Selective Synthesis of Gold Nanoparticles in Water/Alcohol Binary Solution Systems by Ultrasonic Irradiation

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We have synthesized stable gold nanoparticles (AuNPs) by a simple ultrasonic irradiation in water/alcohol binary solutions without additive stabilizer agents. Methanol, ethanol, and 1-propanol are used as solvents. The morphology and optical properties of the sonochemically synthesized AuNPs are characterized using SEM and UV-vis spectroscopy. The average particle diameter of as-prepared AuNPs was 36 ± 10 nm for water/methanol system (methanol: 25 vol%), 56 ± 17 nm for water/ethanol system (ethanol:35 vol%), and 24 ± 7 nm for water/1-propanol system (1-propanol: 35 vol%). The water/1-propanol system give the smallest average particle diameter together with the narrowest particle size distribution. This fact also support that the hydrophobicity of 1-propanol is higher, because the side chain of 1-propanol is longer than those in the other alcohols. Thus, it can be concluded that the dispersion of AuNPs is enhanced and their aggregation and growth are suppressed.

Keywords: Selective preparation; Gold nanoparticle; Absorption spectroscopy; Water/alcohol binary solution

I. INTRODUCTION

Gold nanoparticles (AuNPs) have been so far investigated because of their exceptional optical, electronic, catalytic and photonic properties [1-3]. The precise dimensions of these nanocrystals are very critical to their usefulness in various applications. For example, the shape and size-directed surface plasmon resonance (SPR) in the visible and near-infrared range renders them useful in sensing, imaging, and cancer therapy [4, 5]. Colloidal synthesis have proven extremely useful to prepare a wide variety of nanocrystals with tight control of size and shape [5]. Still, much of the knowledge in this area is empirical and no general rules can be provided for a rational design of nanomaterials.

Recently shape control synthesis of metallic nanocrystals has been the subject of intense research, with several methods reported for the preparation of AuNPs in particular. Some of the methods include surfactant-directed, templated electrochemical method, photochemical method and ultrasonic irradiation of gold salt [6-9]. Some researchers have so far reported that the ultrasonic irradiation method is simple and very useful for the preparation of AuNPs [10-13].

In this paper, we attempt to synthesize stable AuNPs by a simple ultrasonic irradiation in water/alcohol binary solutions without additive reductant and stabilizer agents and to characterize the morphology and optical properties of as-prepared AuNPs. Based on the results of concentration dependence of absorption spectra and SEM images, we investigate the formation of AuNPs in water/alcohol binary solutions.

II. EXPERIMENTAL

All materials such as hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), methanol, ethanol, and 1-propanol used in this work were analytical grade and commercial available from Wako Pure Chemical Industries, Ltd. The synthesis of AuNPs was performed in water/alcohol binary solution systems, with methanol, ethanol, or 1-propanol as the alcohol using ultrasonic irradiation. An aqueous HAuCl₄ solution, water, and each alcohol were mixed in a vial to afford a total volume of 5 mL. The concentration of HAuCl₄ was adjusted to be 1.0 mM, and the experiments were performed by varying the alcohol concentration. The mixed solutions were subjected to ultrasonic irradiation with a commercial ultrasonic wave apparatus (SND US-103, 38 kHz) at 25°C for 1 h. In order to conduct experiments under constant temperature condition at 25 ± 1°C, a circulating thermostat tank (Tokyo Rikakikai, Eyela NTT-1300) was used.

The morphology and optical properties of the sonochemically synthesized AuNPs were characterized using SEM and UV-vis spectroscopy. SEM images (Hitachi SU-70) were measured after dropping a colloidal solution of as-synthesized AuNPs onto a titanium plate and by drying naturally at room temperature. Immediately after the ultrasonic irradiation, absorption spectra of AuNPs in the water/alcohol mixed solutions were recorded on Shimadzu UV-1800 spectrophotometer.

III. RESULTS AND DISCUSSIONS

Figure 1 shows absorption spectra of AuNPs just after ultrasonic irradiation in water/alcohol solutions with varying alcohol concentration. In each system, the dependence of alcohol content (vol%) caused the change of absorption spectral features of AuNPs and also showed alcohol content dependence of absorbance at each absorption band (534 ~ 538 nm). These peaks in Fig. 1 are conventional plasmon band for spherical gold particles and for the nearly spherical-shaped particles. This result indicates that the alcohol content influences the generation of AuNPs in this work.

In order to investigate how the change of absorbance corresponding to AuNP formation is dependent on the alcohol concentration and also depend on the kind of al-
In this work, we summarized the results of alcohol content (vol%) dependence of gold nanoparticle formation from Fig. 1 and compared with each other. As shown in Fig. 2, the absorbance at the maximum absorption peak wavelength are plotted against water content (vol%) in each water/alcohol system. To compare the results obtained for each of the water/alcohol systems, the vol% of water content was considered as a reference. The change of absorbance of AuNPs produced depended on the water content (vol%), and then AuNPs were significantly formed in water content ranges of 64–84 vol% (water/methanol system), 57–75 vol% (water/ethanol system), and 50–77 vol% (water/1-propanol system), respectively. These interesting results show that AuNPs form in the relative narrow range of water content (vol%) in each system. In addition, the formation amount of AuNPs in water/ethanol system was larger than that in water/methanol and water/1-propanol systems, as shown in Fig. 2.

To clarify why AuNPs form in the range of narrow water content (vol%) and what factors influence this interesting behavior for the formation of AuNPs. In the preparation of AuNPs, the reduction of Au$^{3+}$ to Au$^0$ is also one of the key steps. As a factor which contribute to the present results, we conduct experiments under ultrasonic irradiation in this work. Under this condition, some radicals in the cavitation are known to be produced from the solvent in high-temperature and high-pressure reaction sites [14–16]. In case of the present systems, water molecules or alcohol molecules undergo homolytic cleavage and form -OH and H· radicals. It can be considered that the alcohol (water) content range observed in water/alcohol systems is preferable environment for the formation of these radicals and contribute to the formation of AuNPs. Furthermore, under ultrasonic irradiation, the alcohol concentrations are known to influence the growth of bubbles [17–19]. Accordingly, since the formation of reaction sites depends on the alcohol concentration, the formation of gold nanoparticles under ultrasonic irradiation may also be dependent on the alcohol concentration.

Figure 3 shows SEM images and the particle size distributions obtained from SEM images. The particle size was dependent on the alcohol content (vol%) in water/alcohol binary systems. The average particle diam-

![FIG. 1](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))
FIG. 3. SEM images and particle size distributions of AuNPs in water/alcohol systems: (a) water 75 vol%/methanol 25 vol%, (b) water 65 vol%/ethanol 35 vol%, and (c) water 65 vol%/1-propanol 35 vol%.

| water content/vol% | particle size/nm |
|--------------------|------------------|
| Methanol 64-84     | 36 ± 10          |
| Ethanol 57-75      | 56 ± 17          |
| 1-Propanol 50-77   | 24 ± 7           |

TABLE I. Summary of the results of water content (vol%) forming AuNPs in water/alcohol systems and of average particle size of AuNPs produced.

meter was 36 ± 10 nm for the water/methanol system (water 75 vol%, methanol 25 vol%), 56 ± 17 nm for the water/ethanol system (water 65 vol%, ethanol 35 vol%), and 24 ± 7 nm in the water/1-propanol system (water 65 vol%, 1-propanol 35 vol%) and the results are summarized in Table 1. A comparison of these data clearly indicates that the 1-propanol system gave the smallest average particle diameter together with the narrowest particle size distribution. To synthesize homogeneous microparticles, a large number of nuclei are considered to be generated simultaneously. In case of the present water/alcohol systems, it can be expected that nuclei are readily formed in water/1-propanol system to obtain smaller uniform particles compared with other water/alcohol systems. AuNPs synthesized in the present systems were found to remain stable in suspension without precipitation for two weeks after the synthesis. This fact also support that the hydrophobicity of 1-propanol is higher, because the side chain of 1-propanol is longer than those in the other alcohols. Thus, it can be concluded that the dispersion of AuNPs is enhanced and their aggregation and growth are suppressed.

Finally, in order to investigate the formation kinetics of AuNPs in this system, we carried out preliminary experiments on the time dependence of the change in absorbance of AuNPs for water/1-propanol (water 65 vol%, 1-propanol 35 vol%) system. The aim of this experiment is to determine rate constant for the formation of AuNPs and to study the effect of HAuCl$_4$ on the rate constant of AuNP formation in this system. The absorbance versus time plot for [HAuCl$_4$] = 0.1, 0.25, and 1.0 mM showed that this AuNP formation follows a pseudo first-order reaction kinetics (data not shown). The observed rate constant ($k$) was 0.19, 0.05, and 0.04 h$^{-1}$ for [HAuCl$_4$] = 0.1, 0.25, and 1.0 mM, respectively. With decreasing concentration of HAuCl$_4$, the formation rate constant of AuNPs increased and rate constant at [HAuCl$_4$] = 0.1 mM be-
came to be higher. Thus, this fact indicates that there is the optimum value of [HAuCl$_4$] for the formation of AuNPs and very stable AuNPs can be quickly formed in water/1-propanol system.

IV. CONCLUSION

AuNPs have been synthesized by ultrasonic irradiation of an aqueous solution of HAuCl$_4$ in water/alcohol binary mixed systems. The amount of AuNPs produced was found to be dependent on the alcohol content in water/alcohol binary mixed systems. Detail theoretical studies on the formation mechanisms of AuNPs in the present systems are now in progress.

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