

PULSED Nd:YAG LASER-SYNTHESIZED SILVER NANOPARTICLES WITH HIGH SENSITIVITY FOR GLUCOSE DETECTION

Nur Safinatun Najah¹, Latifatul Aisyah Nabila¹, Reni Rusidah¹, Siti Azimatul Luthfiyyah¹, Ahmad Taufiq¹ and Nurul Hidayat^{1,2,*}

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Abstract

Diabetes Mellitus (DM) affects not only adults but also children, leading to an urgent need for the development of a reliable glucose sensors. This study introduces a simple method to develop a Localized Surface Plasmon Resonance (LSPR)-based glucose sensor utilizing silver nanoparticles (AgNPs). AgNPs were synthesized using pulsed Nd:YAG laser ablation in liquid at different laser-pulse diameters ranging from 1 mm to 5 mm. The wavelength, energy, and frequency of the Nd:YAG laser were fixed at 1064 nm, 200 mJ, and 4 Hz, respectively. The morphology of AgNPs was observed to be spherical, with an average diameter of 42.5 nm. Analysis of the UV-Vis results showed that the interaction of AgNPs with glucose at various concentrations (i.e., 0–10%), resulted in changes in the LSPR wavelength. The wavelength shifted to longer values as the glucose concentration increased. The AgNPs' sensing sensitivity to detect glucose was 0.421 nm/%, with excellent linearity (0.98) and a detection range from 0% to 10%. These findings provide significant contributions to the development of reliable glucose sensors, with important application prospects in the management of diabetes mellitus.

Keywords: Silver nanoparticles; Nd:YAG laser ablation; Localized surface plasmon resonance; Glucose sensing

Introduction

Diabetes Mellitus (DM) is a metabolic disease characterized by high blood sugar levels due to insulin deficiency or resistance. Glucose, a carbohydrate used as the body's main energy source, circulates in the blood and cells in the human body. The body tightly controls glucose

levels through humoral factors such as insulin, glucagon, and cortisol. Normally, blood glucose levels are around 3.9-5.6 mmol/L (70-100 mg/dL) when fasting, and increase to 5.7-6.9 mmol/L (100-125 mg/dL) in individuals at risk of prediabetes (Lesmana and Broto, 2019). According

¹ Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia. E-mail: nurul.hidayat.fmipa@um.ac.id

² Center for Instrumentation and Sensing Technology, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia.

* Corresponding author

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to Cano Perez *et al.* (2021) and the International Diabetes Federation (IDF), the number of adults with diabetes has reached 540 million and is predicted to increase by 21.3 million by 2030. To prevent serious complications such as heart attacks and organ damage, regular blood sugar checks are vital (Cano Perez *et al.*, 2021).

One of the simple approaches for detecting glucose levels is using colorimetric analysis, which employs metal nanoparticles with excellent plasmonic properties. Silver nanoparticles (AgNPs) are considered as one of the superior plasmonic materials for this purpose (Rivero *et al.*, 2012; Chen *et al.*, 2015). AgNPs are known for their distinct localized surface plasmon resonance (LSPR) characteristic (Barghouti *et al.*, 2020). LSPR is an important phenomenon in the field of photonics, where light at a certain transmission frequency is absorbed by metal nanoparticles due to the resonance of collective oscillations of free electrons interacting with the electric field of incident light (Hidayat *et al.*, 2023). It has gained significant attention as a promising optical sensing approach for chemical detection, including glucose sensing, due to its high sensitivity, label-free detection capability, and miniaturized sensor designs (Hidayat *et al.*, 2023). AgNPs have been used to detect heavy metal ions, organic or biomolecules (Choudhary *et al.*, 2020), and glucose levels (Jayarambabu *et al.*, 2023).

To date, chemical methods have been the predominant approach for producing AgNPs. However, chemical synthesis techniques often involve hazardous chemicals, leading to environmental pollution risks and potential health hazards (Santhosh *et al.*, 2022; Ying *et al.*, 2022). Moreover, chemical methods tend to be costly and require precise chemical calculations to ensure controlled synthesis and reproducibility (Ramanathan *et al.*, 2021). These limitations highlight the need for cleaner, simpler, more environmentally friendly, and cost-effective alternatives for AgNP synthesis.

This study promotes the use of a Nd:YAG laser ablation technique for this purpose. The pulsed Nd:YAG laser ablation in liquid approach is capable of producing pure nanoparticles without the presence of hazardous chemicals and waste. Pulsed laser ablation in liquids can produce nanostructured materials with various shapes and sizes, which are influenced by a number of factors such as energy, wavelength, and duration of the laser pulse (Mendivil *et al.*, 2013; Khashan *et al.*, 2021). Hence, the objectives of this study are to synthesize AgNPs using Nd:YAG laser technology and apply them for glucose sensing. Ultraviolet-visible (UV-Vis) spectroscopy characterization was performed

to analyze the plasmonic properties of the synthesized AgNPs and their interactions with various glucose concentrations.

Materials and Methods

In this study, 1 gram of pure silver plate (99.999%) and deionized water (DIW) were used to synthesize AgNPs. Meanwhile, glucose ($C_6H_{12}O_6$) was used for sensing purposes. No additional materials were required to synthesize AgNPs using the Nd:YAG laser ablation approach and to explore their sensitivity to glucose.

Method for the Synthesis of AgNPs using Pulsed Nd:YAG Laser Ablation in Liquid

The pure silver plate was initially sonicated for 10 minutes for cleaning purposes. The silver plate was then placed in a glass containing 20 ml DIW. The pulsed Nd:YAG laser was set at a wavelength of 1064 nm with laser beam diameters of 1 mm, 2 mm, 3 mm, 4 mm, and 5 mm. Other controlled lasing parameters included repetition rate, laser energy, and ablation time of 4 Hz, 200 mJ, and 20 minutes, respectively. The synthesis procedure of AgNPs using the Nd:YAG laser in liquid is illustrated in Figure 1.

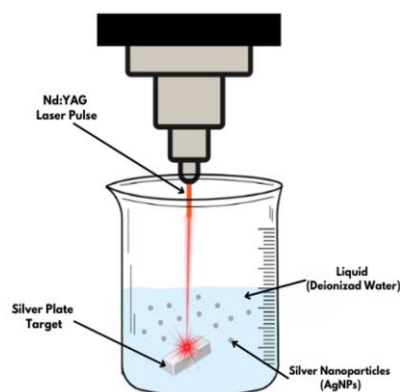


Figure 1. Synthesis of AgNPs using pulsed Nd:YAG laser ablation in liquid

Characterization of AgNPs

AgNPs were characterized by UV-Vis (Analytik Jena, Specord 200 Plus) spectroscopy to determine their plasmonic properties. Before the UV-Vis test was carried out, AgNPs were diluted using DIW at a ratio of 1:1. A Scanning Electron Microscope (SEM) test was also conducted to determine the morphology and size distribution of the synthesized AgNPs. For SEM characterization, the sample was prepared in the form of a thin film

using the drop casting method on a 1×1 cm glass substrate.

Glucose Detection Using AgNPs

The optimized AgNPs, based on the varying laser beam diameter optimization, were applied for glucose sensing. The glucose was added to the AgNPs' nano-colloidal solutions in such a way that the glucose concentrations varied at 0%, 2%, 4%, 6%, 8%, and 10%. The plasmonic characteristics of the AgNP/glucose solutions were tested using UV-Vis spectroscopy. Furthermore, the UV-Vis data obtained from AgNP solutions with varying glucose concentrations were evaluated to obtain their sensing sensitivity.

Results and Discussion

Optimization of AgNPs Synthesis

Figure 2 shows the AgNPs produced by a pulsed Nd:YAG laser ablation at various laser beam diameters. It is clearly seen that the laser beam diameters, or laser fluence, changed the color of the prepared AgNPs. The laser fluence (energy per unit area) changes with the laser beam size, as provided in Table 1. Furthermore, Figure 3 shows the plasmonic characteristics of AgNPs obtained from UV-Vis characterization. Provided in Table 2, the LSPR peaks occurred at around 405 nm to 410 nm. In terms of absorbance, the values varied from 0.680 au to 0.191 au.

Table 1. Laser beam diameter and its corresponding laser fluence

Laser Beam Diameter (mm)	Laser Fluence (J/cm ²)
1	25.46
2	6.37
3	2.83
4	1.59
5	1.02

Table 2. Plasmonic data of AgNPs produced by Nd:YAG laser ablation at various laser beam diameters

Laser Beam Diameter (mm)	Wavelength (nm)	Absorbance (au)
1	405	0.680
2	409	0.249
3	410	0.189
4	405	0.545
5	408	0.191

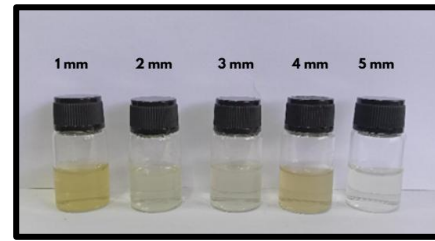


Figure 2. AgNPs produced by pulsed Nd:YAG laser ablation in liquid

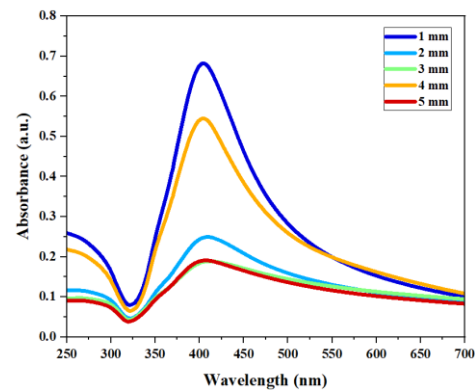


Figure 3. UV-Vis spectra of AgNPs

Figure 4 shows that the absorbance decreased significantly from 1 mm to 3 mm, then increased almost threefold at 4 mm, before decreasing again at 5 mm. This decrease was in line with the reduced laser fluence, while the increase at 4 mm could be due to factors such as a more homogeneous nanoparticle size distribution or changes in plasma dynamics during ablation. If the diameter of the laser beam is enlarged (e.g. from 1 mm to 5 mm), the surface area of the target exposed to the laser will increase. As a result, the fluence (au) will decrease if the applied laser energy remains the same (Salim *et al.*, 2020).

From the UV-Vis analysis, it was implied that the lowest wavelengths that corresponded to the LSPR peak were also observed at laser beam diameters of 1 mm and 4 mm. As AgNPs synthesized at a laser beam diameter of 1 mm showed the highest absorbance peak (i.e., 0.682), showing the best plasmonic properties, this sample was therefore selected as the optimized AgNPs and used as the glucose sensor. The LSPR wavelength can be associated with the size and optical properties of nanoparticles (Rivera *et al.*, 2024).

A higher absorbance peak indicates that the nanoparticles absorb more light, which may be influenced by the concentration, size, shape, or distribution of the particles in the sample (Devaraj *et al.*, 2018).

Morphological Characteristics of AgNPs

Figure 5 depicts the morphological characteristics of AgNPs prepared using the pulsed Nd:YAG laser ablation in liquid approach. This is important to determine the shape and size distribution of AgNPs, as these characteristics dictate their plasmonic properties. The size distribution of the AgNPs is shown in Figure 6. From the analysis, AgNPs were spherical in shape and had an average diameter of 42.5 nm, with a standard deviation of 6.6 nm and a coefficient of variation of 15.5%. This statistical analysis indicated a moderate level of dispersion in the particle size distribution of AgNPs produced using ND:YAG laser ablation.

Evaluation of Glucose Sensing Using AgNPs

The presence of glucose in AgNP nano colloidal solutions was tracked using UV-Vis data

of their mixtures. Figure 7 displays the AgNPs solutions with varying glucose concentrations. It was observed that there was a gradual change to the AgNP/glucose solution as the concentration of glucose increased. This indicated the presence of molecular interaction between glucose and nanoparticles. Furthermore, the spectroscopic data obtained from UV-Vis spectroscopy are shown in Figure 8. Spectral modality - that is, changes in LSPR wavelength - was detected as more glucose was added to the AgNP nano-colloidal solution. In the AgNP solution containing glucose, the incoming light affects the collective oscillation of free electrons on the AgNPs' surface. This interaction is strongly influenced by the refractive index of the solution around the AgNPs, where glucose with a large concentration has a higher refractive index which causes a change in the LSPR effect. The LSPR effect strongly depends on various factors, such as the size and shape of the nanoparticles and the refractive index of the surrounding medium (Hidayat *et al.*, 2023). This change in refractive index also results in an LSPR wavelength shift that gets progressively higher to the right. In other words, this study indicated that the glucose sensor exhibited a redshift characteristic.

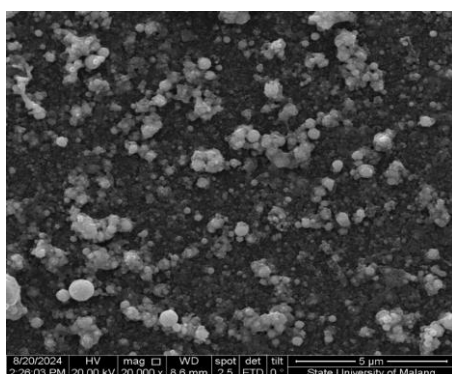


Figure 5. SEM image of AgNPs

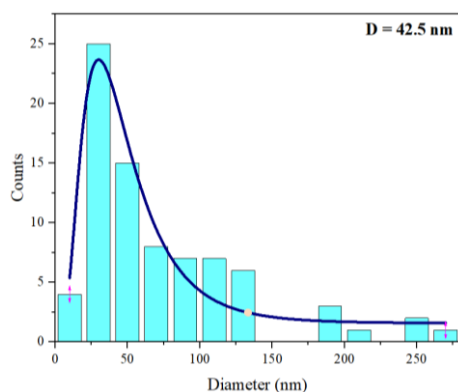


Figure 6. Size distribution of AgNPs



Figure 7. AgNP nanocolloidal solutions containing glucose with different concentrations

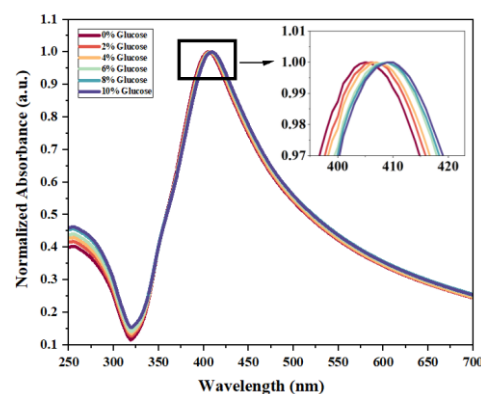


Figure 8. UV-Vis spectra of AgNP nano colloidal solution containing glucose with different concentrations

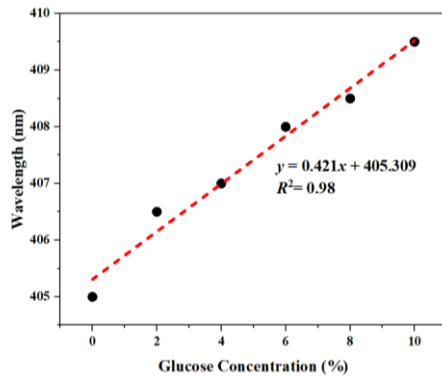


Figure 9. Fitting for sensitivity evaluation of glucose sensor using AgNPs

The plot of wavelength vs. glucose concentration, as displayed in Figure 9, showed that AgNPs demonstrated a strongly linear correlation, providing the linear regression coefficient reached 0.98. From the linear fitting analysis, it was obtained that the AgNPs' sensitivity to glucose was 0.421 nm/% with a detection range of 0-10% glucose. In this measurement, the Limit of Quantification (LOQ) and Limit of Detection (LOD) are important parameters in the validation of analytical methods, where the LOD indicates the minimum concentration that can still be detected, while the LOQ is the lowest concentration value that can be measured and quantified with precision. LOD and LOQ are derived using the following formulas (Chibério *et al.*, 2020):

$$\text{LOD} = \frac{(3.3 \times \sigma)}{S}$$

$$\text{LOQ} = \frac{(10 \times \sigma)}{S}$$

where σ is standard error value and S is the slope value. In this study, the LOD and LOQ were 0.2236% and 0.7453%, respectively. The redshift response of the plasmonic AgNPs towards glucose was also reported by other studies (Xu *et al.*, 2024). This study showed that glucose can be detected using simple colorimetric analysis, where the UV-Vis test could be used as the instrument to record the spectral changes of the LSPR characteristics of AgNP nanocolloidal solutions with the addition of glucose.

In addition, the Full Width at Half Maximum (FWHM) value and the detection accuracy (DA) were also analyzed. The DA value was inversely proportional to the FWHM, as depicted in Table 3. From this analysis, it can be inferred that the FWHM of the glucose sensor was around 127-130 nm, and the DA was around 0.0076-0.0078 /nm.

Table 3. Effect of glucose concentration on FWHM and DA

Concentration of Glucose	FWHM (nm)	DA (/nm)
0	130.396	0.0076
2	128.618	0.0077
4	128.603	0.0077
6	129.557	0.0077
8	128.084	0.0078
10	127.558	0.0078

Conclusions

Synthesis of AgNPs by means of pulsed Nd: YAG laser ablation with various laser beam diameters was successfully conducted. The optimized AgNPs were obtained when the laser beam diameter was 1 mm, indicated by the highest value of absorbance or LSPR peak: 0.682 au at a wavelength of 405 nm. The analysis of the UV-Vis results indicated that the interaction between AgNPs and glucose at different concentrations caused a redshift in the LSPR spectra. The wavelength linearly shifted to longer values as the glucose concentration increased. The coefficient of determination, showing a linear response of the LSPR wavelength towards glucose concentration, was 0.98. The glucose sensing sensitivity of AgNPs was 0.421 nm/% in the detection range of 0-10%. Early glucose detection can be achieved by using AgNPs for further diabetes mellitus monitoring and management.

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