

# Colloidal Stability of Gold Nanoparticles in 2-Propanol under Laser Irradiation

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The influence of laser light irradiation at the surface plasmon frequency of the gold nanoparticles suspended in 2-propanol is examined by the UV–vis absorption spectral measurement and also by a transmission electron microscope. It has been found that the laser light irradiation on the colloidal suspension causes coagulation or dispersion of the particles depending on the particle concentration of the suspension. To investigate the cause of this finding, we have measured the  $\zeta$ -potential of the particles by an electrophoretic light scattering method. This measurement suggests that the dispersion phenomenon of flocculates is due to the increment in the  $\zeta$ -potential of the particles which prevents mutual access of negatively charged particles. The photochemical reaction, in which the gold particles obtain electrons from a solvent molecule, is suggested to be responsible for this process.

## Introduction

Nanometer-sized metallic particles have gathered much attention by their peculiar coloration different from the bulk state, depending on the particle size and on the colloidal dispersion state.<sup>1</sup> The color of metal nanoparticles is originated from an absorption band of the characteristic surface plasmon. This phenomenon is well described by a classical Mie's scattering theory in a diluted system<sup>2</sup> and Maxwell–Garnett theory in a concentrated system.<sup>3</sup> So far we have studied a dispersion–coagulation process of Au nanosuspensions in relation to the optical properties as a function of temperature,<sup>4</sup> the light irradiation by mercury lamp,<sup>5,6</sup> and the addition of salt.<sup>5,6</sup> In some cases, the initial narrow absorption peak was broadened or a new peak appeared at a longer wavelength at the tail of the initial absorption band. It was reported that the surface plasmon peak shifts to a longer wavelength and is broadened or a new peak appears at a low-energy region when well-isolated particles form densely packed aggregates.<sup>7,8</sup> This is explained by the dipole interaction between neighboring particles. Recently, we have reported that the coagulation of nanometer-sized gold colloids in organic media can be promoted by the irradiation of an electromagnetic wave at a Mie resonance frequency based upon a polarization of free electrons and the dipole interaction induced in a surrounding particle.<sup>9,10</sup> The gold ultrafine particles in 2-propanol, being stable over several months in dark conditions, coagulated and sedimented within 30 h upon irradiation with a high-pressure mercury lamp, showing that the acceleration of the rate of coagulation was more than 1000 times higher than in the dark.<sup>5,6</sup> It has also been shown that the acceleration of coagulation is characteristic of the irradiation at the Mie resonance frequency as proven by the wavelength dependence of illuminating light. The same effect has also been observed for gold particles in water.<sup>11</sup> The van der Waals force including the well-known London dispersion force can be enhanced by the irradiation of the light at plasmon frequency due to the photoinduced dipole interaction. Therefore, the van der Waals force becomes more effective under irradiation. This effect was incorporated in a Hamaker constant which is directly related to the van der Waals force.<sup>9</sup> The reduction of the repulsive Coulomb force due to changes of surface charging by photochemical process, involving ad-

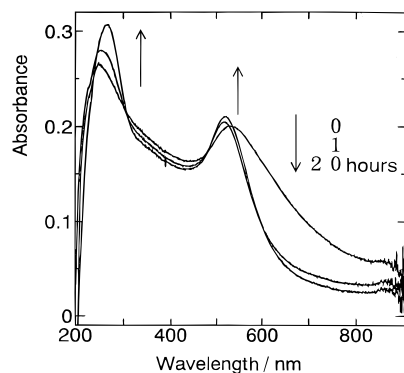
sorbed or chemisorbed ions, can also explain the observed phenomenon. The temperature effect on the coagulation process also cannot be overlooked.<sup>4</sup> In order to examine the cause of these findings, we have measured the change in the  $\zeta$ -potential during a coagulation process of gold nanoparticles dispersed in 2-propanol and compared the result with observations by a transmission electron microscope and the spectra made in the visible region. We have also measured the time course of the absorption spectrum upon laser irradiation as a function of laser power and the number density of particles in a colloidal suspension.

## Experimental Section

Gold nanoparticles were prepared by the gas-flow solution-trap method.<sup>6,12</sup> Although conventional chemical reduction methods in a liquid phase also give a good gold suspension,<sup>13,14</sup> the surfaces of gold particles produced by chemical methods are not clearly defined because of the considerable surface modifications with chemisorption of several kinds of compounds. It is well-known that the optical properties of colloidal ultrafine particles are considerably affected by chemisorbed molecules.<sup>15–17</sup> Therefore these techniques are not suitable for the present purpose. The suspension prepared by our method is stable without any surfactants or stabilizers and is cleaner and simpler than that produced by chemical methods.

Gold (99.999% purity) was evaporated from a tungsten crucible maintained at a constant temperature into an inert gas stream to produce nanometer-sized ultrafine particles (UFPs) in a stainless sample preparation chamber. The mixture of He (99.9999% purity) and Ar(99.9999% purity) was supplied as a carrier gas.<sup>18</sup> The partial pressures of He and Ar were 1.2 and 0.3 kPa, respectively. We can control the size of particles by the change of gas species, the gas pressure, and the evaporation temperature.<sup>19</sup> The particles thus produced were carried away with the gas stream to be trapped into cold organic liquids forming colloidal sol in a Pyrex glass sample container, which is dipped into almost freezing ethanol. Special grade 2-propanol(99.9% purity) without further purification was used as a trapping substance giving a good dispersion. Immediately after the preparation, the suspension was carefully transferred to a quartz rectangular cuvette with a 1 cm optical path length. During this process, the temperature of the suspension was

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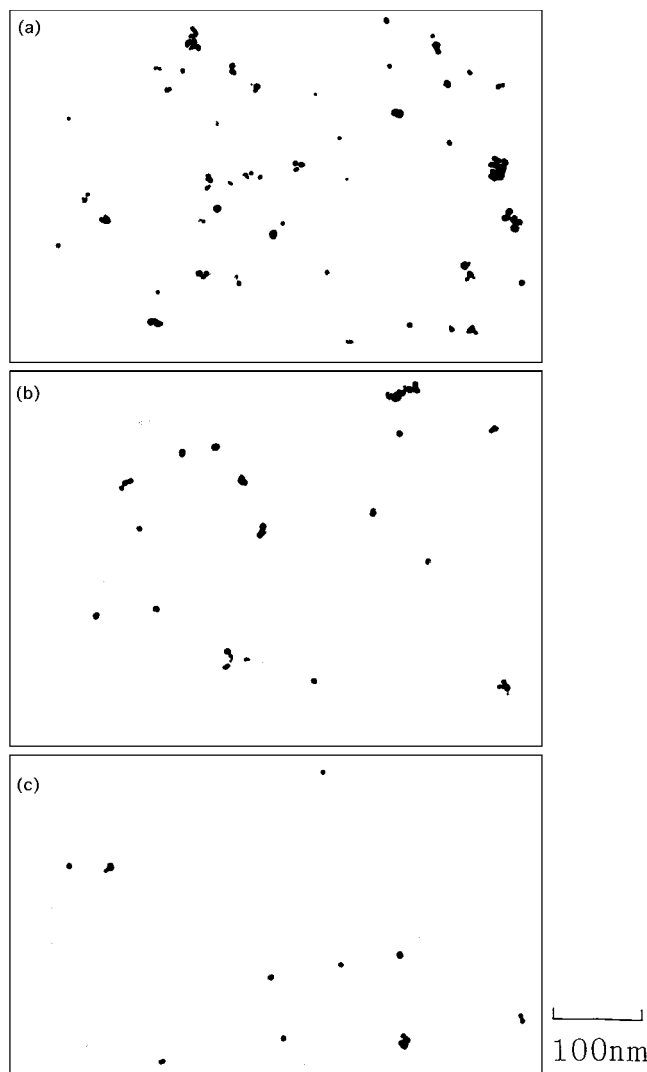
**Figure 1.** Optical absorption spectra of AuUFP-2-propanol suspension as a function of time without laser irradiation. The numbers in the figure are the passage of time after the preparation of the sample.

increased up to room temperature from about  $-50\text{ }^{\circ}\text{C}$ . This quartz cuvette and sample container were washed thoroughly beforehand with aqua regia, distilled water, and 2-propanol itself, in this order, because the suspension is very sensitive to any stain on a glass wall; even a little stain can affect the colloidal state of the suspension.

The suspension thus prepared was illuminated by an Ar-ion laser (Coherent Innova 90) operating at 514 and 488 nm wavelengths, which nearly correspond to the surface plasmon frequency of the gold particles. The gold particles gradually coagulate or disperse with the illumination, although they were stable for more than several months in dark conditions. UV-vis extinction spectra were recorded by a Hitachi UV-3210 spectrophotometer at room temperature at an appropriate time interval. The extinction spectra were practically equivalent to the absorption spectra because the scattering effect is not important when the particle diameter is less than 10 nm. We have compared two spectra taken by a normal absorption method with those using an integrating sphere and have found no difference between them except for the signal-to-noise level. Hence, we will call hereafter the extinction spectrum the absorption spectrum. The colloidal state and particle size were observed with a Hitachi H-8100 transmission electron microscope (TEM) operating at 200 kV in a high-resolution mode. The specimen for TEM was obtained by dropping a sample solution onto a Cu mesh coated with an evaporated carbon film of 50 nm in thickness, which was allowed to dry in air. The evaporation of 2-propanol is so fast that coagulation is not perceptible in the sample preparation process. The  $\zeta$ -potential of the particles in a liquid was measured by an electrophoretic light-scattering method using an Ohtsuka Electronics ELS-800 electrophoretic photometer at  $20\text{ }^{\circ}\text{C}$ . To measure the  $\zeta$ -potential accurately, we have carefully determined the measurement position of the quartz cell so as to extinguish the light scattering from a cell wall. In order to monitor reaction products in the course of laser irradiation without the disturbance caused by the gold plasmon absorption, gold particles were completely removed by a filtration technique using the  $0.2\text{ }\mu\text{m}$  hydrophobic filter MILLEX-FG (Millipore Corporation) after precipitation caused by adding 10 mM NaCl, and the resulting effluent was analyzed by a spectrophotometer and a NMR spectrometer.

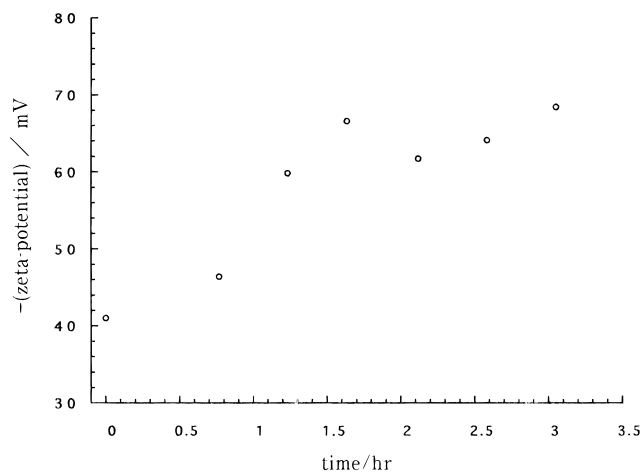
## Results and Discussion

**Initial Instability of Suspensions.** We have noticed that the suspension shows a color change at an initial stage. Figure 1 shows the time course of the optical absorption spectra of the AuUFP-2-propanol system starting from just after being prepared without laser irradiation. During this period, the temperature of the sample is elevating from  $-50\text{ }^{\circ}\text{C}$  up to the



**Figure 2.** TEM micrographs of Au particles shown in Figure 1 undergoing the redispersion: (a) just after preparation, (b) 1 h later, (c) 20 h later.

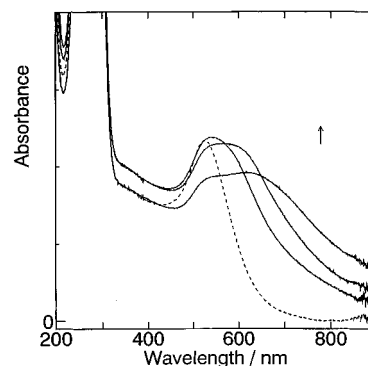
room temperature. The color of the suspension changed from purple to reddish purple. The peak located around 530 nm is due to the surface plasmon band which strongly depends on not only the size of the particles but also the colloidal state of the suspension, whether it is isolated, coagulated, or so on. The plasmon band of coagulated particles shifts to a longer wavelength than that of isolated ones. With the proceeding of the coagulation, the plasmon band shows a broadening of the line width along with a shift to a longer wavelength side, because the absorption band is a superposition of many bands of the various particles having different colloidal states. This plasmon band overlaps with the 5d-6s interband transition starting from about 600 nm. With an increase of the intensity of the 530 nm peak, the intensity of an absorption band at longer wavelength decreased, indicating the redispersion of flocculates at room temperature. Since gold UFPs in gas phase are well separated from each other in the course of the preparation,<sup>18</sup> it is thought that the formation of flocculates occurs after trapped in the cold solution. This color change from purple to reddish purple did not take place while the sample was kept in a cold condition and did not return to purple by a cooling method once reddish purple color has been attained, implying that this is an irreversible process. After this period, the suspension was very stable and no change was found for several months. Figure 2 shows the transmission electron micrographs of the gold particles corresponding to the spectral change in Figure 1. The



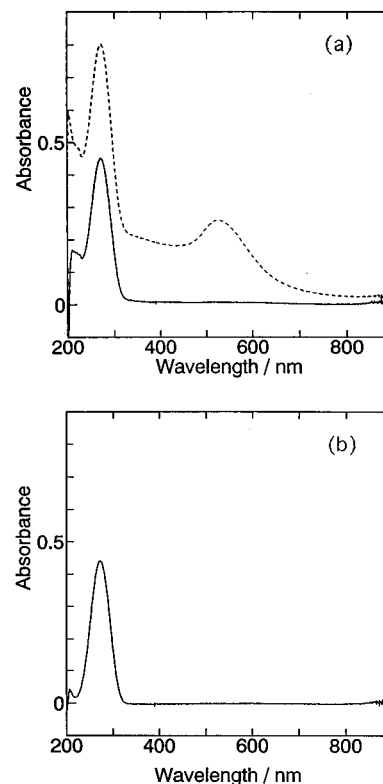
**Figure 3.** Time development of  $\zeta$ -potential of particles corresponding to the change in UV-vis absorption spectra shown in Figure 1.

slightly aggregated particles just after preparation, Figure 2a, are isolated and regarded as being nearly monodispersed having a diameter of 8 nm as shown in Figures 2b,c. It is confirmed from these micrographs that the trapped gold particles forming flocculants in a cooled glass container are gradually redispersed in a liquid as time passed. In the previous paper,<sup>4</sup> we qualitatively explained the reason why the redispersion occurs on the bases of Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The existence of a shallow second minimum in the total interaction potential between neighboring particles, which results from an attractive van der Waals potential and a repulsive electrostatic potential, allows the weak coagulation of particles at a low temperature and the dissociation of particle cluster at an elevated temperature. However this simple interpretation cannot explain the irreversible process. If the absolute value of the  $\zeta$ -potential increases during the initial redispersion process, the dispersion state will be more enhanced. Figure 3 shows the time development of the  $\zeta$ -potential measured by an electrophoretic light-scattering method after the sample preparation. The final  $\zeta$ -potential thus determined is found to be  $-68$  mV. Several final values were obtained depending on the sample preparation conditions. In many cases, it was  $-40$  or  $-45$  mV as mentioned later. Figure 3 suggests that the charge of the particles gradually increased, causing the gradual increase of a repulsive coulomb force, hence promoting the separation of the flocculates. That is, the increased absolute value of the  $\zeta$ -potential stabilizes the redispersion state. The charging mechanism is discussed in the following section. It is usually assumed that a  $\zeta$ -potential or a surface charge is unchanged during the sedimentation or dispersion process in an aqueous dispersion. For a nonaqueous dispersion, however, this is not well established because the charging mechanism itself is not yet clear.

**Effect of Salt.** To investigate whether the coagulation states of the particles in the solution cause the change in the  $\zeta$ -potential or not, we measured both the  $\zeta$ -potentials of the well-separated particles and of the coagulated particles. The particles will coagulate if the electrostatic Coulomb repulsion becomes smaller than the van der Waals attraction within the framework of the DLVO theory. Coagulated particles were prepared by an addition of NaCl up to a concentration of  $0.2 \times 10^{-4}$  M. Figure 4 is a spectral change corresponding to the coagulation process. The color of the suspension turned from an initial reddish purple to blue in the end. This spectral behavior of plasmon band, namely, red-shifted and broadened, is compatible with the finding that coagulation proceeds in the suspension.<sup>7,8</sup> The  $\zeta$ -potential of the particles was unchanged through this process



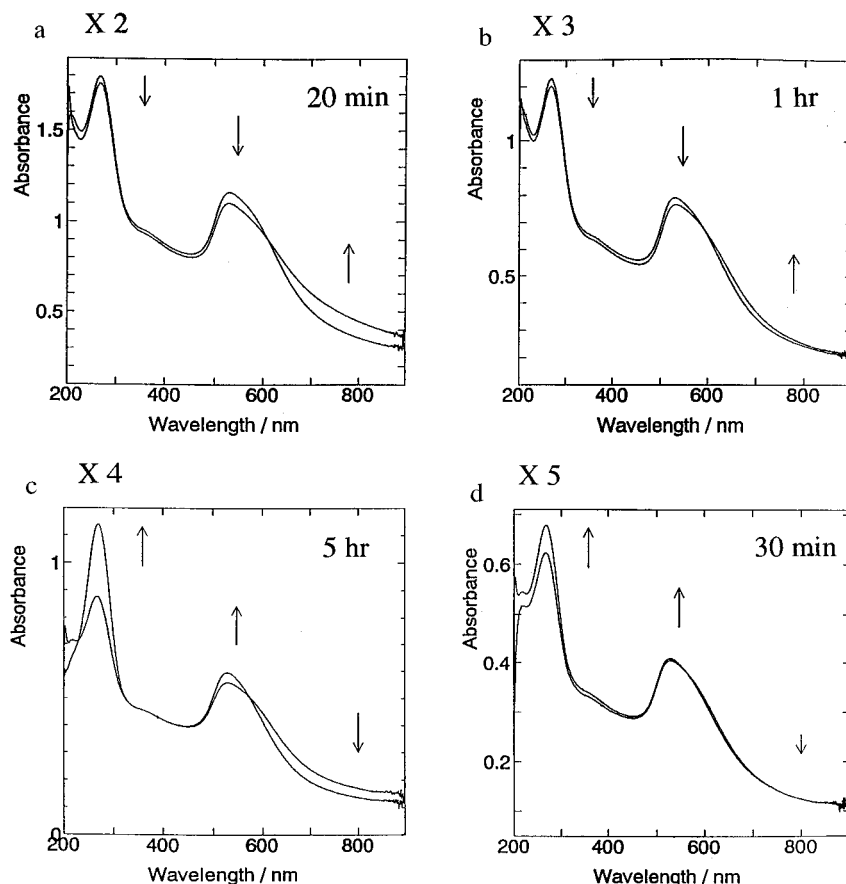
**Figure 4.** Effect of NaCl addition to Au-2-propanol suspension. Broken line, spectrum before addition of NaCl; solid line, spectrum at 1 min, 8 h, and 11 days after addition of NaCl.



**Figure 5.** Optical absorption spectra: (a) solid line, 2-propanol after the removal of Au particles; broken line, AuUFP-2-propanol suspension and (b) 0.25% acetone added to 2-propanol.

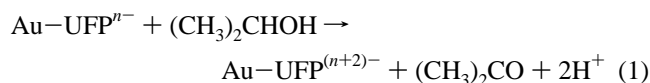
and was at about  $-45$  mV as expected from DLVO theory and an assumption of constant surface potential during particle sedimentation process. This result shows that the change of  $\zeta$ -potential found in an initial warming up process is not induced by the redispersion process itself, but it is a cause of redispersion.

**Assignment of a UV Peak.** In the previous paper,<sup>6</sup> we did not clearly identify the species giving the absorption peak at 273 nm wavelength, although we suggested that acetone or alkoxide is responsible for this absorption. To investigate the species relevant to this absorption of the suspension, we have measured the UV spectrum of the effluent after gold particles were removed by precipitation and filtration. Figure 5a shows the absorption spectra of the filtrate (solid line) and the original suspension (broken line). It shows that the peak at 273 nm wavelength is due to the substances dissolved in the solution but not to the gold particles themselves and/or adsorbates on a particle. Figure 5b shows the absorption spectrum of a control solution of 2-propanol in which 0.25% acetone was added, suggesting acetone in 2-propanol has the peak at 273 nm



**Figure 6.** Effect of the irradiation of the laser light to the different concentration of AuUFP-2-propanol suspension: (a)  $\times 2$ , the suspension was diluted twice; (b)  $\times 3$ , triple; (c)  $\times 4$ , four times; (d)  $\times 5$ , five times. The numbers in the inset are irradiation times.

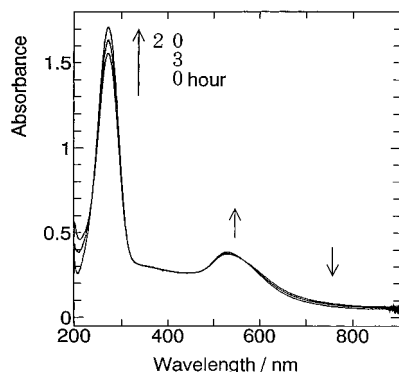
wavelength in the absorption spectrum. These spectra are almost the same in the shape and the intensity.  $^1\text{H-NMR}$  measurement was also done to assign the origin of the unknown species in the effluent. It almost gave the same quantities of acetone (0.18%) from the suspension calibrated with a control solution (0.25% acetone in 2-propanol), while no acetone was detected in 2-propanol itself. These results indicate that the absorption peak at 273 nm is due to acetone which is produced in a suspension. In Figure 1, the intensity of the peak of acetone gradually increased as time passed. The acetone is suggested to be produced from 2-propanol with the help of gold particles being a catalyst as suggested in the following scheme, which resembles the case when silver cluster was the catalyst.<sup>20</sup>



In this reaction, the gold particle obtains electrons from 2-propanol, which decomposes into acetone and two protons even in dark conditions. The intermediate radicals 1-(hydroxymethyl)ethyl radicals, normally formed by gamma irradiation or UV irradiation, have reducing properties. This scheme explains why the absolute value of the  $\zeta$ -potential increased (repulsive Coulomb force became enhanced), causing the redispersion of the particles.

**Laser Light Irradiation.** The irradiation of the laser light at 514 nm was performed with stable suspension systems. There was no change in optical absorption spectra under the dark conditions of the experimental period for the stable suspension, except for the initial instability period where the 273 nm peak gradually increases to a stationary level. First, the laser irradiations were performed at 0 °C under a vigorous circulation

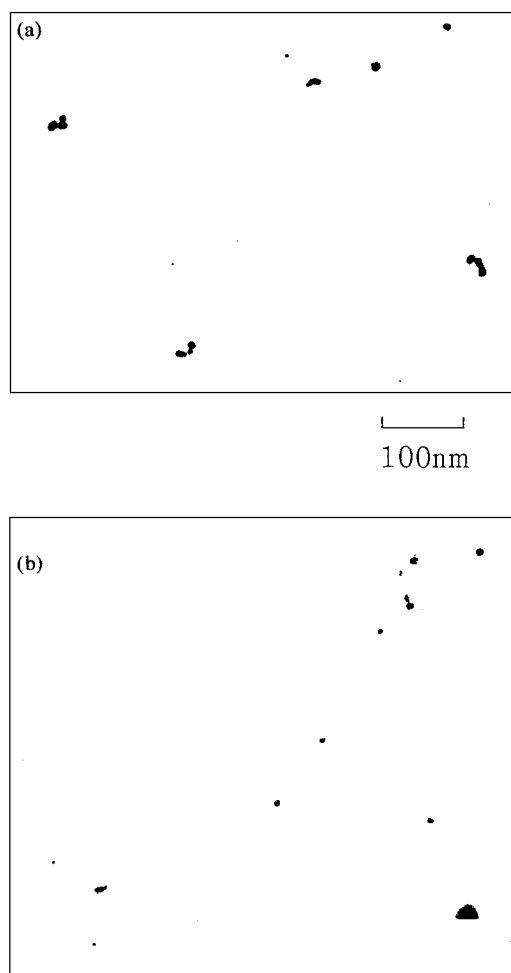
of water to completely reduce the thermal effect. The laser irradiation with the water filter did not cause any measurable change. Hence, temperature effect induced by the light irradiation is important. However, the heating of the 0 °C suspension to room temperature did not cause any remarkable change. To investigate the temperature effect, the sample solution was divided in two, one was for a heating experiment at 30 min at 75 °C and the other for laser irradiation at 1.7 W for 20 min. Although the heat effect promoted the coagulation to some extent, the effect was found to be weaker than that caused by laser irradiation with the above-mentioned conditions in which the steady state temperature was 59 °C. Figure 6 shows the spectral changes by the light irradiation for different concentrations of suspensions without temperature control. Various concentrations of samples were obtained by the dilution of the original suspension with 2-propanol. Comparing Figures 6a–b at time 0, there was no change in the shapes of the absorption spectra with the different concentrations of the suspension, suggesting that the colloidal state of the suspension is unchanged during dilution process. As shown in Figures 6c,d, when the concentration of gold particles is low, the flocculates dispersed to a single particle by the light irradiation as indicated by the increase of the plasmon peak. On the contrary, in high particle concentration as shown in Figures 6a,b, the coagulation of the particles occurred. The threshold value lies between three and four times the dilution concentration. The difference of the response of the different concentrations to the laser light irradiation suggests that there is possibly a change in the electrostatic charge on the particles by diluting the suspension with 2-propanol. Therefore, the  $\zeta$ -potential of the gold particles was measured before and after the dilution of the suspension.  $\zeta$ -potentials of diluted and nondiluted suspension are almost the



**Figure 7.** Time course of the absorption spectra of AuUFP-2-propanol suspension during the irradiation of the laser light. The numbers in the figure are the illumination times.

same and independent on the extent of dilution, showing always around  $-40$  mV. Consequently, the particle concentration cannot be related to the  $\zeta$ -potential. The concentration of the electrolyte, which may accidentally have been introduced as an impurity if exist, simultaneously decreased when the suspension was diluted. It is well-known that the existence of electrostatic double layer around particles prevents further approach of other particles and that the thickness of the double layer increases with a decrease in the concentration of electrolyte. That is to say, the diluted suspension is more stable than the nondiluted suspension. The coagulation is not liable to occur in more stable suspensions. However, we must reserve a final decision in future. We notice that the intensity of the peak at 273 nm is gradually increased along with the increase of the intensity of the plasmon peak and the decrease of the intensity at the longer wavelength side in the dispersion process of Figures 6c,d. To the contrary, in the coagulation process of Figures 6a,b, the intensity of the peak at 273 nm is almost unchanged irrespective of the broadening of the plasmon peak in the spectra.

We have continued the laser irradiation for up to 20 hr and then recorded the changes of the absorption spectra for the diluted sample. In Figure 7, the intensity of the peak at 273 nm due to acetone has increased, suggesting the further dispersion of particles as time passed. We assume that this phenomenon is similar to the process represented by eq 1. Figure 8 shows electron micrographs of the particles before and after irradiation corresponding to Figure 7. These micrographs confirm that the flocculates were redispersed by the light irradiation. We measured the  $\zeta$ -potential of the particles before and after light irradiation. The value of the  $\zeta$ -potential decreased from  $-45$  to  $-60$  mV after the light irradiation. That is to say, the repulsive Coulomb force became stronger than before, causing the particles to gradually disperse. The gold particles could get electrons from 2-propanol through a photochemical process that produces the acetone. This proposition is supported by the spectra shown in Figure 7 in which the acetone peak is growing. In a relatively concentrated suspension where the particles gradually coagulated by the light irradiation, the  $\zeta$ -potential did not change before and after the light irradiation. In fact, the reaction of producing acetone was not observed in Figures 6a,b (concentrated system). It seems that the energy carried with the radiation field is used to overcome the interparticle repulsive energy barrier in a concentrated system, whereas in a diluted system, the field energy may be converted to chemical energy. The coagulation took place for the particles having a kinetic energy higher than the potential barrier. This irreversible coagulation was promoted by the laser light irradiation. The dispersion and coagulation induced by the illumination were found to be irreversible. No further change was found



**Figure 8.** TEM photographs of Au particles: (a) before the light irradiation, (b) 20 h under the irradiation.

once the light irradiation has extinguished. The reason of why acetone was formed from 2-propanol in one case (diluted suspension) and did not in other case (concentrated suspension) is now an open question.

The laser irradiation at 488 nm wavelength was performed, and the result was nearly the same as that for 514.5 nm. Power dependence of the irradiation was also examined. With the low-power light irradiation (0.45 and 0.9 W) with a long irradiation period, any measurable change was not observed. But when intense laser irradiation (1.35 and 1.8 W) was applied to the system, the changes of the colloidal state were observed as described above. The existence of the threshold in the laser power means that this photoinduced coagulation or redispersion is caused by a nonlinear process by light irradiation.

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