Hindawi
Journal of Nanomaterials
Volume 2020, Article ID 1327868, 5 pages
https://doi.org/10.1155/2020/1327868

Research Article

Synthesis and Characterization of Aluminum Nanoparticles Prepared in Vinegar Using a Pulsed Laser Ablation Technique

Reem M. Altuwirqi, Bayan Baatiyah, Eman Nugali, Zeina Hashim, and Hala Al-Jawhari

Physics Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

Correspondence should be addressed to Reem M. Altuwirqi; raltuwirqi@kau.edu.sa

Received 16 July 2019; Accepted 30 December 2019; Published 9 January 2020

Academic Editor: Giuseppe Compagnini

The second harmonic wavelength of a neodymium-doped yttrium-aluminum-garnet (Nd-YAG) laser ($\lambda = 532$ nm) was used in a pulsed laser ablation technique (PLAL) to synthesize aluminum nanoparticles suspended in white vinegar from an aluminum target. The nanoparticles were characterized by HRTEM and UV-Vis spectrophotometry. They were found to range in size between 2 and 50 nm in diameter, with an average diameter of 12 ± 9 nm. The nanoparticles had a maximum absorption peak at 237 nm and were found to exhibit a core-shell structure with an Al core coated by a thin layer of an amorphous material which could be attributed to amorphous carbon. HRTEM results revealed that the small nanoparticles (<20 nm) had an fcc phase of aluminum crystalline structure, where the larger particles represented alumina (γ-Al_2O_3) nanoparticles. Such observation suggests that the use of white vinegar as an ablation medium could facilitate the synthesis of aluminum nanoparticles with minimal evidence of the existence of aluminum oxide nanoparticles in the resultant suspension.

1. Introduction

Aluminum nanoparticles (Al NPs), nowadays, have attracted a great interest due to their significant and diverse applications. They are found to be perfect catalysts for rocket fuel reactions [1], with many other promising applications in biomedical [2] and antimicrobial [3] fields. Yet, the synthesis of high purity Al nanoparticles is a major challenge due to their capability to oxidation forming Al_2O_3 nanoparticles instead [4]. In recent years, pulsed laser ablation in liquid (PLAL) has emerged as a promising method for producing pure active metal nanoparticles [5]. PLAL is a simple one-step method in which a bulk or powder metal target is placed in an aqueous solution and irradiated with laser pulses of a short period of time, typically about a few nanoseconds. PLAL is considered as a simple and low-cost technique that does not require any vacuum apparatus [6]. It could provide size-controlled nanoparticles without any chemical contamination [7].

However, the nanomaterials obtained through this method depend greatly on the used liquid medium [8, 9], laser wavelength [10], laser energy [11–13], and irradiation time [8] along with other parameters. Applying the first harmonic wavelength of a Nd:YAG laser ($\lambda = 1064$ nm), irradiated aluminum targets immersed in ethanol, acetone, or ethylene glycol resulted in Al nanoparticles with different diameters ranging between 30 and 100 nm [8, 9]. It was noticed that finer particles (mean diameter of 30 nm) were obtained in acetone [8] or ethanol [9], when longer ablation durations are applied [8]. Likewise, irradiated aluminum targets in dry tetrahydrofuran (with or without the addition of oleic acid) resulted in Al nanoparticles with an average size of 21 nm [14]. One reason for using oleic acid in this reaction is to serve as a surfactant that decreases aggregation. It has been reported that the pH of the liquid medium in PLAL affects the sizes and surface charge of the synthesized nanoparticles [6]. On the other hand, when pure Al nanoparticles are needed, a prevention of oxide formation is required. One method for achieving this is by introducing hydrocarbons, such as oleic acid, which reduce the Al/O ratio and minimize the oxidation of the nanoparticles [14].

In this work, we demonstrate the ability of fabricating Al nanoparticles in an acidic medium using the PLAL technique. The second harmonic wavelength (532 nm) of a

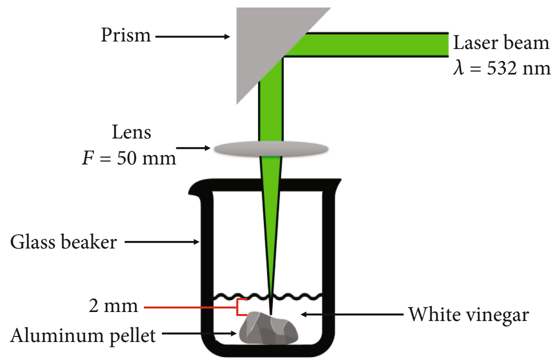


FIGURE 1: A schematic diagram of the experimental setup used in the fabrication of Al nanoparticles by laser ablation in vinegar.

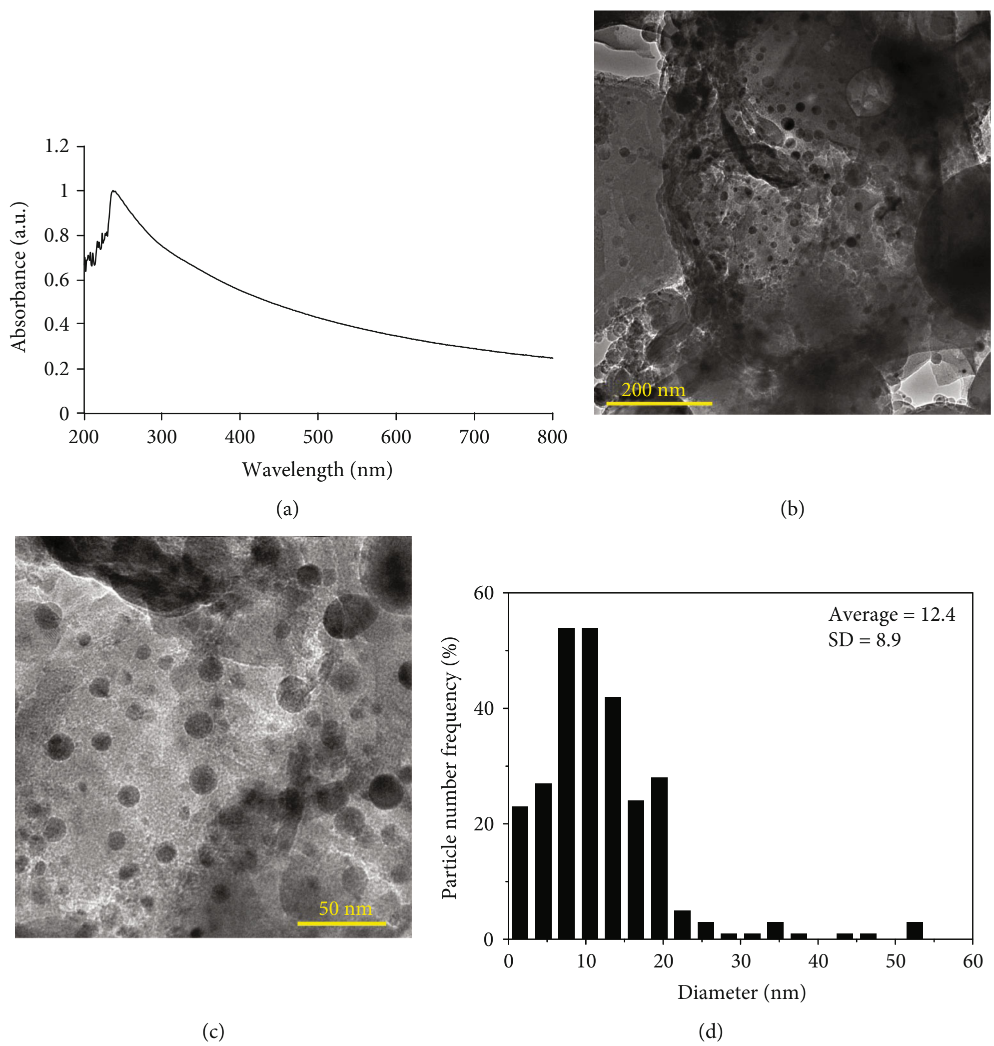


FIGURE 2: (a) UV-Vis absorption spectrum. (b, c) TEM images at two different magnifications. (d) Plots of particle size distribution of Al nanoparticles obtained with PLAL in vinegar.

Nd:YAG laser was employed as a laser source, while white vinegar has been used as a liquid medium. To the best of our knowledge, no previous work has used vinegar in the preparation of aluminum nanoparticles using PLAL.

2. Experiment

Aluminum pellets 99.99% trace metal basis (Sigma-Aldrich) with the dimensions of 3–12 mm were used as targets, and

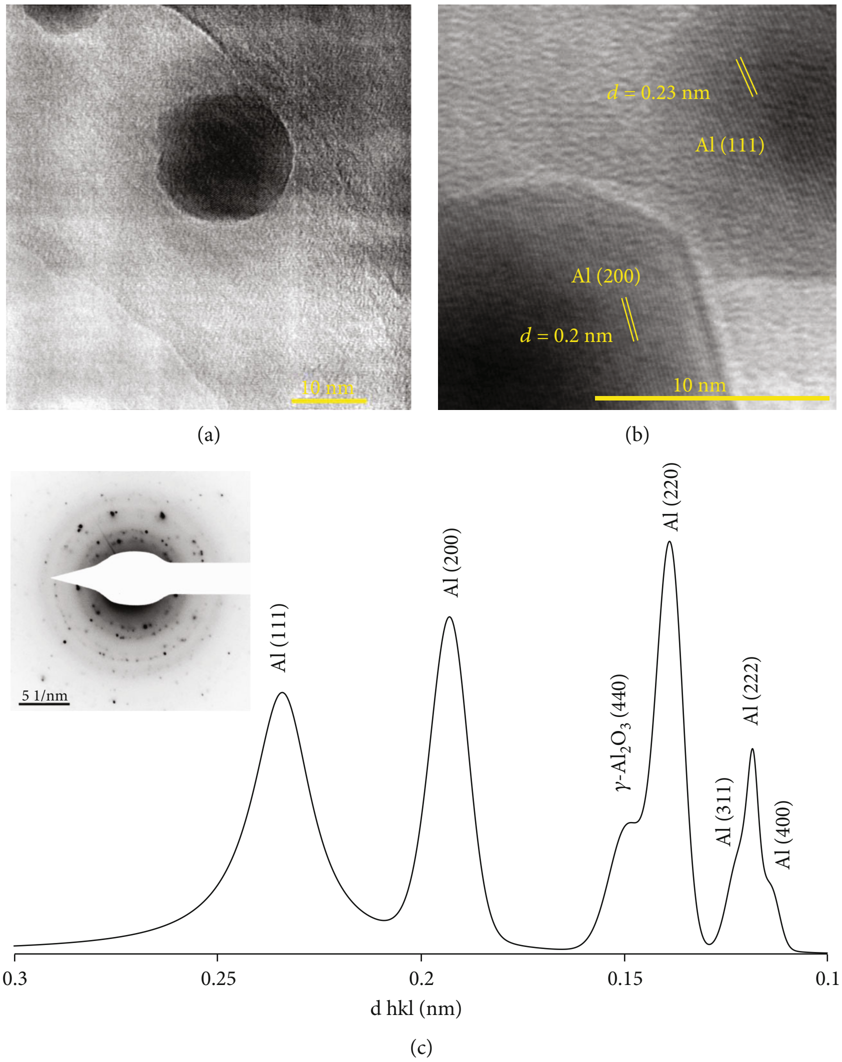


Figure 3: (a) HRTEM of Al particles obtained with PLAL. (b) Zoom of the core of the fabricated particles showing the Al (200) and Al (111) orientation. (c) SAED pattern and plot.

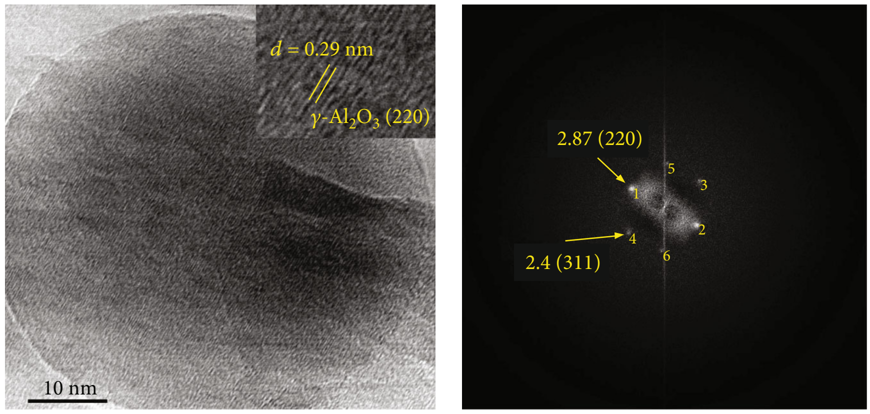
highly acidic white vinegar with a pH of 2 was used as the medium. The white vinegar used is this work is an organic substance found in the local market with acidity not less than 5%. In a typical experiment, the pellet was polished with sand paper to remove any corrosion on its surface just before ablation, then washed with acetone. The pellet was then placed in a glass beaker and covered with white vinegar (level ~2 mm above the target). The beaker was then positioned on an XY stage to allow the movement of the target under the laser beam. This procedure was necessary to avoid the formation of a deep crater on the target surface.

The second harmonic wavelength of a Nd:YAG laser ($\lambda = 532$ nm, Quanta Ray, Spectra Physics) was used with a laser repetition rate of 10 Hz and a pulse length of 6 ns. The laser power was set to 2 W. The laser beam was focused on the surface of the target using a 50 mm lens, and the target was irradiated for 15 min. The experiment was conducted in ambient conditions. Figure 1 shows a schematic diagram of the experimental setup. After irradiation, the pellets were removed and the solution was analyzed using UV-Vis spectrophotometry (Thermo, Genesys 10S). Structural and morphological properties of the nanoparticles were investigated using HRTEM (Tecnai G2 F20 Super Twin TEM microscope). The pallet was weighted before and after the ablation process to determine the mass of the suspended particles in the solution.

3. Results and Discussion

Spherical aluminum nanoparticles suspended in white vinegar resulted from the 532 nm Nd:YAG laser ablation of the submersed aluminum target after 15 minutes of exposure. The suspended aluminum mass was calculated to be 3.8 mg which indicates the formation of a considerable quantity of nanomaterials.

The absorption spectrum of the nanoparticle solution suspension is shown in Figure 2(a). The spectrum shows a single peak below the visible range, with the maximum absorption at 237 nm. The presence of such a peak (below 250 nm) indicates the formation of aluminum nanoparticles



(a) (b)

Figure 4: (a) HRTEM of γ-Al_2O_3 nanoparticles obtained with PLAL. Inset shows the (220) orientation. (b) Fourier transform image of lattice.

in the suspension [8]. Previous studies [8, 13, 15] reported that a peak around 200 nm corresponds to nanoparticles in the range of 10 nm in diameter and that a red shift is associated with larger particles [13]. Moreover, Figure 2(a) shows a wide absorption shoulder in the domain 300–400 nm, which is attributed to nanoparticles with a core-shell structure [13, 15]. TEM images of the suspension, as illustrated in Figures 2(b) and 2(c), indicate the existence of nanospheres varying in size from 2 nm to 50 nm. The measurements of the nanoparticles were taken directly from the TEM images using the ImageJ software. The size distribution of those nanoparticles was then plotted and illustrated in Figure 2(d) where the average diameter was found to be 12 ± 9 nm.

By investigating the nanoparticles of the different sizes, it was noticed that the smaller nanoparticles (<20 nm) have a different structure than the larger ones. Zooming into the smaller nanoparticles with the HRTEM analysis (Figures 3(a) and 3(b)), the rectilinear distance in the crystal structure of the particles can be seen to be 0.2 nm and 0.23 nm which corresponds to (200) and (111) planes of fcc aluminum, respectively. This is further confirmed by the Selected Area Electron Diffraction (SAED) analysis shown in Figure 3(c) where its plot shows the existence of Al (111), (200), (311), (222), and (400) with the onset of γ-Al_2O_3 (440) based on the Joint Committee on Powder Diffraction Standard-International Center for Diffraction Data (JCPDS-ICDD) Card nos. 85-1327 for pure Al and 29-0063 for γ-Al_2O_3. Additionally, the particles exhibit a core-shell structure with Al at the core and coated by a thin layer. The nature of the coated thin layer may require further investigation. It is predicted that the thin layer could be alumina (Al_2O_3) or amorphous carbon that originates from the decomposition of the vinegar medium during the laser ablation [8].

For larger nanoparticles (>50 nm), shown in Figure 4(a), the HRTEM structure shows a grain orientation of (220) and a lattice spacing of 0.28 nm which correspond to γ-Al_2O_3 nanoparticles. This is further confirmed by the Fourier transform image of the lattice in Figure 4(b), which indicates the presence of the (220) and (311) orientations of γ-Al_2O_3. It is worth mentioning that the intensity of the (311) phase of γ-Al_2O_3 is very weak; hence, it did not appear in the SAED pattern in Figure 3(c).

According to the TEM images, nanoparticle size distribution, and SAED pattern (Figures 2 and 3), it could be concluded that the amount of Al nanoparticles in the prepared solution exceeded that of Al_2O_3. Specifically, the ratio of Al/Al_2O_3 was found to be around 9.5. This might be attributed to the abundance of H^+ ions in acidic medium, which makes O^{2-} ions resulted from photolysis and thermolysis prefer to combine with H^+ ions. Consequently, most of the Al^{3+} ions miss the chance to recombine with O^{2-} ions and exist in the form of metallic Al [14, 16].

From a crystalline structure point of view, aluminum oxide (alumina; Al_2O_3) has many forms [17, 18]. These different forms are called "transition alumina" and are denoted by the prefixes γ, δ, θ, κ, χ, η, and ρ. The alumina changes from one form to another due to the increase in temperature. The final product of this transition alumina is the α-Al_2O_3, which is regarded as the most stable form. Under our experimental condition, the final product of the alumina transformation was the γ-Al_2O_3, that is, the temperature was not high enough to reach the α-Al_2O_3 phase.

4. Conclusion

As a conclusion, aluminum and alumina (γ-Al_2O_3) nanoparticles, suspended in white vinegar, were synthesized using a PLAL technique. The aluminum nanoparticles were more abundant and varied in size between 2 and 50 nm, with an average diameter of 12 ± 9 nm. However, very limited number of alumina nanoparticles was found with sizes above 50 nm in diameter. Alumina nanoparticles could be caused by the reaction of the Al pellets with oxygen resulting from the decomposition of the white vinegar by the laser pulses. The white vinegar, which was used here as an ablation medium for the first time as per our knowledge, acted as an oxidation-inhibitor facilitating the synthesis of aluminum nanoparticles with minimal alumina nanoparticles.

Data Availability

The HRTEM images and excel files used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are thankful to the Science Research and Innovation Unit in the Faculty of Sciences and KAU Endowment (WAQF) at King Abdulaziz University, Jeddah, Saudi Arabia for supporting this work (Grant Number: Scigriu38/10).

References

[1] L. Galfetti, L. T. D. Luca, F. Severini et al., "Nanoparticles for solid rocket propulsion," *Journal of Physics: Condensed Matter*, vol. 18, no. 33, pp. S1991–S2005, 2006.

[2] P. Hassanpour, Y. Panahi, A. Ebrahimi-Kalan et al., "Biomedical applications of aluminium oxide nanoparticles," *Micro & Nano Letters*, vol. 13, no. 9, pp. 1227–1231, 2018.

[3] L. Wang, C. Hu, and L. Shao, "The antimicrobial activity of nanoparticles: present situation and prospects for the future," *International Journal of Nanomedicine*, vol. 12, pp. 1227–1249, 2017.

[4] C. O. Nyapete, A. H. H. Benziger, S. W. Buckner, and P. A. Jelliss, "Fabrication and characterization of aluminum nanoparticles entrapped in hollow polymer capsules," *Nano-Structures & Nano-Objects*, vol. 16, pp. 282–287, 2018.

[5] T. Sasaki, Y. Shimizu, and N. Koshizaki, "Preparation of metal oxide-based nanomaterials using nanosecond pulsed laser ablation in liquids," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 182, no. 3, pp. 335–341, 2006.

[6] S. A. Al-Mamun, R. Nakajima, and T. Ishigaki, "Tuning the size of aluminum oxide nanoparticles synthesized by laser ablation in water using physical and chemical approaches," *Journal of Colloid and Interface Science*, vol. 392, pp. 172–182, 2013.

[7] D. Sapkota, Y. Li, O. R. Musaev, J. M. Wrobel, and M. B. Kruger, "Effect of electric fields on tin nanoparticles prepared by laser ablation in water," *Journal of Laser Applications*, vol. 29, no. 1, article 012002, 2017.

[8] A. Baladi and R. S. Mamoory, "Investigation of different liquid media and ablation times on pulsed laser ablation synthesis of aluminum nanoparticles," *Applied Surface Science*, vol. 256, no. 24, pp. 7559–7564, 2010.

[9] M. H. Mahdieh and B. Fattahi, "Size properties of colloidal nanoparticles produced by nanosecond pulsed laser ablation and studying the effects of liquid medium and laser fluence," *Applied Surface Science*, vol. 329, pp. 47–57, 2015.

[10] H. R. Dehghanpour, "Al nanoparticles generation and characterization by Nd:YAG laser ablation in deionized water," *Optik*, vol. 127, no. 13, pp. 5380–5382, 2016.

[11] V. Piriyawong, V. Thongpool, P. Asanithi, and P. Limsuwan, "Effect of laser pulse energy on the formation of alumina nanoparticles synthesized by laser ablation in water," *Procedia Engineering*, vol. 32, pp. 1107–1112, 2012.

[12] V. Piriyawong, V. Thongpool, P. Asanithi, and P. Limsuwan, "Preparation and characterization of alumina nanoparticles in deionized water using laser ablation technique," *Journal of Nanomaterials*, vol. 2012, Article ID 819403, 6 pages, 2012.

[13] V. Damian, I. Apostol, D. Apostol et al., "Correlation between irradiation conditions and nanoparticles obtained in case of laser ablation of aluminum targets in liquids," *Optics & Laser Technology*, vol. 59, pp. 93–98, 2014.

[14] C. A. Crouse, E. Shin, P. T. Murray, and J. E. Spowart, "Solution assisted laser ablation synthesis of discrete aluminum nanoparticles," *Materials Letters*, vol. 64, no. 3, pp. 271–274, 2010.

[15] M. H. Mahdieh and H. Mozaffari, "Characteristics of colloidal aluminum nanoparticles prepared by nanosecond pulsed laser ablation in deionized water in presence of parallel external electric field," *Physics Letters A*, vol. 381, no. 38, pp. 3314–3323, 2017.

[16] F. Luo, Y. Guan, W. Ong et al., "Enhancement of pulsed laser ablation in environmentally friendly liquid," *Optics Express*, vol. 22, no. 20, pp. 23875–23882, 2014.

[17] T. Shirai, H. Watanabe, M. Fuji, and M. Takahashi, "Structural properties and surface characteristics on aluminum oxide powders," セラミ⊠クス基盤工学研究センター年報, vol. 9, 2009.

[18] P. S. Santos, H. S. Santos, and S. P. Toledo, "Standard transition aluminas. Electron microscopy studies," *Materials Research*, vol. 3, no. 4, pp. 104–114, 2000.