Transactions of the Materials Research Society of Japan 27 [1] 101-104 (2002)

Sonochemical Preparation of Gold Nanoparticles in Clay Solution

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Sonochemical preparation of gold nanoparticles has been studied in aqueous surfactant solutions such as sodium dodecylsulfate (SDS) or dodecytrimethylammonium bromide (CTAB) surfactants with or without hectorite type synthesized clay particles (Laponite XLG). Ethanol was also tested for the additive under the ultrasonic field. The experiment was carried out at 298 K and pH = 10.5. When a ultrasonic probe operated at 20 kHz was used, the reduction rate was accelerated in the presence of surfactant or ethanol. However, when clay particles was added in the solution, the chloroauric ion could not be reduced in the CTAB solution due to the adsorption to the clay particles. For the SDS solution, gold nanoparticles were dispersed much stabler as the addition of Laponite XLG clay. When the ultrasonic cleaning bath was also used to irradiate ultrasound of 28 and 200 kHz, gold nanoparticles were prepared in ethanol solution both with and without clay particles. The SDS solution with clay particles did not affect the preparation gold nanoparticles under the ultrasonic field of neither 28 nor 200 kHz operated by the cleaning bath.
Key words: Sonochemical preparation, gold nanoparticles, synthesized clay, ethanol, surfactant

1. INTRODUCTION

Nanoparticles have already been utilized as functional materials such as electric, magnetic, and optical materials, and have been put to use in catalysis, cosmetics, ceramics, medicines, paint colorants, microscopic probe, and so on. The characteristics of the nanoparticles, such as their size, size distribution, structure, orientation, and morphology, must be controlled if the particles are to be used in these applications. An unique attribute of nanoparticles is their extremely high particle surface area that has many active sites for applications. The high particle surface area also leads to the easy aggregation of particles.

To obtain dispersed nanoparticles, aggregation must be prevented, and many approaches to preventing aggregation have been proposed such as the preparation in sol-gel materials, polymer solutions[1, 2], clay suspensions[3, 4], and glass[5]. We found that gold nanoparticles were well dispersed for several months even if particles were above 50 nm diameter, when the preparation was performed in the clay solution[3]. However, the disadvantage of this method was the difficulty to produce small sized particles.

Sonochemistry is the use of ultrasound to enhance or alter chemical reactions, and applies to the preparation of colloid particles[6-8]. Gold nanoparticles were also prepared under the ultrasound, and their size was about 10 nm[9-12]. However, gold nanoparticles sometime aggregated and precipitated even if such a small size. To prevent from those coagulation, we tested the effects of the addition of clay particles on the preparation of gold nanoparticles under the sonication. The influences of pH value in the solution and the sound frequency were also discussed.

2. EXPERIMENTAL

A ultrasonic probe system of 20 kHz frequency (US-150T, Nihon Seiki Seisakusho) was used for the preparation of gold nanoparticles in a glass beaker of 100 mL. The experiment was carried out in air at 298 K and pH = 10.5.

An ultrasonic cleaning bath (VS-100 III, Iuchi Seieidou) was used for the frequency of 28 kHz. A multiwave ultrasonic generator (TA-4021, Kaijo) and a submersible transducer (4611, Kaijo) were also used to generate 200 kHz ultrasonic frequency. The reactions were carried out in a cylindrical stainless steel cell of 100 mL which was dipped in a water bath controlled at 298 K. The bottom of the cell was suitably arranged at a constant position relative to a nodal plane of the sound wave, due to the effective transmission of ultrasonic energy. Some experiments were performed with a cylindrical Pyrex sample cell having a thin flat bottom plate, and no distinct difference was observed from the results used the stainless steel cell.

The synthetic clay used for the experiments is Laponite XLG for cosmetic or medical use (Laporte Industry Ltd., UK), which has the same properties as Laponite RD (Laporte Industry Ltd., UK). Laponite XLG or Laponite RD particles were reported to be discrete plate-like crystals. The edge of this clay is charged positive and the face has negative charges at higher pH value than 8, *i.e.* zwitterions-type particle.

The water used in the all experiments was supplied by a mili-Q system (Nihon Milipore Ltd.) and passed twice through a 0.1 μm filter (ADVANTEC MFS). Laponite and the water treated above were slowly mixed in 0.5 wt% mass fraction and dispersed for 5 min at room temperature in an ultrasonic cleaner bath (Branson Cleaning Co.). After the dispersion, centrifugation at

5000 r.p.m. for one hour was used to remove any large dust in the suspension. Tetrachloroauric acid, ethanol, sodium dodecylsulfate (SDS), dodecytrimethyl ammonium bromide (CTAB), and other chemicals were analytical grade reagents purchased from Wako Chemicals, and were used without further purification. The concentration of tetrachloroauric acid was 0.1 mM in all experiments.

Absorbance spectra of a solution during the reaction were measured by a Shimadzu UV-1600 or Shimadzu MultiSpec-1500 with quartz fiber detection system. The average size and size distribution of gold nanoparticles produced in a solution were observed by TEM (H-8100, Hitachi).

3. RESULTS AND DISCUSION

3.1 Ultrasonic Probe System

The color of the solution containing tetrachloroauric acid ion turned into reddish at first and then into wine red. Figure 1 shows the example of absorption spectra obtained from tetrachloroauric acid ion solution irradiated by the ultrasonic probe with 20 kHz for 90 minutes in the presence of 4 mM SDS. The absorbance around 520 - 540 nm wavelength increased with the sonication due to the formation of gold nanoparticles. The wavelength at the maximum absorption in this range moved slightly during the sonication. At the latter stage of the sonication, the wavelength of the maximum absorbance, λ_{max}, approached a constant value, which depended on the size of the gold nanoparticles. As the time courses of the absorbance at λ_{max} and the gold ion concentration during the reaction were similar as reported in previous paper [13], the formation rate of gold nanoparticles could be estimated using the time courses of the absorbance at λ_{max}.

Figure 2 shows the time courses of the absorbance at λ_{max}, which represents the formation rate of gold nanoparticles during the sonication in the presence of surfactant or ethanol with or without clay particles. The concentration of ethanol was 10 mM. Although surfactant was somewhat adsorbed to clay particles, the initial concentration of surfactant was the critical micelle concentration of each surfactant, i.e. 8 mM for SDS and 0.9 mM for CTAB. The absorbance increased continuously in all cases, and the formation rates were hardly affected by the presence of 0.5 wt.% clay particles. The formation rate in the presence of ethanol was larger than that in the surfactant solution. Nagata and Maeda [11] found that the formation rate of gold sol in SDS solution was faster than that in ethanol solution. with 200 kHz ultrasound in argon atmosphere. Barbour *et al.*[12] also compared both additives using pulsed sound field of 514 kHz, and their results were different from ours. This difference may be attributed to the experimental conditions, especially the irradiation atmosphere and pH value of the solution. We will discuss this topics in detail at latter section.

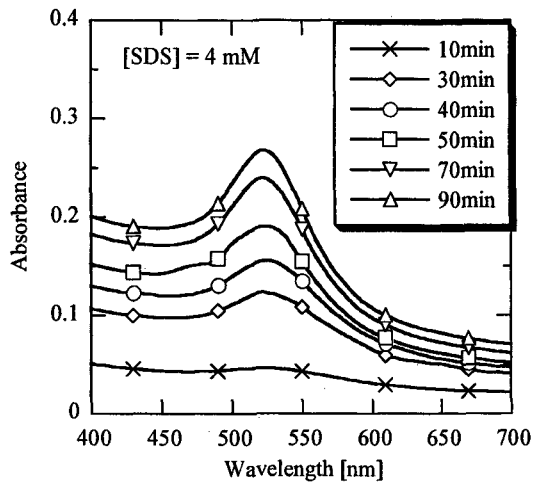

Fig. 1 Absorbance spectra obtained from $HAuCl_4$ solution irradiated by the ultrasonic probe system of 20 kHz for 90 min in the presence of 4 mM SDS.

The histograms of particle size of gold nanoparticles prepared in SDS or CTAB surfactant solution were measured from TEM images, and shown in Fig. 3. Gold nanoparticles of 13 nm average diameter were formed in SDS solution for 40 minutes sonication period, and dispersed well for few days. When CTAB solution was used, gold nanoparticles had an average diameter of 24 nm, and wide size distribution. They aggregated for one day. On the other hand, as clay particles were added in SDS surfactant solution, the average size of gold nanoparticles grew up to 36 nm. In general, if the suspension had such large size particles, particles agglomerate very quickly. However, the suspension containing clay particles kept well in the dispersion state. This reason may be explained that the electrostatic interaction between clay particles and gold nanoparticles, and the gelation of the clay suspension, as mentioned in the previous paper [3].

3.2 Cleaning Bath Type

When a cleaning bath of 28 kHz was used for the preparation of gold nanoparticles, absorption spectra after 90 minutes sonication period were shown in Fig. 4. The spectrum used ethanol as an additive showed high absorbance comparing with that used SDS, that means the formation rate of gold nanoparticles in the presence

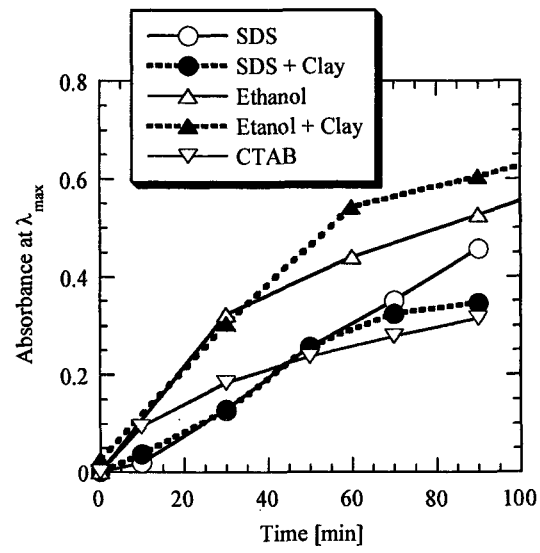

Fig. 2 Time courses of the absorbance of solution at λ_{max} during sonication used the ultrasonic probe system of 20 kHz.

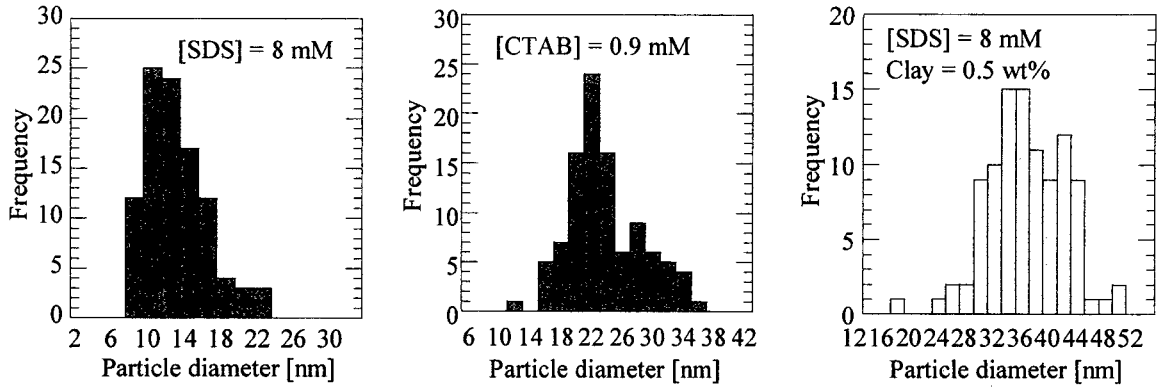

Fig. 3 Histograms of particle size of gold nanoparticles in different surfactant solutions with or without clay particles. $[HAuCl_4]$ = 0.1 mM, sonication time = 40 min, ultrasonic probe system of 20 kHz

of ethanol was faster than that in the presence of SDS. This tendency was same as the results used the ultrasonic probe system.

However, the particle formation was not observed for 90 minutes sonication when SDS solution containing clay particles was used as an additive. On the other hand, the formation rate used ethanol solution with clay particles was almost same as that without clay particles. The absorption spectrum in the presence of ethanol with clay particles indicated that particle size was small, and size distribution was sharp comparing with the results of the additive of ethanol without clay particles, as shown as Fig. 4.

3.3 Effects of Frequency of Ultrasound

In order to discuss the effect of frequency of ultrasound on the formation of gold nanoparticles, a multiwave ultrasonic generator of 200 kHz with a submersible transducer was used. Figure 5 shows the absorbance spectra for 30, 60 and 90 minutes sonication periods. The pH value of the solution was 8.0. The influence of the additives on the absorbance due to the formation of gold nanoparticles at 200 kHz ultrasonic field was also same tendency as the conditions mentioned above. That is, the formation rate used ethanol was faster than that used SDS solution. But the absorbance used SDS as additive was in the same order of that used ethanol at this time.

The shoulder in the absorbance spectrum appeared in for 60 minutes sonication period when used ethanol as an additive, and it was clearly observed for 90 minutes sonication period. This means the existence of the particle agglomeration in the solution. The idea was also supported from the fact that the maximum absorbance due to gold nanoparticles at 90 minutes sonication was smaller than that at 60 minutes sonication. However, the maximum absorbance for the additive of ethanol with clay particles grew up during the sonication, and no shoulder in the absorbance spectrum appeared. It may be concluded that ethanol solution containing clay particles is one of the suitable additives to prepare stable gold nanoparticle suspension, due to the electrostatic interaction among clay particles and gold nanoparticles [3].

On the other hands, the evidence of the particle

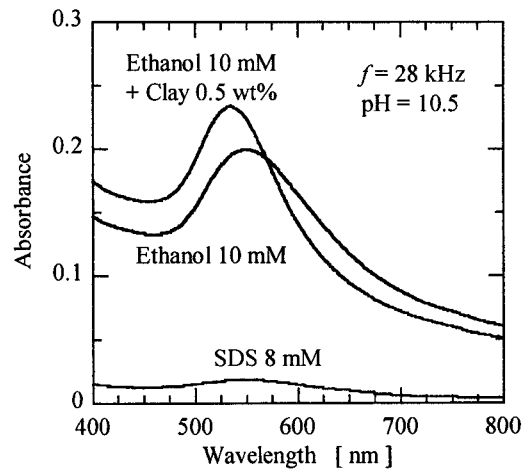

Fig. 4 Absorbance spectra obtained from $HAuCl_4$ solution irradiated by the ultrasonic bath of 28 kHz for 90 min.

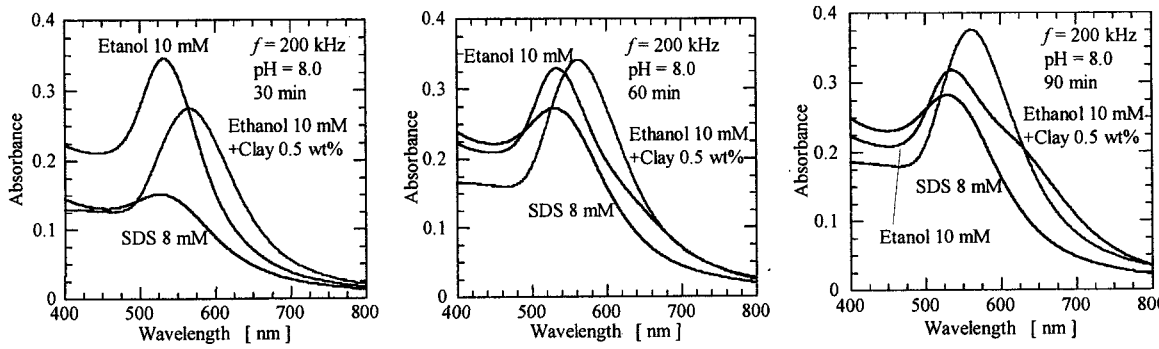

Fig. 5 The absorbance spectra obtained from the solutions by the ultrasonic generator of 200 kHz with a submersible transducer for 30, 60 and 90 minutes sonication periods. pH = 8.0

formation was not observed in the condition of Fig. 5, when SDS solution containing clay particles was used as additive.

3.4 Effects of pH

The experiments were performed at various pH values using ethanol or SDS as additive. Figure 6 shows the time courses of the absorbance at λ_{max} during the sonication, which represents the formation rate of gold nanoparticles[13]. In the case of ethanol, the particle formation rate was almost constant for the pH values. But the formation rate for SDS clearly depends on pH values.

The pH values of the solutions of tetrachloroauric acid or its sodium salt were usually 3 - 4 or 5 - 6, respectively. Nagata and Maeda [11] used tetrachloroauric acid sodium salt, and Barbour *et al.*[12] prepared a solution at pH 3.2. Their results did not consist completely with

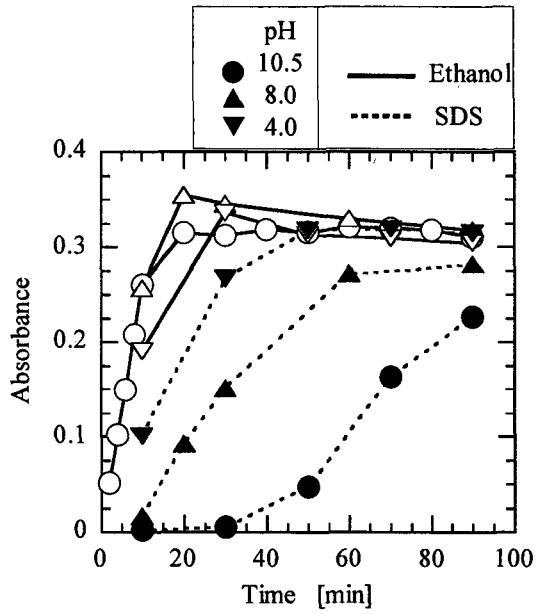

Fig. 6 The time courses of the absorbance at λ_{max} of ethanol or SDS solution at various pH values during the sonication.

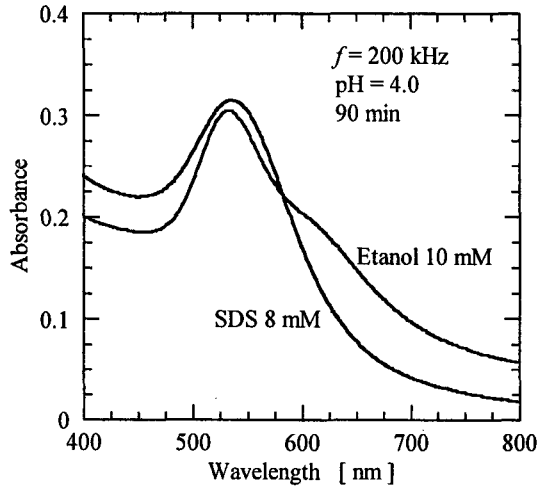

Fig. 7 The absorbance spectra obtained from ethanol or SDS solution for 90 minutes sonication period. pH = 4.0

our results at pH 4.0, but it might be satisfied considering with the difference of the irradiation atmosphere.

4. CONCLUSION

Gold nanoparticles were prepared under the ultrasound field with ethanol or surfactant as additives. The effect of the addition of clay particles on the formation of gold nanoparticles was investigated in order to prevent aggregation. The following conclusions were obtained.

The formation rate of gold nanoparticles was almost constant for the pH values when ethanol was used as an additive. On the other hands, the formation rate increased as pH value decreased, when SDS was used as an additive.

The gold nanoparticles prepared from ethanol solution aggregated easily, but the addition of clay particle in ethanol solution can prevent aggregation, due to the electrostatic interaction among clay particles and gold nanoparticles.

The tendency of the phenomena on the particle formation was not affected on the sonication system and the sound frequency.

5. ACKNOWLEDGMENT

The authors gratefully acknowledge support for this research by a grant to RCAST at Doshisha University from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This work was also partly supported by a Grant-in-Aid for Scientific Research (C) (No. 13650819) of the Japan Society for Promotion of Science.

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(Received December 21, 2001; Accepted January 30, 2002)