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Effect of Ultrafine Bubbles on Reducer-free Synthesis of Gold Nanoparticles by Ultrasound
超音波による還元剤フリーの金ナノ粒子合成に及ぼすウルトラファインバブルの効果

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1. Introduction

Gold nanoparticles have catalysis activity, optical and magnetic characteristics depending on their sizes and shapes. It is widely expected to apply to biosensing and optical instrument. Gold nanoparticles are normally synthesized from a gold ion solution and a reducer in boiling condition. A surfactant is used to control particle size and improve colloid stability. Ultrasound irradiation to aqueous solution of $HAuCl_4$ at room temperature is able to safely synthesize gold nanoparticle of high purity because of reducer-free[1]. However, size control and stability improvement without surfactant is difficult.

Bubbles of less than 1 μm in diameter are called ultrafine bubbles (UFB). UFB have very long life time and high charge in water. UFB attract attention in many fields such as medical. In this study, gold nanoparticles were synthesized by ultrasound in the presence of UFB. Effects concentration and gas kind of UFB on particle size and colloid stability were investigated.

2. Experiment

Sample was aqueous solution of 0.1 mM $HAuCl_4$. Water containing UFB was prepared from ultrapure water (Millipore) by pressurized dissolution method (ultrafineGaLF, IDEC) and used as solvent. Number concentration of UFB in the diameter range from 30 to 1000 nm was measured by nanoparticle tracking method (NanoSight, Malvern). The mode diameter of UFB was about 120 nm. Except for Fig. 3, initial number concentration of UFB was $4 - 5 \times 10^9$ mL^{-1}. Gas inside UFB was air, argon, and nitrogen. For comparison, ultrapure water with no UFB was used.

Ultrasound was indirectly irradiated to 50 mL sample in a glass vessel[2]. A plate-type transducer (PZT, Honda Electronics) was driven by a power amplifier and a signal generator at 495 kHz. Electrical power to the transducer was 50 W. Sample temperature was 283 K. After 10 minutes ultrasonic irradiation, synthesized gold particles were analyzed by scanning electron microscope.

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3. Results and discussion

After ultrasonic irradiation, sample color for air-UFB and no UFB were changed from transparent to dark red and pale blue, respectively. Absorbance at peak wavelength of colloid for air-UFB was higher than that for no UFB. This result means that UFB enhances synthesis of gold particle. **Fig. 1** shows electron micrographs of gold nanoparticles for air-UFB and no UFB. In the case of air-UFB, particle shape is almost sphere. For the case of no UFB, plate shape is also often observed.

Fig. 2 shows diameter distribution of gold nanoparticles for air-UFB and no UFB. Compared with no UFB, diameter for air-UFB is very small

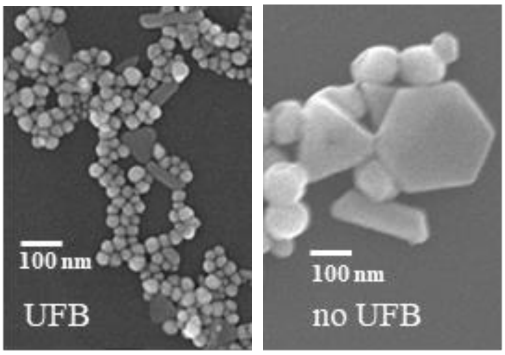

Fig. 1 Electron micrographs of gold nanoparticles with air ultrafine bubbles and no ultrafine bubbles.

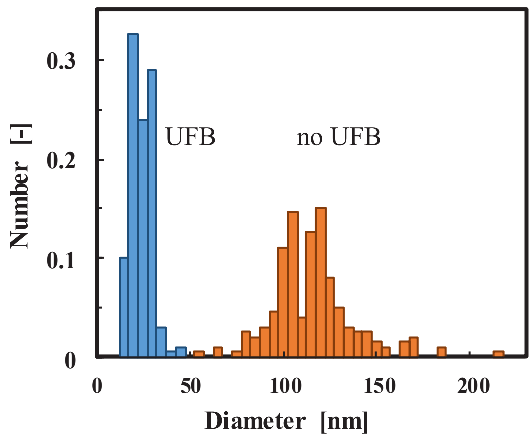

Fig. 2 Diameter distribution of gold nanoparticles for air ultrafine bubbles and no ultrafine bubbles.

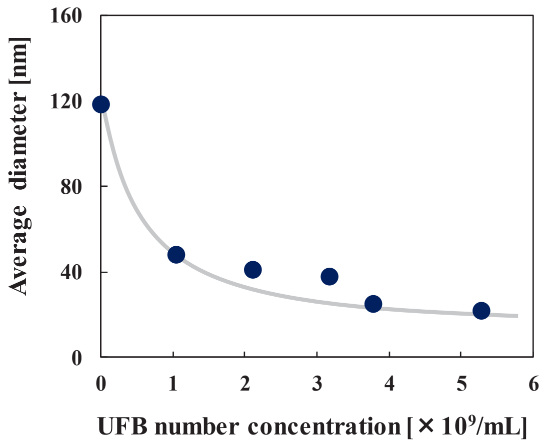

Fig. 3 Effect of number concentration of air ultrafine bubble on mean diameter of gold nanoparticles.

Fig. 4 Photographic observations of dispersion stability of gold nanoparticle for no ultrafine bubbles and air ultrafine bubbles.

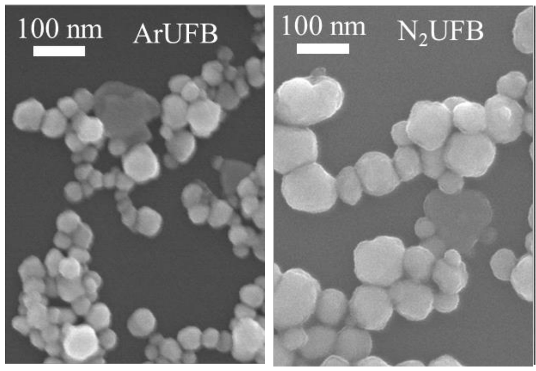

Fig. 5 Electron micrographs of of gold nanoparticles for argon and nitrogen ultrafine bubbles.

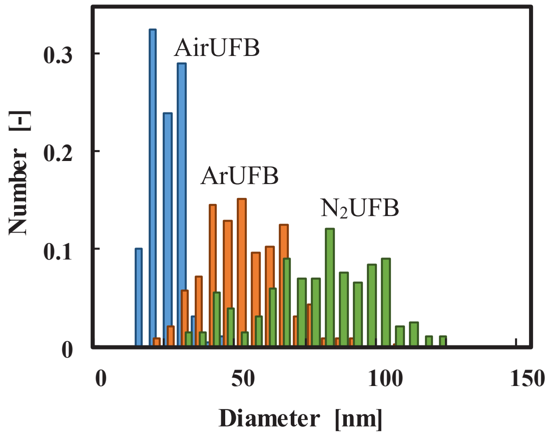

Fig. 6 Diameter distribution of gold nanoparticles for air, argon and nitrogen ultrafine bubbles.

and distribution for air-UFB is narrow. The mean diameter for air-UFB and no UFB are 22 and 119 nm. Standard deviation for air-UFB and no UFB are 6 and 80 nm. The size and shape of gold nanoparticle are typically determined by competition between nucleation (metal ion reduction in bulk) and growth (metal ion reduction on nuclei) processes[1]. It is thought that UFB mainly accelerate nucleation process.

Fig. 3 shows effect of number concentration of air-UFB on mean diameter of gold nanoparticles. Mean diameter decreases with increasing number concentration of air-UFB.

Fig. 4 shows photographs of gold nanoparticle colloid for no UFB and air-UFB. Compared with freshly synthesized colloid, colloid for air-UFB after two days is stable dispersed. On the other hand, nanoparticles for no UFB after two days almost precipitate. These results indicate that UFB is effective for dispersion stability. Since the pH of sample is 3.5, charge of fine bubbles is positive. It is thought that gold nanoparticles are adsorbed on UFB and stabilize in solution.

Colloid color of gold nanoparticle for argon-UFB and nitrogen-UFB were purple and blue, respectively. **Fig. 5** shows electron micrographs of gold nanoparticles for argon- and nitrogen-UFB. Nanoparticles for argon-UFB are smaller than those for nitrogen-UFB.

Fig. 6 shows diameter distribution of gold nanoparticles for air-, argon-, and nitrogen-UFB. The mean diameter for argon- and nitrogen-UFB are 49 and 73 nm. Standard deviation for argon- and nitrogen-UFB are 14 and 21 nm. It is found that gold nanoparticles synthesized in the presence of air-UFB are smallest and have most narrow distribution. It is thought that reducers such as hydrogen peroxide and nitrous acid which are generated by ultrasonic cavitation in water in the presence of air are important to form fine and uniform gold nanoparticles.

As surfactant- and reducer-free methods, ultrasonic method is able to control gold nanoparticle size and improve stability by optimizing number concentration and gas kind of UFB.

References

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