

Protective Agent-free Preparation of Gold Nanoplates and Nanorods in Aqueous HAuCl_4 Solutions Using Gas-Liquid Interface Discharge

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Gas-liquid interface discharge at atmospheric pressure above HAuCl_4 solutions containing no protective agents generates triangular and hexagonal nanoplates and nanorods of gold. Experimental results under several different conditions indicate that the plates and rods rapidly grow on the surface of the solution. In contrast, the spherical nanoparticles slowly grow in the solution.

Recently, the preparation and characterization of nanostructured materials have received significant attention. Especially, gold nanoparticles have unique optical, electrical, catalytic properties, and biocompatible features that should be applicable to biosensors and gene therapy.¹ Various methods have been reported on the preparation of the gold nanoparticles,² where a polymer or surfactant added to the reactant solution plays a crucial role in preparing triangular and hexagonal nanoplates and nanorods.

Glow discharge electrolysis (GDE) is not very common but has been a part of the electrochemistry field since 1887.^{3,4} In GDE, one electrode is set in the gas phase above the electrolyte solution, and the other is immersed in the solution. The glow discharge is generated between the surface of the solution and the end of the electrode placed in the gas phase in a pressure range of $3.3 \times (10^3\text{--}10^4)$ Pa. Charged particles produced by the discharge in the gas phase are accelerated toward the surface of the solution and then collide with solvent molecules to produce various radicals, ions, and excited species, which cannot be generated by ordinary electrolysis in the solution. The formation of hydrogen peroxide (H_2O_2) in various aqueous solutions and of hydrazine (N_2H_4) in liquid ammonia has been examined by GDE in detail.³ However, this method has very limited applications in chemical synthesis to date. Other applications of the discharge in systems containing liquid have recently been tried on the formation of carbon nanotubes using an arc discharge in solution⁵ and on the decomposition of phenol ($\text{C}_6\text{H}_5\text{OH}$) using a pulsed gas-liquid interface discharge.^{6,7}

In this letter, we show that the gold nanoplates and nanorods can be prepared in simple aqueous HAuCl_4 solutions containing no protective agents such as a polymer and surfactant, using a gas-liquid interface discharge at atmospheric pressure. The experimental method used here is very similar to that of GDE. However, nucleation and crystallization instead of electrolysis has occurred in the present experiment. In addition, the discharge form differs from that of an ordinary glow discharge. Hence, the expression "GDE" is not appropriate in this report. Therefore, we describe the present experimental method as a Discharge-Induced Chemical REaction in Solution (DICRES).

Two kinds of solutions were prepared. One was an aqueous solution of 0.33 mM hydrogen tetrachloroaurate(III) tetrahydrate (Wako Chemicals, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99%) using Millipore water

(Millipore Systems, resistivity $18 \text{ M}\Omega \cdot \text{cm}$). The other was 0.33 mM HAuCl_4 and 1.33 mM sodium hydrogen carbonate (Kishida Chemical, NaHCO_3 , 99.5%). The anode of Cu was fixed at 1–2 mm above the gas-solution interface, while the Cu cathode, which was grounded, was immersed in a 25-mL solution in a 50-mL beaker. A DC voltage was applied to the anode using a DC high voltage power supply (MAX-ELECTRONICS, HV α -10K50P/DPM/100), where the power supply confined the electric current to 50 mA. The applied voltage depended on the distance between the end of the anode and the surface of the solution and on the distance between the two electrodes, which was typically 1 to 1.5 kV. A steady discharge was generated between the anode and the surface of the solution. The solution was stirred using a magnetic stirrer during the discharge. Within 15 s, the solution changed from faint yellow to dark red, a well-known color for gold nanoparticle solutions.

The transmission electron microscope (TEM; JEOL JEM-2100XS) images and electron diffraction patterns of the particles prepared by the DICRES method were observed at an electron energy of 200 kV.

Figures 1a and 1b show the TEM images of the nanoparticles prepared by the discharge of the $\text{HAuCl}_4/\text{NaHCO}_3$ solution in the air during 14-s and 10-min discharges, respectively. Triangular and hexagonal plates and rods are clearly observed. Observing the selected-area electron diffraction (SED) patterns of these nanoparticles, we confirmed that these are gold crystals. Figure 2 shows the TEM image of a triangle nanoplate and its SED pattern. The hexagonal symmetry of the SED pattern indicates that the triangle nanoplate is a single crystal and that the incident electron beam is perpendicular to the $\{111\}$ facet of the plate. The obtained colloidal gold solution was dispersed a few days, and it took about one month for the complete aggregation of the nanoparticles. Very recently, Irie et al.⁸ have reported the preparation of gold nanoparticles by pulsed discharge where both electrodes were immersed into aqueous $\text{HAuCl}_4/\text{KCl}$ /gelatin solutions. However, only spherical particles with about 10-nm diameter have been observed in the TEM image. To our best knowledge, this is the first report on the protective agent-free

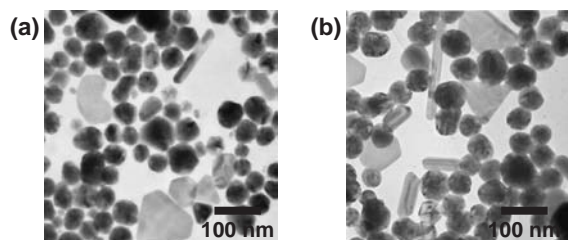


Figure 1. TEM images of gold nanoparticles prepared by the discharge of the $\text{HAuCl}_4/\text{NaHCO}_3$ solution in the air during (a) 14 s and (b) 10 min.

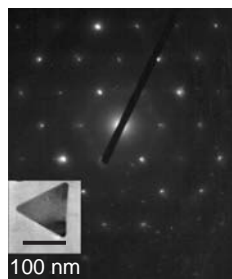


Figure 2. TEM image (left bottom) and SED pattern of a triangular gold nanoplate.

preparation of gold nanoplates and nanorods. The size of the plates and rods in Figure 1a is almost the same as those in Figure 1b, although the discharge time was quite different. In contrast, the fraction of small spherical particles with less than 50-nm diameter in Figure 1a is significantly greater than that in Figure 1b. This finding indicates that the growth rate of the plates and rods is much faster than that of the spherical particles.

Yang et al.⁹ have demonstrated that the gold nanoparticles can be prepared by synchrotron X-ray irradiation to aqueous $\text{HAuCl}_4/\text{NaHCO}_3$ solutions, but only spherical particles with 5–10-nm diameters have been observed in the TEM image. An analogy of the reaction mechanism between GDE and radiation chemistry has been pointed out about the decomposition of solvent molecules by the collisions with energetic particles.³ The formation of the gold nanoplates and nanorods presented here demonstrates that DICRES can lead to a unique nucleation or crystallization of gold nanoparticles, which is difficult by X-ray irradiation.

In order to investigate the formation mechanism of the gold nanoplates and nanorods in detail, we further conducted experiments under several different conditions. Firstly, similar experiments were conducted using a U-tube without stirring the solution, where two electrodes were placed at two open sides of the U-tube one by one. Consequently, the solution changed to red only in the anode side, especially near the gas–solution interface where the discharge was generated. At the other side of the U-tube where the cathode was immersed, the solution did not change color and boiled near the electrode. Secondly, the electrode material was exchanged from copper to gold. The solution changed to dark red after the discharge, similarly to that in the case of the copper electrodes. Thirdly, a colloidal gold solution, which contained only spherical gold nanoparticles with 10–20-nm diameter and was prepared in advance by a citrate reduction method, was used for the DICRES experiment. As a result, the aggregation of the nanoparticles was observed in the TEM image, but no nanoplates and nanorods were observed. Finally, the DICRES experiment was conducted under an atmosphere of Ar or N_2 . The formation of gold nanoplates and nanorods was confirmed in their atmospheres, similarly to the experiment conducted in the air. Especially, the TEM image of the nanoparticles collected near the gas–liquid surface after a one-minute discharge using the HAuCl_4 solution without stirring the solution in the Ar atmosphere contained rich nanoplates, as shown in Figure 3.

Judging from these findings, the formation mechanism of the gold nanoparticles in the DICRES method is summarized as follows; (1) The positive ions generated through the discharge

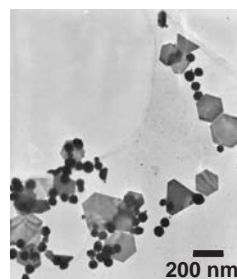


Figure 3. TEM image of gold nanoparticles collected near the gas–liquid surface.

above the solution are accelerated in the gas phase and then collide with the water molecules which are the solvent molecules. Chemically active species such as the H and OH radicals and their positive ions are produced by the collisions. (2) The Au^{3+} ions, which are present in the form of AuCl_4^- ions in the solution, are reduced to Au^0 by the H radicals. This reduction mechanism is the same as that induced by the X-ray irradiation and by the pulsed discharge in the solution. (3) The gold nanoplates and nanorods rapidly grow only on the surface of the solution. This growth mechanism is supported by the fact that the nanoplates and nanorods were not produced by the X-ray radiation and by the pulsed discharge in the solution. The report that the gold crystal is easy to grow on the surface of the solution in a chemical reduction method¹⁰ also supports this growth mechanism in the DICRES method. Once the plates and rods grow on the surface of the solution up to a certain size, they sink into the solution because of their weight, and then their growth stops. (4) The spherical particles slowly grow in the solution. This is the same growth mechanism of the spherical particles as that by the X-ray irradiation and by the pulsed discharge in the solution.

In conclusion, we have successfully demonstrated that the DICRES method can prepare gold nanoplates and nanorods in aqueous HAuCl_4 solutions containing no protective agents. This method is promising as a simple, rapid preparation method of nanocrystals.

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