Journal of Materials Science and Engineering B 4 (10) (2014) 279-283
doi: 10.17265/2161-6221/2014.10.002

# Overlapping of Laser Pulses and its Effect on the Yield of Silver Nanoparticles in Water

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Received: October 11, 2014 / Accepted: October 21, 2014 / Published: October 25, 2014.

**Abstract:** Laser pulse overlapping is one of the least studied parameters involved in the production of nanoparticles by laser ablation confined in liquids. In order to explore its effect on the yield of nanoparticles, we employed a motorized XY translation stage with speed control, which allowed us to regulate the overlapping of laser pulses on the target. Four different XY speed settings were used in the laser ablation of a silver target in distilled water; each process in a virgin surface, using the 532 nm emission of a Nd:YAG laser, with fixed spot diameter of 1 mm and pulse energy of 0.5 J/pulse. Peak optical absorption, in UV-Visible measurements of each nanoparticle suspension, decreases as the employed pulse overlapping increases. According to the well known Beer-Lambert relation, this implies that nanoparticle yield decreases as the pulse overlapping increases.

**Key words:** Silver nanoparticles, nanoparticle yield, confined laser ablation, absorption spectra.

## 1. Introduction

The first use of laser ablation confined in a liquid medium for the generation of nanoparticles was made in 1993 year [1]. It is an alternative method for the production of nanoparticles, which consists in the laser irradiation of a solid target immersed in a liquid environment, where the ions of laser generated plasma rapidly quench to form nanoparticles.

Laser parameters in combination with optical properties of the target material play a key role in the yield and size of nanoparticles [2-4]. For instance, if laser frequency is close to that of plasmonic oscillations of the nanoparticles, they will most probably be fragmented, leading to smaller sizes [5]. In addition, it has been observed that average nanoparticle size decreases when the laser fluence is increased [6]. On the other hand, a comparison of the yield, using the same energy/pulse for fundamental and second harmonic emissions (1,064 nm and 532 nm) on an aluminum target in ethanol, showed that more material was ablated when infrared radiation was used [7]. However, there is a mechanical parameter in the experimental procedure that influences the yield of nanoparticles, the overlapping of consecutive pulses. There are reported works where the totality of pulses overlap, since the point of incidence in the target is fixed during the synthesis [8, 9]. Meanwhile, there are other works where the overlapping is reduced by moving the target, several of them with a rotational motion and a few with an XY drift mechanism [10-14].

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Nevertheless, the main objective of these works, with moving targets, was to avoid the formation of craters or holes on the target's surface. Only Barcikowski et al. have explored the effect of pulse overlapping, employing a $CO_2$ laser with 120 *fs* of pulse duration and a repetition rate of 1 kHz, to ablate silver and titanium targets in gaseous environments, concluding that overlapping has influence on the mass ablated per pulse [14]. However, in spite of their tabulation of a couple percentages of overlapping between consecutive pulses, they seem unattainable with the presented laser and XY drift parameters; since they used a slower drift with a faster repetition rate, which should lead to higher overlapping values.

In this paper, we explore the influence of overlapping of consecutive laser pulses on the yield of silver nanoparticles by laser ablation confined in distilled water; showing the parameters of target's XY drift mechanism and spot diameter, which defines the overlapping percentage of consecutive laser pulses.

## 2. Experiments

Schematic of the experimental setup employed for the synthesis of nanoparticles by laser ablation confined in a liquid medium is shown in Fig. 1. We employed the second harmonic emission of a pulsed Nd: YAG laser (532 nm), with an energy of 0.5 J/pulse, having pulse duration of 5 ns and a repetition rate of 10 *Hz*. Furthermore, we used a silver target with 99.99% purity, immersed vertically in a glass vessel with 25 ml of distilled water, fixed to an XY drift mechanism with controllable speed. By combination of the 10 *Hz* repetition rate and the displacement speed, four different laser pulse overlapping conditions were used to explore the influence of this parameter on the yield of nanoparticles; generating pulse densities of 2,500, 5,102, 8,264 and 10,000 pulses/cm$^2$. Target's drift sequence is schematically shown in Figure 1b. The diameter of laser spot on the target was adjusted to 1 mm and a fixed time of 111 s was used for laser irradiation, with the purpose of using the same amount of pulses in every synthesis. Each synthesis was made using a virgin section of the target's surface, in order to observe clearly the effect of pulse overlapping.

Thus obtained nanoparticle suspensions were characterized by UV-Visible absorption spectroscopy (with a Thermo Genesys 10 spectrophotometer) and transmission electron microscopy (with a 100 kV Jeol JEM1010 microscope).

Table 1 shows the four horizontal displacement speeds ($v_x$) employed in order to attain the different overlapping percentages, where speed $v_y$ is adjusted to 2.5 mm/s in every synthesis. Horizontal displacement ($d$) between consecutive pulses is determined from this speed and the laser repetition rate ($R_{rep}$); meanwhile, the square of its reciprocal, gives the number of pulses per square centimeter. As shown in the following equations:

$$d = \frac{v_x}{R_{rep}} \quad \text{(mm)} \tag{1}$$

$$\rho = \left( \frac{R_{rep}}{v_x} \right)^2 \quad (\text{pulses/cm}^2) \tag{2}$$

The lowest pulse density, 2,500 pulses/cm$^2$, was achieved for the fastest displacement of the target, 2 mm/s; corresponding to an overlapping percentage of 74.7% between consecutive pulses, for the used spot diameter of 1 mm. Meanwhile, using a speed of $v_x$ = 1 mm/s, we obtained a density of 10,000 pulses/cm$^2$, with the highest percentage of overlapping 87.2%. The calculation of this percentage among two consecutive pulses is shown in the appendix.

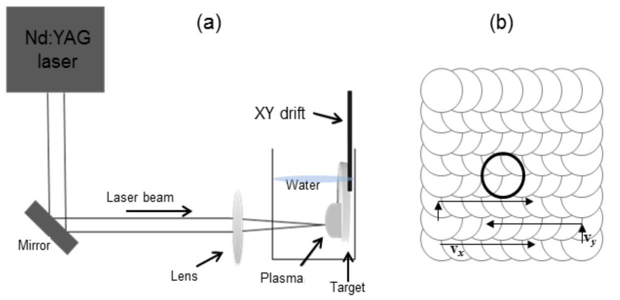


**Fig. 1 (a) Experimental setup employed for the synthesis of nanoparticles by laser ablation confined in distilled water, (b) target´s displacement in X-Y directions and the overlapping of the laser pulses.**

**Table 1 Experimental parameters to explore the overlapping effect; values of the speed ($v_x$) and displacement of the target ($d$); density of pulses ($\rho$) and percentage of overlap among two consecutive pulses.**

| $v_x$ (mm/s) | $d$ (mm) | $\rho$ (pulses/cm$^2$) | $O(\%)$ |
|---|---|---|---|
| 2 | 0.2 | 2,500 | 74.7 |
| 1.4 | 0.14 | 5,102 | 82.2 |
| 1.1 | 0.11 | 8,264 | 85.3 |
| 1 | 0.1 | 10,000 | 87.2 |

The scheme used for the calculation of overlapping percentage of two consecutive pulses is shown in Fig. 2 (shaded area). Considering the diameter ($D_p$) and the radius ($r$) of the laser spot. Meanwhile, $d$ represents the target's displacement between consecutive pulses and $x_0$ the intersection's $x$ coordinate of the two circumferences.

According to this scheme, the overlapping area can be written as:

$$S_O = 4\int_{x_0}^{r} \sqrt{r^2 - x^2}\, dx \quad (3)$$

solving this integral, it is obtained that:

$$S_O = \pi r^2 - 2x_0\sqrt{r^2 - x_0^2} - 2r^2 sen^{-1}\left(\frac{x_0}{r}\right) \quad (4)$$

Considering that the center of the circles are (0, $y_0$) and ($d$, $y_0$), we can write the next circumference equations:

$$\begin{aligned} x_0^2 + y_0^2 &= r^2 \\ (x_0 - d)^2 + y_0^2 &= r^2 \end{aligned} \quad (5)$$

Since both radii are equal, and vertical positions are the same, we obtain that $x_0 = d/2$. Substituting this and the radius ($r = D_p/2$) into the Eq. (4), we can rewrite the expression for the area of overlapping between two consecutive pulses like:

$$S_O = \frac{\pi D_p^2}{4} - \frac{d}{2}\sqrt{D_p^2 - d^2} - \frac{D_p^2}{2} sen^{-1}\left(\frac{d}{D_p}\right) \quad (6)$$

Then, the overlapping percentage between two consecutive pulses is obtained by the ratio of $S_O$ to the area of a spot (assumed circular); given by the following relation:

$$O(\%) = [1 - \frac{2}{\pi}\frac{d}{D_p}\sqrt{1 - (\frac{d}{D_p})^2} - \frac{2}{\pi} arcsen(\frac{d}{D_p})] \times 100 \quad (7)$$

## 3. Experimental Results

Transmission electron micrographs of nanoparticles synthesized in distilled water with densities of 2,500, 5,102 and 10,000 pulses/cm$^2$, are shown in Fig. 3. In spite of the few nanoparticles observed in micrograph of sample with 87.2% of pulse overlapping, it is apparent that particle sizes are at least in the same range as those for nanoparticles obtained with 74.7% and 82.2% overlapping.

Fig. 4 shows the UV-Vis absorption spectra of the silver nanoparticles obtained in distilled water with the four different overlapping percentages. We can observe clearly that peak absorption decreases by increasing the pulse density; in other words, the intensity of maximum absorption is smaller for larger percentages

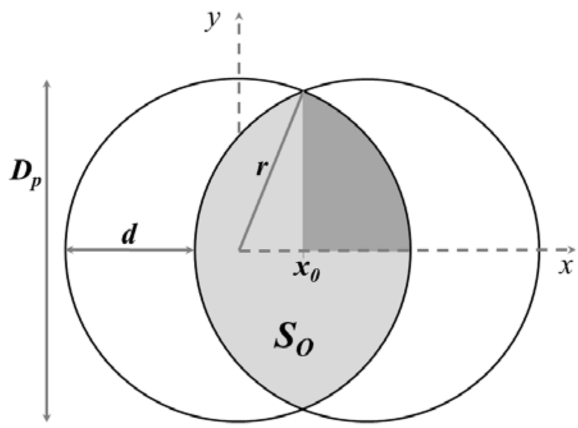


**Fig. 2 Schematic of the overlapping among two consecutive laser pulses.**

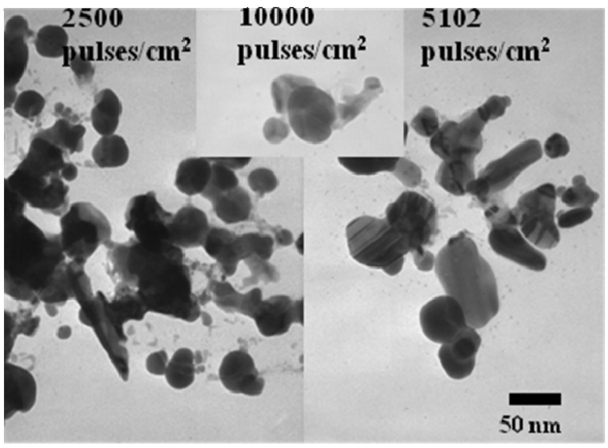


**Fig. 3 Transmission electron micrographs of nanoparticle samples obtained with different pulse densities.**

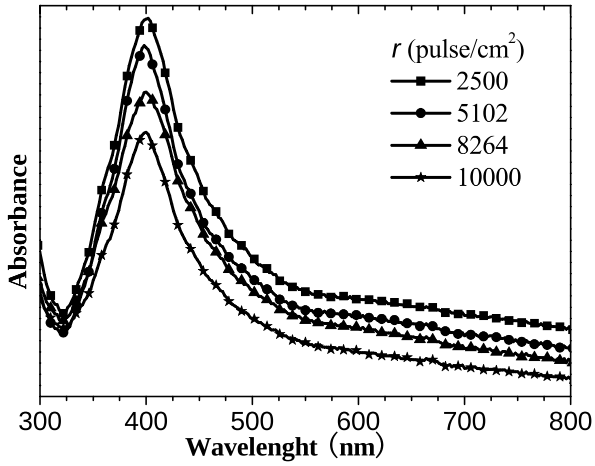


**Fig. 4 UV-Vis absorbance spectra for nanoparticles prepared with different pulse densities.**

of pulse overlapping. Additionally, from the appearance and position of the absorption peaks, we can assume that the four nanoparticle suspensions have similar size and shape distributions. According to Mie theory, the shape of the absorption spectra would be different if the size distributions of nanoparticles were different in each sample, due to differing plasmon resonance peak for each different nanoparticle size and shape.

If we consider the following linear relation, from Lambert-Beer law:

$$A = \alpha \cdot l \cdot C \tag{8}$$

where, $A$ is the absorbance, $\alpha$ is the absorption coefficient, $l$ is the path length that the radiation travels in the sample and $C$ is the concentration of the absorbent, which corresponds to the suspended nanoparticles. This linear relation indicates that a greater concentration of nanoparticles in a suspension corresponds with a larger absorbance. Consistently with this, Baladi et al. [7], exploring the effect of laser irradiation time on the production of aluminum nanoparticles in ethanol, found that the more intense absorption spectrum was obtained for the larger amount of ablated material.

According to these results, the decrease in absorption intensity could be understood as a decrease in the yield of nanoparticles with the increase of pulse overlapping. This can be illustrated if we consider the following relation obtained from the previous linear relation

$$\frac{C_k}{C_{2500}} = \frac{A_k(\lambda_{\max})}{A_{2500}(\lambda_{\max})} \tag{9}$$

where, $C_k$ and $A_k(\lambda_{\max})$ represent the concentration and the intensity of maximum absorbance ($\lambda_{\max} \approx 400$ nm) of sample with $k$ = 2,500, 5,102, 8,264 and 10,000 pulses/cm$^2$.

Thus, from the values of the absorption maximum, we can obtain the ratio of nanoparticle concentrations. This concentration ratio is plotted vs density of pulses in Fig. 5. The observed behavior shows that nanoparticle yield is smaller when a larger pulse overlapping (or pulse density) is used. In spite of the abrupt decreasing observed in the nanoparticle yield, this must represent only part of the behavior, since the continuation of this tendency would lead to a yield equal to zero, which is not possible. Additional experimentation would be needed in order to clarify this issue.

The following are two possible explanations for this behavior. The first is that because of the high percentage of overlapping, the material ablated by the first pulses attenuates part of the irradiation from the following pulses, and so on, preventing pulse energy from distributing homogeneously on target`s surface, decreasing the amount of ablated material, and then the yield of nanoparticles. The second possibility is that the

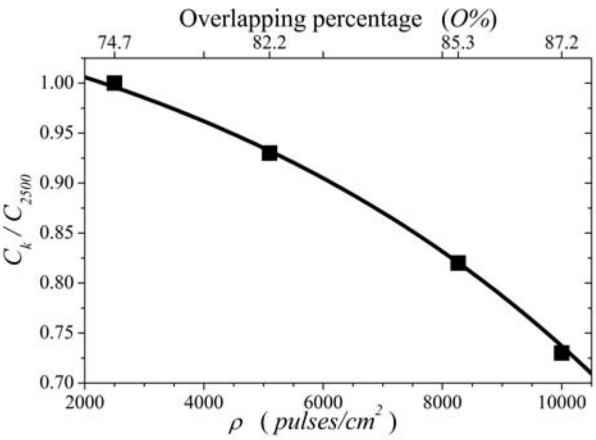


**Fig. 5 Ratio of nanoparticles concentrations as a function of pulse density.**

material surface suffers such a modification after each laser pulse, due to the shock waves produced by the plasma ejection and the surrounding medium, that every other laser pulse tends to ablate less material.

## 4. Conclusions

Overlapping of successive laser pulses was controlled by manipulating the translation speeds of an XY drift mechanism. The 4 different pulse densities produced nanoparticle suspensions which have similar absorption spectra; allowing us to observe a decrease of nanoparticle yield when pulse overlapping is increased. Indicating that, the lower the pulse density used in the production of nanoparticles, the more quantity will be obtained. Perhaps, this occurred because after every pulse, the ejected nanoparticles, with the lateral inertia of the target, tend to screen the intensity of the following pulses; or because target´s surface undergoes modifications with each impact of the laser, such that the next pulse tend to ablate less material.

This is the first time that parameters of the scanning method are clearly described in order to control the overlapping of laser pulses over the target’s surface, which definitely has an effect on the yield of nanoparticles.

## Acknowledgments

Authors want to thank the financial support from CONACyT (under grant CB2010/156773) and UdeG (under programs proSNI and PROINPEP). DOOG and AMB want to thank CONACyT for their scholarships.

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