

## Microwave-assisted Preparation of Silver Nanoparticles

Tetsushi Yamamoto, Yuji Wada,\* Takao Sakata,<sup>†</sup> Hirotarō Mori,<sup>†</sup> Masaki Goto,<sup>††</sup> Shingo Hibino,<sup>††</sup> and Shozo Yanagida\*

Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

<sup>†</sup>Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047

<sup>††</sup>Tokai Rubber Industries Ltd., 3-1 Higashi, Komaki, Aichi 485-8550

(Received September 8, 2003; CL-030828)

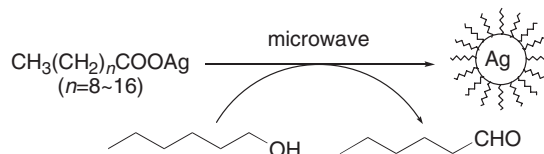
We succeeded in preparing silver (Ag) nanoparticles by alcohol reduction of fatty acid silver salts under microwave irradiation (2.45 GHz) for 1–5 min at 413–430 K. The average sizes of Ag nanoparticles were controlled in the range from 4.9 to 7.4 nm only by changing length of the alkyl chains in the fatty acids.

Silver (Ag) nanoparticles have attracted a great deal of interest in recent years because these are a good candidate of a material applied for optics,<sup>1</sup> electronics,<sup>2</sup> and catalysis.<sup>3</sup> Until now, silver nanoparticles have been prepared by various methods, such as chemical reduction using NaBH<sub>4</sub> or N<sub>2</sub>H<sub>4</sub>,<sup>4a,b</sup> ethanol,<sup>4c</sup> polyol medium<sup>4d</sup> and *N,N*-dimethylformamide (DMF),<sup>4e</sup> aerosol technique,<sup>5</sup> thermal decomposition,<sup>6</sup> electrochemical deposition,<sup>7</sup> photochemical reduction,<sup>8</sup> sonochemical deposition,<sup>9</sup> and laser irradiation technique.<sup>10</sup> One of the best methods for chemical preparation of size-controlled Ag nanoparticles reported so far is a chemical reduction using NaBH<sub>4</sub> resulting in the dodecanethiol-capped 1.8–3.5 nm diameter Ag nanoparticles. However, this method requires a technique of size-selective precipitation.<sup>4b</sup>

In recent years, microwave (MW) dielectric heating is fast emerging as a widely accepted new processing technology for variety of inorganic and organic syntheses.<sup>11</sup> The most commonly used frequency is 2.45 GHz. In the microwave frequencies range, polar molecules try to orientate with the electric field. Next, when dipolar molecules try to re-orientate with respect to an alternating electric field, it loses energy in the form of heat, by molecular friction.<sup>11c</sup> The dissipation of microwave energy to thermal energy depends on dielectric loss factor,  $\epsilon''$ .<sup>11a</sup> In the MW-assisted syntheses of inorganic nanoparticles, size of nanoparticles can be effectively controlled in narrower distribution than the conventional heating due to a homogeneous and fast nucleation induced by MW heating.<sup>4d,12</sup>

As a simple method for rapid preparation of Ag nanoparticles at low temperatures without the technique of size-selective precipitation, we propose here a novel microwave-assisted alcohol reduction of fatty acid silver salts, “microwave-alcohol reduction” (Scheme 1). As the precursors of silver nanoparticles, we selected fatty acid silver salts CH<sub>3</sub>(CH<sub>2</sub>)<sub>*n*</sub>COOAg (*n* = 6 (C<sub>8</sub>-Ag), *n* = 8 (C<sub>10</sub>-Ag), *n* = 10 (C<sub>12</sub>-Ag), *n* = 12 (C<sub>14</sub>-Ag), *n* = 14 (C<sub>16</sub>-Ag), and *n* = 16 (C<sub>18</sub>-Ag)), oleic acid silver salt CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>COOAg (C<sub>18</sub>:1-Ag) and linoleic acid silver salt CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH=CHCH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>COOAg (C<sub>18</sub>:2-Ag), because long-chain counter anions of silver salts should prevent the agglomeration of Ag nanoparticles. We selected 1-pentanol, 1-hexanol, 1-heptanol, or 1-octanol as a solvent, instead of methanol, ethanol, 1-propanol, or 1-butanol, using the microwave-alcohol reduction because these alcohols have (a) low water solubilities, (b) appropriate dielectric loss

factors at 2.45 GHz, (c) high boiling points (411–468 K), and (d) weak reducing power.



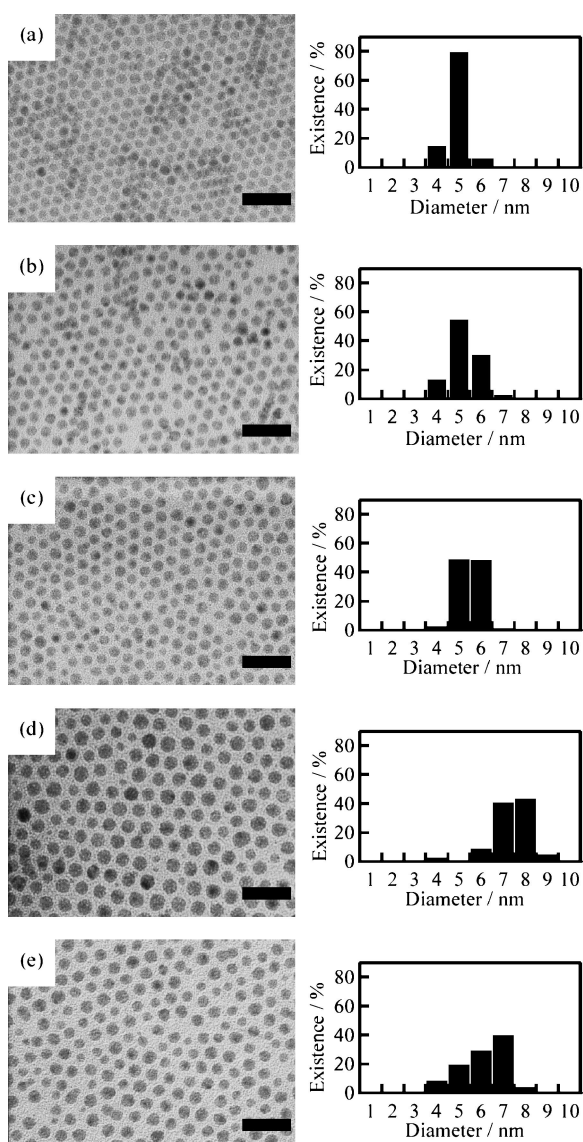
**Scheme 1.** Microwave-alcohol reduction of fatty acid silver salts for silver nanoparticles.

MW irradiation experiments were performed using a multi-mode MW apparatus (Micro Denshi MMG-213VP, 2.45 GHz). A fiber optic sensor (Anritsu SP-SM5176FL) was inserted into the reaction solution and the reaction temperature was controlled by the repeated on–off MW irradiation. A three-stub tuner was used to achieve optimal MW power absorption with a forward and reverse power monitor. The reaction was carried out using a three-neck quartz flask equipped with a water-cooled condenser outside the MW cavity and the reaction solution was stirred by a Teflon magnetic stirrer. In a typical experiment, an aqueous solution (10 mL) of silver nitrate (5 mmol) was added to an aqueous solution (20 mL) of lauric acid sodium salt (5 mmol), stirred by Teflon magnetic stirrer. The resulting water-insoluble precipitate was filtered and was washed by ethanol and was finally dried under vacuum to produce a white lauric acid silver salt (3.8 mmol). Lauric acid silver salt (1 mmol) was added to 1-hexanol (25 mL) in a 100 mL three-neck quartz flask. Fatty acid silver salt was not dissolved totally, giving a suspended solution. The solution stirred by a Teflon magnetic stirrer was heated up to 413 K under MW (150 W) irradiation within 2 min under nitrogen atmosphere. The color of the solution changed to dark-brown within 2 min. This rapid heating rate could not be achieved by conventional heating. The solution was maintained for 5 min at 413 K under the repeated on–off MW (150 W) irradiation. After the MW irradiation, the suspension was cooled down immediately by an air blower. For characterization of the silver nanoparticles, transmission electron microscopic (TEM) analyses were performed with Hitachi H-9000 operating at 300 kV. The *n*-hexane solution dispersing silver nanoparticles (5 drops of 10  $\mu$ L) was dried slowly on an amorphous carbon film supported on a copper mesh TEM grid by self-assembly techniques.<sup>5,13</sup>

TEM images show that 2-D structure of silver nanoparticles were formed on a carbon film (Figure 1). Four diffraction rings ((111), (200), (220), and (311)) indicated that the products were face-centered cubic (fcc) metal silver. The image reveals that silver nanoparticles were formed by 1-hexanol reduction of the fatty acid silver salts under microwave irradiation. It is remarkable that the average diameter of silver nanoparticles was controlled

from 4.9 to 7.4 nm only by varying alkyl chain of fatty acid silver salts; 4.9 nm (0.4 nm)(C<sub>10</sub>-Ag), 5.2 nm (0.7 nm)(C<sub>12</sub>-Ag), 5.5 nm (0.6 nm)(C<sub>14</sub>-Ag), 6.0 nm (1.1 nm)(C<sub>16</sub>-Ag), 5.8 nm (0.9 nm)(C<sub>18</sub>-Ag), 7.4 nm (0.9 nm)(C<sub>18</sub>:1-Ag), and 6.1 nm (1.0 nm)(C<sub>18</sub>:2-Ag), where the values in parenthesis are the standard deviation, compared with 5 nm silver nanoparticles synthesized by a thermal decomposition of fatty acid silver salts at 523 K.<sup>6a</sup> From UV-vis spectrum of Ag nanoparticle prepared from C<sub>16</sub>-Ag in hexane solution, an absorption maximum peak was observed at 418 nm due to the surface plasmon absorption,<sup>1a</sup> in good agreement with the reported values.<sup>6b</sup>

At low temperature (383 K), the size of Ag nanoparticles prepared for 40 min was similar to those obtained at 413 K for 5 min. At high temperature (430 K), Ag nanoparticles prepared



**Figure 1.** TEM images of Ag nanoparticles prepared in 1-hexanol under microwave irradiation at 413 K for 5 min from silver salts; (a) C<sub>10</sub>-Ag, (b) C<sub>12</sub>-Ag, (c) C<sub>14</sub>-Ag, (d) C<sub>18</sub>:1-Ag, and (e) C<sub>18</sub>:2-Ag. Scale bar is 25 nm. The size distributions were determined for the randomly selected 200–300 particles from the 2-D structures of TEM images observed mainly in the samples.

for only 1 min were similar to those obtained at 413 K for 5 min under MW irradiation. As alkyl chains of alcohols became longer, average diameter of Ag nanoparticles, which were prepared from C<sub>16</sub>-Ag at 413 K for 5 min under MW irradiation, decreased slightly: 6.4 nm (0.9 nm)(1-pentanol), 6.0 nm (1.1 nm)-(1-hexanol), 5.4 nm (0.9 nm)(1-heptanol), and 5.3 nm (0.7 nm)-(1-octanol). The intense peak was observed at 1395 cm<sup>-1</sup> in the FT-IR spectrum of the Ag nanoparticles prepared using C<sub>12</sub>-Ag, which should be assigned to the symmetric stretching vibration of a carboxylate group  $\nu_s(\text{COO}^-)$ . This suggests strongly that silver nanoparticles are capped by fatty acids as Lee et al. suggested based on the observation of the peak at 1396 cm<sup>-1</sup> in the literature.<sup>6b</sup>

In our MW-synthesis, silver ion was reduced by alcohol and converted into silver nanoparticles under the precise size-control, which were stabilized by surface modification with fatty acid.

The present study was mainly supported by “21<sup>st</sup> Century Center of Excellence Program.” A part of this work was supported by “Nanotechnology Support Project” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

## References

- a) A. Henglein, *J. Phys. Chem.*, **97**, 5457 (1993). b) C. P. Collier, R. J. Saykally, J. J. Shiang, S. E. Henrichs, and J. R. Heath, *Science*, **277**, 1978 (1997).
- W. P. McConnell, J. P. Novak, L. C. Brousseau, III, R. R. Fuierer, R. C. Tenent, and D. L. Feldheim, *J. Phys. Chem. B*, **104**, 8925 (2000).
- N. R. Jana, T. K. Sau, and T. Pal, *J. Phys. Chem. B*, **103**, 115 (1999).
- a) C. Petit, P. Lixon, and M.-P. Pileni, *J. Phys. Chem. B*, **97**, 12974 (1993). b) J. R. Heath, C. M. Knobler, and D. V. Leff, *J. Phys. Chem. B*, **101**, 189 (1997). c) L. M. L.-Marzán and I. L.-Tourinho, *Langmuir*, **12**, 3585 (1996). d) S. Komarneni, D. Li, B. Newalkar, H. Katsuki, and A. S. Bhalla, *Langmuir*, **18**, 5959 (2002). e) I. P.-Santos and L. M. L.-Marzán, *Langmuir*, **18**, 2888 (2002).
- S. A. Harfenist, Z. L. Wang, M. M. Alvarez, I. Vezmar, and R. L. Whetten, *J. Phys. Chem.*, **100**, 13904 (1996).
- a) K. Abe, T. Hanada, Y. Yoshida, N. Tanigaki, H. Takiguchi, H. Nagasawa, M. Nakamoto, T. Yamaguchi, and K. Yase, *Thin Solid Films*, **327–329**, 524 (1998). b) S. J. Lee, S. W. Han, H. J. Choi, and K. Kim, *J. Phys. Chem. B*, **106**, 2892 (2002).
- R. M. Stiger, S. Gorer, B. Craft, and P. M. Penner, *Langmuir*, **15**, 790 (1999).
- T. Itakura, K. Torigoe, and K. Esumi, *Langmuir*, **11**, 4129 (1995).
- V. G. Pol, D. N. Srivastava, O. Palchik, V. Palchik, M. A. Slifkin, A. M. Weiss, and A. Gedanken, *Langmuir*, **18**, 3352 (2002).
- J. P. Abid, A. W. Wark, P. F. Brevet, and H. H. Girault, *Chem. Commun.*, **2002**, 792.
- a) C. Gabriel, S. Gabriel, E. H. Grant, B. S. J. Halstead, and D. M. P. Mingos, *Chem. Soc. Rev.*, **27**, 213 (1998). b) K. J. Rao, B. Vaidyanathan, M. Ganguli, and P. A. Ramakrishnan, *Chem. Mater.*, **11**, 882 (1999). c) B. Wathey, J. Tierney, P. Lidström, and J. Westman, *Drug Discovery Today*, **7**, 373 (2002). d) “Microwaves in Organic Synthesis,” ed. by A. Loupy, Wiley-VCH, Weinheim (2002).
- a) Y. Wada, H. Kuramoto, T. Sakata, H. Mori, T. Sumida, T. Kitamura, and S. Yanagida, *Chem. Lett.*, **1999**, 607. b) X. Yan, H. Liu, and K. Y. Liew, *J. Mater. Chem.*, **11**, 3387 (2001).
- Z. L. Wang, *Adv. Mater.*, **10**, 13 (1998).