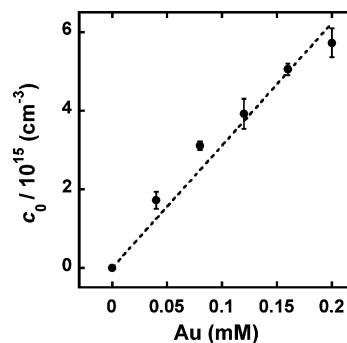
Figure 4. Number density of the solvated electrons at $t = 0$ as a function of the concentration of gold nanoparticles in a 0.02-M SDS solution.
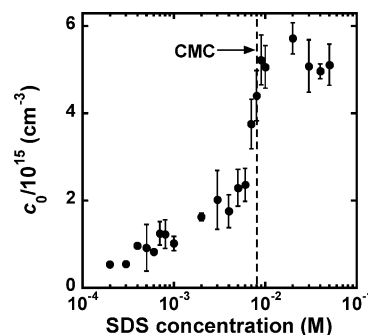
Figure 5. Number density of the solvated electrons at $t = 0$ as a function of the SDS concentration.
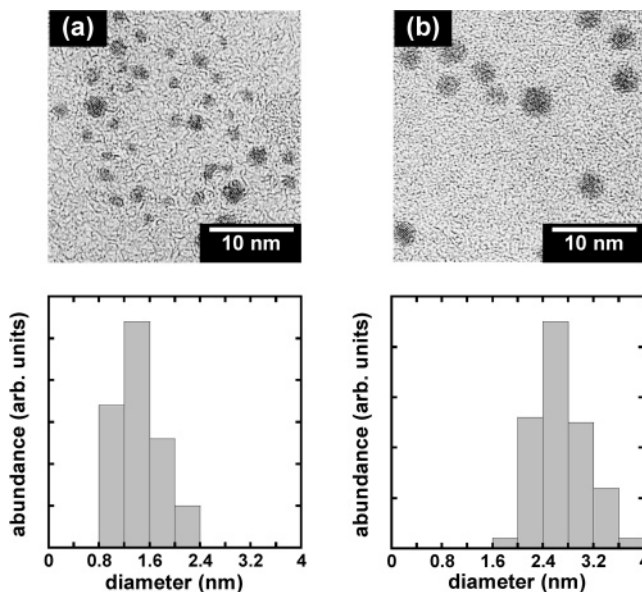
Figure 6. Transmission electron micrographs and size distributions of the gold nanoparticles produced by 355-nm laser irradiation (50 mJ/pulse, 6000 shots) in an SDS aqueous solution. The concentrations of the solutions in panels (a) and (b) are 5×10^{-2} and 5×10^{-3} M, respectively.

ground state. The lifetime of the excited state of gold nanoparticles is known to be as short as several picoseconds, because of the efficient electron−phonon coupling.[19] This photoabsorption and subsequent relaxation is repeated within the duration of a 10-ns laser pulse. As a result, the absorbed photon energy is converted into thermal energy for the nanoparticles. Electrons are ejected through thermionic emission after the laser irradiation.[36] The electrons ejected into the aqueous solution are solvated by the water molecules. On the other hand, excited gold nanoparticles can also absorb a second photon and be
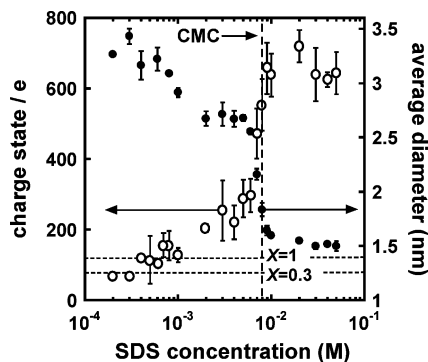
Figure 7. Average diameter of gold nanoparticles after 355-nm laser irradiation (50 mJ/pulse, 6000 shots) as a function of SDS concentration. The charge state of gold nanoparticles is also shown for comparison. See text for details.

ionized in the solution. The ionization potential of a gold nanoparticle in an aqueous solution is expected to be slightly lower than the work function of Au (5.3 eV), so a two-photon absorption (7.0 eV) would surely exceed the ionization potential of the particle.[37] Regardless of the mechanism of electron emission, it is the gold nanoparticles that act as the chromophore for the ejected electrons.

As mentioned in the previous section, the number density of the solvated electrons was estimated to be 5.7×10^{15} cm^{-3} in the 2×10^{-2} M SDS aqueous solution containing 0.2-mM gold nanoparticles. A gold nanoparticle with the diameter of $\approx$8 nm consists of about 15 000 gold atoms; hence, the number density of the nanoparticles in the present solution is 8×10^{12} cm^{-3}. These calculations lead us to infer that each gold nanoparticle can be multiply ionized by a single laser shot, and the nascent charge state can reach $\approx +710$.

As shown in Figure 5, the number density of the solvated electrons increases with an increase in the SDS concentration. The charge state of gold nanoparticles should have a linear relationship with the number density of solvated electrons. The estimated charge state of the gold nanoparticles after the laser irradiation is plotted in Figure 7; the photoionized nanoparticles carry an average charge of $+60$ to $+70$ in the 2×10^{-4} to 3×10^{-4}-M SDS solution, and $> +630$ above 10^{-2} M.

Size-reduction of Gold Nanoparticles by Coulomb Explosion. Highly charged gold nanoparticles are so electronically unstable that they can undergo Coulomb explosion. According to the liquid drop model for Coulomb explosion,[38–40] a multiply charged particle becomes unstable as soon as the disruptive Coulombic force exceeds the attractive cohesive force. The criterion for the Coulomb explosion is expressed quantitatively by "fissility" defined as $X = E_c/2E_s$, where E_c and E_s are the Coulombic energy and the surface energy of the particle of interest, respectively. In the gas phase, multiply charged cluster ions are expected to readily dissociate into the small ones (multi-fragmentation) when $X \geq 1$ (Rayleigh limit), both the evaporation and fission competitively occur in the range $0.3 < X < 1$ and only evaporation takes place when $X < 0.3$.[38–40] The fissility is also expressed as

$$X = \left(\frac{q^2}{n}\right) \Big/ \left(\frac{16\pi r_{\mathrm{WS}}^3 \sigma_{\mathrm{S}}}{e^2}\right) \tag{3}$$

where q, n, r_{WS}, and σ_{S} are the charge state, the cluster size, the Wigner–Seits radius (1.65×10^{-10} m), and the surface tension, respectively.[38] This fissility parameter is calculated using the surface tension of a gold particle in a vacuum,

assuming that the surface tension of the particle does not change drastically by the interaction with the surrounding DS$^-$ ions. As $(16\pi r_{WS}^3 \sigma_S/e^2) = 1.1$ for the multiply charged gold cluster ions in the present case, the fissility is then given by

$$X = 0.9 \frac{q^2}{n} \tag{4}$$

The gold nanoparticles of $n \approx 15\,000$ become extremely unstable ($X \geq 1$) when $q \geq +130$. The broken lines drawn in Figure 7 correspond to $X = 1$ and $X = 0.3$, respectively.

Now, we are in a position to discuss the dissociation dynamics of gold nanoparticles after the laser irradiation on the basis of the liquid droplet model described above. In the dilute SDS solution (2×10^{-4} to 3×10^{-4} M), the gold nanoparticles are prepared in a charge state ranging from $+60$ to $+70$ by the 355-nm laser irradiation. As the fissility is less than 0.3, the disruptive Coulombic force is smaller than the cohesive force of the particles. Although the particles are stable against Coulomb explosion, they are rather unstable energetically as a result of multiphoton absorption/ionization. Under such circumstances, the particles are size-reduced primarily through the evaporation of neutral gold aggregates. As the evaporation proceeds to some extent, the particles become smaller so that the fissility is apt to exceed 0.3. Then, the gold nanoparticles are possibly fragmented into much smaller pieces by the Coulomb explosion, resulting in the formation of nanoparticles with an average diameter of 3.2–3.5 nm. In the 4×10^{-4} to 6×10^{-4}-M SDS solution, the photoionized gold nanoparticles are formed in the charge states of $+100$ to $+120$. As the fissility lies in the range $0.3 < X < 1$, both the evaporation and fission contribute to the size reduction of the nanoparticles. The size distribution of the nanoparticles tends to shift toward smaller diameters. Eventually, the average diameter is observed to be 3.0–3.2 nm after the laser treatment. In the concentrated SDS solution ($>8 \times 10^{-3}$ M), the nascent charge state of the photoionized nanoparticles exceeds $+550$. The fissility becomes much larger than unity and, as a result, the nanoparticles are severely fragmented by the disruptive Coulombic force. This inference is consistent with the observation that the average diameter of the gold nanoparticles is reduced down to $\approx$1.5 nm by the laser irradiation.

In the size-reduction scheme discussed above, we assume a two-step mechanism where the nanoparticles are initially prepared in a highly charged state via the multiple ionization and subsequently undergo a Coulomb explosion. It is, however, also possible that the ionization and fragmentation occur competitively within the time duration of a single laser pulse: in the meantime of a 10-ns laser pulse, multiply ionized nanoparticles dissociate into smaller ones and the resultant particles further absorb multiple photons to reach highly charged states. As we measured the number density of solvated electrons right after the 10-ns laser irradiation, the "charge state" discussed above corresponds to the nominal charge that the nanoparticles which survive the Coulomb explosion during the laser pulse would finally possess after the 10-ns laser irradiation. In any case, we can conclude that gold nanoparticles are fragmented into small pieces by the Coulomb explosion.

SDS Concentration Dependence of the Charge State. As shown in Figure 7, the average charge state of gold nanoparticles after the 10-ns laser irradiation depends characteristically on the SDS concentration. We propose here a possible scheme which reasonably explains the observed nanoparticle charge state dependence on the SDS concentration. Although the observed quantity c_0 is free from the decay processes occurring in the

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nanosecond time scale, it is probably subjected to ultrafast decay processes in the realm of <1 ns. One of those ultrafast processes to be taken into consideration is the geminate recombination of solvated electrons. When gold nanoparticles are ionized by the photoabsorption at 355 nm, the electrons are released into the liquid phase with an initial kinetic energy given by the ionization processes. During thermalization processes in the liquid phase, the ejected electrons have a chance to recombine with the parent gold nanoparticles.

In general, SDS is homogeneously dissolved in water below CMC, whereas it forms a micelle above CMC. According to our preliminary ζ-potential measurement, ζ-potential decreases with an increase in the SDS concentration, indicating that gold nanoparticles are covered with more DS^- ions in the more concentrated SDS solution. In addition, the gold nanoparticle is known to be located in the hydrophobic core of the DS^- micelle above the CMC.[41] The negative charge of DS^- covering gold nanoparticles provides a repulsive barrier for both the electrons leaving from the gold nanoparticles and returning toward them.[42,43] The leaving electrons with a certain kinetic energy must overcome the repulsive barrier, whereas the returning electrons are so thermalized that they can be repelled. When the nanoparticles are not fully covered with DS^-, on the other hand, the recombination proceeds swiftly, whereas it can be retarded to a considerable extent when DS^- densely covers the surface of the nanoparticles. Consequently, the charge state of the ionized nanoparticles tends to increase drastically at CMC with an increase in the SDS concentration. In addition, the lifetime of solvated electrons was obtained to be 50−150 ns in a concentrated SDS solution, probably because the repulsive barrier formed by DS^- prevents geminate recombination. Solvated electrons with such a long lifetime have also been observed by Naik and co-workers in an SDS aqueous solution.[43]

Aggregation of Gold Nanoparticles. In our previous study,[25] we found that laser irradiation of gold nanoparticles in a dilute SDS solution brings about the aggregation of nanoparticles to form a network structure, when the SDS concentration is lower than 10^{-4} M. As the gold nanoparticles are only weakly stabilized by the surrounding DS^- in dilute SDS solution, the electrons ejected by multiple ionizaion recombine with the parent nanoparticles. In fact, solvated electrons are scarcely observed in the SDS concentration range <10^{-4} M by the nanosecond transient absorption spectroscopy in the present study, indicating dominant occurrence of the electron−nanoparticle recombination. As described in the previous section, the nanoparticles are readily excited to the electronically excited state by the 355-nm laser irradiation. Through the rapid relaxation processes, the gold nanoparticles are likely to be prepared in a ground state. The photoabsorption and relaxation are repeated within a single laser pulse, and the absorbed photon energy is converted to the thermal energy of nanoparticles. Koda et al. found that gold nanoparticles are thermally excited up to their melting (1338 K) and boiling points (3080 K) by the nanosecond pulse-laser excitation.[20] As the "thermally excited" gold nanoparticles are rather weakly passivated by the SDS molecules, they can easily encounter one another to coalesce, forming network structures of the gold nanoparticles.

5. Conclusion

The mechanism of the size reduction of SDS-stabilized colloidal gold nanoparticles by 355-nm laser irradiation was examined by nanosecond transient absorption spectroscopy. A number of photoelectrons were observed as solvated electrons right after each laser shot; the abundance of solvated electrons increases significantly with SDS concentration. This finding indicates that gold nanoparticles are photoprepared in a highly charged state under the existence of a certain amount of SDS surroundings. An excellent correlation was observed between the extent of size reduction and the nascent charge state of gold nanoparticles after the laser irradiation, indicating that the size reduction is caused by the Coulomb explosion of highly charged nanoparticles. The observed phenomenon is quantitatively illustrated by the Coulomb explosion mechanism employing the liquid drop model for highly charged cluster ions.

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(37) In general, the ionization potential of small metal clusters is slightly higher than the work function of the bulk material. For instance, the ionization potential of a 10-nm nanoparticle is higher by ∼0.04 eV than

the work function of the bulk material. On the contrary, the ionization potential of small metal clusters decreases by ~1 eV, when they are solvated in the condensed phase. This is because the final ionic state is more stabilized by solvation via electrostatic interactions than the initial neutral state is.

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