

Analysis of growth mechanism of Au seed particles synthesized by sonochemical reduction of Au(III) in Ar dissolved aqueous solution

Ar 溶存水溶液中で超音波還元合成される
Au シード粒子の成長メカニズムの解析

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1. Introduction

Application of Au nanoparticles to various fields has been studied actively because of its unique characteristics different from those of bulk¹. However, the formation mechanism of Au nanoparticles of via reduction of Au(III) is still unclear.

In this study, Au nanoparticles were synthesized by sonochemical reduction method to clarify the generation mechanism. The reducing radicals formed in the sonolysis of solution containing Au(III), colloidal stabilizers, etc., result in the formation of Au seed particles via reduction of Au(III). In this method, reduction can be carried out under ambient temperature and pressure, therefor, the reaction can be controlled easily.

Generally, chemical reduction methods using citric acid have been applied under air atmosphere and high temperature condition. In contrast, in this experiment, by ultrasonic irradiation in Ar dissolved aqueous solution, some of Au (III) in the solution was reduced in a short time, and the growth behavior of the produced Au seed particles was observed. The influences of various parameters on the formation of Au seed particles and the growth mechanism were investigated.

2. Materials and Methods

Gold (III) chloride trihydrate (HAuCl₄·3H₂O) was used as a raw material of Au (III), and citric acid and sodium citrate were used as one of citrate ions.

An aqueous solution containing citrate ions and Au (III) was prepared to glass vessels, respectively, and both vessels were connected with a tube. Then, both solutions were done Ar bubbling for 30 min at a flow rate of 100 mL / min to be under Ar atmosphere. Thereafter, these solutions were mixed so as not to be exposed to air, and immediately ultrasonic irradiation of 200 kHz was carried out at 20 °C to prepare Au seed particles. At

this time, the concentration of citrate ion is 1.5 mM, Au (III) is 0.42 mM, and total amount of solution is 60mL. In this experimental condition, 100% of Au (III) in the solution is reduced by ultrasonic irradiation for 12 min. Therefore, a sample solution of Au seed particles was prepared for 4 min ultrasonic irradiation and then the growth behavior of particles with the standing time was investigated.

3. Analysis

In order to analyze the Au (III) reduction reaction and the growth behavior of the prepared Au seed particles, a sample solution was added to a quartz cell and the reaction occurring in the solution was analyzed using a UV-vis spectrophotometer. The average particle diameter and the number of Au nanoparticles were estimated by the following equations (1) and (2).²⁾

$$d = \exp\left(B_1 \frac{A_{\text{spr}}}{A_{450}} - B_2\right) \quad (1)$$

$$N = \frac{A_{450} \times 10^{14}}{d^2 \left[-0.295 + 1.36 \exp\left(-\left(\frac{d - 96.8}{78.2}\right)^2\right)\right]} \quad (2)$$

where D (nm) is the mean diameter of spherical Au nanoparticles, N is the number of particles, A_{spr} is the absorbance at the surface plasmon peak wavelength, A_{450} is the absorbance at the 450 nm wavelength, B_1 is 3.55, and B_2 is 3.11.

4. Results and discussion

First, samples were taken after irradiation for 4 min, and UV-vis absorption spectra were continuously measured as a function of standing time. Absorbance at surface plasmon peak wavelength peculiar to Au nanoparticles (A_{spr}) was small just after sample collection but increased gradually with standing time. Fig.1 shows the changes in the particle diameter and the number of particles.

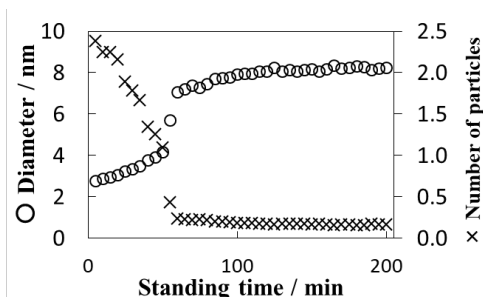


Figure 1 Changes in the diameter and the number of Au nanoparticles synthesized by 4min ultrasonic irradiation as a function of standing time.

This trend of increase in particle diameter suggested that Au seed particles were formed during ultrasonic irradiation and their particle growth occurred even after ultrasonic irradiation was stopped. However, the increase in particle diameter must be caused not only by surface catalysis from Au (III) to Au but also by aggregation because the number of particles tended to decrease with the growth. Also, absorption was observed on the longer wavelength region at the initial growth stage. This represents the formation of non-spherical aggregates³⁾, suggesting the possibility that Eqs. (1) and (2) cannot be applied here.

To analyze the above growth behavior in detail, pH of the solution was adjusted and the solution including Au seed particles was analyzed in the same procedure. It has been reported that aggregation behavior during synthesis of Au nanoparticles under other experimental condition is greatly affected by pH of the solution containing citric ions⁴⁾. Fig.2 shows the time course of A_{spr} when the citrate ion concentration is kept constant and pH of the solution is adjusted before ultrasonic irradiation.

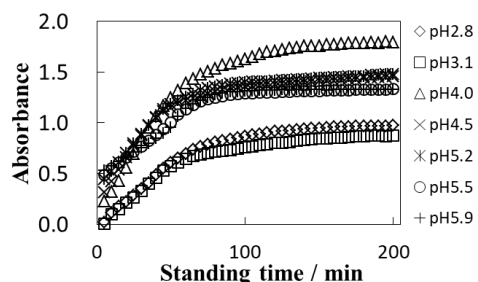


Figure 2 Changes in A_{spr} at different pH as a function of standing time.

As shown in Fig.2, when pH was 2.8 and 3.1, A_{spr} was extremely small and uniformly increased over standing time. The increase in A_{spr} over standing time might be due to the change in aggregation behavior by changing the surface charge of citric acid-coated Au seed particles. At the same time, however, the absorption at the longer

wavelength than peak wavelength also increased over standing time. This suggests that the particles do not exist as spheres. In order to discuss the aggregation behavior of Au nanoparticles in detail, Fig.3 shows the time course of absorbance at 800 nm (A_{800}) which is considered as an index of aggregates formation.

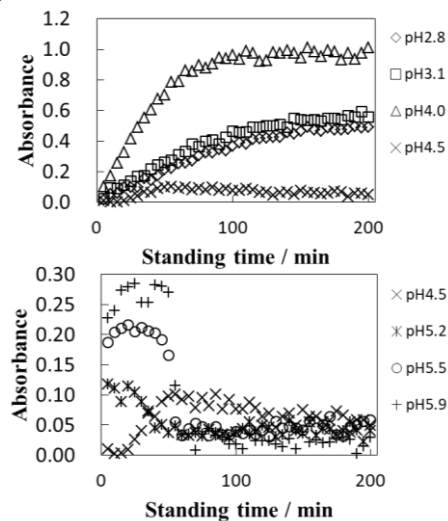


Figure 3 Changes in A_{800} at different pH as a function of standing time.

A_{800} increased with increasing pH and reached a maximum at pH 4.0 under our conditions. This may be due to the fact that pH at this point is close to the isoelectric point of the citric acid-coated Au nanoparticles and thus the stabilization function by citric acid has been lost. This is also supported by the fact that the particle diameters after growth under pH 5.2, 5.5, and 5.9 conditions were 15.4, 10.5, and 8.2 nm, respectively. Also, under the condition that pH was higher than 4.5, A_{800} decreased over standing time. This is due to the formation of string-like particles at the beginning and gradually becoming spherical³⁾. As shown in Fig.3, the time at which the decrease of A_{800} starts is accelerated as pH of the solution closes to 4.5. This tendency suggested that aggregation of string-like to spheres particles was affected by pH, during seed growth. To investigate this reason, the effect of pH on standing was studied in more detail.

4. References

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