Silver nanoparticle formation by femtosecond laser induced reduction of ammonia-containing AgNO₃ solution

Y Herbani¹, T Nakamura² and S Sato²

¹ Research Center for Physics, Indonesian Institute of Sciences, Bldg 442 Kawasan Puspiptek Serpong, Banten, INDONESIA.
² Institute of Multidisciplinary Research in Advanced Materials (IMRAM), Tohoku University, Katahira Campus, Katahira 1-1-1, Sendai, JAPAN.

E-mail: yuliati.herbani@lipi.go.id

Abstract. This paper reports the synthesis of silver colloids by femtosecond laser ablation of ammonia-containing AgNO₃ solution. Effect of ammonia concentration in solution on the production of Ag nanoparticles was discussed. It is found that ammonia rules out significantly to the formation of Ag nanoparticles at which no Ag nanoparticle were formed in the solution without ammonia. Using the solution with the optimum ratio of ammonia to Ag⁺ ions, we further investigate the growth process of Ag nanoparticle by monitoring the evolution of its absorption spectra at 402 nm as a function of irradiation time. The result showed that the growth process was fit to the simple exponential function, and confirmed that the addition of ammonia alone to the metal ion system can boost the particle production by femtosecond laser.

1. Introduction

These days the uses of metallic nanoparticles (NPs) in various regions of science and technology are expanding. Many efforts have been devoted to synthesize these materials and to study their optical properties, which strongly depend on the size and shape of the NPs [1]. The surface plasmon resonance (SPR) which consists in a resonance coupling between the electromagnetic field frequency and the free electrons oscillation frequency on the metal NPs is one of the important aspects of the study, at which a strong absorption of the electromagnetic field energy by metallic NPs happened when resonance conditions are matched. On account of these properties, Ag NPs have been generally utilized as antimicrobial agents [2-4], as biolabelling [5], as well as in the application of optical [6] and catalysis science [7]. Different biological [8, 9], chemical [10, 11] and physical [12-14] techniques have been utilized to get Ag NPs, among them is the pulse laser induced photoreduction [15] which is not fully explored.

Here, by using a femtosecond laser induced reduction of metal salts, Ag NPs were synthesized. Differs from pulse laser ablation of metal target in liquid (PLAL) [2, 14], here metal nanoparticles were obtained by photoreduction of metal salts during irradiation by femtosecond laser which is apparently a bottom up process. Photoreduction of metal salts was promoted in the abundantly presence of the hydrated electrons which were produced by Coulomb explosion of the solution due to interaction of intense femtosecond laser pulses with neat solvent [16]. Using this method, several noble metal nanoparticles [17-20] and their alloys [21-22] have been produced in our lab with good stability for months. In the previous report [18], Ag NPs was successfully fabricated at high concentration of Ag⁺ ions. The limit concentration of Ag⁺ ions was about 0.3 M; none of Ag
nanoparticles were observed below this concentration. This fact has the important disadvantage in the production of its alloy with Au, for example, since it will lead to the formation of stable AgCl precipitates even before femtosecond laser irradiation was started. Therefore, we tried to use ammonia (NH$_4$OH) to modify the chemistry of Ag ions so that the reduction becomes easy. It was reported by D. Goia [23] that redox potential of the Ag ion changes as a result of complex formation. Ag and ammonia, for example, are easy to make a stable complex ion, Ag(NH$_3$)$_2^{2+}$, resulting from strong affinity of ammonia to Ag ions and its reduction potential is much higher than that of free ions, $E_0([\text{Ag(NH}_3]^{2+}, \text{Ag}^+ \text{NHE}]) = +0.38$ V. Therefore, the ammonia concentration and the nature of the reductant play a major role in the formation of Ag nanoparticles in aqueous solution. In this paper, the result of femtosecond laser irradiation of Ag nitrate solution in the presence of NH$_4$OH was reported.

2. Methods
Colloidal dispersion of Ag nanoparticles was synthesized by direct irradiation of silver salts using highly intense femtosecond laser pulses at room temperature in the presence of ammonia. All chemicals were used without further purification. Firstly, the solutions of silver ions with the concentration of $2.54 \times 10^{-4}$ M were prepared by dissolving AgNO$_3$ (Sigma-Aldrich, +99.998%) in extra-pure water containing 0.01wt% of polyvinylpyrrolidone (PVP) as a dispersant. The fresh aqueous liquid ammonia (NH$_4$OH, 25wt%, Sigma-Aldrich, 99.8%) in a variation volume of 1, 3 and 5 $\mu$l was added to the Ag$^+$-PVP solution. In laser irradiation experiment, the ammonia containing solution was introduced into a quartz glass cuvette and irradiated for 30 minutes by the highly intense femtosecond laser pulses (Spitfire, Spectra-Physics Co.) at the fundamental wavelength of 800 nm with the typical pulse width, repetition rate and maximum pulse energy per pulse were 100 fs, 100 Hz and 6 mJ, respectively. The laser beam was directed perpendicularly to the surface of the cuvette into the solutions after tightly focused using an aspheric lens with a focusing length of 8 mm (NA = 0.5). Taking no account for the aberration and considering the diameter of the laser beam before focusing was approximately 3.2 mm, the theoretical laser intensity is about $3.2 \times 10^{18}$ W/cm$^2$ at the focal spot considering. This intensity is expected to exceed the optical breakdown threshold of any solvent.

After irradiation, samples were characterized by a UV-visible spectrometer (V630iRM, JASCO Co, Tokyo, Japan) to observe an absorption spectrum in 200 – 700 nm range and then confirm the nanoparticles formation by observing a surface plasmon resonance (SPR) of Ag nanoparticles around 400 nm. TEM experiments were performed using a JEOL2000-EXII (200kV, JEOL Ltd., Tokyo) to obtain the electron micrographs for all samples. Several drops of sample were placed on a carbon coated microgrid and left to dry in room temperature for this TEM observations. The bright field image of each sample was then processed using image analysis software Image J to measure the size of each nanoparticle. At least 500 particles were counted for each sample, taken from three separate areas on the microgrid.

3. Results and Discussion
Figure 1 shows the spectra of colloidal Ag nanoparticle prepared by femtosecond laser irradiation of $2.54 \times 10^{-4}$ M AgNO$_3$ solution with different concentrations of ammonia for 30 minutes. The irradiation of 3-ml AgNO$_3$ containing 1 $\mu$l of 25 wt% ammonia results in the generation of a sharp-symmetric SPR peak at 402 nm which is originated from Ag nanoparticles. It is also confirmed by yellow color of the solution after irradiation. It can also be seen that the increase of ammonia content in solution increases the absorbance before it turns to decrease slightly after the ammonia content reach to 5 $\mu$l. This is in contrast with the result that the solution without ammonia which is still transparent after irradiation by femtosecond laser (figure 1 (b)), confirming that no particles were generated in the solution.
The corresponding TEM images of Ag colloids samples presented in figure 1 were shown in figure 2. No particle was found for the sample without ammonia. Using ammonia with the dosage of 1 μl per 3 ml AgNO₃ solution, Ag flakes with 100 nm width were generated. If the dosage increases to 3 μl, Ag nanoparticle were observed and the average diameter was found to be 10.3 ± 8.5 nm with a broad size distribution. With 5 μl ammonia, large aggregates were also found besides small particles with size of 10 nm. This result indicated that the ammonia enhanced the formation rate of Ag nanoparticles, and hence the aggregates were generated due to the absence of dispersant. At this point, it was considered

![Absorbance vs Wavelength](image)

**Figure 1.** (a) UV-visible absorption spectra of the irradiated Ag ion solution with various concentrations of ammonia, and (b) the corresponding photographs of the solutions.

![TEM images](image)

**Figure 2.** TEM images of the irradiated Ag ion solution for 30 minutes with various content of 25 wt% NH₄OH: (a) 0, (b) 1, (c) 3 and (d) 5 μl in every 3 ml of Ag ions.
that the dosage of 3 µl per 3 ml of AgNO₃ was optimum to produce Ag nanoparticles with reliable concentration.

For the monitoring of Ag nanoparticle formation, we followed the evolution of the absorption spectra at 402 nm during laser irradiation. The spectra were collected every 5 minutes for a typical experiment conducted at a solution with 3 µl ammonia. Figure 3(a) shows the UV-vis spectra of the solution every 5 minutes for a total of 30 minutes irradiation. As shown in the figure, the absorbance of Ag nanoparticles started from zero and increased rapidly at the beginning of the reaction without any significant induction time. The black arrow indicates the growth of the SPR at 402 nm, corresponding to the conversion of Ag ions to Ag nanoparticles. If the plasmon feature over the spectral range of 400 – 450 nm is magnified, the maximum plasmon absorbance blue shifts as the reaction upon the continued irradiation and then the absorbance remained stayed at the same absorbance level near the commencement of irradiation. The latter behaviour may be attributed to the inhibited Ag nanoparticle production due to the absorption of laser energy by the produced nanoparticles along the path to the focusing point or to Ag nanoparticle fragmentation by the laser. The maximum plasmon absorbance (peak position) as a function irradiation time is not cubic spline function like the formation of Au nanoparticles [24], but rather fit to the negative exponential function, indicating the formation of Ag nanoparticles goes quickly to completion in the presence of ammonia (figure 3(b)). Within 1 minute, a broad absorption band at 419 nm appeared and it smoothly blue-

Figure 3. (a) UV–visible absorption spectra of Ag nanoparticles at different reaction time during the irradiation with femtosecond laser. (b) The corresponding time evolution of the absorbance recorded at λ = 402 nm and peak position. [AgNO₃] = 2.54 × 10⁻⁵ M, [PVP] = 0.01 wt% and [NH₄OH] = 25 wt%, dosage = 3 µl per 3 ml ion solution.

Figure 4. Comparison of TEM image of peak absorbance evolution of Au and Ag nanoparticles during the formation by femtosecond laser for 30 minute irradiation.
shifted to a constant value of 402 nm with the irradiation time. It suggested that the particles size became smaller as the time increases, as confirmed in figure 4. The absorbance reached maximum approximately after 20 minutes of the irradiation. No significant change in this final value was observed afterward. In addition, the absorbance in the range of 250 – 280 nm increased with the irradiation time (blue arrow in figure 3(a)). The same absorption band has been observed for the reduction of Ag$^+$ ions in the solution with 2-propanol in alkaline environment [25] as well as during the radiation induced synthesis using synchrotron X-ray [26] and pulsed $\gamma$-ray [27]. The cluster Ag$^{2+}_4$ has been identified as the species corresponding to the absorption at 250 – 280 nm [28]. Accordingly, it was assumed in this study that the absorption in the 250 – 280 nm range is due to Ag$^{2+}_4$ clusters.

The evolution of absorption spectra of the Ag$^+/NH_4OH$ without PVP during laser irradiation was also monitored (figure 5). In comparison to the one with PVP, the changes in absorbance with irradiation time for the system were investigated to study the global kinetics behaviour of Ag nanoparticle formation by femtosecond laser irradiation in the absence of additives. A key fact was that the reaction proceeds faster in the absence of PVP. This result confirmed that ammonia alone can boost the formation of Ag nanoparticles without need any dispersant. To test the result, we also conducted the same laser irradiation experiment for ammonia containing [AuCl$_3$] ion solution. Its evolution curves of absorbance shown in figure 4 evinced that Au and Ag have very different reduction and clustering rates under the same reaction condition (blue open triangle for Ag/NH$_4$OH/PVP and filled green circle for Au/PVP/NH$_4$OH). Even in the presence of PVP or any other additives, the kinetic process that governs the Au nanoparticles formation followed the sigmoidal kinetics, different from the kinetics for Ag nanoparticles which was simply exponential trend. It was also clear that ammonia promoted the formation of both nanoparticles, resulting in fast growth of nanoparticles. The nanoparticles might eventually be aggregated when there is no dispersant used in the system. Nevertheless, the reaction speed is a key factor for multimetallic nanoparticle synthesis, by which alloying process will be assisted, especially for Au and Ag with large difference in reduction potential.

4. Conclusions
We have, for the first time, demonstrated that ammonia addition to the Ag$^+$ ion solution may boost the production of Ag nanoparticle by femtosecond laser irradiation in the concentration below 0.3 M, at which the mixture of metal ions can be feasibly prepared without introduced any precipitates. The optimum volume is about 3 µl per 3ml of Ag$^+$ in water. In the presence of ammonia, the growth
monitoring of Ag nanoparticle production showed that the process rapidly occurred to fit the exponential function without any significant elapsed time once the irradiation started, even for the system without dispersant. The relative importance of this result is expected to enable greater control over the properties of uncapped Ag nanoparticles using femtosecond laser induced photoreduction, making it possible to use the properties for a variety of application.

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