Journal of Photochemistry and Photobiology A: Chemistry 226 (2011) 64–67

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

High concentration silver nanoparticles stably dispersed in water without chemical reagent

Teppei Nishi*, Noritomo Suzuki, Hidehiko Sugiyama, Kazuhisa Yano, Hirozumi Azuma

Toyota Central Research and Development Laboratories Incorporation, Nagakute, Aichi 480-1192, Japan

ARTICLE INFO

Article history:
Received 30 July 2011
Received in revised form 3 October 2011
Accepted 20 October 2011
Available online 29 October 2011

Keywords:
Laser ablation in liquid
Nanoparticle yield
Bactericidal activity

ABSTRACT

New laser ablation method to drastically improve nanoparticle yield was developed. In this method, laser was irradiated from the bottom of a piriform flask to the precipitated powder target. Nanoparticle yield became much higher than that obtained by the conventional method. Silver nanoparticle colloid with high concentration was prepared in a single step and the colloid has been stable for more than 6 months without any chemical reagents. The shape of nanoparticles was estimated to be four-sided pyramid or octahedral by scanning transmission electron microscopy (STEM) observation. In addition, STEM image showed narrow size distribution. A typical bacteria, *Bacillus coli*, became extinct within 24 h in silver nanocolloid with the concentration of 20 mg/L.

1. Introduction

Because of the interesting optical properties (surface plasmon, surface enhanced Raman scattering [1–3] and applicability (an antibacterial agent [4–6])), silver nanoparticles have attracted a lot of attention for a decade. In general, silver nanoparticles stably dispersed in liquid work as an antibacterial agent. However, chemical reagent such as surfactants [7,8] is needed to prevent aggregation and disperse nanoparticles stably. It results in loss of surface area albeit specific nanoparticle properties largely arise from their surface. Therefore, properties specific to nanoparticles may be diminished.

In general, nanoparticles can be mechanically [9,10], physically [11,12], chemically [13–15] fabricated. In particular, nanoparticles can be produced by pulsed laser irradiation to target immersed in liquid [16–24]. This method has advantages such as the capability to produce nanoparticles in high purity. In addition, nanoparticles stably dispersed in liquid without other treatments can be prepared in some cases [21]. However, nanoparticle yield is very low [22] because nanoparticles produced by previous pulse are again ablated and laser power irradiating the target is decreased. Therefore, laser ablation for a prolonged time does not bring high nanoparticle yield.

In the previous reports, silver has been often used as the target. However, applications have rarely been investigated because of low nanoparticle yield. In this paper, we present the preparation of silver nanoparticles by new laser ablation method in water. In this method, laser is irradiated to powder target precipitated in a piriform flask filled with water. This setup enables continuous laser ablation with high nanoparticle yield. The produced particles were stably dispersed in water more than 6 months without chemical reagent and pH adjustment. In addition, it turned out that the produced silver nanoparticles had narrow size distribution and a unique morphology.

2. Experimental

Schematic illustration of experimental set up is shown in Fig. 1. Target silver powder (Nilaco) was precipitated on the bottom of a piriform flask filled with pure water. Second harmonic light from Nd:YAG laser system (Spectro Physic Pro-290) operated in the Q-switch mode at the wavelength of 532 nm with a repetition rate of 10 Hz and pulse duration of 7 ns was used. The pulsed laser energy was 400 mJ corresponding to the fluence of ca. 0.5 J/cm^2. After laser ablation for 60 min, silver nanocolloid was obtained. Target powder was observed by SEM (Hitachi S-3600N) operated at 15 kV. Products were analyzed by STEM (JEOL JEM-2100F) operating at 200 kV. Absorption spectrum was measured using spectral photometer (Shimadzu UV-2100PC). Light path was 10 mm and the measurement range was from 300 to 900 nm. Antibacterial activity against *Bacillus coli* (*B. coli*) was measured as follow. First, *B. coli* were inoculated into 10 mL of Luria–Bertani (LB) broth. Then, it was shaken and preculture was carried out for 15 h. Culture fluid was added to physiological salt solution to dilute by 5000 times. A 0.5 mL of the diluted solution, 2.5 mL of LB broth diluted by 2 times, 1.5 mL of sterilized water and 0.5 mL of silver nanocolloid

* Corresponding author. Tel.: +81 561 71 7728.
E-mail address: e1481@mosk.tytlabs.co.jp (T. Nishi).

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.10.016

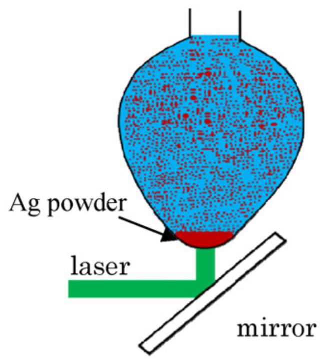

Fig. 1. Schematic illustration of experimental setup. Silver powder employed as the target was precipitated on the bottom of a piriform flask filled with pure water. Laser was irradiated through the bottom of a piriform flask.

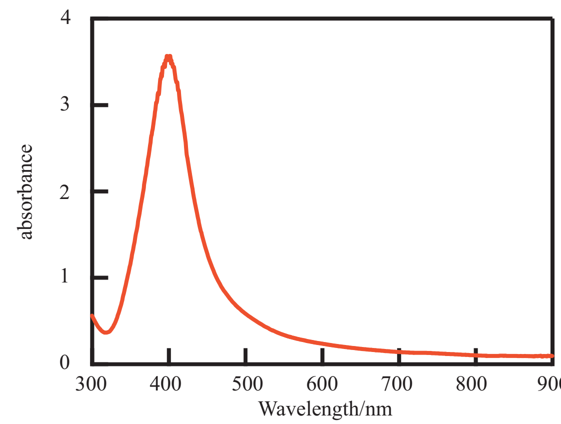

Fig. 3. Absorbance spectrum of silver nanocolloid prepared by laser ablation.

(diluted by 10 times) were mixed. Then, they were shaken at 37 °C and 100 rpm. In 0, 6, 24 h, colonies were respectively counted after static culture on agar at 37 °C.

3. Results and discussion

We used a new laser irradiation method. Laser is irradiated to the precipitated silver powder through the bottom of a piriform flask filled with water as shown in Fig. 1. In this method, the interaction between nanoparticles produced by previous pulse and incident laser light can be practically prevented. Therefore, laser light irradiating the target is stable because laser power is never attenuated. As the result, the improvement of nanoparticle yield could be attained. Scanning electron microscopy (SEM) image of the target silver powder is shown in Fig. 2. An inhomogeneous distribution of particle size and shape can be confirmed. Absorbance spectrum of silver nanocolloid prepared by laser ablation for 60 min in water is shown in Fig. 3. The spectrum consists of strong absorption due to plasmon band around 400 nm, indicating the presence of silver nanoparticles. This peak intensity is much higher than any other result reported so far for the silver nanoparticles prepared by laser ablation in liquid [23,24]. Although absorbance spectrum is influenced by the concentration, scattering, optical path, particle size, this result indicates that the concentration of nanoparticles in liquid is much higher than any other reports as one of the possibilities. In fact, the concentration of silver nanoparticles is estimated to be 0.2 g/L as described below. This must be higher than any other report. In the conventional method, laser is attenuated by the interaction between existed nanoparticles produced by the previous laser pulse. Therefore, it is difficult to obtain a great amount of nanoparticles by laser ablation even irradiated for a long time. Hence, most of reports show the results of laser ablation for shorter period of time. On the other hand, the interaction between nanoparticles produced by the previous pulse and incident laser light can be practically prevented in our new method. In consequence, laser light with stable energy reaches the target and nanoparticles can be continuously produced at a constant rate. It is expected that this method leads to steady increase of nanoparticle concentration with ablation time. Therefore, nanocolloid with desired concentration can be prepared by a single step. Actually, nanoparticle yield was estimated by the decrease in the amount of target powder after laser ablation for 60 min four times. As a result, average nanoparticle yield of 20 mg/h which corresponds to 1.39 μg/J could be obtained. This is much higher than that reported by the other groups [22]. The concentration of silver nanoparticles dispersed in water was about 0.2 g/L because amount of water was about 100 mL in our experiments.

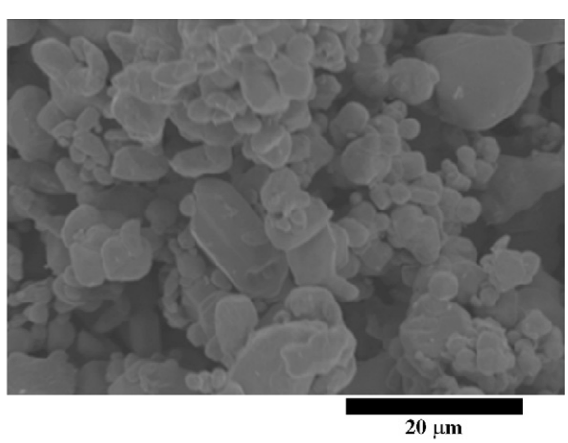

Fig. 2. SEM image of target silver powder.

Next, the mechanism of the production of nanoparticles is discussed. It is well known that the temperature and pressure of the plume produced by laser ablation in liquid are very high [25–30]. The plume can heat the target, which results in melting, vaporization and ionization. In the case of the conventional method using powder target in liquid, a part of plume contact with target particles and they are heated. If another target particles that are not irradiated present near the heated ones, they can also be heated. However, this heating effect is rather limited in the conventional method due to the low probability of the presence of target particles around the laser-induced plume. In contrast, target powder can be effectively heated in our new method because a lot of target particles are expected to be around irradiated particles. It is deduced that target particles not directly irradiated by pulsed laser are heated to be melting, vaporizing, in plasma. Therefore, it is possible to consider that nanoparticle yield can be drastically improved by the heating effect in our method. Another rational reason for the improvement of nanoparticle yield is the effect of scattering of incident laser light by target particles. Laser can be scattered by target powder. Then, scattering light irradiates target particles which are not directly irradiated by the incident laser light. If the fluence is higher than the threshold value, target powder can be ablated. If the fluence is not high enough to induce ablation, laser light may be expected to heat target particles, resulting in melting. Hence, both the heating and the scattering effect might contribute to the improvement in nanoparticle yield.

Silver nanoparticles prepared by our method have been stably dispersed for more than 6 months. Preparation of stable nanocolloid was reported in some cases. For example, laser ablation of gold target can produce Au–O$^-$ on the surface of gold nanoparticles and they are stably dispersed by electrostatic repulsion [21]. It is

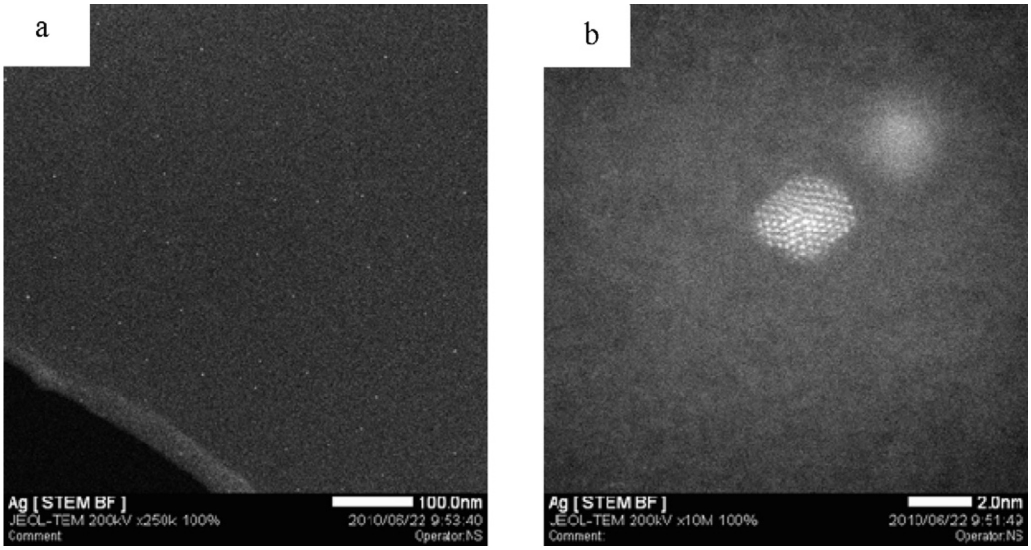

Fig. 4. (a) Low and (b) high magnifications of TEM images of products.

possible to consider that the stability of silver nanoparticles prepared in our experiments can also be attributed to electrostatic repulsion.

Scanning transmission electron microscopy (STEM) of silver nanoparticles is shown in Fig. 4. Fig. 4(a) indicates that the size distribution of produced particles is very narrow and the average particle size is about 2 nm. Additionally, Fig. 4 (b) shows that the shape of the particles is not sphere but square pyramid or octahedral structure. In general, the shape of nanoparticles produced by laser ablation in liquid is spherical. Irradiation of laser light to nanoparticles dispersed in liquid induces the change of particle shape in some cases. Tsuji et al. reported the formation of silver wires and sheets, probably due to fusion of nanoparticles [31]. In our experiments, laser light can be scattered by target powder. And nanoparticles produced may be irradiated by scattered and attenuated laser light. Therefore, the production of unique shape cannot be expected. However, the average particle size is 2 nm and its distribution is very narrow. It is needed to further investigate the mechanism of the production of nanoparticles with peculiar shape.

Antibacterial activity of silver nanoparticles against *B. coli* was investigated and shown in Fig. 5. Nanocolloids prepared by laser ablation were diluted and tested. The concentration of as-prepared colloid was estimated to be 200 mg/L and estimated concentration used in this experiment was ca. 20 mg/L. The number of bacteria decreased with time and bactericidal activity was observed. The intrinsic property of silver nanoparticles has been demonstrated because the surface of nanoparticles prepared by laser ablation in liquid is absolutely pure.

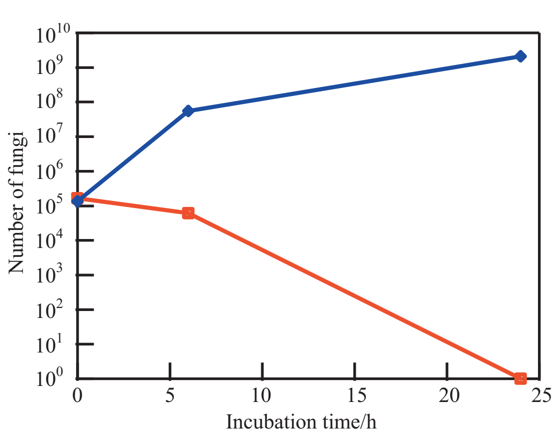

Fig. 5. Antibacterial activities of a silver nanocolloid diluted to be 20 mg/L (□). Control experiment (◆) without silver nanocolloid is also shown.

4. Summary

New laser ablation method was developed to improve nanoparticle yield. In this method, laser is irradiated to the precipitated target powder through the bottom of a piriform flask. High nanoparticle yield of 20 mg/h was attained because the interaction between produced nanoparticles and incident laser light could be practically prevented. The average size of produced particles was ca. 2 nm and its distribution was very narrow. Moreover, nanoparticles have been dispersed for more than 6 months without any chemical reagent and pH adjustment. Bactericidal activity of silver nanocolloid could be demonstrated. We expect that this method enable the production of various types of nanoparticles and leads to the discovery of new functional materials.

References

[1] T. Dadosh, J. Sperling, G.W. Bryant, R. Breslow, T. Shegai, M. Dyshel, G. Haran, I. Bar-Joseph, ACS Nano. 3 (2009) 1988–1994.
[2] W.E. Doering, S.M. Nie, J. Phys. Chem. B 106 (2002) 311–317.
[3] J. Theiss, P. Pavaskar, P.M. Echternach, R.E. Muller, S.B. Cronin, Nano Lett. 10 (2010) 2749–2754.
[4] D. Lee, R. Cohen, M. Rubner, Langmuir 21 (2005) 9651–9659.
[5] S. Pal, Y.K. Tak, J.M. Song, Appl. Environ. Microbiol. 73 (2007) 1712–1720.
[6] S. Tarimala, N. Kothari, N. Abidi, E. Hequet, J. Fralick, L.L. Dai, J. Appl. Polym. Sci. 101 (2006) 2938–2943.
[7] B.P. Binks, J.A. Rodrigues, Langmuir 23 (2007) 7436–7439.
[8] N. Wu, L. Fu, M. Su, M. Aslam, K.C. Wong, V.P. Dravid, Nano Lett. 4 (2004) 383–386.
[9] A.K. Singh, A.K. Singh, O.N. Srivastava, J. Alloys Compd. 227 (1995) 63–68.
[10] M. Inkyo, Y. Tokunaga, T. Tahara, T. Iwaki, F. Iskandar, C. Hogan, K. Okuyama, Ind. Eng. Chem. Res. 47 (2008) 2597–2604.
[11] K. Imasaka, Y. Kanatake, Y. Ohshiro, J. Suehiro, M. Hara, Thin Solid Films (2006) 250–254, 506–507.
[12] J. Cole, E. Lin, C. Barry, H. Jacobs, Appl. Phys. Lett. 95 (2009) 113101.
[13] N.R. Jana, L. Gearheart, C. Murphy, Chem. Mater. 13 (2001) 2313–2322.
[14] J.B. Jackson, N.J. Halas, J. Phys. Chem. B 105 (2001) 2743–2746.
[15] T. Teranishi, I. Kiyokawa, M. Miyake, Adv. Mater. 10 (1998) 596–599.
[16] F. Mafune, J. Kohno, Y. Takeda, T. Kondow, H. Sawabe, J. Phys. Chem. B 105 (2001) 5114–5120.
[17] F. Mafune, J. Kohno, Y. Takeda, T. Kondow, H. Sawabe, J. Phys. Chem. B 104 (2000) 8333–8337.
[18] S. Besner, M. Meunier, J. Phys. Chem. C 114 (2010) 10403–10409.
[19] J.S. Golightly, A.W. Castleman, J. Phys. Chem. B 110 (2006) 19979–19984.
[20] Y. Tamaki, T. Asahi, H. Masuhara, J. Phys. Chem. A 106 (2002) 2135–2139.

[21] J.P. Sylvestre, S. Poulin, A.V. Kabashin, E. Sacher, M. Meunier, J.H.T. Luong, J. Phys. Chem. B 108 (2004) 16864–16869.
[22] W.T. Nichols, T. Sasaki, N.J Koshizaki, Appl. Phys. 100 (2006) 114912.
[23] T. Tsuji, K. Iryo, N. Watanabe, M. Tsuji, Appl. Surf. Sci. 202 (2002) 80–85.
[24] T. Tsuji, K. Iryo, Y. Nishimura, M. Tsuji, J. Photochem. Photobiol. A 145 (2001) 201–207.
[25] Y. Kawaguchi, X. Ding, A. Narazaki, T. Sato, H. Niino, Appl. Phys. A 79 (2004) 883–885.
[26] K. Saito, T. Sakka, Y.H. Ogata, J. Appl. Phys. 94 (2003) 5530–5536.
[27] X. Zeng, S.S. Mao, C. Liu, X. Mao, R. Greif, R.E. Russo, Spectrochim. Acta B 58 (2003) 867–877.
[28] X. Zeng, S.S. Mao, C. Liu, X. Mao, R. Greif, R.E. Russo, Appl. Phys. Lett. 83 (2003) 240–242.
[29] L. Berthe, R. Fabbro, P. Perye, E. Bartnicki, J. Appl. Phys. 85 (1999) 7552–7555.
[30] L. Berthe, R. Fabbro, P. Peyre, L. Tollier, E. Bartnicki, J. Appl. Phys. 82 (1997) 2826–2832.
[31] T. Tsuji, Y. Okazaki, T. Higuchi, M. Tsuji, J. Photochem. Photobiol. A 183 (2006) 297–303.