

# Growth of Gold Clusters into Nanoparticles in a Solution Following Laser-Induced Fragmentation

Fumitaka Mafuné, Jun-ya Kohno, Yoshihiro Takeda, and Tamotsu Kondow\*

Cluster Research Laboratory, Toyota Technological Institute, and East Tokyo Laboratory,  
Genesis Research Institute, Inc., 717-86 Futamata, Ichikawa, Chiba 272-0001, Japan

Received: March 22, 2002; In Final Form: April 30, 2002

Colloidal gold nanoparticles having an average diameter of 8 nm were prepared by laser ablation at 1064 nm of a gold metal plate in an aqueous solution of sodium dodecyl sulfate (SDS) and were subjected to fragmentation under irradiation of a pulsed laser at 532 nm. Gold clusters exhibiting no significant optical absorption in the visible wavelength region were produced in a solution, together with nanoparticles. UV–visible optical absorption spectroscopy revealed that the gold clusters grow gradually through attachment to the nanoparticles and through mutual aggregation. The growth processes depend crucially on the concentration of SDS in the aqueous solution of nanoparticles.

## 1. Introduction

Metal nanoparticles have attracted much attention because of their size-dependent physical and chemical properties.<sup>1–7</sup> In this relation, considerable efforts have been directed to preparation of nanoparticles having a desired diameter.<sup>8–12</sup> Size-selected nanoparticles with diameters less than 10 nm have been typically prepared using wet-chemistry techniques because of its readiness despite possible contamination by the reducing agents used. More recently, a laser ablation method has been developed to prepare metal nanoparticles in a solution.<sup>13–21</sup> This contaminant-free physical method allows us to prepare nanoparticles with ease, but the size-distribution of the nanoparticles tends to be broadened, because aggregation processes of the ablated atoms can hardly be controlled. In combination with the laser ablation method, a laser-induced size control is one of the most promising methods for preparation of metal nanoparticles having a narrow diameter-distribution with a small average diameter.<sup>22–29</sup> The size control is performed by irradiation of a laser, of which wavelength is in the vicinity of the wavelength of the surface plasmon excitation of metal nanoparticles of interest. Several attempts have been made on gold nanoparticles in a solution by means of lasers having various performances. For instance, gold nanoparticles of 10 nm in diameter aggregate in a solution under irradiation of a 1064 nm pulsed laser,<sup>23</sup> while those of 40 nm in diameter are pulverized under irradiation of a 532-nm pulsed laser.<sup>27,28</sup>

To establish the method of the size-control, it is necessary to elucidate the mechanism of how the size-control proceeds.<sup>27–29</sup> We have so far investigated the fragmentation dynamics of gold nanoparticles of 8.0 nm diameter under irradiation of a pulsed laser at 532 nm by using optical-absorption spectroscopy, and have found that the gold nanoparticles are fragmented into smaller nanoparticles.<sup>29</sup> The average diameter decreases and their size-distribution is narrowed as the laser fluence is increased. We have also observed a phenomenon that the average diameter of the gold nanoparticles begins to increase gradually after the laser is switched off. This finding implies

that the smaller nanoparticles produced by the laser irradiation grow gradually by collecting the clusters and other nanoparticles.<sup>29</sup>

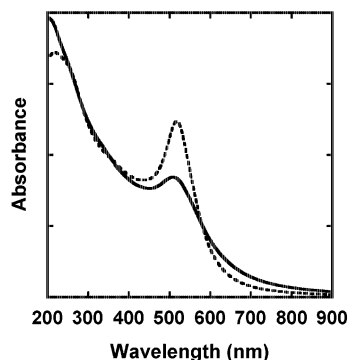
In the present study, we studied the mechanism of the nanoparticle growth and the cluster aggregation, which proceeds concurrently with the laser-fragmentation. On the basis of the mechanism, we developed a method for preparing much smaller nanoparticles by suppressing the nanoparticle growth.

## 2. Experimental Section

Gold nanoparticles were prepared by laser ablation of a gold metal plate in an aqueous solution of sodium dodecyl sulfate (SDS).<sup>21</sup> The metal plate (>99.99%) was placed on the bottom of a glass vessel filled with 10 mL of an aqueous solution of SDS. The metal plate was irradiated with an output of the fundamental (1064 nm) of Quanta-ray GCR-170 Nd:YAG pulsed laser operating at 10 Hz, which was focused by a lens having a focal length of 250 mm. Our previous study shows that the average diameter of gold nanoparticles decreases with an increase in the concentration of SDS.<sup>21</sup> In the present experimental condition, the average diameter of gold nanoparticles was measured to be 8.0 nm by means of electron microscopy, where the laser fluence is 800 mJ/pulse cm<sup>2</sup> and the concentration is 0.01 M. An SDS solution containing the parent gold nanoparticles was placed in a conventional optical absorption cell made of silica, and was irradiated with an output of the second harmonic (532 nm) of Quanta-ray GCR-170 Nd:YAG laser operating at 10 Hz. The laser was focused to a spot (0.1 cm<sup>2</sup>) on the solution surface by a lens having a focal length of 250 mm. The cell was bathed inside water whose temperature was maintained at 298 K.

The dynamics of the nanoparticles after the laser irradiation was observed on the basis of the optical absorption spectroscopy, because the surface plasmon band of gold nanoparticles in the visible region is sensitive to their size. The optical absorption spectra of the SDS solutions were measured by a Shimadzu UV-1200 spectrometer based on an NEC personal computer. A transmission electron microscope (JEOL JEM-100S  $\times 50000$ ) was employed to take electron micrographs of the nanoparticles in the solutions studied. A drop of a sample solution was placed

\* Corresponding author. E-mail: kondow@mail.cluster-unet.ocn.ne.jp



**Figure 1.** Optical absorption spectra of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution before (dotted line) and immediately after (solid line) irradiation of  $3 \times 10^4$  shots of a pulsed laser having the wavelength of 532 nm and the fluence of 400 mJ/pulse  $\text{cm}^2$ .

on a copper mesh coated with collodion and sputtered in advance, and was dried by heating to 320 K. After repeating this procedure five times, the mesh was washed with water so as to remove free SDS. Each sampling was performed within 1 min after the laser irradiation. The diameters of more than 500 nanoparticles in sight on a given micrograph were directly measured, and the distribution of the particle diameters (size-distribution) was obtained.

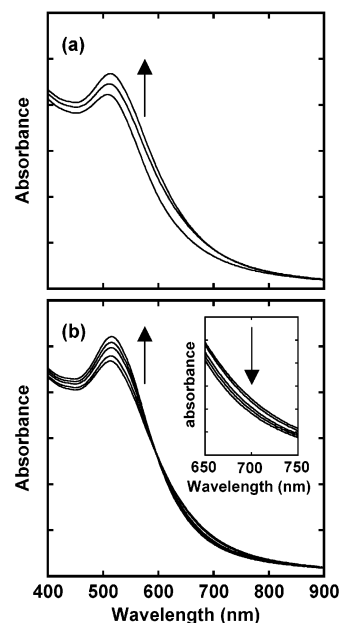
### 3. Results

Figure 1 shows typical optical absorption spectra of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution before (dotted line) and immediately after (solid line) irradiation of  $3 \times 10^4$  shots of a pulsed laser having the wavelength of 532 nm and the fluence of 400 mJ/pulse  $\text{cm}^2$ . The height and the width of a peak centering at 520 nm were found to be lowered and broadened by the laser irradiation, respectively. This spectral change shows that the nanoparticles are pulverized by the laser irradiation and hence the average diameter of the nanoparticles is reduced (see eqs 3 and 4 for the relation between the peak profile and the average diameter). The absorbance at the wavelength of 200 nm increases by the laser irradiation, as well.

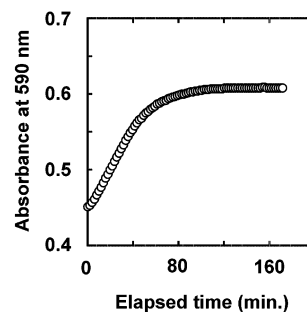
Figure 2 shows optical absorption spectra of gold nanoparticles in the  $1 \times 10^{-3}$  M-SDS solution as a function of the time elapsed after the laser employed for the size reduction at the wavelength of 532 nm and the fluence of 400 mJ/pulse  $\text{cm}^2$  is switched off. As shown in panel a, the absorbance in the entire wavelength range of 400–900 nm increases with the time for 2 h after the laser irradiation. The height of the peak at 520 nm continued to increase even after 2 h, whereas the absorbance of the longer wavelength tail at 700 nm decreases with a further increase in time after 2 h passed (see panel b). As a result, the optical absorption spectrum changes systematically with time while keeping the absorbance at 590 nm constant. These spectral changes show that the gold nanoparticles turn to grow slowly with time in the solution after the laser employed for the size reduction is switched off.

The absorbance at 590 nm was measured as a function of the elapsed time after the irradiation of the pulsed laser at the wavelength of 532 nm and the fluence of 400 mJ/pulse  $\text{cm}^2$ . Figure 3 shows the absorbance plotted as a function of the elapsed time. Evidently the absorbance increases gradually and then levels off completely at 2 h after the laser irradiation.

To scrutinize the spectral change with respect to the elapsed time after the laser irradiation, the difference spectra,  $A(t) - A(0)$ , of the gold nanoparticles in the  $1 \times 10^{-3}$  M-SDS solution were plotted in Figures 4a and b, where  $A(0)$  and  $A(t)$  represent



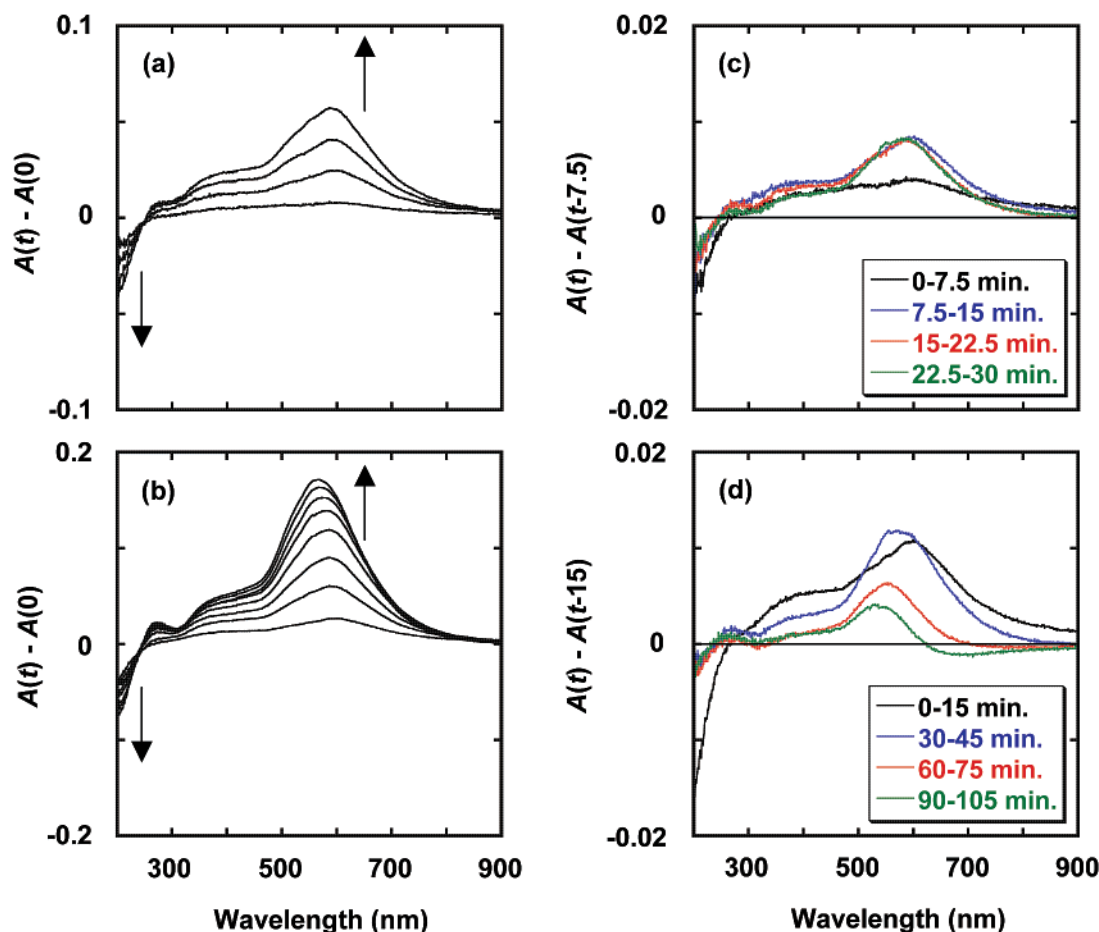
**Figure 2.** Optical absorption spectra of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution as a function of the time elapsed after the laser employed for the size reduction is switched off (the wavelength of 532 nm and the laser fluence of 400 mJ/pulse  $\text{cm}^2$ ). Spectra measured at 0, 1, and 2 h after the laser irradiation (panel a) and at 2, 3, 5, 7, and 9 h after the laser irradiation (panel b).



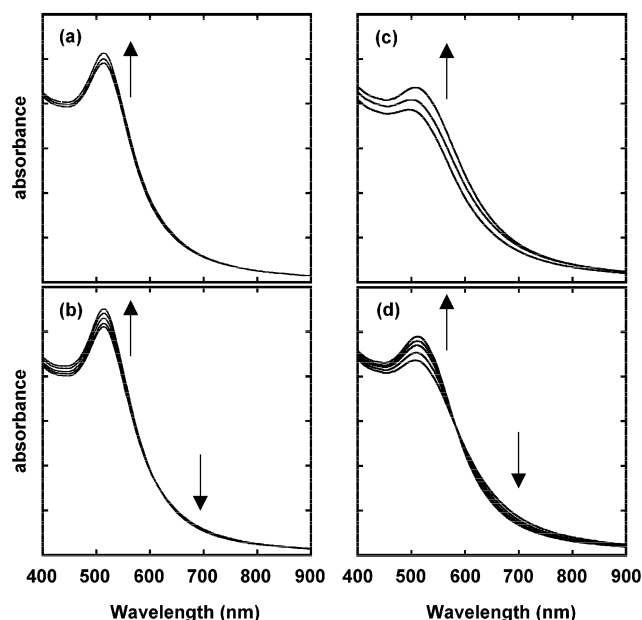
**Figure 3.** Absorbance of gold nanoparticles at the wavelength of 590 nm in a  $1 \times 10^{-3}$  M-SDS solution as a function of a time after the laser employed for the size reduction is switched off (the wavelength of 532 nm and the laser fluence of 400 mJ/pulse  $\text{cm}^2$ ).

the absorbance at a given wavelength immediately after the laser irradiation and at the elapsed time,  $t$ , after the laser irradiation, respectively. In the time window of 0–30 min (see panel a), the absorbance in the vicinity of 600 nm increases and the absorbance at 200 nm decreases with the elapsed time. After 30 min passed, the peak position shifts to a shorter wavelength (see panel b). These spectral changes are exhibited more distinctly in difference spectra of gold nanoparticles in panels c and d.

The growth dynamics of nanoparticles after the laser irradiation for the size reduction depends on the laser fluence. Figure 5 shows absorption spectra of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution as a function of the elapsed time after the laser irradiation at 200 mJ/pulse  $\text{cm}^2$  (panels a and b) and 800 mJ/pulse  $\text{cm}^2$  (panels c and d). Similarly to Figure 2, the absorbance in the wavelength range of 400–900 nm increases with time in the entire wavelength range studied until the elapsed time of 2 h after the laser irradiation. After 2 h, the height of the peak at 520 nm continues to increase, while the absorbance of the longer wavelength tail at 700 nm turn to decrease with a further increase of the elapsed time (see panels b and d). The change is more significant at 800 mJ/pulse  $\text{cm}^2$ . To scrutinize the growth



**Figure 4.** Difference spectra,  $A(t) - A(0)$ , of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution, where the spectra immediately after the laser irradiation and at time,  $t$ , after the laser irradiation at 400 mJ/pulse  $\text{cm}^2$  are denoted as  $A(0)$  and  $A(t)$ , respectively. Spectra obtained at 7.5, 15, 22.5, and 30 min after the laser irradiation are shown from the bottom to the top in panel a, and at 15, 30, 45, 60, 75, 90, 105, and 120 min after the laser irradiation are shown from the bottom to the top in panel b. Difference spectra,  $A(t) - A(t - 7.5)$ , of gold nanoparticles are shown in panel c, while difference spectra,  $A(t) - A(t - 15)$ , of gold nanoparticles are shown in panel d.



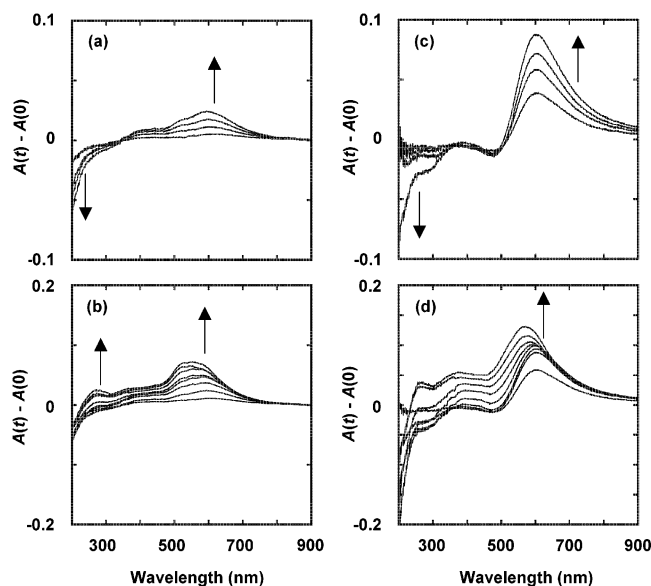
**Figure 5.** Optical absorption spectra of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution as a function of the elapsed time after laser irradiation at the wavelength of 532 nm and the laser fluence of 200 mJ/pulse  $\text{cm}^2$  (panels a and b) and 800 mJ/pulse  $\text{cm}^2$  (panels c and d).

dynamics, difference spectra,  $A(t) - A(0)$ , of gold nanoparticles in the  $1 \times 10^{-3}$  M-SDS solution after the laser irradiation at

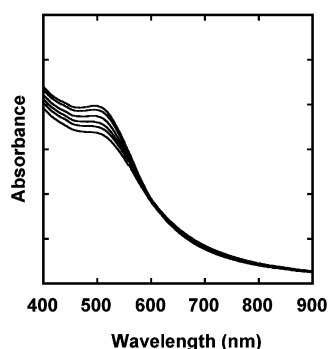
200 mJ/pulse  $\text{cm}^2$  (panels a and b) and 800 mJ/pulse  $\text{cm}^2$  (panels c and d) were observed as shown in Figure 6. The spectral features of the gold nanoparticles after the irradiation at 200 mJ/pulse  $\text{cm}^2$  are similar to those of the 400 mJ/pulse  $\text{cm}^2$  irradiation (see Figure 4). On the other hand, the absorbance at 600 nm increases greatly with the elapsed time in the time window of 0–30 min at 800 mJ/pulse  $\text{cm}^2$ , whereas no appreciable increase in the absorbance is observed at 500 nm. After 30 min, the peak position shifts gradually to a shorter wavelength.

The growth dynamics of nanoparticles after the laser irradiation depends on the concentration of SDS in a solution. Figure 7 shows absorption spectra of gold nanoparticles in a  $5 \times 10^{-2}$  M-SDS solution as a function of the elapsed time after the laser irradiation at 400 mJ/pulse  $\text{cm}^2$ . The peak height and the absorbance increases monotonically with the elapsed time over 9 h after the laser irradiation in the entire spectral range studied. The spectral change of the gold nanoparticles is much less than that in the  $1 \times 10^{-3}$  M-SDS solution. Figure 8 shows difference spectra  $A(t) - A(0)$ , of gold nanoparticles in a  $5 \times 10^{-2}$  M-SDS solution after laser irradiation at 400 mJ/pulse  $\text{cm}^2$ . The absorbance in the vicinity of 500 nm increases with the elapsed time, in contrast to the gold nanoparticles in the  $1 \times 10^{-3}$  M-SDS solution where the dominant spectral change at 600 nm is shown (see Figure 4).

Figure 9 shows typical optical absorption spectra of gold nanoparticles before and immediately after laser irradiation at



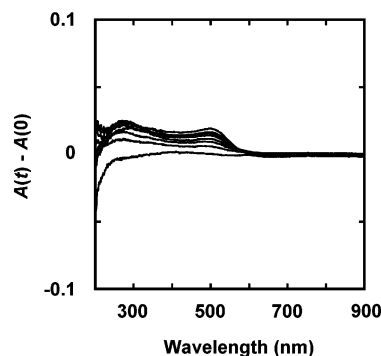
**Figure 6.** Difference spectra,  $A(t) - A(0)$ , of gold nanoparticles in a  $1 \times 10^{-3}$  M-SDS solution after the laser irradiation at the wavelength of 532 nm and the laser fluence of 200 mJ/pulse  $\text{cm}^2$  (panels a and b) and 800 mJ/pulse  $\text{cm}^2$  (panels c and d). Spectra obtained at 7.5, 15, 22.5, and 30 min after the laser irradiation are shown from the bottom to the top in panels a and c, and at 15, 30, 45, 60, 75, 90, 105, and 120 min after the laser irradiation are shown from the bottom to the top in panels b and d. See detailed explanation in the caption of Figure 4.



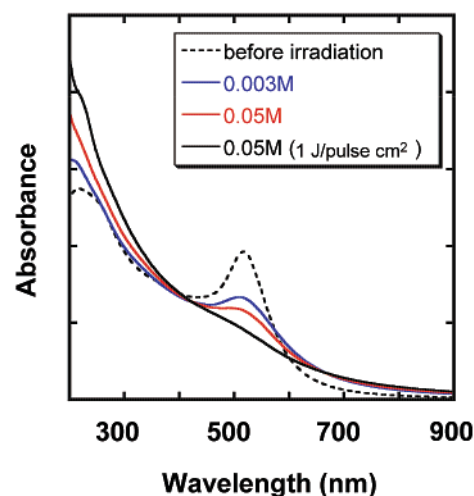
**Figure 7.** Optical absorption spectra of gold nanoparticles in a  $5 \times 10^{-2}$  M-SDS solution as a function of the elapsed time after laser irradiation at the wavelength of 532 nm and the laser fluence of 400 mJ/pulse  $\text{cm}^2$ . Spectra measured at 0, 1, 2, 4, 6, and 8 h after the laser irradiation are shown from the bottom to the top.

532 nm (400 mJ/pulse  $\text{cm}^2$ ) in a  $3 \times 10^{-3}$  and 0.05 M SDS solutions. As mentioned above, the spectral change implies that the average diameter of the parent gold nanoparticles is reduced by the laser irradiation. A more prominent spectral change in a more concentrated SDS solution indicates that the nanoparticles are pulverized more significantly in a more concentrated SDS solution. The spectrum of the gold nanoparticles prepared by laser irradiation at 1000 mJ/pulse  $\text{cm}^2$  in the 0.05 M SDS solutions (see black solid line in Figure 9) shows that the average diameter of the parent gold nanoparticles is reduced more greatly by the laser irradiation.

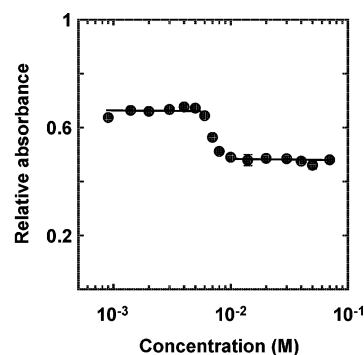
Figure 10 shows a relative absorbance of gold nanoparticles at the wavelength of the plasmon peak (520 nm) immediately after the laser irradiation as a function of the concentration of SDS. The relative absorbance shows a steep stepwise decrease at the SDS concentration of  $8 \times 10^{-3}$  M, otherwise it does not change with the concentration. Namely, the average diameter of the nanoparticles is reduced drastically at  $8 \times 10^{-3}$  M. In fact, distributions of the diameters of nanoparticles (size-distribution) produced immediately after laser irradiation at 1000



**Figure 8.** Difference spectra,  $A(t) - A(0)$ , of gold nanoparticles in a  $5 \times 10^{-2}$  M-SDS solution after laser irradiation at the wavelength of 532 nm and the laser fluence of 400 mJ/pulse  $\text{cm}^2$ . Spectra obtained at 15, 30, 45, 60, 75, 90, 105, and 120 min after the laser irradiation are shown from the bottom to the top.



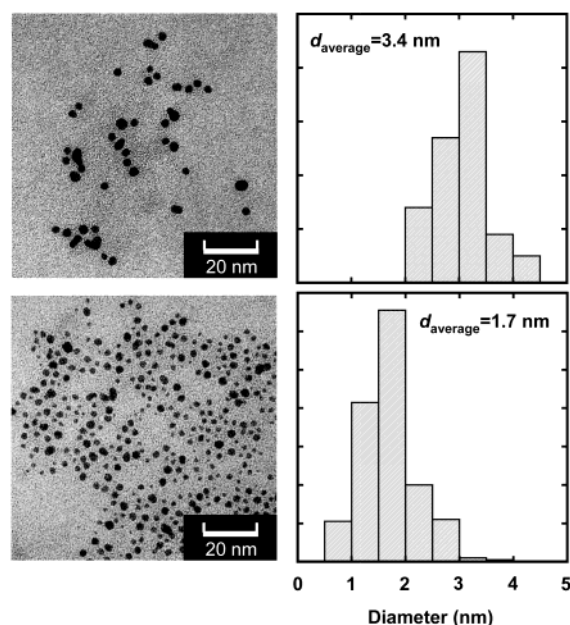
**Figure 9.** Optical absorption spectra of gold nanoparticles before and immediately after laser irradiation at the wavelength of 532 nm and the laser fluence of 400 mJ/pulse  $\text{cm}^2$  in  $3 \times 10^{-3}$  and 0.05 M SDS solutions. The black solid line shows the spectrum obtained after the laser irradiation at 532 nm (1000 mJ/pulse  $\text{cm}^2$ ) in the 0.05 M SDS solution.



**Figure 10.** Relative absorbance of gold nanoparticles at the wavelength of the plasmon peak immediately after the laser irradiation as a function of the concentration of SDS. The relative absorbance decreases with the concentration of SDS and levels off above 0.01 M. The value at the steepest decrease of the concentration coincides with the critical micelle concentration of SDS.

mJ/pulse  $\text{cm}^2$  in  $1.4 \times 10^{-3}$  and 0.05 M SDS solutions are shown in Figure 11. Evidently, the size-distribution shifts to a smaller diameter in a more concentrated SDS solution. The average diameters of the nanoparticles obtained in the  $1 \times 10^{-3}$  and the 0.05 M solutions are obtained to be 3.4 and 1.7 nm, respectively, by using the relation





**Figure 11.** Size-distributions of nanoparticles produced after the laser irradiation at the wavelength of 532 nm and the laser fluence of 1000 mJ/pulse cm<sup>2</sup> in  $1 \times 10^{-3}$  M (panel a) and 0.05 M (panel b) SDS solutions.

$$d_{\text{average}} = \frac{\sum_i^{N_0} d_i w_i}{\sum_i^{N_0} w_i} \quad (1)$$

$$w_i = \pi d_i^3 / 6 \quad (2)$$

where  $d_i$  is the diameter of the  $i$ th nanoparticle and  $N_0$  is the total number of nanoparticles in sight.<sup>21</sup> The average diameter decreases with the concentration of SDS.

#### 4. Discussion

**4.1. Scheme of Fragmentation and Growth.** The optical absorption spectrum exhibits one prominent surface plasmon peak at 520 nm on a tail part of a broad band arising from an interband transition (see Figure 1).<sup>30–35</sup> The Drude theory shows that the average diameter,  $d_{\text{average}}$ , of the nanoparticles is expressed in terms of the height,  $h$ , and the width,  $w$ , of the surface plasmon peak as

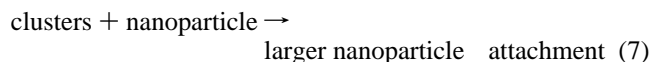
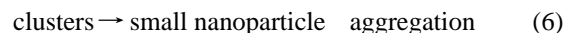
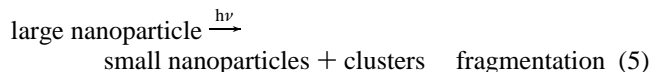
$$d_{\text{average}} \sim h/h_0 \quad (3)$$

$$d_{\text{average}} \sim w_0/w \quad (4)$$

where  $h_0$  and  $w_0$  are constants. By taking advantage of the relations, the decrease of the peak height and the increase of the peak width by irradiation of the 532-nm laser are interpreted as that the parent nanoparticles are fragmented into smaller nanoparticles by the laser irradiation (see Figure 1). Similarly, the increase of the peak height and the decrease of the peak width with the elapsed time imply that the smaller nanoparticles produced by the fragmentation grow after the laser is off (see Figure 2).

Under irradiation of a 532-nm laser, a parent gold nanoparticle in an SDS solution absorb more than a thousand photons during a single laser pulse,<sup>29</sup> and is heated to its boiling point, because of efficient transmission of the absorbed energy to the internal energy of the nanoparticles due to a strong electron–photon interaction.<sup>28</sup> The heated nanoparticle is fragmented into smaller nanoparticles with releasing atoms and clusters. The smaller

nanoparticles grow by assembling the clusters and other nanoparticles. These processes are expressed as



The growth by the aggregation and the attachment takes place simultaneously. The coagulates formed by the aggregation and the attachment are subjected to coalescence.<sup>36</sup> Hereafter, we define assembling of clusters as “aggregation” and attachment of clusters onto the nanoparticles as “attachment”.

**4.2. Change of Spectral Features by Aggregation and Attachment.** Under irradiation of the pulsed 532-nm laser onto a solution containing gold nanoparticles, gold atoms or gold clusters must be released from the nanoparticles. The gold atoms released in a solution are stable so that they are not ionized or oxidized even in an aqueous solution. According to our preliminary study, transition metal atoms are found to be oxidized in an aqueous solution. The gold atoms rapidly aggregate into small gold clusters in a nanosecond time scale.<sup>37</sup> These clusters are so small that they are regarded to be nonmetallic. Therefore, they exhibit no significant optical absorption in the wavelength of the surface plasmon peak (“colorless”), although the nonmetallic clusters show a broad absorption corresponding to the HOMO–LUMO gap.<sup>38</sup> The gold clusters begin to contribute to the optical absorption as they grow into nanosized particles by aggregation (see eq 6) and attachment to the nanoparticles (see eq 7), followed by coalescence. In addition to the direct attachment of clusters to the nanoparticles, nanoparticles can grow by the atomic diffusion (Ostwald ripening), where atoms evaporating from clusters diffuse and attach to the nanoparticles in a solution. Figure 2a demonstrates the growth process of the clusters. The growth of the gold clusters into nanoparticles completes within 2 h after the pulsed laser for the size reduction is switched off (see Figure 3).

The absorbance in the whole wavelength range of 400–900 nm ceases to increase any more when the “colorless” clusters are exhausted for the particle growth, and instead the 520-nm plasmon peak rises and is sharpened due to further growth by assembling “colored” nanoparticles while conserving the absorbance summed in the entire wavelength range measured. In other words, the absorbance at 520 nm increases whereas the absorbance at 700 nm decreases with the elapsed time. These growth processes are shown in panel b of Figure 2.

The growth processes of the nanoparticles produced by the laser fragmentation (size reduction) are not influenced by the laser fluence in the entire fluence range studied (200, 400, and 800 mJ/pulse cm<sup>2</sup>) (see Figure 5): The nanoparticle formation from the clusters ceases within 2 h after the laser irradiation, and the nanoparticles thus formed grow further via aggregation and attachment. The comparison of the spectra shown in Figures 2 and 5 reveals that the nanoparticles grow faster at a higher fluence, probably because more dense clusters are produced at a higher fluence.

**4.3. Growth Processes.** Let us construct a scheme for aggregation and attachment of gold clusters produced by irradiation of the laser for the size reduction. Immediately after the laser irradiation is switched off, the “colorless” gold clusters attach to the surface of nanoparticles; the coagulates seemingly

show the optical absorption at around 600 nm.<sup>39</sup> The coagulates are subjected to coalescence into nanoparticles, and the nanoparticles begin to contribute to the absorption band at 520 nm. It is also likely that the clusters assemble into aggregates and contribute to the optical absorption at 600 nm.

The change of the spectral features shown in Figure 4c,d is explained in terms of this scheme. In the time window of 0–30 min, the absorbance at 600 nm increases gradually with the elapsed time because of cluster attachment onto a nanoparticle surface. The peak shifts to a shorter wavelength after the elapsed time of 30 min indicates nanoparticle formation by coalescence. Note that the coagulates are still being formed by assembling the clusters even at this elapsed time. The formation of coagulates is decelerated due to a decreasing concentration of the clusters by the coagulation, whereas the nanoparticle formation continues until the coagulates are supplied by the attachment of clusters onto the nanoparticles. As a result, the absorbance at 500 nm continues to increase, whereas  $A(t) - A(t - 15)$  has a negative value at 650 nm due to depletion of the coagulates.

This conjecture is supported by the difference spectra,  $A(t) - A(0)$ , of solutions after the laser irradiation at different laser fluences (see also Figure 6). The absorbance at 600 nm increases greatly with the elapsed time in the time window of 0–30 min at 800 mJ/pulse cm<sup>2</sup>, whereas no appreciable increase in the absorbance is observed at 500 nm. After 30 min, the peak position gradually shifts to a shorter wavelength. The spectral change is slightly different from that of gold nanoparticles after the laser irradiation at 200 mJ/pulse cm<sup>2</sup>, where the absorbance around 400–700 nm monotonically increases with time (see Figure 6a,b). The increment of the absorbance at 600 nm is more greatly pronounced under irradiation at a higher fluence, probably because more dense clusters are produced, and hence, coagulates of clusters and nanoparticles are more rapidly formed due to a frequent encounter of the clusters.

**4.4. Optical Absorption of Gold Clusters.** The absorbance of the solution containing gold nanoparticles at the wavelength of 200 nm increases significantly after the laser irradiation at 532 nm (see Figure 1), but decrease with the time elapsed after the laser irradiation (see Figure 4a). These findings imply that the “colorless” gold clusters have an optical absorption in the vicinity of 200 nm. This absorption is likely to be related to several intense atomic lines of gold in the vicinity of 200 nm.<sup>40</sup> In fact, the absorbance at 200 nm was depleted, when the gold clusters start to aggregate (see Figure 4c). In addition, the absorbance at 200 nm does not change, when the gold clusters in the solution are mostly consumed.

Gold nanoparticles with a diameter as small as 1.4 nm (Au<sub>80</sub>) are known to have a surface plasmon band in the visible region.<sup>41</sup> The gold clusters formed in the present study is considered to be much smaller than Au<sub>80</sub>, because the gold clusters obtained in this experiment have most intense absorption band in the vicinity of 200 nm.

**4.5. Aggregation during Laser Irradiation.** During laser irradiation, gold clusters grow mainly by aggregation and attachment at a sizable rate as argued below. Let us consider an example that parent gold nanoparticles of 8.0 nm in diameter are pulverized into those of 3.4 nm in diameter under irradiation of a 532-nm laser having the fluence of 1000 mJ/pulse cm<sup>2</sup>. Suppose that all the gold clusters produced by the laser irradiation are dispersed to be free in the solution. Then, the number of the constituent gold atoms in all the nanoparticles in the solution should be reduced by 92% by the laser irradiation, by taking into account the fact that the gold clusters do not

contribute to the optical absorption in the region where the plasmon peak is present. Therefore, the absorbance at the peak should be reduced by >96%, taking the size effect into consideration. In reality, a very small portion of the gold atoms (~8% of the gold atoms in the solution) was found to remain in the solution as free clusters, calculated from the absorbance of the nanoparticles in the solution immediately after the laser irradiation. It turns out that a considerable portion of the clusters released from the nanoparticles by laser irradiation aggregate and attach readily to other nanoparticles and the rest remains in the solution. If all the gold clusters aggregate into nanoparticles in the solution immediately, the absorbance of the nanoparticles increases linearly with  $d_{\text{average}}$ .

In the previous study, we have studied the dependence of the average diameter of nanoparticles on the fluence of the laser for the size reduction at 532 nm. It has been found that under irradiation of a 532-nm laser the average diameter decreases until 700 mJ/pulse cm<sup>2</sup> and levels off, as the laser fluence increases.<sup>29</sup> The leveling off behavior is explained in terms of a competitive contribution of the fragmentation, and the aggregation which operates dominantly above 700 mJ/pulse cm<sup>2</sup>. In fact, the present experiment also shows that the growth by the aggregation and the attachment tends to dominate, as the fluence of the irradiation laser increases (see Figure 6). Nanoparticles must be more greatly fragmented into clusters by a more intense laser. Hence, the growth by the aggregation and the attachment proceeds more rapidly. The average diameter of the nanoparticles turns out to be unchanged when the rate of the fragmentation coincides with that of the growth. Seemingly, the two process are balanced at a fluence of ~700 mJ/pulse cm<sup>2</sup>.

**4.6. Formation of Small Nanoparticles by Suppression of Particle Growth.** Taking the fragmentation and the growth mechanisms into account, one devises a method for preparing small nanoparticles with optimizing a concentration of SDS. As shown in Figure 7, the absorbance of gold nanoparticles increases more slowly in the 0.05 M SDS solution than in the  $1 \times 10^{-3}$  M SDS solution. In addition, the difference spectra shown in Figure 8 exhibit the monotonic increase of the absorbance with the elapsed time in the vicinity of 500 nm. Namely, the gold clusters formed by the laser irradiation in a concentrated SDS solution tend to attach to the nanoparticles, where the gold nanoparticles are coated with SDS molecules. The slow growth of the nanoparticles is ascribable to the tight coating of SDS. Gold clusters have to travel through bulky SDS molecules to reach gold nanoparticles in a concentrated SDS solution. As the SDS concentration increases, the diffusion rate of the small fragments decreases, and hence, the rate of the aggregation decreases. On the other hand, the fragmentation does not change significantly with the SDS concentration, because the fragmentation is driven by absorption of more than a thousand photons during a single laser pulse.

As mentioned above, a stationary condition is fulfilled between the fragmentation by the laser irradiation and the growth by the aggregation in a SDS solution under irradiation of the laser. When SDS molecules are added to the solution, the growth by the aggregation is greatly retarded so that smaller nanoparticles tend to be produced in a more concentrated SDS solution (see Figure 9). The conjecture is supported by the dependence of the relative absorbance on the SDS concentration (see Figure 10). The relative absorbance or the average diameter of nanoparticles decreases most significantly at the critical micelle concentration of SDS ( $8 \times 10^{-3}$  M). It seems that several layers of SDS molecules cover tightly the nanoparticles above the

critical micelle concentration and/or the micelle formation hinders diffusion of nanoparticles in the solution.<sup>19,42</sup> To elucidate the role of SDS in a microscopic level, the structure of SDS molecules covering a nanoparticle needs to be observed by a spectroscopic method. Figure 11 shows size-distributions of nanoparticles produced in the  $1 \times 10^{-3}$  and the 0.05 M SDS solutions. Evidently, the size-distribution shifts to a smaller size when the concentration of SDS is higher. In summary, much smaller nanoparticles with a narrow size-distribution are prepared by irradiation of a more intense laser in a more concentrated SDS solution.

## 5. Conclusions

Growth processes occurring concurrently with laser-induced fragmentation were studied for gold nanoparticles of  $\sim 8$  nm in diameter by optical-absorption spectroscopy and electron microscopy. Gold nanoparticles were found to grow by aggregation of gold clusters and by attachment to other nanoparticles. We showed that much smaller gold nanoparticles with a narrow size-distribution were prepared by optimizing the laser fluence, the concentrations of nanoparticles, and SDS in water.

**Acknowledgment.** This work is financially supported by the Cluster Research Project of Genesis Research Institute, Inc.

## References and Notes

- (1) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.
- (2) Sakurai, H.; Haruta, M. *Appl. Catal. A: General* **1995**, *127*, 93.
- (3) Takagi, M. *J. Phys. Soc. Jpn.* **1954**, *9*, 359.
- (4) Hodak, J. H.; Martini, I.; Hartland, G. V.; Link, S.; El-Sayed, M. A. *J. Chem. Phys.* **1999**, *108*, 9210.
- (5) Wilcoxon, J. P.; Martin, J. E.; Parsapour, F.; Wiedenman, B.; Kelley, D. F. *J. Chem. Phys.* **1998**, *108*, 9137.
- (6) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.
- (7) Ahmadi, T. S.; Logunov, S. L.; El-Sayed, M. A. *Nanostructured Materials*; Shalaev, V. M., Moskovits, M., Eds.; American Chemical Society: Washington, DC, 1997.
- (8) Hirai, H.; Wakabayashi, H.; Komiyama, M. *Chem. Lett.* **1983**, 1047.
- (9) Hirai, H.; Wakabayashi, H.; Komiyama, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 367.
- (10) Petit, C.; Lixon, P.; Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 12974.
- (11) Pileni, M. P. *Nanostructured Materials*; Shalaev, V. M., Moskovits, M., Eds.; American Chemical Society: Washington, DC, 1997.
- (12) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
- (13) Fojtik, A.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 252.
- (14) Neddersen, J.; Chumanov, G.; Cotton, T. M. *Appl. Spectrosc.* **1993**, *47*, 1959.
- (15) Sibbald, M. S.; Chumanov, G.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 4672.
- (16) Yeh, M. S.; Yang, Y. S.; Lee, Y. P.; Lee, H. F.; Yeh, Y. H.; Yeh, C. S. *J. Phys. Chem.* **1999**, *103*, 6851.
- (17) Yeh, Y. H.; Yeh, M. S.; Lee, Y. P.; Yeh, C. S. *Chem. Lett.* **1998**, 1183.
- (18) Chen, Y. H.; Yeh, C. S. *Colloids Surf.* **2002**, *197*, 133.
- (19) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem.* **2000**, *104*, 8333.
- (20) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem.* **1999**, *104*, 9111.
- (21) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem.* **2001**, *105*, 5114.
- (22) Eckstein, H.; Kreibig, U. *Z. Phys. D* **1993**, *26*, 239.
- (23) Niidome, Y.; Hori, A.; Sato, T.; Yamada, S. *Chem. Lett.* **2000**, 310.
- (24) Niidome, Y.; Hori, A.; Takahashi, H.; Yamada, S. *Stud. Surf. Sci. Catal.* **2001**, *132*, 359.
- (25) Niidome, Y.; Hori, A.; Takahashi, H.; Goto, Y.; Yamada, S. *Nano Lett.* **2001**, *1*, 365.
- (26) Kamat, P. V.; Flumiani, M.; Hartland, G. V. *J. Phys. Chem. B* **1998**, *102*, 3123.
- (27) Kurita, H.; Takami, A.; Koda, S. *Appl. Phys. Lett.* **1998**, *72*, 789.
- (28) Takami, A.; Kurita, H.; Koda, S. *J. Phys. Chem. B* **1999**, *103*, 1226.
- (29) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T. *J. Phys. Chem. B* **2001**, *105*, 9050.
- (30) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1983.
- (31) Doremus, R. H. *J. Chem. Phys.* **1964**, *40*, 2389.
- (32) Kreibig, U.; Fragstein, C. v. *Z. Phys.* **1969**, *224*, 307.
- (33) Kreibig, U. *J. Phys. F* **1974**, *4*, 999.
- (34) Gramqvist, C. G.; Hunderi, O. **1977**, *16*, 3513.
- (35) Charle, K.-P.; Frank, F.; Schulze, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 350.
- (36) Abid, J.-P.; Girault, H. H.; Brevet, P. F. *Chem. Commun.* **2001**, 829.
- (37) Dawson, A.; Kamat, P. V. *J. Phys. Chem. B* **2001**, *105*, 960.
- (38) Link, S.; Beeby, A.; FitzGerald, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2002**, *106*, 3410.
- (39) Galletto, P.; Brevet, P. F.; Girault, H. H.; Antoine, R.; Broyer, M. *J. Phys. Chem. B* **1999**, *103*, 8706.
- (40) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Frederikse, H. P. R., Eds.; CRC Press: New York, 1997.
- (41) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706.
- (42) It has been reported that gold nanoparticles sustain more firmly against centrifugation in a more concentrated SDS solution, because the gold nanoparticles are more fully coated by SDS molecules and/or are contained in micelles of SDS molecules.<sup>25</sup>