Effect of Laser Parameters on the Characteristics and Stability of Ag NPs Produced by Laser Ablation in Stationary Conditions

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Abstract: The effect of laser ablation parameters on the size and stability of synthesized silver nanoparticles (Ag NPs) by laser ablation in deionised water was investigated. The results showed that the selected laser parameters (laser pulse wavelength and laser fluence) and ablation of the target in a fixed beam position had a direct effect on the size and size distribution of Ag NPs. The stability of all Ag nanoparticle samples prepared in different laser parameters has been studied. All the samples of Ag NPs presented remarkable long-term stability up to two months.

Keywords: Ag nanoparticles; Laser Ablation; ambient conditions.

1. Introduction

Silver nanoparticles Ag NPs are particles of silver that range in diameter from 1 to 100 nm [1]. When the size of the material reduces from macroscale to nanoscale range, its physical properties change. Therefore, the Ag NPs possess unique electronic, optical and biological properties compared to metal silver (bulk) [2]. In general, there are two main procedures are used to produce nanomaterials: bottom-up and top-down. Bottom-up procedure begins with the reduction of ions, which are combined to generate nanostructures such as electrochemical and chemical reduction methods. In the top-down strategy, a part of the bulk material is removed to produce the desired nanostructures such as photolithography and pulsed laser ablation in liquids techniques [3].

The method of pulsed laser ablation in liquids is a single-step process for processing colloidal nanoparticles [4,5]. This process is environmentally friendly and clean and can produce free of chemicals nanoparticles compared to chemical methods that require purification processes for several times before carrying out the medical and biological applications [6-8]. The size and shape of nanoparticles produced by laser ablation in liquid mainly depend on many factors: laser fluence, pulse duration, repetition rate, temperature, ablation time, and laser wavelength [9]. Metal nanoparticles are an attractive material which can be used in many fields from biological to industrial applications [10]. Among them, Ag NPs are the most widely accepted nanomaterials in the medical and biological applications. For instance, it has been widely used as an antibacterial and antifungal material in many applications such as water purification, cosmetics, and medical fields including wound dressings or creams and ointments and disinfection of medical devices [11,12]. Moreover, previous studies pointed out that the smaller size of silver nanoparticles (less than 10 nm) have a greater antibacterial efficiency than the silver nanoparticles of larger sizes (bigger than 10 nm) [12]. Therefore, the control of Ag NPs size is a very significant factor in colloid generation. Most of studies concern with miniaturization; for example, Anastasiya E. Tyurnina et al. produced silver nanoparticles Ag NPs by pulsed laser ablation method in deionized water using Q-switched Nd: YAG laser at wavelength 1064 nm with a pulse duration 100 ns. The study showed that the size of the generated Ag NPs reduced by decreasing the laser fluence and increasing the ablation time [13]. Elmira Solati et al. prepared Ag NPs using a Q-switched Nd: YAG laser at two different
wavelengths (532 and 1064 nm) for the same laser fluence ranges and ablation time duration with pulse duration 7 ns at 10 Hz repetition rate. The ablation process was performed by the laser beam with a fluence 14-22 J/cm² for 4 minutes exposure time. The size of prepared Ag NPs at 1064 nm wavelength was increased by increasing the laser fluence while the size of silver nanoparticles generated at 532 nm wavelength was reduced with increasing the laser fluence [14]. Another mechanism was used to reduce the size of Ag NPs is preforming of ablation process in stirred liquid [15]. For instance, Prochazka et al. showed that the liquid stirring during the ablation the ablation process leads to increase the ablation yield and reduction the particle size of generated Ag NPs . They showed that liquid stirring increased the amount of Ag NPs crossing the laser beam which promoted the laser induced fragmentation [16].

In general, the stability of silver nanoparticles can affect their activity in many applications; for instance, the stability of silver nanoparticles is an important factor affecting their antibacterial efficacy [12]. It was found that the stability of the silver nanoparticles depends on their size surface charge and storage conditions.

Most of the studies concern the stability of silver nanoparticles produced by chemical methods, on the other hand, some research has been reported on the stability of Ag NPs prepared by pulsed laser ablation method in the liquid. For example, Raid Baiee et al. investigated the stability of Ag NPs kept at different storage conditions during six months which produced in different solutions (deionised water and Polyvinylpyrrolidone as a stabilizing agent). Their results indicated that the Ag NPs prepared in Polyvinylpyrrolidone solution (with sizes less than 10 nm) were more prone to agglomeration and their stability depended on the storage conditions. While, the stability of Ag NPs prepared in deionised water (bigger than 10 nm) showed high stability over six months regardless their storage conditions [12]. Another study was conducted by Anastasiya E. Tyurnina et al. to inspect the effect of the ablation parameters on the stability of Ag NPs for one month. They found that the stability of prepared Ag NPs was enhanced by increasing the laser fluence and ablation time and decreasing the water layer above the target surface [13]. Until now, no work has been reported on the generation of silver nanoparticles under stationary conditions. In this present work, Ag NPs were prepared by pulsed laser ablation in deionised water under stationary conditions (Both the laser beam and the liquid were fixed during ablation process). This technique was used to synthesize smaller size of nanoparticles by pulverization of freshly produced nanoparticles. Moreover, the effect of the ablation parameters on the stability of produced nanoparticles was taken into account.

2. Experimental details

Silver nanoparticles were synthesized by (PLA) of silver plate in deionized water. Nanoparticles were produced using Nd:YAG laser operating at 355 nm and 532 nm wavelengths. A silver plate (99.99% purity) with a thickness of 1 mm and a surface area of (1.5 × 1.5 mm²) was placed at the bottom of a glass vessel filled with a 10 ml deionized water. Then the laser beam was focused on the silver plate with a spot size of 0.5 mm in diameter. The ablation process was carried out at laser fluence of 38.2, 76.4 and 144.6 J/cm² with pulse duration 7 ns at 6 Hz repetition rate. During the experiments, 500 laser shots were applied for preparing each sample. The laser ablation process was performed in deionized water under stationary conditions by fixing both the laser beam scanning and the liquid movement during the ablation process which is applied for the first time. In order to study the effect of changes in silver Ag NPs properties occur over time which impacts their stability and ageing mechanism, each of the prepared samples of the Ag NPs solution was poured immediately into glass vial covered with aluminium (Al) foil and stored in the dark at room temperature.

The optical properties of the silver nanoparticles were examined by a UV-Visible absorption spectrophotometer (CECIL CE 7200, ENGLAND). A zeta analyzer (Brookhaven, USA) was used to measure the surface charge of the prepared silver nanoparticles. Particle size and size distribution of synthesized silver nanoparticles were measured by transmission electron microscopy (TEM) (Model: LEO 912 AB, Germany). A Fourier-transform infrared spectroscopy (FTIR) (BOKER, Germany) was used to identify the compounds of the generated silver nanoparticles.

Table 1 Laser wavelength and laser fluence of samples produced by (PLA).

| Sample | Laser Wavelength | Laser fluence |
|--------|------------------|--------------|

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3. Results and discussion

3.1 Optical properties

The optical properties of prepared Ag NPs were investigated using a UV-Visible absorption spectrophotometer. Figure 1 shows UV-Visible absorption spectra of fresh colloidal solutions synthesized by laser ablation of a silver plate in deionised water at different laser fluences and wavelengths. All samples presented a single absorption peak around 400 nm, which indicates that the Ag NPs in the solutions are spherical or semispherical [17,18]. This was confirmed by the TEM results as shown in figure 3. From figure 1, one can observe that the absorption intensity increased with increasing the laser fluence, which indicates an increase in the production of nanoparticles [18,19]. This means that the ablation efficiency was increased by increasing the laser fluence which leads to an increase in the concentration of nanoparticles [20]. Another effect which should also be taken into account is that the ablation efficiency strongly depended on the laser wavelength where the concentration of Ag NPs prepared by laser ablation at 355 nm laser wavelength was higher than that prepared at 532 nm laser wavelength at the same values of laser fluence as shown in figure 2 [19,20]. The concentration of produced Ag NPs was confirmed by weighing the metal target before and after the laser ablation process. It is obvious from figure 2 that the concentration of Ag NPs depended on the laser wavelength where the amount of ablated material increases, when the ablation process was carried out with 355 nm laser pulses. When the ablation process was carried out with 532 nm laser pulses, the concentration of prepared Ag NPs are 13.33, 21.11 and 26.66 µg/ml for 38.2, 76.4, and 144.6 J/cm² laser fluence respectively. Compared with the concentration obtained with 532 nm laser pulses, the concentrations obtained with 355 nm laser pulses are 33.33, 40 and 46.66 µg/ml for 38.2, 76.4 and 144.6 J/cm² laser fluence respectively. This could be attributed to an increase the amount of ablated material that is more probable at wavelength close to the target absorption spectrum (Ag) [18].

|       | (J/cm²) | (nm) |
|-------|---------|------|
| A     | 38.2    |      |
| B     | 76.4    | 532  |
| C     | 114.6   |      |
| D     | 38.2    |      |
| E     | 76.4    | 353  |
| F     | 114.6   |      |

Figure 1. Absorption spectra of freshly Ag NPs prepared at (a) 532 nm wavelength and (b) 355 nm laser wavelength.
Figure 2 Variation of synthesized Ag NPs concentration versus the laser fluence at different wavelengths.

![Graph showing concentration vs. laser fluence for different wavelengths](image)

| Laser fluence (J/cm²) | Concentration (µg/ml) | Laser wavelength (nm) |
|-----------------------|-----------------------|-----------------------|
| 38.2                  | 13.33                 | 532                   |
| 76.4                  | 21.11                 |                       |
| 144.6                 | 26.66                 |                       |
| 38.2                  | 33.33                 | 355                   |
| 76.4                  | 40                    |                       |
| 144.6                 | 46.66                 |                       |

Table 2 Concentration of the synthesized Ag NPs by different 355 nm and green 532 nm laser fluences.

![Images of Ag NPs at different concentrations and laser fluences](image)
3.2 Size of nanoparticles

Figure 3 shows TEM images of freshly Ag NPs synthesized by laser ablation in deionised water at different laser fluencies and wavelengths. As clearly seen, all samples showed that prepared Ag NPs had no agglomeration and were scattered with a good dispersity with a spherical shape. It is obvious from figure 3 that the size of Ag NPs prepared at 355 nm laser wavelength is smaller than the Ag NPs prepared at 532 nm laser wavelength. Figure 4 shows the size distribution of Ag NPs synthesized at different wavelengths and fluencies. This figure shows that with increasing the laser fluence, the size distribution of nanoparticles prepared at 532 nm was broader. On the contrary, with increasing the laser fluence, the size distribution of nanoparticles prepared at 355 nm was narrower [19]. The statistical results in figure (5.a) indicated that the average size of Ag NPs depended on the both laser fluence and laser wavelength where the mean size of Ag NPs prepared at 532 nm wavelength was increased by increasing laser fluence. While, the average size of Ag NPs prepared at 355 nm wavelength was decreased by increasing laser fluence [21]. The obtained average particle size of Ag NPs prepared at 532 nm laser wavelength are 14.07 ± 11.87 nm, 15.56 ± 14.28 nm and 20.59 ± 20.24 nm in order for 38.2, 76.4 and 144.6 J/cm² laser fluence. Whereas, the mean size of Ag NPs prepared at 355 nm laser wavelength are 14.7 ± 11.71 nm, 12.3 ± 9.82 nm and 9.2 ± 11.43 nm in order for 38.2, 76.4 and 144.6 J/cm² laser fluence. This could be attributed to the fragmentation process induced by absorption of the laser wavelength 355 nm that had a greater influence on the size of Ag NPs. It has been reported that fragmentation process can happen simultaneously to laser ablation process when colloidal solutions of Ag NPs are synthesized by ablation with 355 nm laser pulses. Therefore, the mean size of nanoparticles usually increase with increasing laser fluence, except when the laser wavelength can be reabsorbed by nanoparticles because of the production of photo fragmentation [22]. As a result, this could be the reason that produces the smaller size of Ag NPs when Ag NPs are prepared by ablation with 355 nm laser wavelength at higher laser fluence due to the photo fragmentation process. More explanation is that using a high fluence could enhance the photo fragmentation process by a 355 nm laser beam [22].

Our methodology depended on the fact that freshly formed nanoparticles are irradiated by incoming laser pulses to induce fragmentation. Therefore, our technique to reduction the size is that implementation of laser ablation process in stationary conditions to keep the formed nanoparticles over the laser spot for a long time, which leads to enhancement of the photo fragmentation. This was confirmed by increasing the number of Ag NPs less than 10 nm as depicted in figure (5.b).
Figure 4 Particle size distribution of silver nanoparticles.

Figure 5 (a) Effect of laser ablation parameters on producing Ag NPs sized less than 10 nm. (b) Influence of laser wavelength on the average size of Ag NPs synthesize at different values of laser fluence.
It is obvious from figure (5.b) that the laser fluence and laser wavelength have a direct effect on producing ultrafine Ag NPs with size less than 10 nm where the number of particles with size less than 10 nm was increased with increasing laser fluence when the ablation process was carried out only using 355 nm laser wavelength. As a result, the average size of produced Ag NPs was decreased with increasing the laser fluence when the ablation process was implemented using 355 nm laser wavelength. On the other hand, the number of particles with size less than 10 nm was decreased with increasing the laser fluence when the ablation process was implemented using 532 nm laser wavelength. Therefore, the mean size of produced Ag NPs was increased by increasing the laser fluence when the ablation process was implemented using 532 nm laser wavelength. To explain this behavior, one should bear in mind that the 355 nm laser wavelength lies within the surface plasmon band of all the Ag NP samples. Therefore, we believe that implementation of ablation process in a stationary conditions could reabsorb 355 nm laser wavelength by freshly produced nanoparticles leading to enhancing the fragmentation process. As a result, the population of smaller particles (less than 10 nm) was increased due to fragmentation process leading to decreasing both the average size and the size distribution [23].

3.3 FTIR analysis

FTIR measurements were employed immediately after preparation to analyze the composition of the freshly prepared Ag NPs. All of the FTIR analysis in figure 6 showed the presence of Ag NPs. The bands in figures 6 found at the range of 1631-1636 cm⁻¹ which can be assigned to Ag NPs bonding with hydroxyl group [24]. The peaks in figure 6 found at the range of 3252-3276 cm⁻¹ which can be attributed to silver metal (Ag⁺) [25].
3.4 Zeta Potential analysis

The zeta potential value that ranges from 0-10 mV shows a highly unstable colloid, with zeta potential value of 10 - 20 mV, 20 - 30 mV and > 30 mV shows relatively, moderately, and highly stable colloid in the respective order [26,27]. In this study, zeta potential measurements were carried out immediately after preparation for each sample in order to study the surface charge of the freshly prepared Ag NPs as shown in table 3, the zeta potential values were -36.89,-30.73,-32.22 and -31.90 mV for samples A, C, D and E respectively which indicate a high stability [26,27,28]. Whereas, the zeta potential values for samples B and F were -24.38 ,-28.92 mV respectively that indicate a moderate stability [26,27,28].

| Sample | Zeta Potential(mV) |
|--------|---------------------|
| A      | -36.89              |
| B      | -24.38              |
| C      | -30.73              |
| D      | -32.22              |
| E      | -31.90              |
| F      | -28.92              |

3.5 Effect of Ag NPs storage time on their stability

The stability of bare Ag NPs (with the majority of the particles less than 10 nm), which prepared via different synthesis conditions, was studied for up to two months as a function of the these synthesis conditions. UV-visible , Zeta potential and FTIR measurements were performed immediately post synthesis and subsequently after one to two months of storage.

3.5.1 Changes in size and agglomeration during storage

Figure 8 presents the optical properties of Ag NPs storage in the dark at room temperature for two months. As shown in figure 7,UV–Visible measurements presented some changes in the nanoparticles dispersity during the first month. It is obvious from this figure that almost all the prepared samples of the Ag nanoparticle solution presented a very slight red shift of the peak maximum. The UV-Visible measurements also presented a decrease in the absorption intensity, however, the change for samples 7 (a, d and f) was not as strong as in the case of samples (b, c and e). This could be attributed either to increase in the size of nanoparticles or, more reasonably, to the different oxidation grade of the nanoparticle.
surfaces during the first month [29,30]. The position of the plasmon peak remained unchanged for all samples after one month. There was no significant change observed in the absorption intensity of samples a, b, c, d and f during second month, while, the highest decrease of the absorbance of sample e was again observed during the same period of time, confirming additional oxidation [29,30].

![Graphs showing UV-Visible absorbance spectra of Ag NPs immersed in deionised water after 0, 1, and 2 months.]

Figure 7 UV-Visible of Ag NPs immersed in deionised water after 0, 1, and 2 months.

3.5.2 Impact of storage time on the composition of Ag NP colloids

The FTIR analysis of samples A – F revealed that a new peaks appeared during the storage time, confirming the formation of Ag NPs oxidation. The spectrum in figure 8 show the peaks at the range of (526-592 cm⁻¹) which are a signature of Ag NPs bonding with oxygen from hydroxyl groups [28,31,32].
Figure 8. FTIR spectrum of Ag NPs after one month of preparation.
3.5.3 Changes in surface charge during storage

The variation in surface charge with time are another indicator to monitor the long-term stability of stored Ag NPs. Zeta potential measurements in table 4 revealed that there were no drop in zeta potential values of sample (B, C and F) during the first month. On the other hand, zeta potential values of sample (A, D and E) dropped significantly after one month of storage, especially for sample E which seemed to be sensitive to the storage time. However, zeta potential value of sample A still beyond the stable colloid border value during the first month. The zeta potential value of sample A changed already after one month of storage, and did not differ significantly during the second month. In addition, the zeta potential values of samples B and F were somewhat constant during second month. Although, sample C presented the highest value of zeta potential of −30mV during first month, this value was significantly dropped to −24.6 mV after one month. Moreover, the drop in the zeta potential values of samples D and E continued after one month. However, the zeta potential values of samples C, D and E show that the colloidal Ag NPs samples were moderately stable up to 60 days.

| Sample | zeta potential (mV) | zeta potential (mV) | zeta potential (mV) |
|--------|---------------------|---------------------|---------------------|
|        | Fresh               | After first month   | After second month  |
| A      | -36.89              | -32.17              | -30.26              |
| B      | -24.38              | -25.12              | -25.22              |
| C      | -30.73              | -30.50              | -24.26              |
| D      | -32.22              | -27.40              | -23.26              |
| E      | -31.90              | -23.10              | -20.92              |
| F      | -28.92              | -28.29              | -29.78              |

4. conclusion

Different sizes of Ag NPs were successfully generated by laser ablation in deionised water using different laser ablation parameters. The results show that the experimental set-up played an important role in controlling the size of produced Ag NPs where by the proper selection of the laser ablation parameters, the size was reduced from 20.59 ± 20.24 nm to 9.2 ± 11.43 nm. This study presented a new method to control the size of nanoparticles which involved implementation of the ablation process in stationary conditions to pulverize the produced Ag NPs into smaller nanoparticles by photo fragmentation process. Stability of Ag NPs was also investigated and the results showed that all Ag nanoparticle samples produced in pure deionised water presented remarkable stability up to two months.

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