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Full Physical Preparation of Size-Selected Gold Nanoparticles in Solution: Laser Ablation and Laser-Induced Size Control

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

Colloidal gold nanoparticles with a broad size distribution were prepared by laser ablation of a gold metal plate in an aqueous solution of sodium dodecyl sulfate (SDS) and were fragmented under irradiation of a 532 nm laser at different SDS concentrations and laser fluences. Gold nanoparticles with a desired average size (1.7−5.5 nm in diameter) were prepared by tuning properly the surfactant concentration and the laser fluence. The concentration of SDS was found to be higher than a critical micelle concentration so as to gain a significant size reduction and to obtain stable final products. Laser ablation in combination with the laser-induced size control provides a versatile full physical preparation method of size-selected gold nanoparticles.

Metal nanoparticles have attracted much attention because of their size-dependent physical and chemical properties.[1−6] In this relation, size-selected nanoparticles with diameters less than 10 nm have been prepared using wet-chemistry techniques.[7−15] More recently, laser-ablation method has been developed to prepare metal nanoparticles in a solution.[16−20] This physical method allows us to prepare nanoparticles with ease and without contamination by a reducing agent, but the size distribution of the nanoparticles tends to be broadened because the coagulation processes of atoms can hardly be controlled. On the other hand, a technique of "laser-induced size reduction" was known to be a powerful tool to change size and geometrical structure of gold nanoparticles by taking advantage of the fact that the gold nanoparticles have an intense surface plasmon peak centering at 520 nm.[21−26] In the present study, we investigated laser-induced size reduction of gold nanoparticles prepared by laser ablation in a solution in advance at various laser fluences and surfactant concentrations. We have found that gold nanoparticles of a desired average diameter are prepared by optimizing the

laser fluence and the surfactant concentration, regardless of the initial size distribution of the gold nanoparticles employed, although the nanoparticles thus produced show a slightly broader size distribution than the gold nanoparticles prepared by the conventional wet-chemistry technique.

Gold nanoparticles were prepared by laser ablation (1064 nm) of a gold metal plate (>99.99%) in a 0.01-M aqueous solution of sodium dodecyl sulfate (SDS);[19] the average diameter of the gold nanoparticles was obtained to be ∼8.0 nm at the laser fluence of 800 mJ pulse^{-1} cm^{-2}.[26] The gold nanoparticles thus obtained in the SDS solutions were subjected to laser-induced fragmentation. In practice, a solution in an optical cell made of silica was illuminated by the output of the second harmonic (532 nm) of a Quanta-ray GCR-170 Nd:YAG laser operating at 10 Hz. The laser was focused to a spot as large as 0.12 cm^2 on the solution surface by a lens having a focal length of 250 mm. The sample cell was placed in a heat bath so that the temperature of the sample cell was maintained at the temperature of 278 K throughout the experiment. A Scientech AC2501 power meter was used to monitor the laser power. The absorption spectrum was measured by a Shimadzu UV-1200 spec-
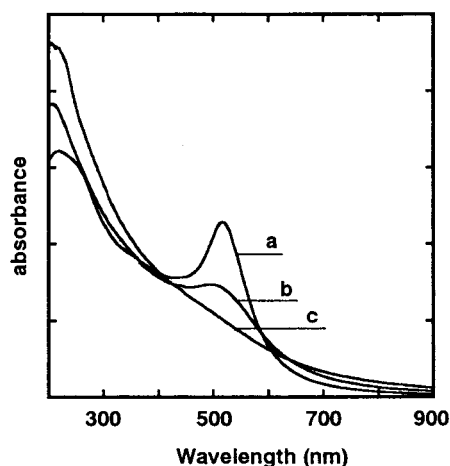
Figure 1. Optical absorption spectra of gold nanoparticles produced before (marked as a) and after irradiation of a 532-nm laser having the fluence of 1200 mJ pulse^{-1} cm^{-2} in (b) 9×10^{-4} and (c) 0.05 M SDS solutions in water.

trometer. Electron micrographs of nanoparticles were obtained by using a transmission electron microscope (JEOL JEM-2000EXII ×500,000). 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.

Figure 1 shows optical absorption spectra of gold nanoparticles produced before and after irradiation of a 532-nm laser having 1200 mJ pulse^{-1} cm^{-2} in 9×10^{-4} and 0.05 M SDS solutions in water. The spectra exhibit the characteristic peak of the surface plasmon band at 520 nm and a tail portion of a broad band extending toward the UV-wavelength range.[27-30] The width of the 520-nm peak is broadened and the height is lowered by the laser irradiation, and more significant change is observed at 0.05 M than at 9×10^{-4} M. This spectral change implies that the diameters of the nanoparticles are reduced more significantly at 0.05 M. This finding accords with the change of the size distribution measured directly from the electron micrographs (see Figure 2). The average sizes of the nanoparticles are obtained to be 3.4 and 1.7 nm at the SDS concentrations of 9×10^{-4} and 0.05 M, respectively.

With the aid of the Drude theory of a conducting droplet, one can translate the 520-nm absorbance into the average diameter of the nanoparticles in the solution.[23-27] Figure 3 shows the dependence of the average diameter of the gold nanoparticles on the SDS concentration after the laser irradiation (532 nm) at the laser fluences of 320, 480, and 1200 mJ pulse^{-1} cm^{-2}. As shown in Figure 3, the average diameter drops abruptly at 8×10^{-3} M and otherwise remains unchanged as the SDS concentration increases. The extent of the abrupt drop increases with the increase of the laser fluence. This implies that the mechanism of the laser-induced fragmentation changes at this SDS concentration.

When the surface plasmon band of gold nanoparticles in an SDS solution is excited by irradiation of a 532-nm laser, the photon energy is readily converted to heat because of efficient transmission of the absorbed energy to the internal energy of the nanoparticles due to a strong electron−photon interaction. During a single laser pulse, one gold nanoparticle is considered to absorb consecutively more than 1000 photons and is heated to its boiling point.[25,26] As a result, the nanoparticle starts to fragment and small fragments (gold clusters, etc.) are produced and dispersed in the solution. The fragmentation rate must increase with an increase in the laser fluence, because the
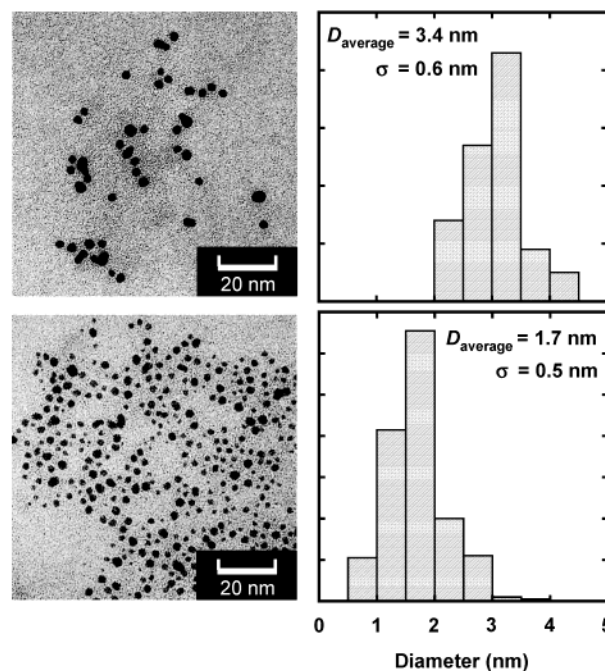

Figure 2. Electron micrographs and size distributions of gold nanoparticles produced after a 532-nm pulsed laser irradiation (1200 mJ pulse^{-1} cm^{-2}) in 9×10^{-4} M (top) and 0.05 M (bottom) aqueous solution of SDS. The average sizes of the nanoparticles are obtained to be 3.4 and 1.7 nm at 9×10^{-4} and 0.05 M, respectively.
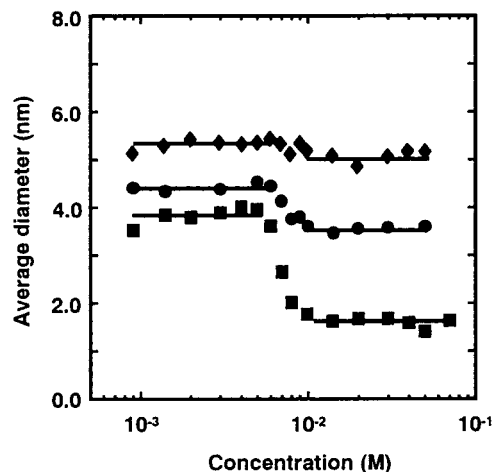

Figure 3. Average diameter of gold nanoparticles after the laser irradiation at 532 nm at the laser fluence of (♦) 320, (●) 480, and (■) 1200 mJ pulse^{-1} cm^{-2} as a function of the SDS concentration in the solution.

internal energy of irradiated nanoparticles increases.[26] On the other hand, the nanoparticles present in the solution grow by collecting these small fragments.[31] The coagulation rate increases with the increase of the concentration of the small fragments. Namely, these fragmentation and coagulation processes are balanced under the irradiation of the 532-nm laser.[25,26] After the laser is off, the fragmentation ceases so that only the coagulation proceeds, until the small fragments are consumed. In fact, the optical absorption spectra of gold nanoparticles after switching off the 532-nm laser for the size reduction show that the height of the surface plasmon peak increases significantly with the elapsed time.[31] This is the case for the gold nanoparticles in a $<8 \times 10^{-3}$ M SDS solution.

When the SDS concentration is higher than 8×10^{-3} M, the small fragments are stabilized by a sufficient amount of the SDS molecules, and hence, coagulation of the small fragments is

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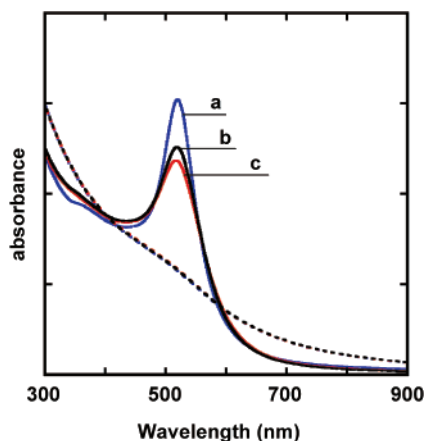*J. Phys. Chem. B, Vol. 106, No. 31, 2002* **7577**

Figure 4. Optical absorption spectra of gold nanoparticles having different initial average diameters of (a) 10.0, (b) 7.5, and (c) 6.0 nm before (solid lines) and after the laser-induced size reduction (dotted lines) onto gold nanoparticles.

greatly decelerated. Evidently, the height of the surface plasmon peak in the absorption spectrum increases more slowly after switching off the 532-nm laser in a 0.005 M SDS solution than in a 0.05 M SDS solution.[31] As a result, smaller nanoparticles tend to be formed when the SDS concentration is higher than 8×10^{-3} M. The critical SDS concentration (8×10^{-3} M) for the size reduction is very close to critical micelle concentration of SDS in water, indicating that the small fragments are readily stabilized when the SDS micelles are formed. 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.

Gold nanoparticles having a different average diameter (10.0, 7.5, and 6.0 nm) were prepared by the laser ablation of a gold metal plate in an aqueous solution of SDS and were subjected to laser-induced size reduction at the SDS concentration of 0.05 M. Figure 4 shows the optical absorption spectra of gold nanoparticles before and after the laser irradiation. The gold nanoparticles with a different average diameter before laser irradiation exhibit a characteristic size dependence of a surface plasmon peak in the optical absorption spectra. On the other hand, the spectra of the gold nanoparticles after the laser irradiation are identical regardless of the average diameter of the initial nanoparticles. Under irradiation of a 532-nm laser, gold nanoparticles with any diameters are fragmented into small nanoparticles of comparable diameters, because the diameters of the nanoparticles are determined by dynamic balance between the rate of the photofragmentation depending solely on the laser fluence and the rate of coagulation depending on the SDS concentration. These findings lead us to conclude that one can prepare, in a controlled manner, gold nanoparticles of a desired average diameter from the larger nanoparticles by selecting properly the laser fluence and the surfactant concentration, regardless of the initial average size and the initial size distribution of the gold nanoparticles employed. Laser ablation in combination with the laser-induced size control provides a versatile full physical preparation method of size-selected gold nanoparticles without contamination by a reducing agent, which is inevitably used in conventional wet-chemical techniques.

References and Notes

(1) Takagi, M. *J. Phys. Soc. Jpn.* **1954**, *9*, 359.
(2) Buffat, D. A.; Borel, J. P. *Phys. Rev.* **1976**, *A13*, 2289.
(3) Ahmadi, T. S.; Logunov, S. L.; El-Sayed, M. A. In *Nanostructured Materials*; Shalaev, V. M., Moskovits, M., Eds.; American Chemical Society: Washington, DC, 1997.
(4) Wilcoxon, J. P.; Martin, J. E.; Parsapour, F.; Wiedenman, B.; Kelley, D. F. *J. Chem. Phys.* **1998**, *108*, 9137.
(5) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.
(6) Sakurai, H.; Haruta, M. *Appl. Catal., A* **1995**, *127*, 93.
(7) Petit, C.; Lixon, P.; Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 12974.
(8) Pileni, M. P. In *Nanostructured Materials*; Shalaev, V. M., Moskovits, M., Eds.; American Chemical Society: Washington, DC, 1997.
(9) Kortenaar, M. V. t.; Kolar, Z. I.; Tichelaar, F. D. *J. Phys. Chem. B* **1999**, *103*, 2054.
(10) Kurihara, K.; Kizling, J.; Stenius, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 2574.
(11) Link, S.; Beeby, A.; FitzGerald, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2002**, *106*, 3410.
(12) Schmid, G.; Pfeil, R.; Boese, R.; Brandermann, F.; Meyer, S.; Calis, G. H. M.; Van der Velden, J. W. A. *Chem. Ber.* **1981**, *114*, 3634.
(13) Yonezawa, T.; Sutoh, M.; Kunitake, T. *Chem. Lett.* **1997**, 619.
(14) Yonezawa, T.; Kunitake, T. *Colloids Surf., A* **1999**, *149*, 193.
(15) Link, S.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B*, **1999**, *103*, 3529.
(16) Fojtik, A.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 252.
(17) Sibbald, M. S.; Chumanov, G.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 4672.
(18) Yeh, M. S.; Yang, Y. S.; Lee, Y. P.; Lee, H. F.; Yeh, Y. H.; Yeh, C. S. *J. Phys. Chem. B* **1999**, *103*, 6851.
(19) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem. B* **2000**, *104*, 8333.
(20) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem. B* **2000**, *104*, 9111.
(21) Eckstein, H.; Kreibig, U. *Z. Phys. D* **1993**, *26*, 239.
(22) Niidome, Y.; Hori, A.; Sato, T.; Yamada S. *Chem. Lett.* **2000**, 310.
(23) Kamat, P. V.; Flumiani, M.; Hartland, G. V. *J. Phys. Chem. B* **1998**, *102*, 3123.
(24) Kurita, H.; Takami, A.; Koda, S. *Appl. Phys. Lett.* **1998**, *72*, 789.
(25) Takami, A.; Kurita, H.; Koda, S. *J. Phys. Chem. B* **1999**, *103*, 1226.
(26) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T. *J. Phys. Chem. B* **2001**, *105*, 9050.
(27) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1983.
(28) Doremus, R. H. *J. Chem. Phys.* **1964**, *40*, 2389.
(29) Kreibig, U.; Fragstein, C. v. *Z. Phys.* **1969**, *224*, 307.
(30) Kreibig, U. *J. Phys. F* **1974**, *4*, 999.
(31) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T. *J. Phys. Chem. B*, in press.