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1. **Draft manuskrip sebelum proses submission**

THE ROLE OF LASER FLUENCE, PULSE REPETITION RATE, AND LIQUID MEDIA IN THE CHARACTERISTICS OF GOLD NANOPARTICLES PRODUCED BY THE LASER ABLATION METHOD USING Nd:YAG LASER 1064 NM AT LOW ENERGY

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ABSTRACT
Pulse laser ablation method using an Nd:YAG laser operated at low-energy laser of 30 mJ has been successfully employed to produce gold nanoparticles. The role of laser pulse repetition rate, laser fluence, and liquid media on the characteristics of the nanoparticles produced, such as particle shape and distribution of particle size, were examined. In this study, an Nd:YAG laser beam (1064 nm, 7 ns) with low energy of 30 mJ was irradiated on a high-purity gold plate (99.95%), which is immersed in a liquid media. A small, luminous plume was induced just above the sheet surface and finally producing gold nanoparticles dispersed in the liquid. The results certified that the average particle diameter and size distribution depended on some parameters of the pulse repetition rate, laser fluence and liquid media used in the synthesis process. The diameters of the GNPs increased when the laser fluence or pulse repetition rate were increased. The particle diameters also changed with a change in the liquid media, the diameters were much larger for aquades compared to ethanol. However, the shape of the GNPs was the same for these parameters. Namely, the GNPs produced by this laser ablation method had a spherical shape. By understanding the effects of these parameters on the characteristics of the GNPs produced by laser ablation method using low-energy Nd:YAG laser, GNPs having specific characteristics can be synthesized for specific applications.

*Keywords***:** GNPs, Gold nanoparticles, Low-energy Nd:YAG laser, laser ablation method, laser fluence, pulse repetition rate, low energy of laser pulse

1. INTRODUCTION

Many scientists and researchers are interested in studying and developing nanoparticles (NPs) for various applications due to their specific characteristics (Zhang et al., 2016, Tran et al., 2013, Mieszawska et al., 2013). NPs have minute size with a diameter of 1 to 100 nm. Recently, production of gold nanoparticles (GNPs) has been made for some applications, such as sensor (Nath and Chilkoti, 2002, Raj et al., 2003), photonics device (Parker and Townley, 2007), catalyst (Turner and Golovko, 2008), and medical applications (Huang et al., 2007, Zhang et al., 2008, Giljohann et al., 2010). Due to their specific properties, GNPs were employed as radiosensitizers, contrast agents, and for drug delivery in the medical field (Butterworth et al., 2012, Cole et al., 2015, Dreaden et al., 2014, Jain et al., 2012).

Colloidal GNPs were first produced by Faraday using a chemical method to reduce gold chloride with phosphorous as a stabilizer (Mie, 1908). Various methods were then developed for the synthesis of GNPs, such as electrochemical deposition, seeded growth, and vapor phase deposition (Rad et al., 2011). However, chemical methods require additional chemical constituents and surfactants during the production process, and, therefore, the GNPs are of lesser purity. Production of high-purity GNPs is necessary for applications in medical field in order to ensure human health. Therefore, alternative methods for synthesis of GNPs are necessary. One such recent method used to produce GNPs is a green process using plants (Aroma et al., 2012).

A physical method based on a pulse laser has been developed as well. This technique conducts NPs synthesis in liquid, producing colloidal NPs (Giorgetti et al., 2012). Experimentally, a laser beam was irradiated by a convex lens on a high-purity metal sheet placed in a liquid medium. Small, luminous plasma is induced just above the sample. The plasma then expands and interacts with the liquid, and, finally, metal NPs are produced in the liquid medium. The metal NPs produced by using this pulse laser ablation (PLA) method have a high purity compared to those produced by conventional methods, such as the chemical method (Al-Azawi et al., 2015). This is because a high-purity metal sample is employed and the synthesis process does not involve additional chemical agents and stabilizers. These NPs are very suitable for specific medical applications which require high-purity NPs, such as being used as contrast agents, for drug delivery, and as radiosensitizers in, for example, cancer and tumor therapy. The PLA method has been applied to the synthesis of silver NPs (AgNPs) and GNPs (Compagnini et al., 2004, Tsuji et al., 2002). Many parameters and variables play an important role in the characteristics of the NPs produced using the PLA method (Abbasi and Dorranian, 2015). These parameters include laser energy, laser pulse repetition rate, and liquid media when metal NPs are produced (Al-nassar et al., 2015, Solati et al., 2013, Zamiri et al., 2013). However, based on our knowledge, the neodomium yttrium aluminium garnet (Nd:YAG) laser pulse used for material ablation in PLA method usually uses high-energy laser (more than 50 mJ) for gold nanoparticle synthesis as reported in elsewhere (Al-Azawi et al., 2015; Shukri et al., 2015).

In this present study, a pulse laser ablation method using Nd:YAG laser operated at low-energy of 30 mJ was employed to produce gold nanoparticles in liquid media. The effects of laser pulse repetition rate, laser fluence, and liquid media in the synthesis of colloidal GNPs using a quiet, low-energy Nd:YAG laser were examined.

2. METHODOLOGY/ EXPERIMENTAL

The basic experimental arrangement for this study is displayed in Fig. 1. A metal gold with high purity (99.95%) was immersed in 10 ml pure aquades placed in a petri dish (a diameter of 50 mm). A laser beam (Nd:YAG laser, New polaris II 1064 nm, max energy of 50 mJ, 7 ns) was irradiated on the gold plate via convex lens (30 mm in focal length). The laser energy and laser repetition rate were set at 30 mJ and 10 Hz, respectively. The laser was bombarded on the gold plate for 20 minutes. During laser irradiation, the gold plate was moved in the XY direction so that the laser always impinged on the new surface of the gold sample in order to obtain homogeneous colloidal GNPs.

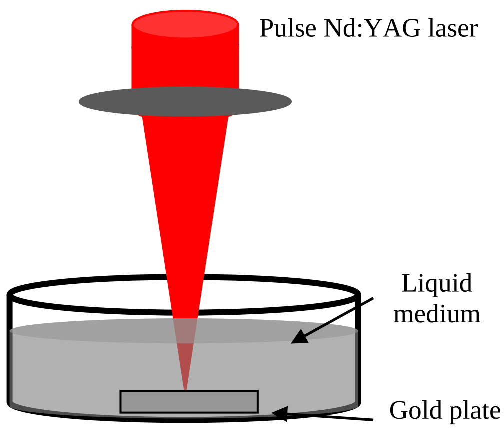


Figure 1. Experimental arrangement used in this study

Various analytical methods were employed for the characterization of the GNPs. The optical properties and surface plasma resonance of the product were characterized by ultra-violet visible (UV-Vis) absorption spectrometer. In addition, scanning electron microscopy – energy diffraction x-ray (SEM-EDX, JEOL JED-2300) was used to study the morphology of the product. Finally, particle size and size distribution were measured using aparticle size analyzer (DelsaNano).

3. RESULTS AND DISCUSSION

The mechanism of PLA-NPs production has been suggested by Semaltianos (Semaltios, 2010). When a pulse laser is irradiated on a solid material target, such as a metal, the laser energy is transferred to the material, and a heating process takes place on the material surface. Due to the high intensity of the laser beam focused on a small region, the material is melted and serious ablation occurs by ejection of excited species and neutrals from the material's surface in the form of high-density luminous plasma. The plasma further expands very fast adiabatically and compresses the surrounding environment, finally cooling down after several microseconds. In the case of a liquid environment, the expanding plasma will be confined much more strongly than it would be in a gas environment, affecting physical properties of the plasma. The confinement of the expanding plasma to the liquid environment also results in a higher- temperature plasma than a gas environment could produce. These two plasmas are mixed, and, therefore, chemical reactions may occur within the mixed plasma. For example, the ablation of a metallic target in water produces metal oxide NPs, with oxygen having been contributed by the water. In this study, the roles of laser fluence, laser pulse repetition rate, and liquid environment in the production of GNPs are discussed.

3.1. Role of laser fluence

Firstly, the role of laser fluence on the characteristics of GNPs was examined. Figure 2 displays the spectra of gold nanoparticles prepared by using UV-Vis spectroscopy. Two different laser fluencies were applied during the experiment, the blue and red lines in Fig. 2 represent the spectrum with a laser fluence of 4 J/cm^2 and 6 J/cm^2, respectively. The GNPs were prepared using the Nd:YAG laser with a repetition rate of 10 Hz and laser beam bombardment duration on gold surface of 20 minutes.

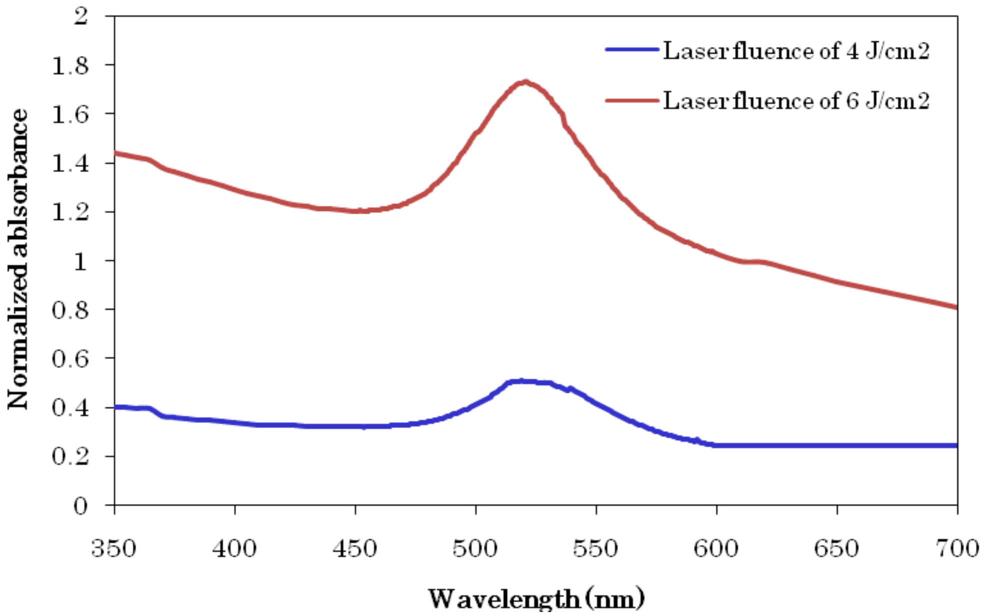
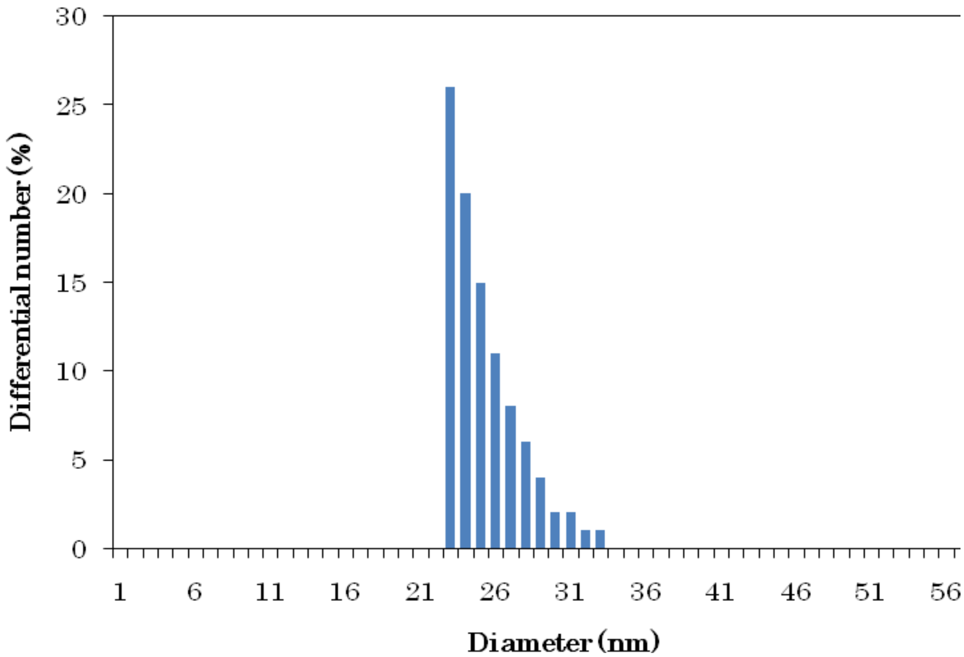


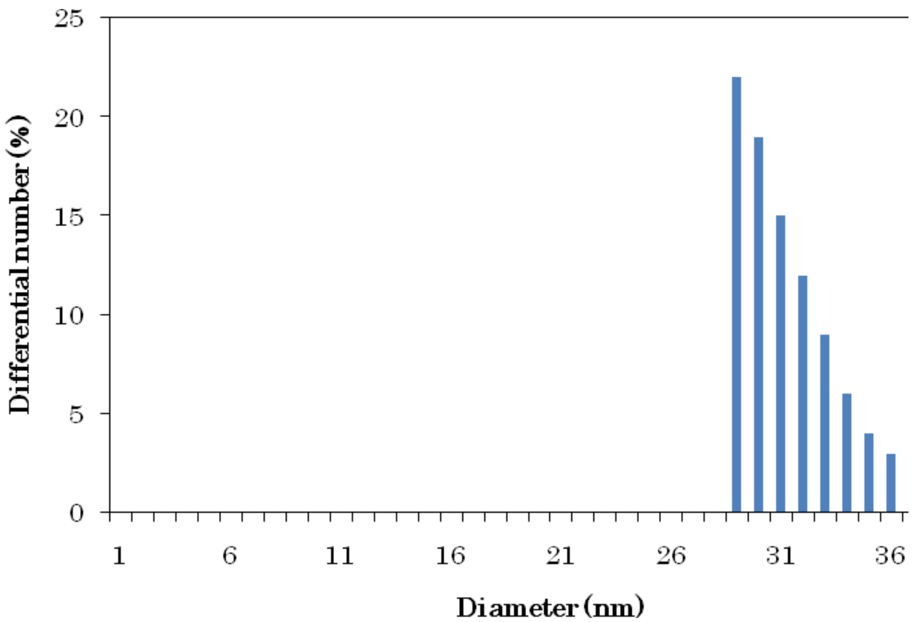
Figure 2. Spectra of gold nanoparticles synthesized by using the pulse laser ablation method with different laser fluencies of (a) 4 J/cm^2 and (b) 6 J/cm^2

The peak of the surface plasmon resonance (SPR) of the GNPs appears clearly for both laser fluences, 4 and 6 J/cm^2. The SPR peak occurs at 519 nm for 4 J/cm^2, and at 521 nm for 6 J/cm^2. The peak shifts by 2 nm toward a longer wavelength with an increment in laser fluence from 4 to 6 J/cm^2, indicating that particle size increases with an increase in laser fluence. This phenomenon was also confirmed by measuring the particle size of GNPs using PSA.

Figures 3(a) and 3(b) display the distribution of the diameters of the particles obtained by using a PSA technique with laser fluences of 4 and 6 J/cm^2, respectively.



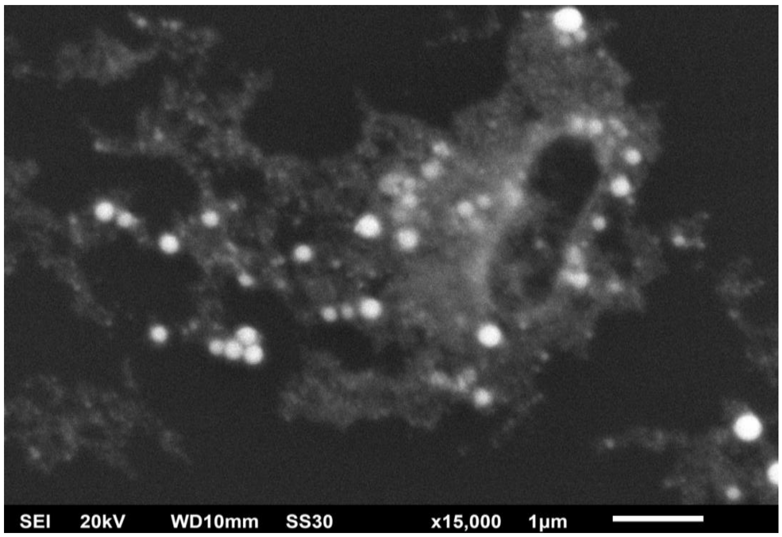
(a)



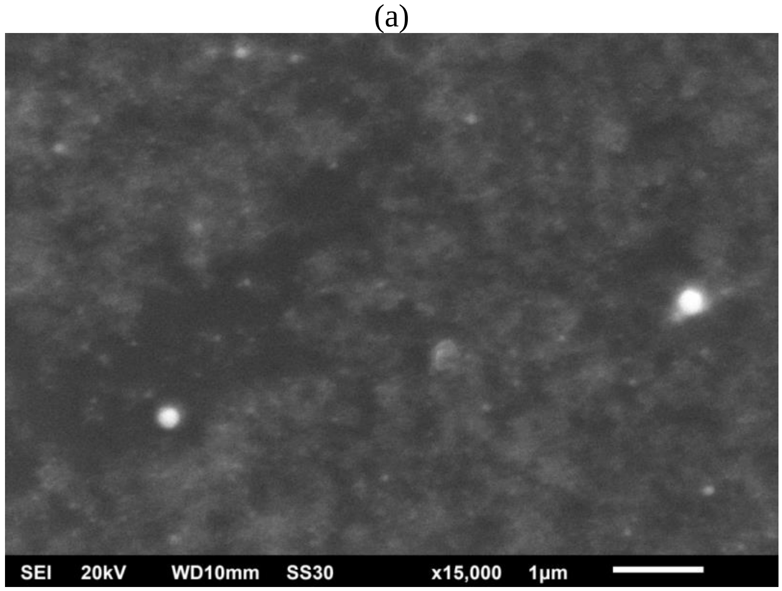
(b)

Figure 3 Diameters of gold nanoparticles produced by laser fluencies of (a) 4 J/cm^2 and (b) 6 J/cm^2

For 4 J/cm^2 in laser fluence, the average diameter is 26 nm ± 4 nm, while they are 32 nm ± 5 nm, respectively, for the case of 6 J/cm. This result certifies that increasing the laser fluence increased the size of the GNPs produced. This is a similar pattern with the results reported by Solati et al. in the synthesis of silver NPs by the PLA technique using an Nd:YAG laser at fundamental wavelength, namely that NPs increase in size and have a broader size distribution with increased laser fluence (Solati et al., 2013). It is assumed that the changes in nanoparticle size and size distribution are due to the explosive ejection of material surface by a high density laser beam. In the case of higher laser fluence, the distribution of particles ejected from the surface increases (Nichols et al., 2006).



(a)



(b)

Figure 4 Photographs of gold nanoparticles obtained by SEM-EDX technique using laser fluencies of (a) 4 J/cm^2 and (b) 6 J/cm^2

To study the morphology of the produced GNPs, the SEM-EDX technique was used. Figures 4(a) and 4(b) show the photographs of GNPs obtained by using the current PLA method. All GNPs show a spherical shape with various diameters. This measurement result confirms the indications of nanoparticle shape displayed in Fig. 2, namely that the absorption spectrum has a single SPR peak. This certifies that the GNPs were successfully synthesized in a spherical shape.

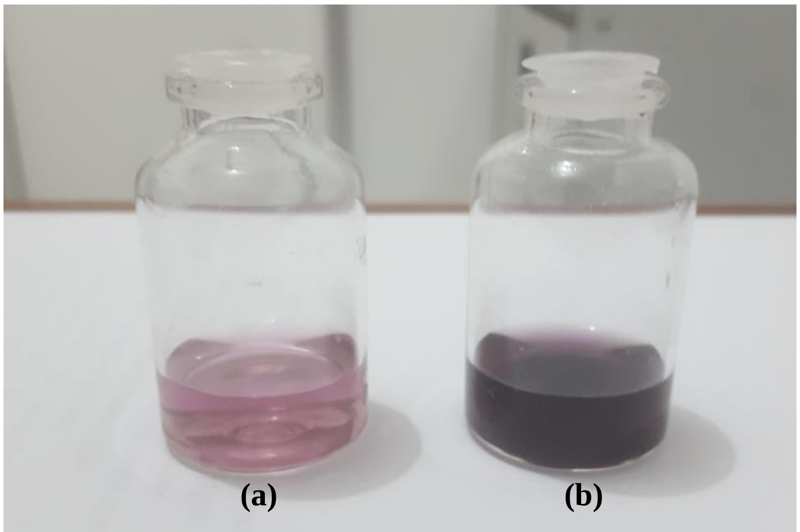


Figure 5 Photographs of colloidal gold nanoparticles produced by laser fluencies of (a) 4 J/cm^2 and (b) 6 J/cm^2

Figure 5 shows the photographs of GNP colloids produced by the current PLA method, Figure 5(a) represents the GNP product obtained when the laser fluence was 4 J/cm^2, while Fig. 5(b) represents the product for 6 J/cm^2 in laser fluence. The color of the colloids changes from light to dark red with the increase in laser fluence. This indicates that the number of GNPs produced by PLA increases by increasing the laser fluence. This result is confirmed by the higher absorption intensity for the higher laser fluence, as depicted in Figure 2.

3.2. Role of pulse repetition rate

The role of the pulse repetition rate in the characteristics of GNPs produced by the current PLA technique was studied next. Figure 6 displays the spectra of GNPs obtained by UV-Vis spectroscopy technique for laser pulse repetition rates of 10 Hz (dotted blue line) and 15 Hz (fixed red line). The single SPR peak occurs clearly for both the10 and 15 Hz repetition rates, indicating that the GNPs produced by this PLA technique have a spherical shape. The increase in the absorbance values at 15 Hz indicates that ablation efficiency effectively increases with increasing repetition rate (Xu et al., 2012).

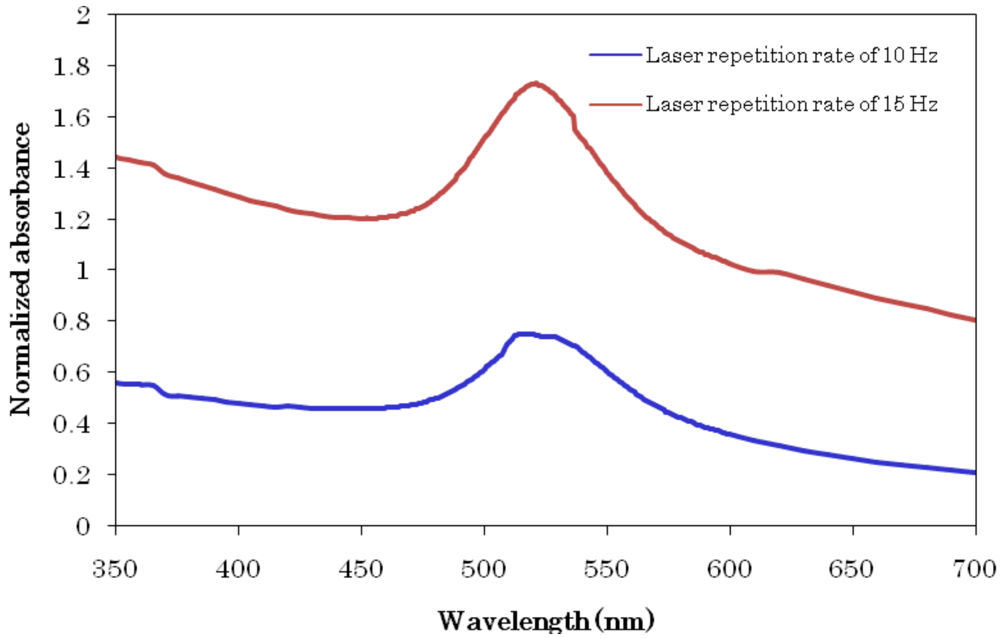
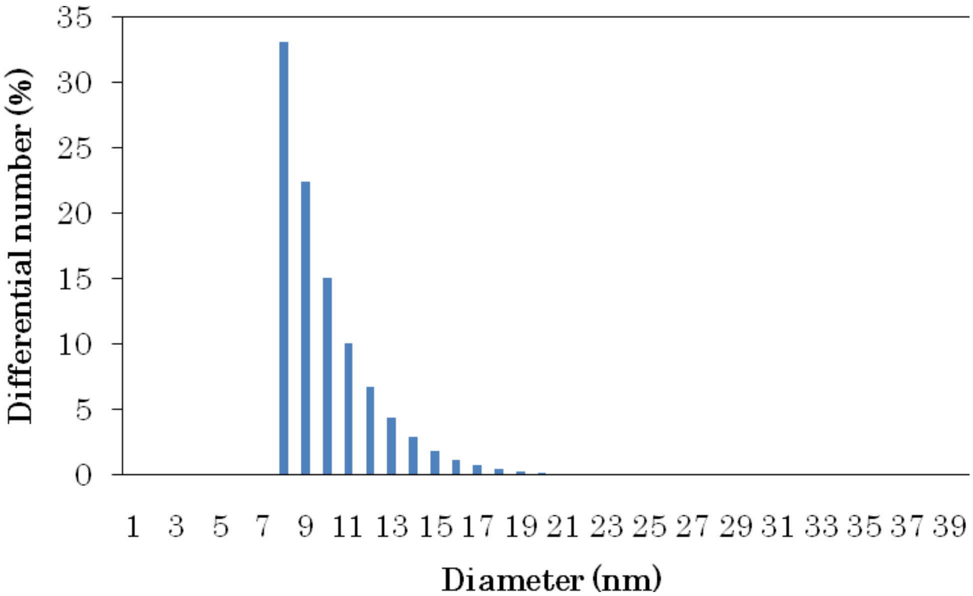
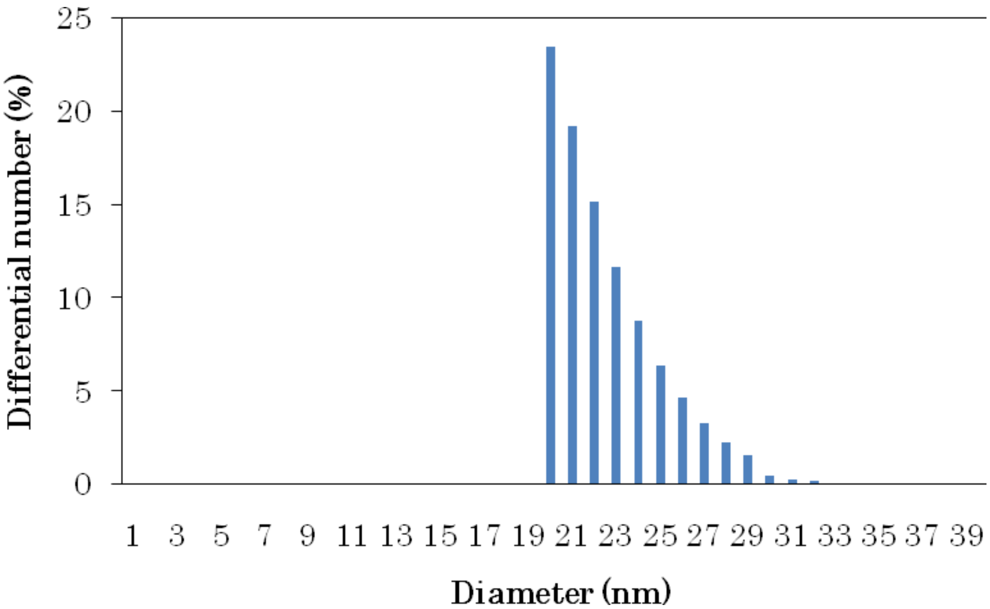


Figure 6. Absorption spectra of gold nanoparticles produced by using the laser ablation method with laser pulse repetition rates of 10 and 15 Hz

The GNPs diameter and their distribution was then examined using the PSA technique. Figure 7 shows the average diameter and size distribution of GNPs obtained by using PSA at the (a) 10 Hz repetition rate, and (b) 15 Hz repetition rate. The laser energy was 30 mJ, and the duration of the laser bombardment onto the pure gold sheet sample was 20 minutes. During the synthesis process, gold metal and its container were shake to obtain homogeneous GNP colloids. The average diameter of GNPs produced in this study was 10 nm ± 3 nm when a laser repetition rate of 10 Hz was used, as seen in Fig. 7(a). In the case of a 15 Hz repetition rate, the average diameter of GNPs produced was 26 nm ± 7 nm, as seen in Fig. 7(b). The results certify that, with increasing laser repetition rate, the size of produced GNPs increases. This result agrees with the work published by Zamiri et. al. concerning the synthesis of silver NPs (Zamiri et al., 2013), namely that the diameter of NPs increased with increment of laser energy.



(a)



(b)

Figure 7 Diameters of GNPs synthesized by using the laser ablation method with laser pulse repetition rates of (a) 10 Hz and (b) 15 Hz

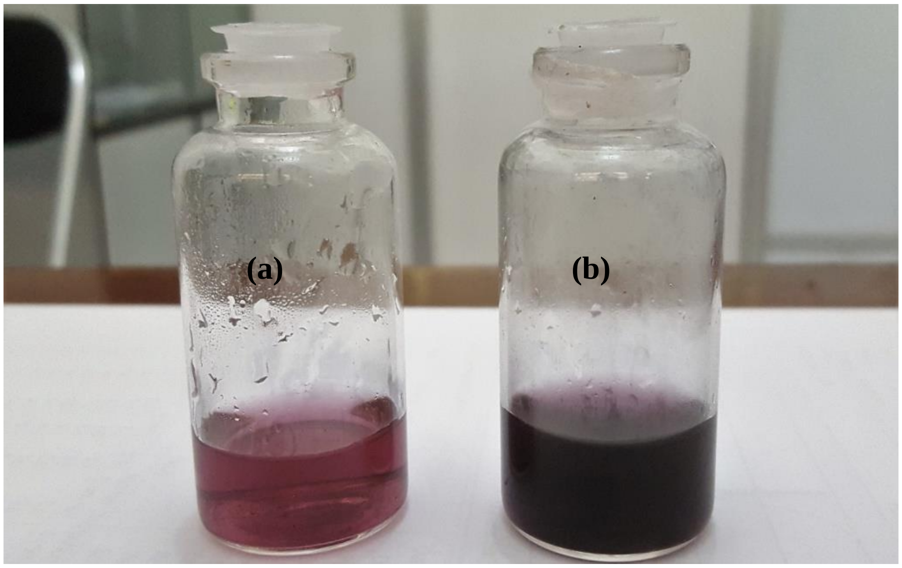


Figure 8 Photographs of colloidal high-purity gold nanoparticles produced using the laser ablation method with laser pulse repetition rates of (a) 10 Hz and (b) 15 Hz

Figure 8 shows a photograph of GNPs produced by the present PLA method with a (a) 10 Hz laser pulse repetition rate and (b) 15 Hz repetition rate. The color changes from light red (Fig. 8a) to dark red (Fig. 8b) when the repetition rate is increased. This result was confirmed by using the UV-Vis technique, for which the absorption spectra are shown in Fig. 6. Namely, the absorption intensity increases with increased laser repetition rate, certifying that the number of GNPs increases with increasing repetition rate.

3.3. Effect of liquid media

Finally, the effect of liquid media on the characteristics of GNPs was studied. To this end, aquades and ethanol were used as liquid media. Figure 9 displays the absorption spectra obtained from the GNPs produced in this experiment with aquades (red line) and ethanol (blue line). A single peak for SPR appears for both aquades and ethanol, certifying the spherical shape of the GNPs produced in both aquades and ethanol. The absorption intensity for aquades is much higher than that for ethanol, which means that more GNPs are produced in aquades than in ethanol.

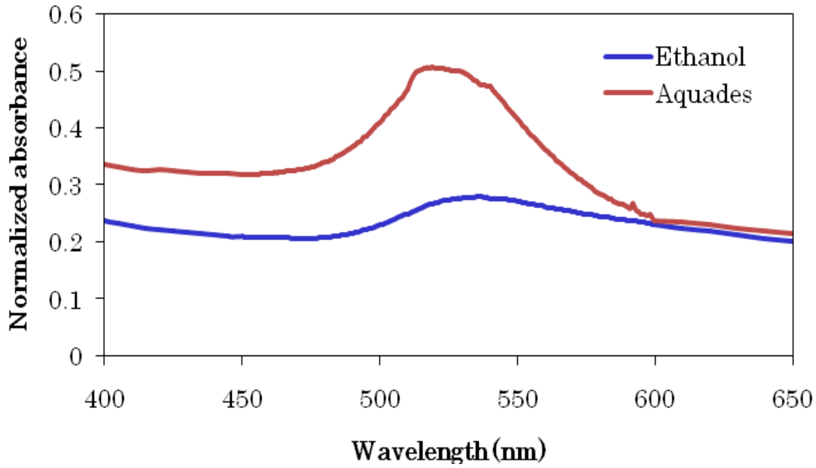
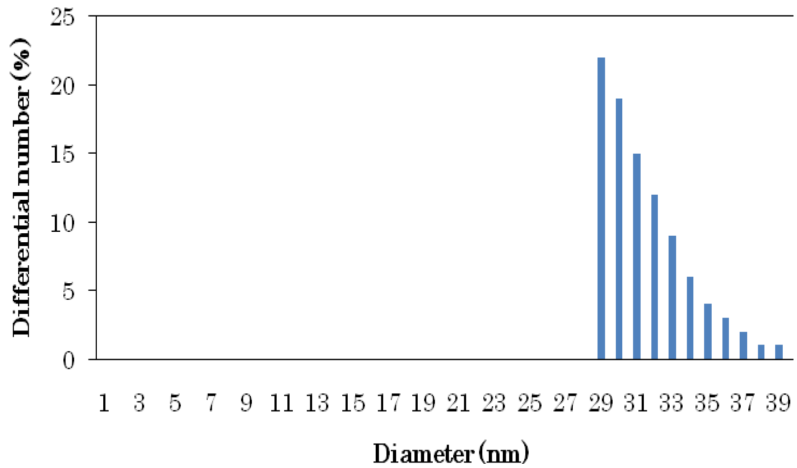
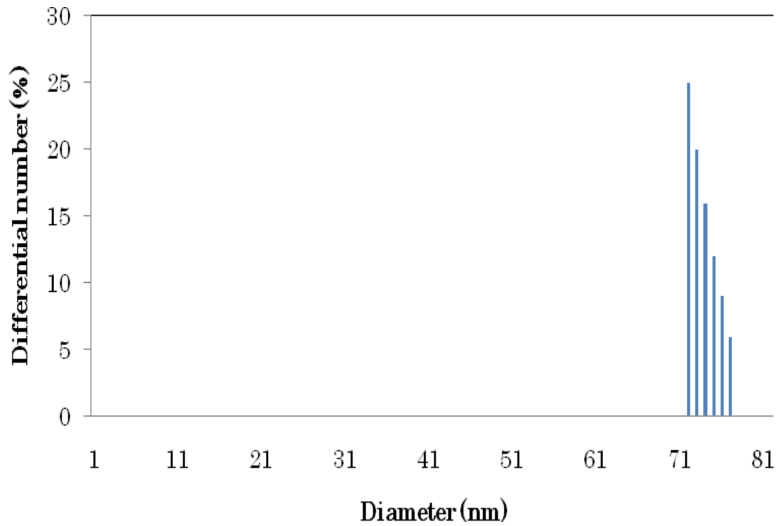


Figure 9. Spectra of gold nanoparticles produced by using the PLA technique with liquid media of aquades and ethanol

The GNPs diameter and their distribution was further examined by particle size analyzer. In this experiment, the laser energy was set at 40 mJ, and the repetition rate was10 Hz. The gold colloid was produced for 10 minutes. The average diameter of GNPs produced in aquades was 9 nm ± 2 nm, as shown in Fig. 10(a). For the case of ethanol, the average diameter was 75 nm with a standard deviation of 27 nm (Fig. 10b). The average size diameter and size distribution of particles in aquades is much smaller than in the case of ethanol. This might relate to the characteristics of dipole moments in liquid media. Aquades has a higher dipole moment than ethanol. As reported by Tilaki et al., ahigher dipole moment of molecules strengthens the bonds between the molecules and surface of produced NPs. Thus,the growth mechanism is retarded (Tilaki et al., 2007).



(a)



(b)

Figure 10 Diameters of GNPs synthesized by using the laser ablation technique with liquid media (a) aquades and (b) ethanol

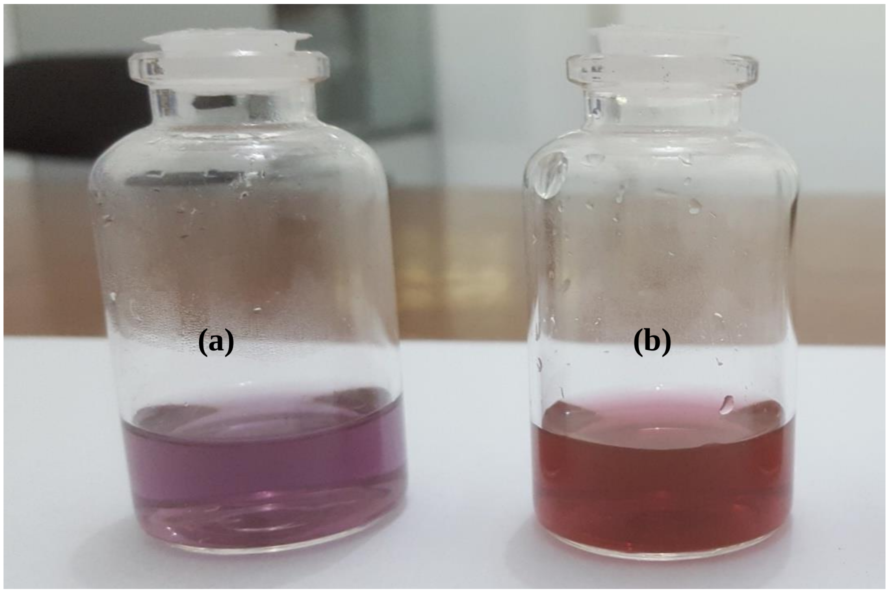


Figure 11 Photographs of GNPs produced in liquid media using the laser ablation method with liquid media (a) aquades and (b) ethanol

Figure 11 shows photographs of GNPs produced in (a) aquades and (b) ethanol. The color of the gold colloid is differs significantly between aquades and ethanol. For aquades, the color is dark red, while it is purple for ethanol. The difference in color was affected by the size and density of the produced NPs. Namely, the concentration of GNPs in aquades is much higher than that in ethanol.

4. CONCLUSION

Gold nanoparticles have been successfully produced in liquid media by using pulse laser ablation method utilizing an Nd:YAG laser operated at low-energy laser of 30 mJ. The role of laser repetition rate, laser fluence, and liquid media on the characteristics of GNPs produced by the pulse laser ablation method using an Nd:YAG laser at fundamental wavelength were studied. The results certified that the laser fluence affects the average size, size distribution, and morphology of the GNPs. Increasing the laser fluence from 4 to 6 J/cm^2 resulted in the diameter of the GNPs increasing from 26 to 32 nm, on average. The spherical shape of GNPs was produced by both laser fluences. The particle size of GNPs also increased for the increment of pulse repetition rate, namely the diameter of particles increased from 10 to 26 nm from the repetition rate of 10 Hzto15 Hz, respectively. When using different liquid media (aquades and ethanol), the diameter of produced GNPs also changes. Namely, the average diameter is 9 nm for aquades and 75 nm for ethanol. All the GNPs produced in this study had a spherical shape.

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3. Editor and reviewers' comments (30 Januari 2019)

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Ali Khumaeni <khumaeni@fisika.undip.ac.id>

[IJTech] Editor Decision

IJTech <noreply@ijtech.eng.ui.ac.id> Wed, Jan 30, 2019 at 12:00 PM
Reply-To: "noreply@ijtech.eng.ui.ac.id" <noreply@ijtech.eng.ui.ac.id>
To: khumaeni@fisika.undip.ac.id
Cc: wahyu.sb@fisika.undip.ac.id, sutanto@gmail.com

International Journal of Technology
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Decision Result : Revise

Dear **Dr. Ali Khumaeni**

We have finished the review and made decision on your manuscript entitled **[THE ROLE OF LASER FLUENCE, PULSE REPETITION RATE, AND LIQUID MEDIA IN THE CHARACTERISTICS OF GOLD NANOPARTICLES PRODUCED BY THE LASER ABLATION METHOD USING Nd:YAG LASER 1064 NM AT LOW ENERGY]** which was submitted to International Journal of Technology.

We have decided that your manuscript **Need to be Revised**

We also send you the review result from the reviewers. Here is the detail review result:

Notes from Editor:
Please revise according to reviewer's comment

Reviewer (1)

Introduction:
• Introduction section: the authors did not state what the problem remains in the synthesis of gold nanoparticles with various techniques, and why with their current method and the studied variables, it is worth and contribute to the area of Gold NPs. In this section, the authors must provide very clear information. • The terminology for laser fluence is rather seldom to use while pulse repetition is more common. Can the terminology for laser fluence be replaced with other more understandble words?

Methodology:
The authors must provide more detail information about the characterization techniques. What they have written is still too general.

Results and Discussion:
The paper just rely on the analysis based on UV-Vis absoprtion spectra (to show the SPR peak for the varied syntheszing parameters), as well as particle size analyzer, and one SEM-EDX result in order to demonstrate the effects of those laser fluence, repetition rate and liquid media on size and shape. Definitely, these are not sufficient. It is strongly required that the authors must put at least TEM and XRD for the evindence. Otherwise, the works are not worth for publication in IJtech.

References:
OK

Other:
OK

Originality	3 *(average)*
Technical	3 *(average)*
Methodology	3 *(average)*
Readability	3 *(average)*
Practicability	3 *(average)*
Organization	3 *(average)*
Importance	3 *(average)*

Additional Comment:
• The title "The Role of Laser Fluence and Pulse Repetition Rate, and Liquid Media in the Characteristics of Gold Nanoparticles Produced by the Laser Ablation Method using Nd:Yag Laser 1064 nm at Low Energy" used conjuction "and" two times closely, which has made it a bit redundant. In addition, what characteristics will be raised up by authors? This word is still too general, please be specific. • Abstract section: ? The authors should put "short background and motivation as well as problems" in the beginning of abstract so that they can claim their current work is worth and contributing to solve the problem in the area of gold nanoparticles. ? The authors also did not put their quantitative data of their findings as a results of process parameters including pulse repetition rate, liquid media etc. The statement was just qualititaive ones such as the diameter and shapes of gold nanoparticles. ? In the end of Abstract, the authors need to state what the implications of their finding to the motivation and research objective(s), what is contribution to the problem solution in the respective area. Decision : Major revision, not enough evidence (TEM and XRD)

Attachment File:
-

Reviewer (2)

Introduction:
Introduction is well revised so that it could guide readers on this particular Laser Pulse Ablation subject.

Methodology:
The methodology is normal and standard.

Results and Discussion:
The revised version bears better discussion on the results, though the theory and mechanism of laser ablation is not discussed.

References:
The revised version has added several references in the Reference List. The references covered well the introduction and discussion.

Other:

Originality	3 *(average)*
Technical	3 *(average)*
Methodology	3 *(average)*
Readability	3 *(average)*
Practicability	3 *(average)*
Organization	3 *(average)*
Importance	3 *(average)*

Additional Comment:
This manuscript should be accepted for publication in IJTech.

Attachment File:
-

Please login into application http://ijtech.eng.ui.ac.id/login for more detail.

You must respond to this revise and resubmit request before **06 Feb 2019**, after which point we will presume that you have withdrawn your submission from International Journal of Technology (IJTech) Online System.

Yours sincerely,

Dr. Mohammed Ali Berawi
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Editor in Chief
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4. Balasan komentar Editor dan Reviewers

List of Changes

Manuscript:

The role of laser fluence, pulse repetition rate, and liquid media in the characteristics of gold nanoparticles produced by the laser ablation method using Nd:YAG laser 1064 nm at low energy

Response and Revision made by Author(s)

Reviewer #1:

No	Comments	Revision/Changes
1	Introduction section: the authors did not state what the problem remains in the synthesis of gold nanoparticles with various techniques, and why with their current method and the studied variables, it is worth and contribute to the area of Gold NPs.	Various methods were developed for the synthesis of GNPs, such as electrochemical deposition, seeded growth, and vapor phase deposition. However, in chemical methods, additional chemical constituents and stabilizer agents are required during the production process, and, therefore, the GNPs contain impurity from the chemical agents. Furthermore, the chemical method produced nanoparticles, which have high-distribution of nanoparticle sizes. The effects of laser pulse repetition rate, laser fluence, and liquid media in the synthesis of colloidal GNPs using a quiet, low-energy Nd:YAG laser were examined to produce nanoparticles having high-purity and small size distribution. Based on experimental results, it shows that the produced gold nanoparticles have much smaller size distribution of the nanoparticle compared to the case of chemical method.
2	• The terminology for laser fluence is rather seldom to use while pulse repetition is more common. Can the terminology for laser fluence be replaced with other more understandble words?	The terminology for laser fluence is commonly used in the field of material to describe laser energy per area (J / cm^2), namely laser beam hits on the material surface. Therefore, it is better to use the term of laser fluence in this present study.
3	The authors must provide more detail information about the characterization techniques. What they have written is still too general.	Various spectroscopic methods were employed for the characterization of the GNPs. The optical properties and surface plasma resonance of the product were characterized by ultra-violet visible (UV-Vis) absorption spectrometer (Shimadzu 1240 SA). For this purpose, the GNPs colloid was placed in a cuvet with a

		dimension of 12.5 x 12.5 x 14 mm^3 and inserted in the cell holder. White light was used as a light source. The morphology of the produced nanoparticles was analyzed using a scanning electron microscope (SEM-EDX, JEOL JED-2300) equipped with an energy dispersive X-ray spectrometer (EDX). SEM samples were prepared by placing and drying a droplet of the nanoparticle solution on a surface of silicone wafer. Finally, particle size and size distribution were measured using a particle size analyzer (DelsaNano).
	The paper just rely on the analysis based on UV-Vis absoprtion spectra (to show the SPR peak for the varied syntheszing parameters), as well as particle size analyzer, and one SEM-EDX result in order to demonstrate the effects of those laser fluence, repetition rate and liquid media on size and shape. Definitely, these are not sufficient. It is strongly required that the authors must put at least TEM and XRD for the evindence. Otherwise, the works are not worth for publication in IJtech.	GNPs image obtained by SEM is representative to show the morphology of produced GNPs, namely GNPs produced in this present research have single spherical shape and the size of the produced GNPs have nanoparticle size ranging from 10 to 70 nm as measured by particle size analyzer. For XRD data, we are now examining the GNPs to see the crystal produced in this present research.
	The title “The Role of Laser Fluence and Pulse Repetition Rate, and Liquid Media in the Characteristics of Gold Nanoparticles Produced by the Laser Ablation Method using Nd:Yag Laser 1064 nm at Low Energy” used conjuction “and” two times closely, which has made it a bit redundant. In addition, what characteristics will be raised up by authors? This word is still too general, please be specific. • Abstract section: ? The authors should put “short background and motivation as well as problems” in the beginning of abstract so that they can claim their current work is worth and contributing to solve the problem in the area of gold nanoparticles. ? The authors also did not put their quantitative data of their	Synthesis of gold nanoparticles having high-purity and small-size distribution is necessary for the application in the medical field. However, it is difficult to be realized using chemical method. In this present study, Pulse laser ablation method using an Nd:YAG laser operated at low-energy laser of 30 mJ has been successfully employed to produce gold nanoparticles having high purity and small-size distribution. The role of laser fluence, laser pulse repetition rate, and liquid media on the characteristics of the nanoparticles produced, such as particle shape and distribution of particle size, were examined. Experimentally, an Nd:YAG laser beam (1064 nm, 7 ns) with low energy of 30 mJ was irradiated on a high-purity gold plate (99.95%), which is immersed in a liquid media. The results certified that the

	findings as a results of process parameters including pulse repetition rate, liquid media etc. The statement was just qualititaive ones such as the diameter and shapes of gold nanoparticles. ? In the end of Abstract, the authors need to state what the implications of their finding to the motivation and research objective(s), what is contribution to the problem solution in the respective area. Decision : Major revision, not enough evidence (TEM and XRD)	average particle diameter and size distribution depended on some parameters of the pulse repetition rate, laser fluence and liquid media used in the synthesis process. The diameters of the GNPs increased from 26 to 32 nm when the laser fluence was increased from 4 to 6 J/cm^2. The diameter of the GNPs also increased from 10 to 26 nm when the pulse repetition rate increased from 10 to 15 Hz. The particle diameters also changed with a change in the liquid media, the diameters were much smaller for aquades (diameter of 29 nm) compared to ethanol (diameter of 75 nm). However, the shape of the GNPs was the same for these parameters. Namely, the GNPs produced by this laser ablation method had a spherical shape. By understanding the effects of these parameters on the characteristics of the GNPs produced by laser ablation method using low-energy Nd:YAG laser, GNPs having specific characteristics, namely low diameter and small-size distribution as well as high-purity, can be synthesized for specific applications in the medical field.

Reviewer #2:

No	Comments	Revision/Changes
1	**Introduction:** Introduction is well revised so that it could guide readers on this particular Laser Pulse Ablation subject.	Thank you very much for your kindness. We have revised following your suggestion.
2	**Methodology:** The methodology is normal and standard.	Thank you very much for your kindness. We have revised following your suggestion.
3	**Results and Discussion:** The revised version bears better discussion on the results, though the theory and mechanism of laser ablation is not discussed.	Thank you very much for your kindness. We have revised following your suggestion.
	References: The revised version has added several references in the Reference List. The references covered well the introduction and discussion.	Thank you very much for your kindness. We have revised following your suggestion.

5. **Paper setelah proses revisi mempertimbangkan masukan Editor dan Reviewers**

THE ROLE OF LASER IRRADIANCE, PULSE REPETITION RATE, AND LIQUID MEDIA IN THE SYNTHESIS OF GOLD NANOPARTICLES BY LASER ABLATION METHOD USING Nd:YAG LASER 1064 NM AT LOW ENERGY

ABSTRACT

Synthesis of gold nanoparticles having high-purity and small-size distribution is necessary for the application in the medical field. However, it is difficult to be realized using chemical methods. In this present study, Pulse laser ablation method using an Nd:YAG laser operated at low-energy laser of 30 mJ has been successfully employed to produce gold nanoparticles having high purity and small-size distribution. The role of laser irradiance, laser pulse repetition rate, and liquid media on the characteristics of the nanoparticles produced, such as particle shape and distribution of particle size, were examined. Experimentally, an Nd:YAG laser beam (1064 nm, 7 ns) with low energy of 30 mJ was irradiated on a high-purity gold plate (99.95%), which is immersed in a liquid media. The results certified that the average particle diameter and size distribution depended on some parameters of the laser irradiance, pulse repetition rate and liquid media used in the synthesis process. The diameters of the GNPs increased from 6.5 to 12.3 nm when the laser irradiance was increased from 12 to 20 GW/cm^2. The diameter of the GNPs also increased from 12.3 to 20.7 nm when the pulse repetition rate increased from 10 to 15 Hz. The particle diameters also changed with a change in the liquid media, the diameters were much smaller for aquades (diameter of 12.3 nm) compared to ethanol (diameter of 15.0 nm). However, the shape of the GNPs was the same for these parameters. Namely, the GNPs produced by this laser ablation method had a spherical shape. By understanding the effects of these parameters on the characteristics of the GNPs produced by laser ablation method using low-energy Nd:YAG laser, GNPs having specific characteristics, namely high-purity and small-size distribution, can be synthesized for specific applications in the medical field.

Keywords: GNPs, Gold nanoparticles, Low-energy Nd:YAG laser, laser ablation method, laser irradiance, pulse repetition rate, low energy of laser pulse

1. INTRODUCTION

Many scientists and researchers are interested in studying and developing nanoparticles (NPs) for various applications due to their specific characteristics (Tran et al., 2013, Khalil et al., 2017). For example, Adiwibowo et al. have successfully produced stable ZnO nanoparticles for detergent applications (Adiwibowo et al., 2018). NPs have minute size with a diameter of 1 to 100 nm. Recently, production of gold nanoparticles (GNPs) has been made for some applications, such as sensor (Raj et al., 2003), photonics device (Parker and Townley, 2007), catalyst (Turner and Golovko, 2008), and medical applications (Giljohann et al., 2010). Due to their specific properties, GNPs were employed as radiosensitizers, contrast agents, and for drug delivery in the medical field (Cole et al., 2015, Dreaden et al., 2014).

Various methods were developed for the synthesis of GNPs, such as electrochemical deposition, seeded growth, and vapor phase deposition (Rad et al., 2011). However, in chemical methods, additional chemical constituents and stabilizer agents are required during the production process, and, therefore, the GNPs contain impurity from the chemical agents. Furthermore, the chemical method produced nanoparticles, which have high-distribution of nanoparticle sizes. Production of high-purity GNPs is necessary for applications in the medical field in order to ensure the human health. Therefore, alternative methods for synthesis of GNPs are necessary. One such recent method used to produce GNPs is a green process using plants (Aroma et al., 2012).

A physical method based on a pulse laser has been developed as well. This technique conducts NPs synthesis in liquid, producing colloidal NPs (Giorgetti et al., 2012). The metal NPs produced by using this pulse laser ablation (PLA) method have a high purity compared to those produced by conventional methods, such as the chemical method (Al-Azawi et al., 2015). These NPs are very suitable for specific medical applications which require high-purity NPs, such as being used as contrast agents, for drug delivery, and as radiosensitizers in, for example, cancer and tumor therapy. The PLA method has been applied to the synthesis of silver NPs (AgNPs) and GNPs. Many parameters and variables play an important role in the characteristics of the NPs produced using the PLA method (Abbasi and Dorranian, 2015). These parameters include laser energy, laser pulse repetition rate, and liquid media when metal NPs are produced (Al-nassar et al., 2015).

In this present study, a pulse laser ablation method using Nd:YAG laser operated at low-energy of 30 mJ was employed to produce gold nanoparticles in liquid media. The effects of laser pulse repetition rate, laser irradiance, and liquid media in the synthesis of colloidal GNPs using a quiet low-energy Nd:YAG laser were examined to produce nanoparticles having high-purity and small size distribution. Based on experimental results, it shows that the produced gold nanoparticles much smaller size distribution of the nanoparticle compared to the case of chemical method. Furthermore, the GNPs also have high-purity, which are required for the application in the medical field.

2. METHODOLOGY/ EXPERIMENTAL

The basic experimental arrangement for this study is displayed in Fig. 1. A metal gold with high purity (99.95%) was immersed in 10 ml pure aquades placed in a petri dish (a diameter of 50 mm). A laser beam (Nd:YAG laser, New polaris II 1064 nm, max energy of 50 mJ, 7 ns) was irradiated on the gold plate via convex lens (30 mm in focal length). In this study, the laser irradiance on the gold plate surface was varied at 12 and 20 GW/cm^2. The laser pulse repetition rate was also varied at 10 and 15 Hz in order to know the ablation efficiency of material. The laser was bombarded on the gold plate for 40 minutes. During laser irradiation, the gold plate was moved in the XY direction so that the laser always impinged on the new surface of the gold sample in order to obtain homogeneous colloidal GNPs.

Various spectroscopic methods were employed for the characterization of the GNPs. The optical properties and surface plasma resonance of the product were characterized by ultra-violet visible (UV-Vis) absorption spectrometer (Shimadzu 1240 SA). For this purpose, the GNPs colloid was placed in a cuvet with a dimension of 12.5 x 12.5 x 14 mm^3 and inserted in the cell holder. White light was used as a light source.

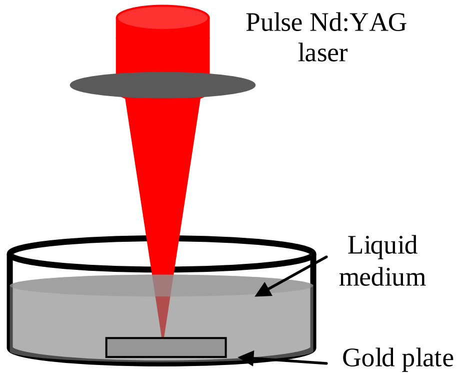


Figure 1. Experimental arrangement used in this study

The morphology of the produced nanoparticles was analyzed using a transmission electron microscope (TEM, JEOL) equipped with an energy dispersive X-ray spectrometer (EDX). TEM samples were prepared in the form of colloidal gold nanoparticles. X-ray diffraction (Rigaku Smartlab, Japan) was used to analyze crystalline nanoparticles produced in this present research. For XRD characterization, the samples were prepared by placing and drying a droplet of the nanoparticle solution on a surface of silicone wafer. Finally, particle size and size distribution were analyzed using imageJ processing software from the photographs obtained by TEM.

3. RESULTS AND DISCUSSION

3.1. Role of laser irradiance

Firstly, the role of laser irradiance on the characteristics of GNPs was examined. Figure 2 displays the absorption spectra of gold nanoparticles prepared by using UV-Vis spectroscopy.

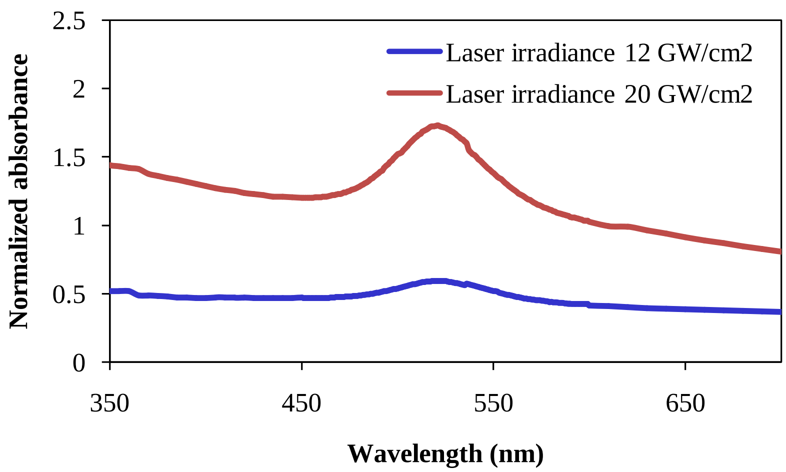
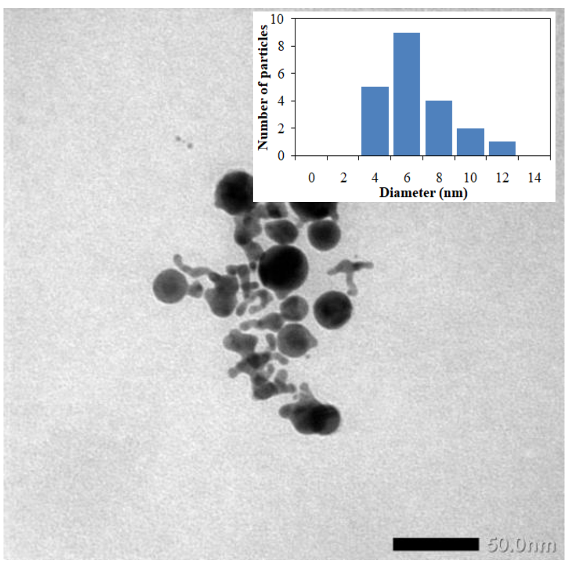


Figure 2. Absorbance spectra of gold nanoparticles synthesized by using the pulse laser ablation method with different laser irradiances of 12 GW/cm^2 and 20 GW/cm^2

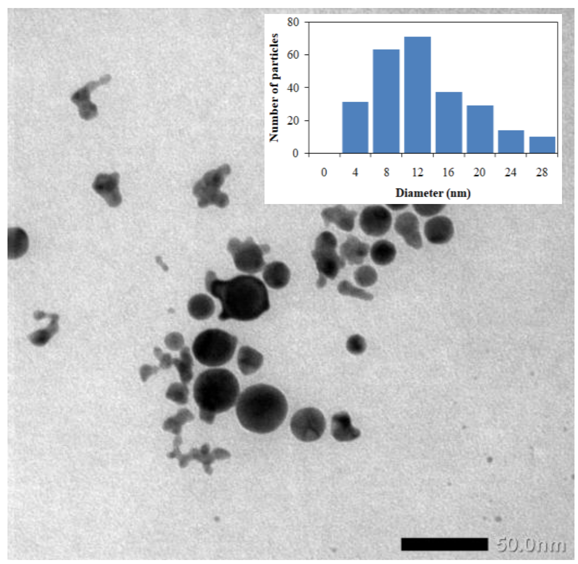
Two different laser irradiances were applied during the experiment, the blue and red lines in Fig. 2 represent the spectrum with a laser irradiance of 12 GW/cm^2 and 20GW/cm^2, respectively. The GNPs were prepared using the Nd:YAG laser with a repetition rate of 10 Hz and laser beam bombardment duration on gold surface of 40 minutes.

The peak of the surface plasmon resonance (SPR) of the GNPs appears clearly for both laser irradiances, 12 and 20 GW/cm^2. The SPR peak occurs at 519 nm for 12 GW/cm^2, and at 521 nm for 20 GW/cm^2. The peak shifts by 2 nm toward a longer wavelength with an increment in laser irradiance from 12 to 20 GW/cm^2, indicating that particle size increases with an increase in laser irradiance. This phenomenon was also confirmed by calculating the particle size of GNPs using imageJ processing software.

To study the morphology of the produced GNPs, the TEM imaging technique was employed. Figures 3(a) and 3(b) show the photographs of GNPs obtained by using the current PLA method. All GNPs show a spherical shape with various diameters. This measurement result confirms the indications of nanoparticle shape displayed in Fig. 2, namely that the absorption spectrum has a single SPR peak. This certifies that the GNPs were successfully synthesized in a spherical shape.



(a)



(b)

Figure 3 TEM images of gold nanoparticles and their distribution sizes (inset) obtained by TEM technique using laser fluencies of (a) 12 GW/cm^2 and (b) 20 GW/cm^2

The distribution of the diameters of the particles obtained by using an imageJ processing software derived from the photographs shown in the inset of Fig. 3 with laser irradiances of 12 and 20 GW/cm^2, respectively. For 12 GW/cm^2 in laser irradiance, the average diameter is 6.5 nm ± 3.7 nm, while they are 12.3 nm ± 8.7 nm, respectively, for the case of 20 GW/cm^2. This result certifies that increasing the laser irradiance increased the size of the GNPs produced. This is a similar pattern with the results reported by Solati et al. in the synthesis of silver NPs by the PLA technique using an Nd:YAG laser at fundamental wavelength, namely that NPs increase in size and have a broader size distribution with increased laser irradiance (Solati et al., 2013). It is assumed that the changes in nanoparticle size and size distribution are due to the explosive ejection of material surface by a high density laser beam. In the case of higher laser irradiance, the distribution of particles ejected from the surface increases (Nichols et al., 2006).

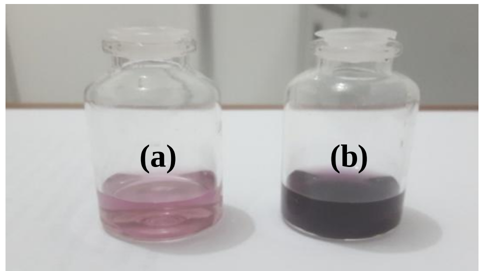


Figure 4 Photographs of colloidal gold nanoparticles produced by laser fluencies of (a) 12 GW/cm^2 and (b) 20 GW/cm^2

Figure 4 shows the photographs of GNP colloids produced by the current PLA method, Figure 4(a) represents the GNP product obtained when the laser irradiance was 12 GW/cm^2, while Fig. 4(b) represents the product for 20 GW/cm^2 in laser irradiance. The color of the colloids changes from light to dark red with the increase in laser irradiance. This indicates that the number of GNPs produced by PLA increases by increasing the laser irradiance.

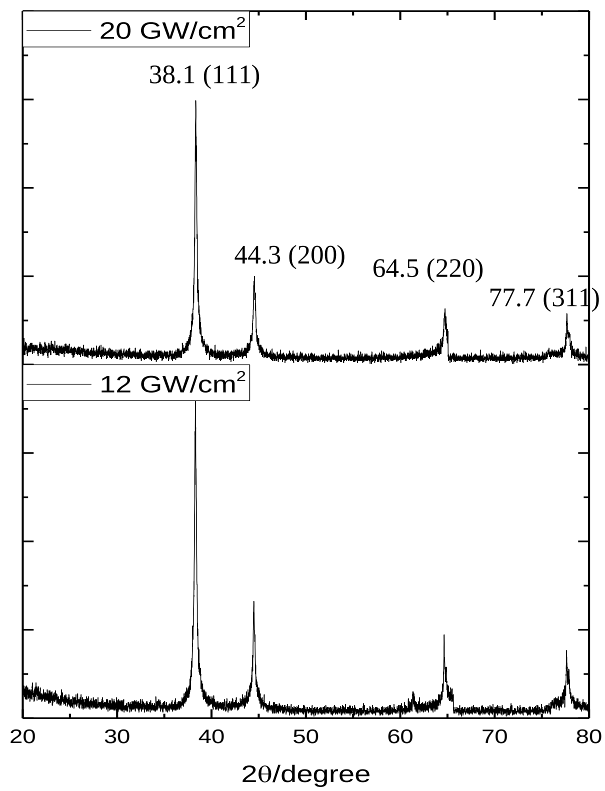


Figure 5 XRD diffractogram from the gold nanoparticles produced by the laser irradiance of 12 GW/cm^2 and 20 GW/cm^2

3.2. Role of pulse repetition rate

The role of the pulse repetition rate in the characteristics of GNPs produced by the current PLA technique was studied next. Figure 6 displays the spectra of GNPs obtained by UV-Vis spectroscopy technique for laser pulse repetition rates of 10 Hz (fixed blue line) and 15 Hz (fixed red line). The single SPR peak occurs clearly for both the 10 and 15 Hz repetition rates, indicating that the GNPs produced by this PLA technique have a spherical shape. The increase in the absorbance values at 15 Hz indicates that ablation efficiency effectively increases with increasing repetition rate (Xu et al., 2012).

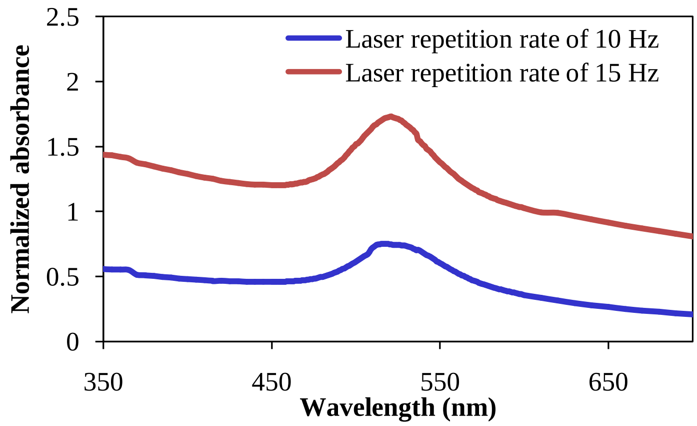
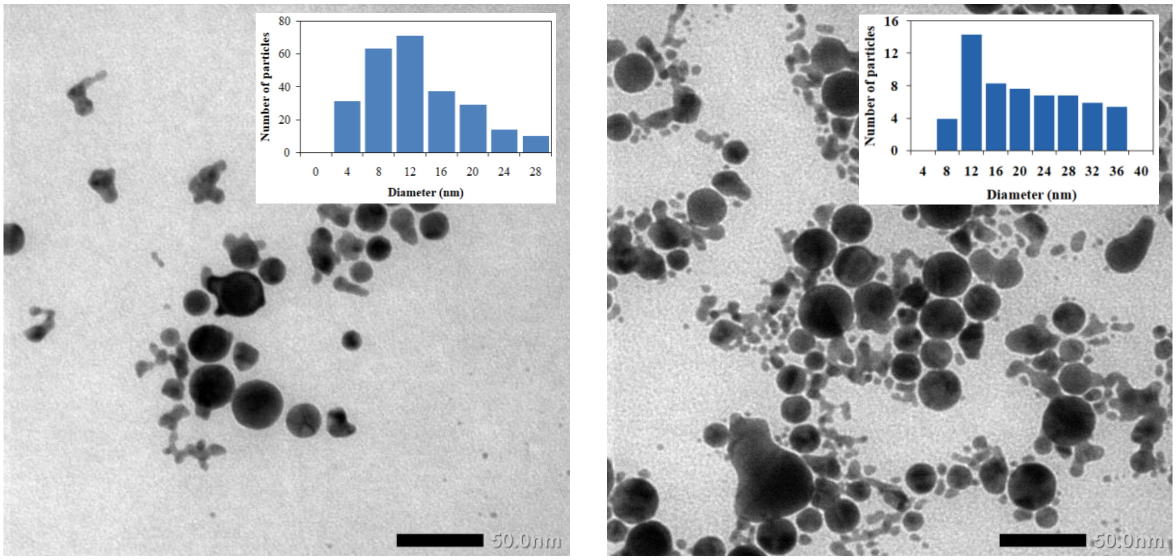


Figure 6. Absorbance spectra of gold nanoparticles produced by using the laser ablation method with laser pulse repetition rates of 10 and 15 Hz

The TEM images of GNPs produced by the laser ablation method with the laser pulse repetition rates of 10 and 15 Hz including their size distribution are shown in Fig. 7. The laser energy was 30 mJ, and the duration of the laser bombardment onto the pure gold sheet sample was 40 minutes. During the synthesis process, gold metal and its container were shake to obtain homogeneous GNP colloids. It can clearly be seen that the shape of the GNPs in both conditions are the same, namely spherical shape. This is similar with the shape of nanoparticles generally produced by pulse laser ablation method as mentioned above. The size distribution of GNPs is displayed in the inset of each figure. The average diameter and size distribution of GNPs obtained by using imageJ software at the (a) 10 Hz repetition rate, and (b) 15 Hz repetition rate. The average diameter of GNPs produced in this study was 12.3 nm ± 8.7 nm when a laser repetition rate of 10 Hz was used, as seen in Fig. 7(a). In the case of a 15 Hz repetition rate, the average diameter of GNPs produced was 20.7 nm ± 9.8 nm, as seen in Fig. 7(b). The results certify that, with increasing laser repetition rate, the size of produced GNPs increases. This result agrees with the work published by Zamiri et. al. concerning the synthesis of silver NPs (Zamiri et al., 2013), namely that the diameter of NPs increased with increment of laser energy.



(a) (b)

Figure 7 TEM images of gold nanoparticles and their distribution sizes (inset) obtained by TEM technique with laser pulse repetition rates of (a) 10 Hz and (b) 15 Hz

3.3. Role of liquid media

Finally, the effect of liquid media on the characteristics of GNPs was studied. To this end, aquades and ethanol were used as liquid media.

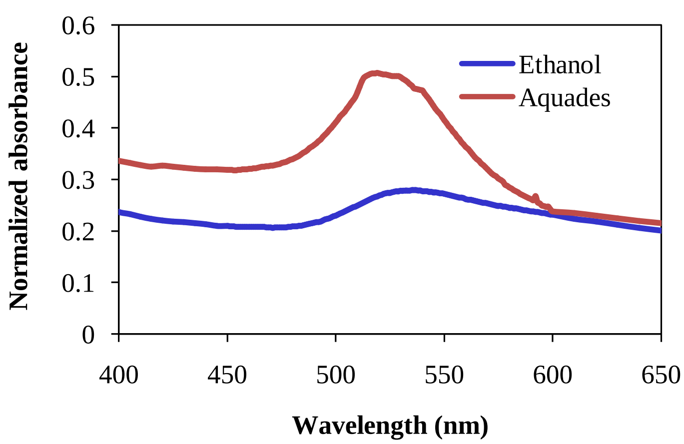
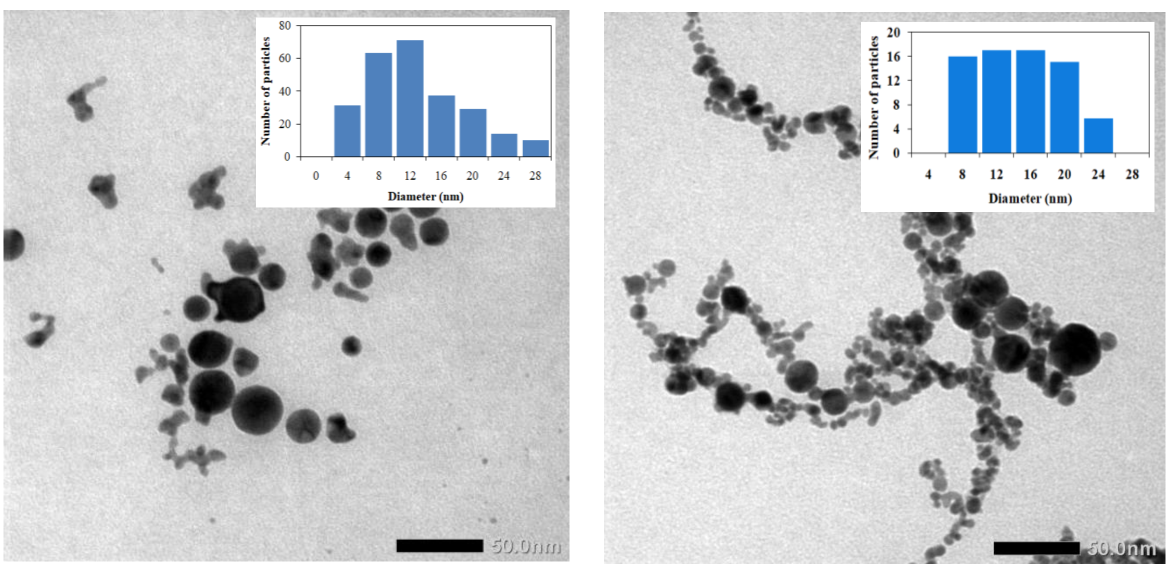


Figure 8. Absorbance spectra of gold nanoparticles produced by using the PLA technique with liquid media of aquades and ethanol

Figure 8 displays the absorption spectra obtained from the GNPs produced in this experiment with aquades (red line) and ethanol (blue line). A single peak for SPR appears for both aquades and ethanol, certifying the spherical shape of the GNPs produced in both aquades and ethanol. The absorption intensity for aquades is much higher than that for ethanol, which means that more GNPs are produced in aquades than in ethanol.

To prove that the shapes of the produced GNPs are spherical for the case of aquades and ethanol, the images of the GNPs were taken by using TEM imaging. Figure 9 shows the photographs of GNPs obtained by using the TEM technique. The distribution of GNPs sizes is shown in the inset of each figure. The shape of the GNPs are spherical both for aquades ad ethanol. The average diameter of GNPs produced in aquades was 12.3 nm ± 8.7 nm, as shown in the inset of Fig. 10(a). For the case of ethanol, the average diameter was 15.0 nm ± 7.5 nm (inset of Fig. 10b). The average size diameter and size distribution of particles in aquades is slightly smaller than in the case of ethanol. This might relate to the characteristics of dipole moments in liquid media. Aquades has a higher dipole moment than ethanol. As reported by Tilaki et al., a higher dipole moment of molecules strengthens the bonds between the molecules and surface of produced NPs. Thus, the growth mechanism is retarded (Tilaki et al., 2007). The other reason is the low ablation efficiency in the ethanol compared to aquades. In the ethanol medium, the ethanol decomposition process happens during laser ablation, which results in ethanol gas indicated by lots of bubble gases produced during laser bombardment. Those gases my retard the laser path, which reduces the laser energy that reaches on the target. The lower energy will increase in the size of produced nanoparticles (Moura et al., 2017).



(a) (b)

Figure 9 TEM images of gold nanoparticles and their distribution sizes (inset) obtained by TEM technique with liquid media (a) aquades and (b) ethanol

4. CONCLUSION

Gold nanoparticles have been successfully produced in liquid media by using pulse laser ablation method utilizing an Nd:YAG laser operated at low-energy laser of 30 mJ. The role of laser repetition rate, laser irradiance, and liquid media on the characteristics of GNPs produced by the pulse laser ablation method using an Nd:YAG laser at fundamental wavelength were studied. The results certified that the laser irradiance affects the average size, size distribution, and morphology of the GNPs. Increasing the laser irradiance from 12 to 20 GW/cm^2 resulted in the diameter of the GNPs increasing from 6.5 to 12.3 nm, on average. The spherical shape of GNPs was produced by both laser irradiances. The particle size of GNPs also increased for the increment of pulse repetition rate, namely the diameter of particles increased from 12.3 to 20.7 nm from the repetition rate of 10 Hz to15 Hz, respectively. When using different liquid media (aquades and ethanol), the diameter of produced GNPs also changes. Namely, the average diameter is 12.3 nm for aquades and 15.0 nm for ethanol. All the GNPs produced in this study had a spherical shape. The results certified that gold nanoparticles with small-size distribution and high-purity can be successfully produced by using the present PLA technique. The produced high-purity GNP has high possibility to be applied to the medical field as a contrast agent for cancer diagnostic using CT scan.

ACKNOWLEDGMENT

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6. **Mengirim komentar dan revisi manuskrip ke jurnal (15 Februari 2019)**

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Submission of final revised manuscript

Ali Khumaeni <khumaeni@fisika.undip.ac.id> Sun, Mar 3, 2019 at 8:10 AM
To: nsuwartha@eng.ui.ac.id, IJTech <ijtech@eng.ui.ac.id>

Dear Dr Nyoma Suwartha

Thank you very much for your kind reminder. We have submitted the final revised manuscript to Ijtech submission system following the suggestion of Reviewer 1. We would like also to attach the submitted manuscript and reviewer letter as in attachment. Thank you very much for your kindness.

Best regards
Ali Khumaeni

3 attachments

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7. **Acceptance letter dari jurnal dari seluruh proses review (1 April 2019)**

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[IJTech] Editor Decision

IJTech <noreply@ijtech.eng.ui.ac.id> Mon, Apr 1, 2019 at 2:36 PM
Reply-To: "noreply@ijtech.eng.ui.ac.id" <noreply@ijtech.eng.ui.ac.id>
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Editor Decision on #R5-CE-1953 : Accepted

Ms ID **#R5-CE-1953**
Title : THE ROLE OF LASER FLUENCE, PULSE REPETITION RATE, AND LIQUID MEDIA IN THE CHARACTERISTICS OF GOLD NANOPARTICLES PRODUCED BY THE LASER ABLATION METHOD USING Nd:YAG LASER 1064 NM AT LOW ENERGY
Author(s) : Ali Khumaeni, Wahyu Setia Budi, Heri Sutanto

Dear **Dr. Ali Khumaeni**

On behalf of the Editorial Board, I am pleased to inform you that your paper entitled: THE ROLE OF LASER FLUENCE, PULSE REPETITION RATE, AND LIQUID MEDIA IN THE CHARACTERISTICS OF GOLD NANOPARTICLES PRODUCED BY THE LASER ABLATION METHOD USING Nd:YAG LASER 1064 NM AT LOW ENERGY has been accepted to be published in International Journal of Technology (IJTech). **Congratulation!**

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8. Galley proof confirmation (22 Oktober 2019)

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[IJTech-CE-1953] Final Proof reading & Copyright form

IJTech <ijtech@eng.ui.ac.id> Tue, Oct 22, 2019 at 8:14 AM
To: khumaeni@fisika.undip.ac.id
Cc: wahyu.sb@fisika.undip.ac.id, sutanto@gmail.com

Dear Dr. Ali Khumaeni,

The editorial boards delighted to inform you that your paper has been accepted to be published in IJTech next Volume 10 issue 5, October 2019.

Congratulations!

We have carried out necessary layouting and editing of your

manuscript. Prior to publication we need your final proof and copyright of the paper. Here is the note from editor:

1. Please provide the corresponding author's telephone and fax number (if any).

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Any confirmation of the final check should be submitted no later than **October 24, 2019.** Copyright form can be printed, signed, scanned and send by email to ijtech@eng.ui.ac.id.

On behalf of editorial boards, we want to express you and your collaborators our deep appreciation for your contribution to IJTech.

We look forward to receiving the copyright form and proofs at your earliest convenience.

Yours sincerely,

Dr. Mohammed Ali Berawi

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Journal Publishing : Volume 10 Issue 5, Oct 2019

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Journal Publishing

Dear Dr. Ali Khumaeni,

Greetings from Depok!

On behalf of the Editorial Board, I am pleased to inform you that your article entitled **The Role of Laser Irradiance, Pulse Repetition Rate, and Liquid Media in the Synthesis of Gold Nanoparticles by the Laser Ablation Method using an Nd:YAG Laser 1064 nm at Low Energy** has been published online in *Volume 10 Issue 5, Oct 2019*. You can check the online version at: http://ijtech.eng.ui.ac.id/issue/57

The articles are available to be accessed and downloaded free of charge. The hardcopy version is being printed and one copy will be delivered to the corresponding author.

Thank you for your contribution to IJTech and we look forward to a good collaboration in the next future.

Yours sincerely,

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