

Exotic shapes of gold nanoparticles synthesized using plasma in aqueous solution

Junko Hieda

Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

Nagahiro Saito^{a)}

Department of Materials, Physics and Energy Engineering and Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan, and CREST, JST, Furo-cho, Chikusa, Nagoya 464-8603, Japan

Osamu Takai

Department of Materials, Physics and Energy Engineering, Graduate School of Engineering and EcoTopia Science Research Institute, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan, and CREST, JST, Furo-cho, Chikusa, Nagoya 464-8603, Japan

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Gold nanoparticles with exotic shapes, such as triangle, pentagon, and hexagon, have been synthesized by glow discharge in aqueous solutions. A pulsed power supply was used to generate discharges in the aqueous solutions. Pulse width and frequency were 2 μ s and 15 kHz, respectively. Discharges were generated at applied voltages of 1600 and 3200 V. The shapes of the gold nanoparticles and electron diffraction patterns were observed by transmission electron microscopy. The nanoparticles obtained were about 20 nm in diameter. In particular, at the higher voltage of 3200 V, nanoparticles with anisotropic shapes were synthesized. In the initial stages of synthesis, diameter decreased with discharge time as the nanoparticles redissolved in the solution. After discharge for 25 min, nanoparticles with anisotropic shapes appeared. This discharge led to the generation of H₂O₂ and a decrease in pH as a result of the consumption of OH radicals during the generation of H₂O₂ and electron donation of H radicals to the solution. After the pH stopped decreasing, H radicals mainly reacted as a reducing agent. The decrease in pH allowed redissolution of the gold nanoparticles. The gold dust particles that were not completely dissolved acted as new seeds for nucleation. Thus, the two reaction steps, nucleation and nuclear growth, occur during the formation of gold nanoparticles with exotic shapes. © 2008 American Vacuum Society.

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I. INTRODUCTION

Plasma processing of materials in the liquid phase has the potential to become an industrial process for the production of metal nanoparticles, because this process would allow extremely rapid reactions under high pressure. In this process, plasma is generated inside microbubbles produced by electrolysis, Joule heating, or the introduction of a gas. At the plasma/gas and gas/liquid interfaces, ultraviolet light, electrons, ions, and radicals are generated at high density. These reactive species efficiently react with chemical species in a liquid solution at the gas/liquid interface, which provides a heterogeneous reaction field where substance transfer can dynamically occur, because a nonlinear coupled motion between the plasma and the solution, such as contraction and expansion, can form a stable system.

Gold nanoparticles have been utilized in the field of nanotechnology and biotechnology because of their optical visibility and high bioaffinity.¹⁻³ It is well known that particle shape influences the optical and catalytic properties of gold nanoparticles.⁴ Therefore, many researchers have studied the

fabrication of anisotropically shaped gold nanoparticles by chemical reduction methods.³⁻⁸ In our previous study, gold nanoparticles were successfully synthesized by discharge in an aqueous solution. By using gelatin as a stabilizer, well-dispersed particles with an average size of \sim 10 nm were obtained from chlorauric acid (HAuCl₄) solutions at different HAuCl₄ concentrations. A unique point regarding the solution plasma process is that it requires no reducing agent, because the plasma generates H radicals, which act as a reducing agent.

In this study, we aimed at controlling the shapes of nanoparticles fabricated by discharge in aqueous solutions.

II. EXPERIMENTAL PROCEDURE

Gold nanoparticles were synthesized from aqueous solutions containing chlorauric acid by using the solution plasma process. Sodium dodecyl sulfonate (SDS) (1.0×10^{-2} mol) (Aldrich) was added to 150 ml of water as a stabilizer. This concentration of SDS is greater than the critical micelle concentration. Chlorauric acid (37 mM) solution was prepared from HAuCl₄·4H₂O (Wako Pure Chemical Industries, Ltd.) as a stock solution, which was mixed into the solution containing SDS. The concentrations of [AuCl₄]⁻ in the solution

^{a)}Author to whom correspondence should be addressed; electronic mail: hiro@eco-t.esi.nagoya-u.ac.jp

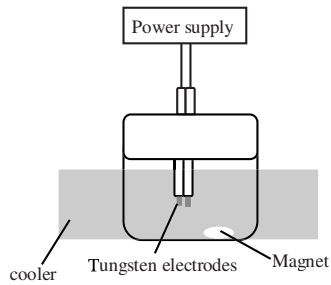


FIG. 1. Schematic of experimental apparatus.

in these experiments were 0.3 and 0.65 mM. Figure 1 shows a schematic of our experimental apparatus. No large chamber was required for this experiment. Tungsten electrodes ($\phi 1$ mm) with a 0.3 mm gap were placed in a glass vessel filled with the solution. The temperature of the aqueous solution was kept at 25 °C by using a cooling system. A pulsed dc power supply (Kurita Co. Ltd.; Kurita-Nagoya MPS-06K06C) was used to generate plasma. The voltages applied were 1600 and 3200 V. The pulse frequency and pulse width employed were 15 kHz and 2 μ s, respectively. During the discharge, HAuCl₄ solutions were stirred with a magnetic stirrer. Shapes and electron diffraction (ED) patterns of gold nanoparticles were observed by transmission electron microscopy (TEM) (JEOL; JEM-2500SE). UV-visible (UV-vis) spectra were measured by UV-vis spectroscopy (Shimadzu; UV-3600 UV-vis-NIR spectrophotometer).

III. RESULTS AND DISCUSSION

Figure 2 shows TEM images of gold nanoparticles prepared from the solution after discharge at 1600 and 3200 V for 45 min. Initial concentrations of [AuCl₄]⁻ were 0.3 and 0.65 mM. The size of particles formed at 0.65 mM was approximately 25–50 nm. Most of the particles were spherical in shape [Figs. 2(a) and 2(b)]. The gold nanoparticles synthesized with discharge at 3200 V were smaller than those synthesized at 1600 V. Gold nanoparticles of approximately 10–20 nm size were formed by using an initial [AuCl₄]⁻ concentration of 0.3 mM [Figs. 2(c) and 2(d)]. Particles syn-

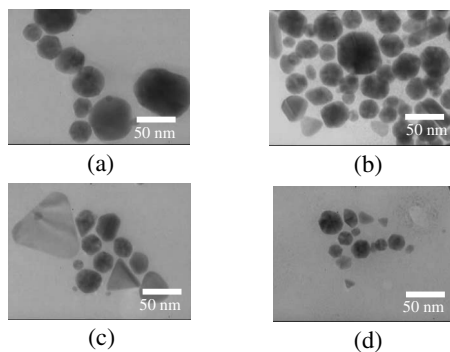


FIG. 2. TEM images of gold nanoparticles synthesized by discharge for 45 min: (a) 0.65 mM [AuCl₄]⁻, discharge voltage of 1600 V; (b) 0.65 mM [AuCl₄]⁻, discharge voltage of 3200 V; (c) 0.3 mM [AuCl₄]⁻, discharge voltage of 1600 V; and (d) 0.3 mM [AuCl₄]⁻, discharge voltage of 3200 V.

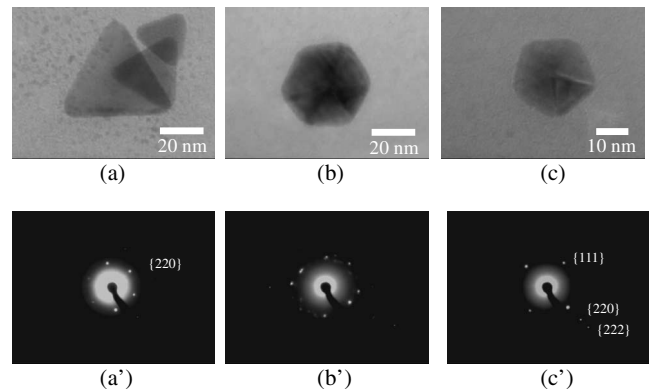


FIG. 3. TEM images of gold nanoparticles and corresponding ED patterns. [(a) and (a')] triangular nanoparticles. [(b) and (b')] hexagonal nanoparticles. [(c) and (c')] pentagonal nanoparticles.

thesized at higher concentration were larger, because the reaction rate for the synthesis was higher and continued to increase until [AuCl₄]⁻ was entirely consumed. At the concentration of 0.3 mM, smaller particles were also obtained by synthesis at a higher applied voltage. As shown in Fig. 2(d), particles with an average size of \sim 10 nm had triangular, pentagonal, and hexagonal shapes. Thus, higher voltage and lower [AuCl₄]⁻ concentration led to size reduction and generation of gold nanoparticles with anisotropic shapes.

TEM images and ED patterns of gold nanoparticles with anisotropic shapes (triangle, pentagon, and hexagon) are shown in Fig. 3. All spots were indexed according to the face centered cubic structure of Au. From the TEM images, the triangular nanoparticles seemed to be platelike. The ED pattern showed a hexagonal diffraction spot pattern corresponding to {220}. The TEM image and the ED pattern [Figs. 3(a) and 3(a')] indicate that the incident axis of the electron beam \langle 111 \rangle is normal to the triangle plate. For the pentagons, patterns corresponding to {111}, {220}, and {222} were observed. The spots corresponding to {111} and {222} are the diffraction from one crystal, and the other spot corresponding to {220} is from another crystal. This indicates that at least the nanoparticles with a pentagonal shape consist of two crystals. On the other hand, many spots corresponding to {111} and {200} could be seen in the ED pattern for the hexagonal particles. This indicates that the particles had a polycrystalline structure.

Time evolution of the formation process was evaluated by using TEM images. Figure 4 shows TEM images of gold nanoparticles synthesized at 3200 V at the [AuCl₄]⁻ concentration of 0.3 mM in relation to discharge time. Hexagonal and dendrite-shaped nanoparticles were observed in the solution after discharge for 5 min. After discharge for 15 min, particles size decreased from approximately 50 to 30 nm and, at the same time, small, new particles \sim 20 nm in size were formed. Discharge for more than 10 min resulted in a significant reduction in gold nanoparticle size, as shown in Fig. 4(c). Nanoparticles with the triangular and hexagonal shapes were observed. Discharge for 45 min produced gold nanoparticles of \sim 20 nm size with exotic shapes, such as

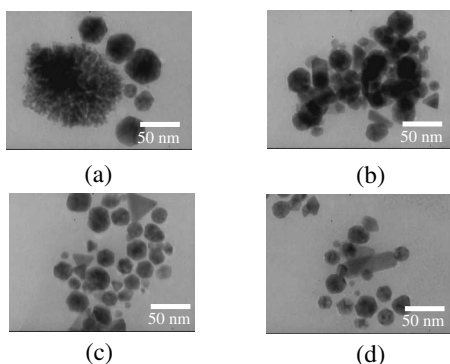


FIG. 4. TEM images of gold nanoparticles prepared by discharge at 3200 V for (a) 5 min, (b) 15 min, (c) 25 min, and (d) 45 min at an initial $[\text{AuCl}_4]^-$ concentration of 0.3 mM.

triangles, pentagons, and hexagons. The reduction in particle size with increasing discharge time indicated dissolution of gold nanoparticles into the solution. This formation mechanism is clearly different from that which occurs with other fabrication methods using solutions containing HAuCl_4 as a precursor.

To investigate the concentration of $[\text{AuCl}_4]^-$, 100 μl of saturated NaBr solution was added to the solutions after discharge. The addition of NaBr led to a shift in absorption due to the displacement of ligands in $[\text{AuCl}_4]^-$ and precipitation of gold nanoparticles. The absorbance at 382 nm attributed to $[\text{AuBr}_4]^-$ was compared to the calibration line, and we then evaluated the concentration of $[\text{AuCl}_4]^-$. A plot of the change in concentration of $[\text{AuCl}_4]^-$ from the initial concentration of 0.3 mM as a function of discharge time is shown in Fig. 5.

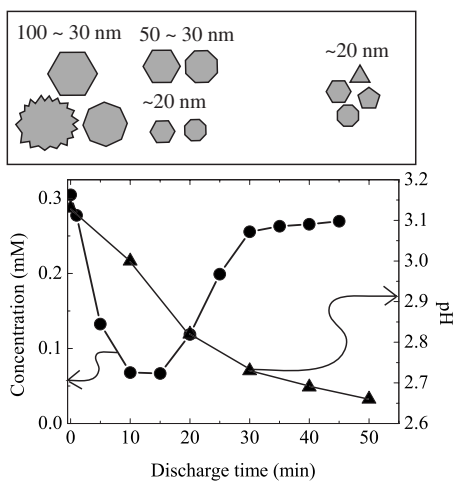


FIG. 5. Plot of $[\text{AuCl}_4]^-$ as a function of discharge time at an initial $[\text{AuCl}_4]^-$ concentration of 0.3 mM in preparations with discharge at 3200 V.

Under this condition, the voltage applied between the electrodes in the solution was 3200 V. $[\text{AuCl}_4]^-$ concentration gradually decreased and subsequently increased with discharge time. During discharge in the aqueous solution, H_2O_2 was produced and the pH gradually decreased from 3.13 to 2.66. This resulted from the consumption of OH radicals for the generation of H_2O_2 and the electron donation of H radicals to the solution. After the decrease in pH stopped, H radicals mainly acted as a reducing agent. Figure 5 suggests that the reaction rate for the synthesis became lower and the dissolution rate became higher at lower pH, because $[\text{AuCl}_4]^-$ is more stable in acidic solutions. The change in particle shape was strongly related to the lower reaction rate for synthesis at low pH and the increase in H radicals reacting with $[\text{AuCl}_4]^-$. The large nanoparticles with a hexagonal shape dissolved and became smaller after discharge for 15 min. Subsequently, triangle- and pentagon-shaped nanoparticles were generated from the dissolved $[\text{AuCl}_4]^-$ as a precursor. Gold nanoparticles that were not completely dissolved acted as seeds for nucleation.

IV. CONCLUSION

We have described the synthesis of gold nanoparticles with exotic shapes by discharge in aqueous solutions. Nanoparticles with triangular, pentagonal, and hexagonal shapes were observed by TEM. Nanoparticles of ~ 50 nm size with hexagonal shape were formed after discharge at 3200 V for 5 min. During discharge, H_2O_2 was generated and the pH decreased, and this led to changes in particle shape. Discharge in aqueous solution caused dissolution of the gold nanoparticles and their size decreased to ~ 20 nm. Anisotropic nanoparticles that were formed after the dissolution of the gold nanoparticles acted as seeds for nuclear growth. Thus, the two reaction steps, nucleation and nuclear growth, occur during the formation of exotic gold nanoparticles.

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