

PRODUCTION OF ALUMINA NANOPARTICLES (AL₂O₃) USING PULSED LASER ABLATION TECHNIQUE IN ETHANOL SOLUTION

Ph.D. Adel K. M.

Mechanical Engineering Department, College of Engineering, University of Diyala, Iraq

Email: adel_alkayali@yahoo.com

Abstract: Pulsed Laser Ablation in Liquid (PLAL) has become an increasingly important technique for metals production and metal oxides nanoparticles (NPs). This technique has its many advantages compared with other conventional techniques (physical and chemical). This work was devoted for production of alumina (Al₂O₃) nanoparticles via PLAL technique from a solid alumina target immersed in ethanol at different values of laser fluences in order to study the effect of laser fluences on the optical properties and structure of Al₂O₃ nanoparticles. The controllability of particle size and size distribution is shown in this paper to be dependent upon laser fluences and it proved that the ablation at lower fluence led to the creation of smaller nanoparticles, smaller aggregates of nanoparticles, and a lower concentration of nanoparticles in contrast an increase of fluence leads to the formation of larger nanoparticles and most of these NPs were aggregated. The produced NPs were characterized by mean of many tests such as UV-visible (UV-Vis.), Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM).

KEYWORDS: ALUMINA NANOPARTICLES, PULSED LASER ABLATION TECHNIQUE, ETHANOL SOLUTION.

1. INTRODUCTION

The properties and behavior of materials at nano levels differ greatly when compared to micro levels. Also these nanoparticles show great differences of their outstanding properties such as physical, chemical, optical and electronic properties from the bulk material of which they are made [1].

PLAL represents one of the most important, effective and simple technique for preparing metal, metal oxide nanoparticles. PLAL has many advantages compared with other conventional physical and chemical methods like purity, stability of the fabricated nanoparticle colloids, and do not require a vacuum chamber. It is the most flexible and promising technique because of its ability to control NPs size by optimizing the laser parameters, Also this technique provides the possibility of generating a large variety of NPs those are free of both surface-active substances and counter ions [2-4].

In general, the produced NPs through PLAL technique pass through three fundamental steps. Firstly plasma generates due to extreme heating during the interaction of laser with matter. Secondly the plasma, containing vapor of target atoms expands adiabatically, this leads to quick cooling of the plume region and hence to the formation of nanoparticles clusters. Finally after plasma extinguishing the formed nanoparticles clusters encounter and interact with the solvent and surfactant molecules in the surrounding solution, typically about a

few microseconds, all these steps take place and nanoparticles are synthesized [5, 6].

Laser ablation in liquid media has been occurred either in nanosecond (ns) or femtosecond (fs) laser pulses. Femtosecond laser ablation (FLA) is one of the best methods to generate free nanoparticles with unique properties such narrower size distribution and with reduced porosity. FLA can be considered as isochoric process since the irradiation of laser pulse causes local heating in short time and it lasts before expansion of metal takes place [3].

Alumina or aluminum oxide one of important metal oxides has many interesting properties such as high hardness, high stability, high insulation, and transparency. Thus, because of these properties, it can be used in various applications e.g. fire retard, catalyst, insulator, surface coating, composite materials, thermal protections etc [7].

Many researchers direct their researches towards studying the effect of laser parameters on reducing particles sizes and collides stabilities. Co-workers later Tsuji have shown that the formation efficiencies and size of particles were changed with power of laser pulses. Recently, Sajti and co-workers found that laser ablation in water yields a greater material removal rate than in air [8].

In this work, alumina nanoparticles were produced by using pulsed laser ablation technique and study the effect of laser fluences on the size and size distribution of NPs in ethanol environment, size and morphology of the nanoparticles were investigated by AFM and SEM., their optical properties were examined by using UV-visible spectroscopy.

2. EXPERIMENTAL WORK

The experimental arrangement for the production of colloidal solution of nanoparticles by using pulsed laser ablation in aqueous media were carried out with a pulsed Ti/Sapphire laser beam (Quadronix IntenC laser) Kocaeli University - Laser Technologies Research and Application Center. The laser operates at 1 kHz repetition rate with a pulse width of ≤ 130 fs at 2.5 mJ/pulse maximum laser beam output.

Figure 1 shows the schematic diagram of PLAL experiment setup for synthesis colloidal solution of alumina NPs. The experiments of producing alumina NP were done at 90 min exposure time at 800 nm wavelength, 10 Hz pulse repetition rate and 130 fs pulse duration at different values of fluences. This laser beam is focused via a 100 mm focal length focusing lens to a minimum spot size at a solid alumina target (purity 99.99%). The alumina target was fixed by a fixture inside the flask and immersed at 10 mm depth in the solution inside the flask. A well designed and fabricated rotator mechanism used to rotate the flask in order to maintain continuous changing of the focused laser spot position at the target. A magnetic stirrer rotator was placed in the solution rotates at 600 r.p.m. to ensure uniform irradiation on target and the movement of solution that can enhance ablated particles diffusion also to disperse the produced NPs. Laser power was measured via a power meter type Newport 841-PE, the measurement was obtained at two locations very near to the final stage of the laser apparatus and before the focusing lens to evaluate the losses of the power in the beam delivery unit. Before starting the experiment the alumina target was cleaned by ultrasonic cleaning device type EMAG 50 HC then wiped with acetone and ethanol solvents. Ethanol was used as a wet environment. A number of tests were done to characterize the produced alumina NPs at different values of laser fluences, before doing the tests the sample was placed in the ultrasonic cleaner to ensure the homogeneity of the NPs solution. UV-visible extinction spectrum of the colloidal solutions was recorded using a spectrophotometer type Varian Cary-50 UV-Visible. NPs Size, morphology and distribution were examined by SEM imaging device type TESCAN VEGA series and AFM test type AA3000 Scanning Probe Microscope is most popular model.

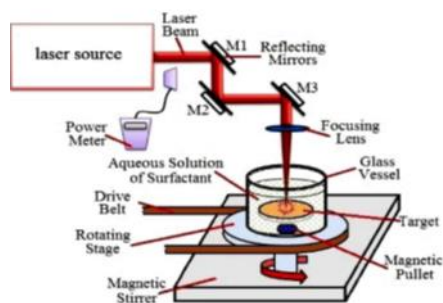


Fig.1 Mapping Experimental set up of femtosecond laser ablation method [9].

3. RESULTS AND DISCUSSION

Table 1 shows the effect of laser fluences and the effect of ablation medium on domain particle size and UV-Visible absorption peak wavelength(nm) in ethanol by using femtosecond laser ($\lambda=800$ nm/pulse, $\tau =130$ fs ,P.R.R =1 KHz) for Al_2O_3 NPs.

Table 1 Shows the effect of laser fluences and the effect of ablation medium on domain size and UV-Visible absorption peak wavelength(nm) by using femtosecond laser ($\lambda=800$ nm mJ/pulse, $\tau =130$ fs ,P.R.R =1KHz) for Al_2O_3 NPs.

Sample Code	Ablation medium	Fluences J/cm^2	Domain size of NPs	UV-Visible Absorption peak wave length (nm)
L1	Ethanol	0.83	80	213
L2	Ethanol	1.04	140	238

Laser fluence, plays an important role in ablated particle's shape, size, structure, phase, and ablation efficiency, the laser ablation of the alumina rod was performed in Ethanol at two fluences $0.83 J/cm^2$ and $1.04 J/cm^2$ corresponding in samples L1 &L2. Ethanol provides a relatively inert environment for the production of nanoparticles. Nanoparticles produced from ablation of Al_2O_3 in ethanol are primarily alumina species. SEM analysis of the nanoparticles produced in ethanol showed a lack of aggregation as shown in Figure 2.

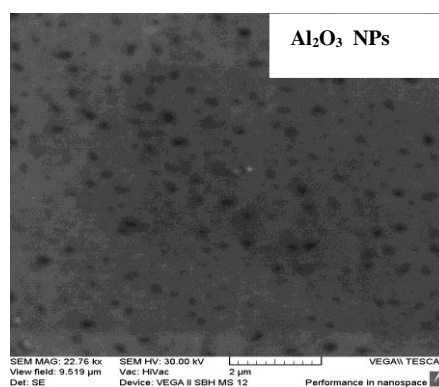


Fig. 2 SEM image of nanoparticles formed from ablation of Al_2O_3 in Ethanol at $0.83 J/cm^2$ laser fluence.

Figure 3 shows an AFM images of an area at a distance of ~ 500 nm from the edge of an ablated crater for samples L1 & L2. It can be seen the average size and the shape of nanoparticles differ between these two samples.

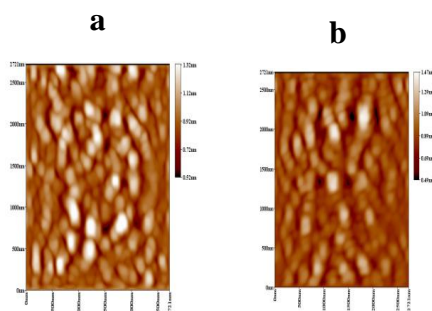


Fig. 3 AFM images of Al_2O_3 NPs produced in water solution at a. 0.83 and b. $1.04 J/cm^2$ laser fluences.

Figure 4 shows a histogram of nanoparticles produced by ablation at $0.83 J/cm^2$ and $1.04 J/cm^2$ laser fluences in ethanol media. The histogram was normalized to represent the particles have a size ranging from 10-170 nm depending on the laser fluences. From figure 4 the dominant sizes of the particles obtained from 0.83 and $1.04 J/cm^2$ is 80 and 140 nm, respectively. At $0.83 J/cm^2$ of laser fluences offered the smallest dominant particle size, whereas that of the $1.04 J/cm^2$ yielded the largest size.

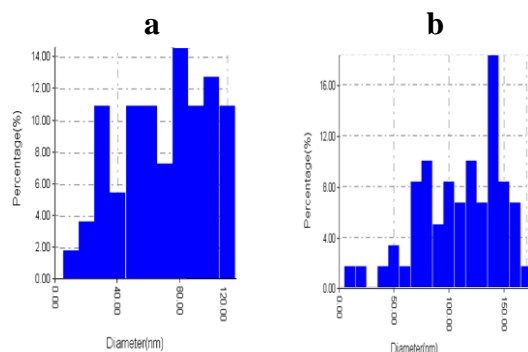


Fig. 4 Histogram of nanoparticles formed by ablation Al_2O_3 in ethanol at a. 0.83 and b. $1.04 J/cm^2$ laser fluences.

During laser ablation of alumina in ethanol small bubbles can be observed in the solution and by increasing fluence results in more alumina being ejected from the rod, thus these bubbles created from ablation is larger. A larger bubble would have a larger volume for interaction, then allowing for longer times of nucleation and easy to form larger nanoparticle a superheated bubble expands until it reaches a critical volume, and after that collapses. The ablation event causes many bubbles to be ejected normal to the surface of the rod but the collapse is not proficient by all bubbles, as there are some that reach the surface. Based upon these results, the bubbles that survive to

reach the surface contain a mixture of volatile gases such as H_2 , CO , CO_2 , as well as small hydrocarbon species. The gases are formed as a direct result of the high energy from the laser irradiation, which is sufficient to break the carbon-hydrogen bonds. During collapse, confined species are subjected to extremely high pressures, which may contribute to the formation of the nanoparticles. The collapse of the bubble also effectively binds solvent molecules to the nanoparticles.

These ethanol molecules form a shell which prevents the nanoparticle from undergoing further reaction. Therefore the solvent molecules surrounding the particles and serve to protect the formed nanoparticles from oxidation [10-12].

Also increasing fluence results in a shift in the size distribution to larger sizes. The shift is due to the presence of more particles at larger sizes, because too high laser fluences, may cause a coalescence or melt of the adjacent particles, which may be not suitable for some applications requiring individual particles. Nanoparticles greater than 100 nm were found at two fluence in this case; these nanoparticles have been excluded from the histogram and calculated averages to provide more accurate representation of the dominant species. The average size of samples L1 & L2 is about 85 nm & 110 nm respectively.

Figure 5 shows the absorption spectra of alumina nanoparticles in Ethanol. The absorption spectra of the particles synthesized showed a strong absorption in the UV range with the maximum absorbance at around 213 nm in sample L1 and 238 nm in sample L2. As mentioned above the difference in the absorbance belongs to the difference in the concentration of nanoparticles in suspension thus the concentration of NPs in sample L1 more than NPs concentration in sample L2.

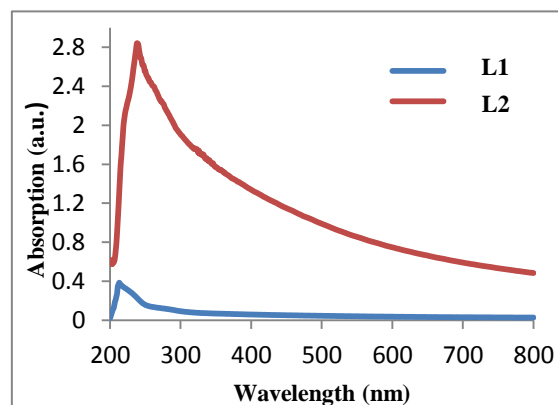


Fig. 5 Shows the absorption spectra of Al_2O_3 NPs in ethanol at two different fluences.

4. Conclusions

In summary, the present research work has successfully demonstrated that alumina nanoparticles with a size of less than 100 nm can be easily produced via laser ablation in ethanol solution with less oxide cladding and different nanostructures formation at different values of laser fluences. The results indicate that lower laser fluences results in higher ablation efficiency and finer spherical nanoparticles in contrast an increase of fluence leads to the formation of larger nanoparticles and most of these NPs were aggregated. However, too high fluences may cause a coalescence or melt of the adjacent particles, which may be not suitable for some applications requiring individual particles and too low energy may have problems with a large fragment of alumina that did not ionized by the laser beam.

This convenient production strategy can be applied as a general approach that Al_2O_3 NPs have attracted significant interest of materials scientists and physicists due to their special properties and have attained a great importance in several technological applications such as industrial applications.

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References

- [1]. Piriya Wong V., V. Thongpool, P. Asanithi, P. Limsuwan, "Effect of Laser Pulse Energy on the Formation of Alumina Nanoparticles Synthesized by Laser Ablation in Water", *Surface Science Direct*, 32, pp. 1107-1112, 2012.
- [2]. Liu Z., Y Yuan, S Khan, A Abdolvand, D Whitehead, M Schmidt and L Li, "Generation of Metal-Oxide Nanoparticles using Continuous-Wave Fibre Laser Ablation in Liquid", *Journal Micromech. Microeng.*, 19, pp. 1-7, 2009.
- [3]. Krishna G. i, S. Hamad, S. Sreedhar, P. Tewari, S. Venugopal, "Fabrication and characterization of aluminum nanostructures and nanoparticles obtained using femtosecond ablation technique", *Chemical Physics letters*, 530, pp. 93-97, 2012.
- [4]. Viau G., V. Collière, G.A. Shafeev, "Internal structure of nanoparticles of Al generated by laser ablation in liquid ethanol", *Chemical Physics Letters*, 501, pp. 419-422, 2011.
- [5]. Baladi A., "Effect of laser wavelength and ablation time on pulsed laser ablation synthesis of Al nanoparticles in ethanol", *International Journal of Modern Physics: Conference Series Vol. 5*, pp. 58-65, 2012.
- [6]. Arash B., Rasoul S., "Investigation of different liquid media and ablation times on pulsed laser ablation synthesis of aluminum nanoparticles", *Applied Surface Science*, 256, pp. 7559-7564, 2010.
- [7]. Lukić, I · Krstić, J · Jovanović, D. Skala, "Alumina/silica supported K_2CO_3 as a catalyst for biodiesel synthesis from sunflower oil", *Journal Bioresource Technology*, 2009.
- [8]. Al-Mamun S., Nakajima R., Zhu X., Ishigaki T., "Generation of alumina nanoparticles by a nanosecond laser-induced liquid plasma in water", *Optics Express*, 17, pp. 12650-12659, 2009.
- [9]. Suha I. Alnassar, Adel K. M., Zainab F. M., "Study the Effect of Sodium Dodecyl Sulfate Surfactant Solution on the Production of Zirconia (ZrO_2) Nanoparticles Synthesized by Laser Ablation Technique", *Second International Conference on Advanced Manufacturing and Automation (INCAMA'13)* 28th to 30th March, 2013.
- [10]. Justin S.G., "Formation and characterization of nanoparticles via laser ablation solution", M.Sc. Thesis submitted to Pennsylvania State University, the Graduate School, Department of Chemistry, 2007.
- [11]. Yavas O., A. Schilling, J. Bischof, J. Boneberg, P. Leiderer, "Bubble nucleation and pressure generation during laser cleaning of surfaces", *Applied Physics/Materials Science and Processing*, 64, pp. 331-339, 1997.
- [12]. Schilling A., O. Yavas, J. Bischof, J. Boneberg, and P. Leiderer, "Absolute pressure measurements on a nanosecond time scale using surface plasmons", *Applied Physical Letters* 69, pp. 4159-4161, 1996.