

Formation of Stable Platinum Nanoparticles by Laser Ablation in Water

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Platinum nanoparticles were produced by laser ablation of a platinum metal plate in an aqueous solution of sodium dodecyl sulfate (SDS). The absorption spectrum of the platinum nanoparticles was essentially the same as that of platinum nanoparticles chemically prepared in a solution. The size distribution of the nanoparticles thus produced was measured to be in the range of 1–7 nm in diameter by an electron microscope. The abundance of the nanoparticles changes with the concentration of SDS in the solution. Stable platinum nanoparticles were found to be produced by this method even in pure water.

1. Introduction

Colloidal metal nanoparticles are of great interest because of their size dependent optical properties, magnetic properties, catalytic activities, etc.^{1–6} For instance, gold nanoparticles smaller than 5 nm in diameter emit intense photoluminescence,⁴ whereas gold nanoparticles smaller than 10 nm in diameter exhibit catalytic activities (low-temperature CO oxidation).^{5,6} It is crucially important, therefore, to develop methods to prepare nanoparticles with a desired diameter.^{7–14} Chemical reduction of metal ions inside reversed micelles in a nonpolar solvent is most commonly employed in the preparation of metal nanoparticles in solutions.^{9–11} A metal salt dissolved in water is confined inside the reversed micelles and is reduced into metal nanoparticles by chemical reduction. The diameters of the nanoparticles are controlled by the effective volumes of the reversed micelles, which are varied by changing the amount of water inside the reversed micelles with changing a molar ratio of water to the nonpolar solvent.

In our previous papers, we have reported investigations on the formation of silver and gold nanoparticles by laser ablation of silver and gold metal plates, respectively, in a sodium dodecyl sulfate (SDS) aqueous solution.^{15–17} We have found that the sizes and the stability of the nanoparticles can be controlled by changing the laser fluence and the SDS concentration. It has been demonstrated in addition that this physical method is free of any reducing agents, which are potential impurities in the nanoparticles produced, and is applicable to the preparation of nanoparticles of any metal elements through ready formation of the metal atoms by laser ablation.^{18–22}

Platinum and its alloy nanoparticles have attracted much attention because they are excellent catalysts for many purposes; for instance, the nanoparticles supported on a porous alumina are used to eliminate NO generated in a combustion process.^{23,24} In this regard, formation of bare and stable platinum nanoparticles is practically important for catalysis involving the platinum element. In the present paper, we studied preparation of stable platinum nanoparticles in solutions containing SDS

and in pure water by the method based on laser ablation of a platinum metal plate in the liquid media. The stability and the formation mechanism of platinum nanoparticles in the SDS solutions were examined.

2. Experimental Section

Platinum nanoparticles were produced by laser ablation of a platinum metal plate in aqueous solutions of SDS. The metal plate (>99.99%) was placed on the bottom of a glass vessel filled with 10 mL of an aqueous solution of SDS and of pure water. The metal plate was irradiated with a focused output of the fundamental (1064 nm) or second harmonic (532 nm) of Quanta-ray GCR-170 Nd:YAG laser operating at 10 Hz with a lens having the focal length of 250 mm. The spot diameter of the laser beam on the surface of the metal plate was varied (1.5–2 mm) by changing the distance between the lens and the metal surface and was measured from the burnt pattern formed on a thermally sensible paper. A Scientech AC2501 power meter was used to monitor the laser power. Upon irradiation of the laser beam, the solution was gradually turned into brown. The absorption spectrum of the solution was measured by a Shimadzu UV-1200 spectrometer. At least five different runs were accumulated on an NEC computer to obtain one spectrum.

The total number of atoms released in the aqueous solution by the laser ablation was measured from the weight loss of the metal plate after the laser ablation. Actually, nanoparticles were produced by the laser ablation as described above, and the procedure was repeated for more than 50 times. The concentration of the atoms in a solution was obtained from the total volume of the solution and the weight loss (~0.02 g).

A transmission electron microscope (JEOL JEM-2000EXII) was employed to take electron micrographs of the nanoparticles in the SDS solutions studied. Each size-distribution was obtained by measuring the diameters of more than 1000 particles in sight on a given micrograph. It is still difficult to estimate the abundance of tiny nanoparticles, because nanoparticles as tiny as ~1 nm cannot be identified and evaluated by the electron micrograph. In practice, we ignored these tiny nanoparticles and it may produce an systematic error of 20% in estimating average diameter. We must adopt mass spectrometry in order to determine size distribution of tiny platinum nanoparticles precisely in the future.

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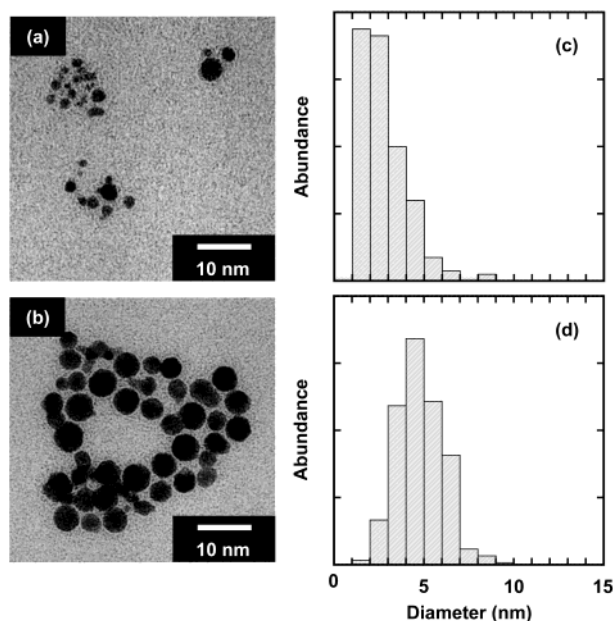


Figure 1. Electron micrographs of platinum nanoparticles produced by laser ablation (532 nm, 1.6 J/pulse cm^2) of a platinum plate immersed in a 0.01-M SDS aqueous solution (panel a) and in pure water (panel b), respectively. The size distributions of the nanoparticles shown in panels a and b are plotted in panels c and d, respectively.

The ζ potential of nanoparticles was measured by the laser Doppler method.^{25,26} The nanoparticles suspended in the solution were illuminated by a laser at 488 nm (10 mW). A frequency shift of the laser light scattered by the nanoparticles was measured under the electric field gradient of 5.0 V cm^{-1} . The velocity of the nanoparticles was calculated from the frequency shift, and the ζ potential was estimated from the velocity and the strength of the field gradient applied.

3. Results

Panels a and b of Figure 1 show typical electron micrographs of platinum nanoparticles produced by laser ablation (532 nm, 1.6 J/pulse cm^2) of a platinum plate immersed in a 0.01-M SDS aqueous solution and in pure water, respectively. Panels c and d of Figure 1 show the size distributions of the nanoparticles shown in panels a and b of Figure 1, respectively. Platinum nanoparticles of 2–5 nm in diameter with the average diameter of 3.0 ± 0.8 nm were found to be produced in the 0.01-M SDS aqueous solution, whereas platinum nanoparticles of 4–7 nm in diameter with the average diameter of 6.2 ± 1.4 nm were produced in pure water. Figure 2 shows a typical optical absorption spectrum of platinum nanoparticles produced by the same experimental condition as that shown in panel a of Figure 1. The spectrum exhibits a structureless broad band extending toward the VUV wavelength range. Figure 3 shows the average diameter of the platinum nanoparticles as a function of the SDS concentration. As the SDS concentration increases, the average diameter remains unchanged up to the SDS concentration of 10^{-3} M and then decreases sharply.

Figure 4 shows the abundance of the platinum nanoparticles (represented by the absorbance in the UV region) as a function of the SDS concentration before (solid circle) and after (open circle) the centrifugation; the abundance is represented by the absorbance in the vicinity of interband transition (~ 300 nm) which is almost proportional to the abundance. In the lower concentration region ($< 10^{-5}$ M), the abundance of the platinum nanoparticles before the centrifugation does not change ap-

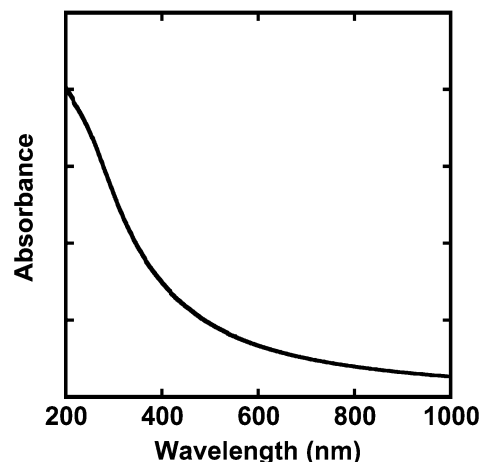


Figure 2. Optical absorption spectrum of platinum nanoparticles produced under the same experimental condition as in Figure 1a.

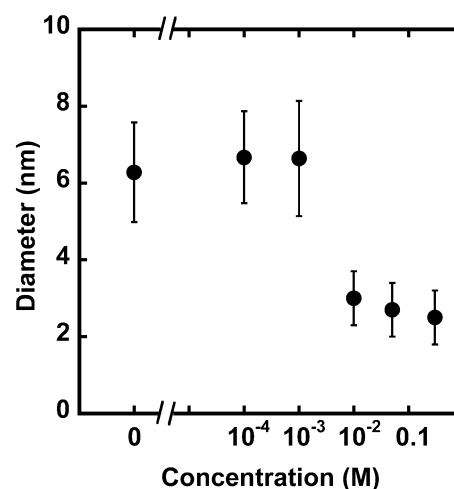


Figure 3. Average diameter of platinum nanoparticles produced by laser ablation (532 nm, 1.6 J/pulse cm^2) as a function of the concentration of SDS in an aqueous solution.

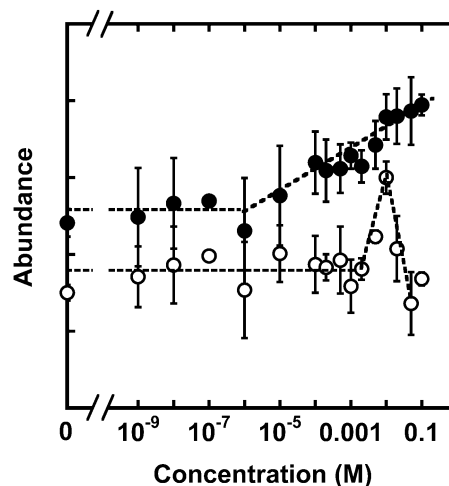


Figure 4. Abundance of platinum nanoparticles produced by laser ablation (532 nm, 1.6 J/pulse cm^2) as a function of the concentration of SDS in an aqueous solution before (solid circle) and after centrifugation (open circle).

preciously with the SDS concentration, whereas the abundance increases with the concentration in the higher concentration region ($> 10^{-5}$ M). After the centrifugation, on the other hand, the abundance is almost unchanged with the SDS concentration below 10^{-3} M, whereas it increases up to 10^{-2} M and then

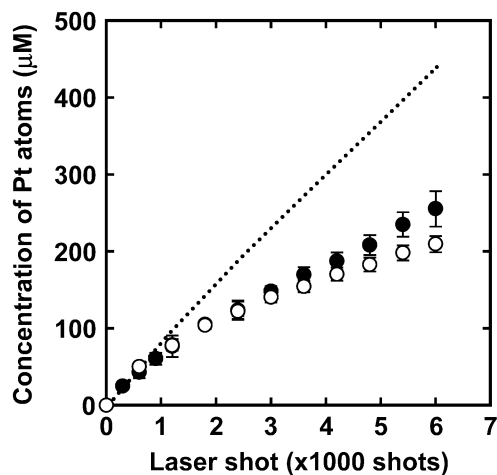


Figure 5. Concentration of platinum atoms released in a 0.01 M-SDS solution (solid circle) and in pure water (open circle) measured as a function of a number of the laser shot (1064 nm, 3.0 J/pulse cm^2). The dotted line shows the estimated concentration of platinum atoms in a liquid as a function of the laser shot. Further details are described in the text.

decreases as the SDS concentration increases. This finding implies that stable platinum nanoparticles are produced, at the SDS concentrations of $\sim 10^{-2}$ M, and have a particularly stable structure. Note that stable platinum nanoparticles resistive against the centrifugation are produced even in pure water (no surfactant is present in it).

The concentrations of platinum atoms ejected in 10 mL of a 0.01 M SDS solution and of pure water by the laser ablation were measured as a function of a number of the laser shots (1064 nm, 3.0 J/pulse cm^2 ; see Figure 5). Here, the concentration of the platinum atoms in a solution is estimated from the absorbance of the solution and the weight loss of the metal plate after the laser irradiation. The concentration of the platinum atoms in the SDS solution and in pure water increases with the number of the laser shots, whereas an increment of the concentration of the platinum atoms by each laser shot decreases with the number of the laser shots more greatly in the pure water than in the 0.01-M SDS solution. A leveling-off tendency of the concentration of the platinum atoms results from covering the metal plate with platinum nanoparticles formed by aggregation of the platinum atoms, as will be discussed in a later section. On the other hand, the concentration of the platinum atoms was found to increase almost linearly, as the number of the laser shots increases within the first ~ 500 shots. The ejection rate of the platinum atoms by one laser shot toward the liquid media was estimated from the concentration of the platinum atoms ejected within the first 500 shots and is shown as a function of the laser power (see Figure 6). The ejection rate of the platinum atoms starts to increase at the threshold power of 25 mJ/pulse or the threshold fluence of 1.0 J/pulse cm^2 as a fluence (1064 nm) and increases with an increase in the laser power or fluence. The ejection rates of silver and gold atoms, which are also shown in Figure 6 for comparison, are slightly higher than that of the platinum atoms at a lower laser power.

Figure 7 shows the ζ potential of the platinum nanoparticles as a function of the SDS concentration. The ζ potential is nearly zero when the concentration is less than 10^{-4} M, whereas the nanoparticles become negatively charged when the concentration exceeds 10^{-2} M. The high abundance of the nanoparticles after the centrifugation at 0.01 M results from the charging of the nanoparticles by the SDS molecules.

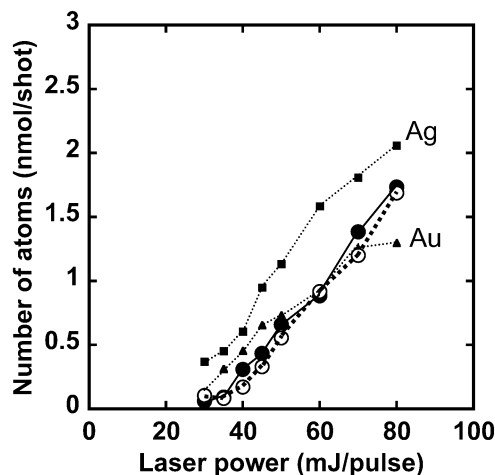


Figure 6. Ejection rates of platinum atoms released in a 0.01-M SDS solution (solid circle) and in pure water (open circle) by a single laser shot as a function of a laser power (1064 nm). Ejection rates of silver (solid square) and gold (solid triangle) atoms in a 0.01-M SDS solution under the identical experimental condition as platinum atoms are also shown.

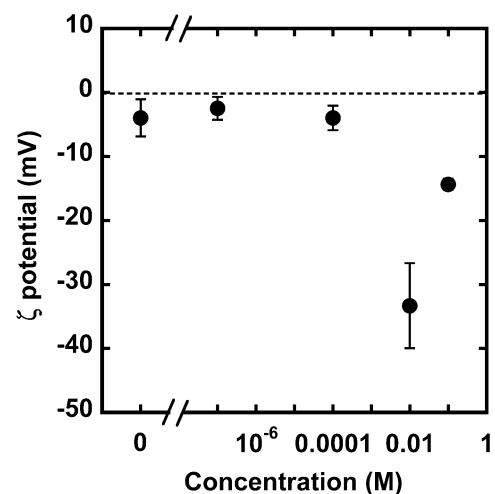


Figure 7. ζ potential of platinum nanoparticles produced by laser ablation at (532 nm, 1.6 J/pulse cm^2) as a function of the concentration of SDS in an aqueous solution.

4. Discussion

4.1. Formation of Platinum Nanoparticles. The optical absorption spectra of an aqueous SDS solution and pure water, in which a platinum metal plate is ablated by a pulsed YAG laser, agree with a solution containing platinum nanoparticles prepared chemically (see Figure 2) reasonably well.²⁷ The agreement proves that platinum nanoparticles are produced in the SDS aqueous solution and in pure water by the laser ablation. The electron micrographs of the platinum nanoparticles show that the average diameter of the nanoparticles ranges from 1 to 10 nm, depending on the experimental condition employed.

In general, an optical absorption of particles in a solution with smaller diameters than the wavelength of an incoming light (< 500 nm) is given by the Mie theory, where the dielectric function is written as a combination of an interband term and a Drude term for the conduction electrons in the particles. Creighton and Eadon calculated the optical absorption of platinum nanoparticles based on the Mie theory and showed that a plasmon peak appears at 215 nm.²⁷ Experimentally, Henglein et al. showed that a peak exists around 215 nm in the optical absorption spectrum of platinum nanoparticles prepared

chemically and that the spectrum is almost independent of the particle size, although the absorption coefficient at the maximum was about 30% higher than the calculated one.²⁸ However, platinum nanoparticles prepared by citrate reduction do not show any maximum around 215 nm, and the plasmon oscillation very slightly contributes to the total absorption. These facts imply that the average size and the size distribution of the platinum nanoparticles cannot be estimated from their spectral feature. Note that average size of the nanoparticles can be estimated from the characteristic spectral feature of the gold and the silver nanoparticles.

The dynamic formation mechanism is applicable to the growth of platinum nanoparticles in an SDS solution.¹⁵ Immediately after the laser ablation of a platinum metal plate immersed in the SDS solution, platinum atoms in a plume built over the laser spot on the metal plate aggregate rapidly into small particles as fast as the platinum atoms collide mutually. This initial rapid aggregation continues until available atoms in the close vicinity are consumed almost completely and embryonic nanoparticles with ~2 nm in diameter appear in the centers of small regions void of any platinum atoms. The embryonic nanoparticles grow slowly with collecting platinum atoms diffusing into the void regions even after the rapid growth ceases. This slow growth terminates when the surfaces of the particles are fully covered with SDS molecules or the free platinum atoms are consumed completely in the solution.

The dynamic formation mechanism is supported by the dependence of the average particle diameter on the SDS concentration as shown in Figure 3. The average diameter of the nanoparticles increases and then levels off below 10^{-3} M, as the SDS concentration decreases. Smaller platinum nanoparticles tend to be formed in a more concentrated solution (SDS concentrations higher than 10^{-3} M), because more efficient coating of the surfaces in the concentrated solution terminates the slow growth more rapidly. On the other hand, at SDS concentrations lower than 10^{-3} M, the supply rate of SDS molecules toward growing embryonic nanoparticles is so low that the growth continues until all of the platinum atoms in the solution are completely consumed.

There is an inherent tendency that relatively small nanoparticles (1–10 nm) are produced by the laser ablation of the platinum metal plate, in comparison with nanoparticles produced by the laser ablation of silver or gold metal plates under the same experimental condition. In fact, under a similar experimental condition, small gold nanoparticles having the average diameter of 4.6 nm are formed in a 0.01-M SDS solution by the laser ablation of a gold metal plate, and the average diameter increases greatly up to ~20 nm with a decrease in the concentration of SDS.¹⁷ On the other hand, larger silver nanoparticles (the average diameter of ~11 nm) are formed in a 0.01-M SDS solution, and the average diameter of the silver nanoparticles increases up to 20 nm with a decrease in the SDS concentration.¹⁵

The diameter distribution differs from metal to metal as described above. The difference is explained, first, by the difference of the diameters of the embryonic nanoparticles formed at the initial stage of the growth process. As shown in Figure 6, the ejection rates of platinum, gold, and silver atoms indicate that silver atoms are most densely dispersed in a plume right above the metal plate by the laser ablation, probably because of its lower boiling point (2466 K) and its lower evaporation enthalpy (254 kJ mol⁻¹; see Table 1). Hence, the diameters of silver embryonic nanoparticles must be larger than gold and platinum embryonic nanoparticles. In fact, the diam-

TABLE 1: Physical Properties of Metals

metal	T/K^a	$\Delta H/\text{kJ mol}^{-1\ b}$	d/nm^c
Pt	4583	447	2
Au	2933	310.5	4
Ag	2466	254	11

^a Boiling point. ^b Enthalpy of evaporation. ^c Diameter of embryonic particle.

eters of the embryonic nanoparticles of platinum, gold, and silver are estimated to be 2, 4, and 11 nm, respectively.^{15,17} Second, a large variation of the diameter by changing the SDS concentration is attributed to the slow growth process after the embryonic nanoparticles are formed: Free atoms which do not participate in the formation of the embryonic nanoparticles contribute to the growth of the embryonic nanoparticles.¹⁷ A greater variation of the diameter in the gold and silver nanoparticle formation with the change of the SDS concentration indicates that a more considerable number of free atoms still remain after the embryonic nanoparticles are formed. Formation of the smallest platinum nanoparticles produced is explained by formation of many more nuclei in a plume of platinum atoms, because of the highest evaporation enthalpy of a platinum metal; too many nuclei have too little share of platinum atoms per particle, and hence resulting platinum particles have the smallest diameter.

4.2. Structure and Stability of Nanoparticles. Stability of a platinum nanoparticle depends on such parameters as an SDS coverage, a charge density on the surface and the diameter of the nanoparticle, etc. Seemingly, these parameters are predetermined by the SDS concentration and the number density of platinum atoms in a solution, in which the nanoparticles are born. If the SDS concentration is less than 10^{-3} M, platinum nanoparticles freshly produced in it are practically bare, because of a low number density of SDS molecules in the solution. Partial precipitation of the platinum nanoparticles by the centrifugation implies that the bare nanoparticles are forced to coagulate under the centrifugal forces (see Figure 4). At SDS concentrations higher than 10^{-3} M, platinum nanoparticles are born to be coated by a sufficient number of SDS molecules and are negatively charged (see Figure 7). The repulsive force exerted among the negatively charged nanoparticles exceeds the van der Waals attractive force among them, so that they are dispersed stably in the solution and resistive against the centrifugation. In a much higher concentration region (~0.1 M), a greater portion of the nanoparticles is precipitated by the centrifugation. This phenomenon is explained by reduction of the negative charge on the nanoparticles because of neutralization of $\text{C}_{12}\text{H}_{25}\text{SO}_4^-$ on the nanoparticles by an excess amount of SDS in the solution through the equilibrium, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na} \rightleftharpoons \text{C}_{12}\text{H}_{25}\text{SO}_4^- + \text{Na}^+$ (see Figure 7). The repulsive forces among the different nanoparticles are weakened by reduction of the surface charge, and hence, the platinum nanoparticles are readily coagulated under the centrifugation. In fact, the ζ potential proportional of the nanoparticles, which is to the surface charge density, decreases with the concentration of SDS.

On the other hand, a sizable amount of platinum nanoparticles remains suspended in an SDS solution after the centrifugation in the entire concentration range studied, as shown in Figure 4. This finding implies that the platinum nanoparticles produced by the laser ablation in the solution are too tiny (<5 nm in diameter) to feel a sufficient centrifugal force for their precipitation by the centrifugation (15000 rpm). Note that platinum nanoparticles are much more stable against the centrifugation than silver and gold nanoparticles produced under a similar condition. For instance, silver and gold nanoparticles produced

in a diluted SDS solution ($<10^{-6}$ M) are precipitated completely by the centrifugation. The ready precipitation by the centrifugation indicates that larger particles tend to be produced by the laser ablation on a silver or gold metal plate. The conjecture is supported by our preliminary result on gold nanoparticle preparation. As described above, gold nanoparticles (~ 5 – 50 nm in diameter) produced in a dilute SDS solution are completely precipitated by the centrifugation. When gold nanoparticles are fragmented by laser-induced size reduction into smaller nanoparticles with diameters of 1–5 nm, no significant precipitation occurs by the centrifugation. Namely, nanoparticles smaller than ~ 5 nm in diameter are hardly precipitated by the present centrifugation.

4.3. Formation of Stable Surfactant-Free Platinum Nanoparticles. As shown in Figures 3 and 4, small platinum nanoparticles having the average diameter of 6.2 nm are found to be produced in pure water (no surfactant) and are stable against the centrifugation. Formation of stable surfactant-free nanoparticles is characteristic of platinum. In addition, they show such a characteristic feature of aggregation (see Figure 1b) that the nanoparticles maintaining finite distances among them are clustered. In general, surfactant-free nanoparticles tend to coagulate and coalesce, because they are bare. It arises probably because the surfactant-free platinum nanoparticles are slightly charged because of adsorption of OH^- on their surfaces, similarly to surfactant-free nanodroplets in water.³⁰ The dielectric constant of pure water is much less than that of a solution dissolved with a salt, and hence, the surface charges of the nanoparticles are not efficiently shielded. In other words, the repulsive forces because of their negative charges among the nanoparticles are likely to exceed the van der Waals attractive forces leading to coalescence, and hence, the nanoparticles are present in a solution without being coalesced even under application of the centrifugation. No such surfactant-free silver and gold nanoparticles are prepared by any methods at the present stage.

4.4. Reduction of Ejection Rate. As shown in Figure 6, the ejection rate of platinum atoms by the laser ablation at 1064 nm does depend on the laser power but does not on the SDS concentration. A similar SDS-concentration dependence was observed in the formation of platinum nanoparticles by the laser ablation at 532 nm. It follows that, as far as the laser power for the ablation is equal, the concentration of the platinum atoms contained in the solution as a form of free atoms and nanoparticles before centrifugation must be independent of the SDS concentration. Figure 4 demonstrates that platinum nanoparticles are more abundantly formed in a more concentrated SDS solution. This behavior is ascribable to reduction of the ejection rate (slope) as the number of the laser shots increases: The concentration of platinum atoms ejected in pure water or in a 0.01-M SDS solution increases with the number of the laser shots, whereas the ejection rate decreases with the number of the laser shots more significantly in pure water than in the 0.01-M SDS solution. The degree of the reduction must depend on the concentrations of the platinum nanoparticles and SDS molecules in the solution.

It is plausible that the ejection rate is reduced because (1) the laser light is absorbed by nanoparticles present over the metal plate and the ablation efficiency is reduced, (2) the surface properties of the metal plate are changed by the continuous irradiation of the pulsed laser, and the ablation efficiency diminishes, or (3) change of the polarizability of the solution in the presence of the nanoparticles causes the ablation efficiency to decrease. Reason 1 is ruled out as described below. As

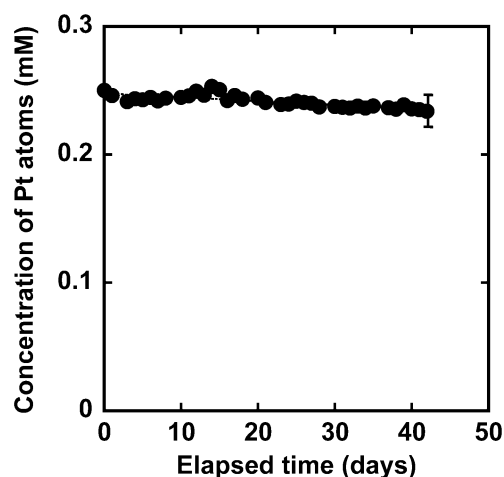


Figure 8. Concentration of platinum atoms remaining in pure water as a function of the elapsed time after platinum nanoparticles are formed by the laser ablation of a metal plate.

platinum nanoparticles show a sizable optical absorption at 532 nm (see Figure 2), the laser power on the surface of the metal plate decreases with an increase in the concentration of the platinum nanoparticles. In fact, the laser power on the metal surface is reduced by 30% of that of the incident laser power, at the platinum concentration of $200 \mu\text{M}$. Therefore, the ejection rate of the platinum atoms would decrease as the number of the laser shots increases at the wavelength of 532 nm.¹⁷ To examine the validity of this mechanism for explaining the reduction of the ablation efficiency, the dependence of the platinum abundance on the number of the laser shots was measured at the wavelength of 1064 nm, where platinum nanoparticles have a weak optical absorption (see Figure 5). In general, the laser power on the surface of the metal plate, I , is given by

$$I = I_0 10^{-\epsilon cl} \quad (1)$$

where I_0 is the incident laser power, ϵ and c represent the absorption coefficient, and the concentration of platinum nanoparticles, respectively, and l is the length of the optical path (1.1 cm). In the present study, for instance, the product, ϵcl , is 0.06, for the platinum concentration of $250 \mu\text{M}$. The dotted line in Figure 5 shows the estimated concentration of platinum atoms in pure water and in the SDS solution as a function of the number of the laser shots, by taking into account the optical absorption of the incident laser by the solution and the ejection rate given in Figure 6. The ejection rate of the platinum atoms measured decreases more significantly with the number of the laser shots. In other words, the optical absorption of the incident laser by the platinum nanoparticles over the metal plate provides a minor effect in the present case, and hence, reason 1 described above should be ruled out.

4.5. Long-Term Stability of Surfactant-Free Platinum Nanoparticles. In pure water, platinum nanoparticles grow by molecular diffusion (Ostwald ripening) and coagulation followed by coalescence because of no surfactant molecules as stabilizers. Figure 8 shows the concentration of platinum atoms remaining in pure water as a function of the elapsed time after platinum nanoparticles are formed by the laser ablation of a metal plate. The concentration of the platinum atoms in water decreases very slowly with the time (a half-life period >500 days). It follows that a significant growth of surfactant-free platinum nanoparticles followed by precipitation does not take place. On the other hand, Figure 9 shows an electron micrograph of platinum

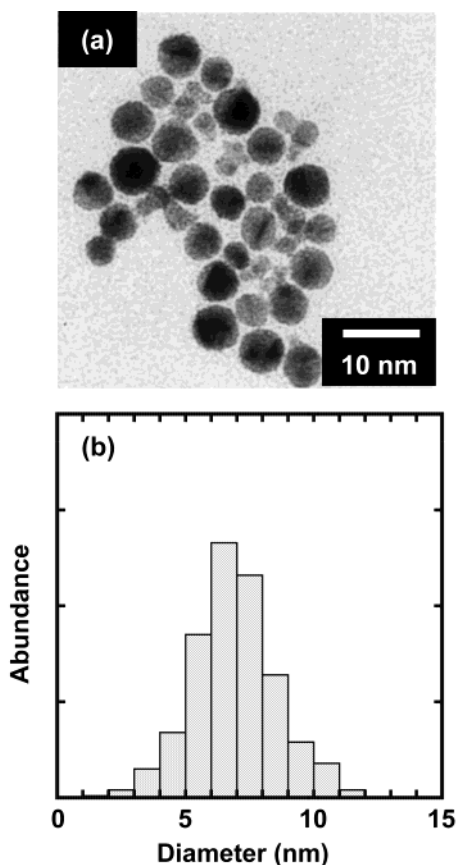


Figure 9. Electron micrograph of platinum nanoparticles one month after the preparation, together with the diameter distribution. The average diameter was measured to be 7.4 ± 1.6 nm.

nanoparticles one month after the preparation, together with the diameter distribution. The distribution slightly shifts to a larger diameter, probably because of slow growth of nanoparticles. In summary, surfactant-free platinum nanoparticles are stable but tend to grow gradually in a time scale of months.

5. Conclusions

Laser ablation of a platinum plate immersed in an aqueous solution of sodium dodecyl sulfate was employed to prepare platinum nanoparticles in the solution. The nanoparticles produced were characterized by optical absorption spectroscopy, electron microscopy, and centrifugation. It is found that platinum nanoparticles produced in a 0.01-M SDS aqueous solution are stable, because they are negatively charged in the presence of SDS molecules on their surfaces. Small nanoparticles with diameters less than 5 nm are not precipitated by the centrifugation. In addition, we succeeded preparing stable surfactant-free

platinum nanoparticles in pure water, which are not precipitated by the centrifugation; this method is proved to be useful for preparation of bare metal nanoparticles in a liquid medium.

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