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# Preparation and characterization of gelatin mediated silver nanoparticles by laser ablation

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ABSTRACT

We successfully prepared colloidal silver nanoparticles (Ag-NPs) using a nanosecond pulsed Nd:YAG laser, $\lambda = 532$ nm, with laser fluence of approximately about 0.6 J/pulse, in an aqueous gelatin solution. The size and optical absorption properties of samples were studied as a function of the laser repetition rates. The results from the UV–vis spectroscopy demonstrated that the mean diameter of Ag-NPs increase with the laser repetition rate increases. The Ag-NPs have mean diameters ranging from approximately 9 nm to 15 nm. Compared with other preparation methods, this work is clean, rapid, and simple to use.


## 1. Introduction

Metallic nanoparticle research is an attractive field in scientific studies due to the wide and varied ranges of potential and available applications, from biological to industrial areas. Recently, researchers have published various preparation methods of metal nanoparticles, including chemical and physical methods [1–3]. Among the physical methods, the photo-irradiation synthesis method offers many advantages, such as space-selective fabrication. The pulsed laser ablation (PLA) method has also attracted attention due to its enormous potential in laser-based materials processing, such as nanocrystals, growth, solid thin film, surface cleaning, and microelectronic device fabrication. In addition, the PLA technique offers advantages in preparation methodology: (I) "*simple and clean*" synthesis, (II) ambient conditions without extreme temperature and any special physical conditions such as pressure, and (III) formation of nanoparticles that may occur in both liquid and solid forms [4]. The optical absorption spectra of metal nanoparticles are evident as shown by surface plasmon resonance (SPR) [5], and the blue-shift to shorter wavelengths with decreasing particle size. For metal nanoparticles the SPR, which occurs in the visible wavelengths, is sensitive to size, shape, and the surrounding media [6]. Silver nanoparticles (Ag-NPs) are well known to have a SPR at approximately 400 nm, with the wavelength dependent on the size and shape of Ag-NPs [7]. However, the size effect using the PLA method in preparing metal nanoparticles has not been thoroughly investigated, although some approaches have considered the effect of PLA parameters and conditions on the size of metal nanoparticles [8,9].

Many studies have recently demonstrated that various organic stabilizers, such as poly ethylene glycol (PEG) [10,11], polyvinylpyrrolidone (PVP) [9,12], and poly (vinyl alcohol) [13], can be used to prepare nanoscale metal particles. Yet, gelatin offers more eco-friendly, available, and cheaper alternative compared to previously tested stabilizers. To date, no approach has been carried out on the preparation of Ag-NPs using gelatin as a stabilizer [14,15] in the PLA method. In this paper, we used the PLA method to focus on the preparation of Ag-NPs from silver plate in water using gelatin as a stabilizer. The effect of the laser-pulsed repetition rate on size of Ag-NPs was studied.

## 2. Material and methods

Silver plate (Sigma–Aldrich, 99.99%, USA) was used as a silver source and gelatin (Sigma–Aldrich, type A, USA) was used as a stabilizer for the fabrication of Ag-NPs. The silver plate was set in glass cell containing 20 mL of a fresh aqueous gelatin (1% wt.) solution, and the laser light was focused on the surface of the silver plate using a quartz lens ($f = 25$ cm). Laser ablation was carried out using a focused 532 nm laser light of a nanosecond Q-switched pulsed Nd:YAG laser (SL400/SL800 system) at 0.6 J/pulse for 15 min on different vessels for different repetition rates (e.g., 10, 20, 30, and 40 Hz).

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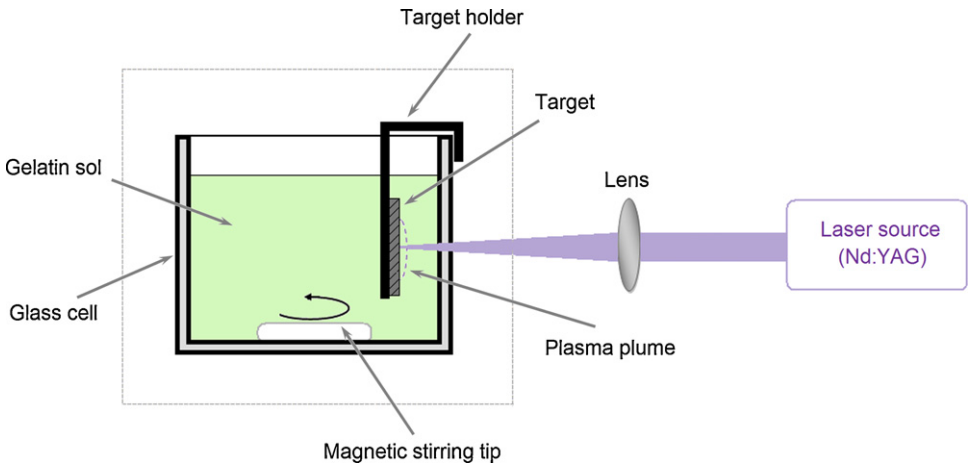


**Fig. 1.** The experimental set-up for preparation of Ag-NPs using the PLA method.

All solutions were freshly prepared using double distilled water. The solutions were continuously stirred with a magnetic stirrer throughout the PLA process. The silver plate was cleaned in an ultrasonic bath containing ethanol and acetone, and washed with double distilled water twice before being used. Fig. 1 shows a graphical plan of the experimental set-up proposed in this study. To show the role of the stabilizer, the container cell was filled using the double distilled water and the silver plate was ablated under the same experimental conditions as before for gelatin at a 10 Hz repetition rate.

Ag-NPs colloids prepared under different repetition rates were characterized by ultraviolet-visible (UV–vis) spectroscopy and transmission electron microscopy (TEM). The particles were tested for their optical absorption property using a UV-1650 PC-Shimadzu UV–vis spectrophotometer over the range of 300–700 nm, to ensure the formation of nanoparticles. TEM observations were performed with a Hitachi H-7100 electron microscopy and the particle size distributions were determined using the UTHSCSA Image Tool software, Version 3.00 program.

## 3. Results and discussions

During the laser ablation of the silver target, the color of the solutions changed from colorless to light yellow, yellow, and finally light brown. Interestingly, the color of solution changed faster for the higher repetition rate than lower at the same intensity (0.6 J/pulse). The deeper the color was, the higher the concentration of Ag-NPs, which was confirmed using the UV–vis absorption spectra.

Fig. 2 shows the UV–vis absorption spectra of silver colloids prepared using the PLA method in water with 532 nm laser light at different repetition rates. The UV–vis spectra show the characteristic SPR peak of Ag-NPs [16], which has a distinguished peak at around 400 nm as; this is consistent with the fact that the nanoparticles present in the solution are spherical [17]. As shown in the UV–vis spectra, the SPR peak increases as the laser repetition rate increases, suggesting that the concentration of particles or the efficiency of particle formation increases at higher repetition rates [18].

From the SPR spectra it is clear that, as the repetition rate increases, a subtle red shift from 398 to 404 nm occurs, which can be attributed to the increase of particle size [5]. This phenomenon contrasts previous work [19] and can be explained by the stirring of the colloidal solution during the PLA process. Stirring is expected to promote particle fragmentation because, in this condition, more particles can be exposed to laser radiation [20]. However, in this experimental set-up the metal plate was placed close to the cell wall, thereby decreasing the efficiency of fragmentation; this effect increased as repetition rates increased. Therefore, broader particle size distributions with high average particle diameters for Ag-NPs prepared in higher repetition rates were obtained.

Fig. 3 shows the TEM images of Ag-NPs in the colloidal solutions and their particle size distributions (displayed next to each image). The mean diameter and the standard deviation of Ag-NPs

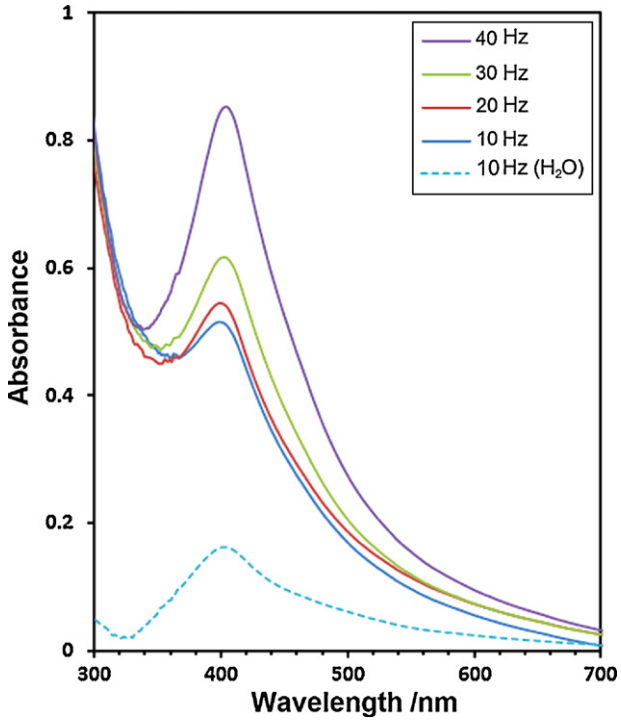


**Fig. 2.** UV–vis spectra of Ag-NPs prepared using the PLA method at different repetition rates.

are also summarized in Table 1. The Ag-NPs with a mean diameter of less than 15 nm in all applied laser repetition rates; thus, it is clear that the size and particle size distribution of Ag-NPs significantly depend on applied laser repetition rates. The mean diameter and the particle size distributions of Ag-NPs increased as laser repetition rate becomes greater. In the repetition rate of 40 Hz, a mean diameter of approximately 14.7 nm was observed, while the mean

**Table 1**
The mean diameter of Ag-NPs prepared using the PLA method in aqueous solutions at different repetition rates (*without gelatin).

| Repetition rate (Hz) | Mean diameter (nm) | Standard deviation (nm) |
|---|---|---|
| 10 | 8.95 | 2.47 |
| 20 | 11.29 | 4.43 |
| 30 | 13.01 | 6.71 |
| 40 | 14.73 | 9.71 |
| 10* | 33.76 | 16.59 |

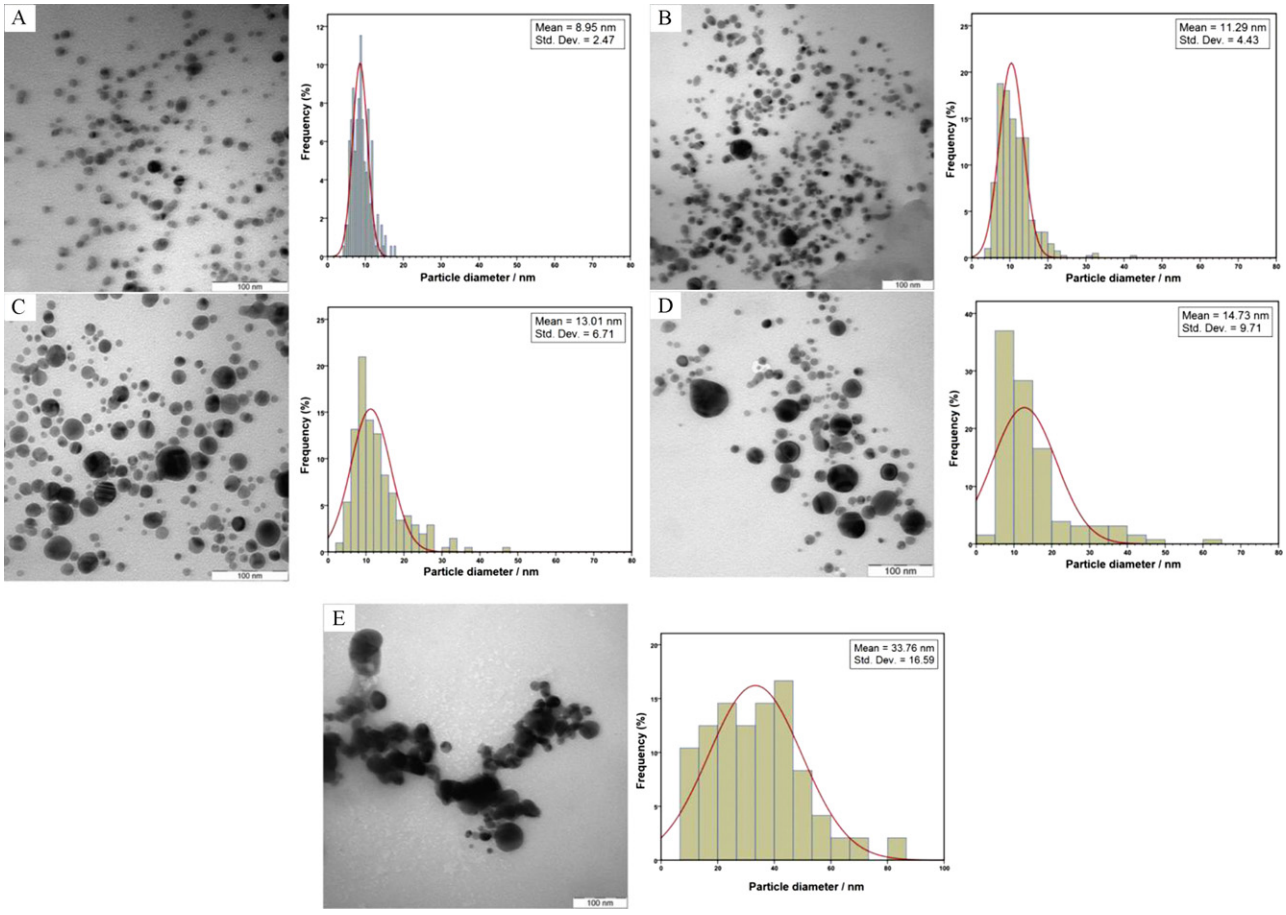


**Fig. 3.** TEM images and particle size distributions of Ag-NPs prepared at different repetition rates; 10 (A), 20 (B), 30 (C), 40 (D), and 10 Hz (E) neat water.

diameter of particles in 10 Hz was around 8.9 nm. The mean diameters of Ag-NPs prepared in 20 and 30 Hz were 11.3 and 13 nm, respectively.

To show the role of gelatin as a stabilizer, the experiment used the same experimental conditions for pure water at a repetition rate of 10 Hz. As shown in the UV-spectrum (Fig. 2, 10 Hz $H_2O$), the results obtained in the absence of gelatin showed that the FWHM of the SPR peak increased and moved to a higher wavelength (403 nm) than the result with gelatin (398 nm). This red shift and peak broadening indicated that the size of Ag-NPs prepared in absence of the stabilizer is larger and has agglomeration compared with the Ag-NPs prepared with the stabilizer. The absorption peak due to SPR of metal nanoparticles shows a red-shift as the particle size increases [5]. This phenomenon was also confirmed in the particle size distribution obtained from the TEM image (Fig. 3E). The TEM images clearly show that Ag-NPs prepared in gelatin solutions were more dispersed than those prepared in neat water. Gelatin as a good stabilizer can cover them and prevent their agglomeration and growth because, in the PLA process the size of particles decreases as the stabilization of nanoparticles increases due to the solvent used [21].

In the PLA process, different materials (e.g., Ag atoms, Ag clusters, and Ag droplets) are emitted from the silver target. This phenomenon consists of rapid formation of an embryonic Ag-NPs and a continuously growth of particle in competition with termination of the growth due to capping gelatin on the particle. In details, after the PLA irradiation, a dense cloud of Ag atoms is instantly built over the laser point from the silver plate. After formation of Ag cloud, Ag atoms are aggregated together because the interatomic interaction is stronger than the other consistent interactions such as Ag atoms-solvent molecules or Ag atoms-gelatin molecules. This aggregation is rapid and continues to finish the Ag atoms in the close vicinity of particle. However, the Ag-NPs forms in a region void of Ag atoms and the supply of Ag atoms outside this space during diffusion cause the particle to grow slowly even after the rapid growth ceases. The slow growth of obtained Ag particle can be limited or terminated by capping surface of Ag particle with gelatin molecules [22,23].

## 4. Conclusion

Preparation of Ag-NPs in the gelatin matrix using the pulsed laser ablation method without any other reagents is simply possible. The particle size distributions of Ag-NPs at different repetition rates indicated that the smallest Ag-NPs were obtained at 10 Hz. Further experiments in this condition demonstrated that an increase in repetition rate caused an increase in particle size as well as size distributions. This work provides important advantages namely, simplicity, speed, and cleanness. This approach is general and may be extended to other noble metals such as Au, Pd and Pt.

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