IJPAS | INTERNATIONAL JOURNAL PURE AND APPLIED SCIENCES
ISSN:2149-0910

Vol. 10(2); 632-641 (2024)
DOI: 10.29132/ijpas.1584049

Research Article

Investigating Sensor Properties of Plasmonic Gold Nanoparticles Produced By Pulsed Laser Deposition

İlhan CANDAN [1,*], Serap YİĞİT GEZGİN[2], Hadice BUDAK GÜMGÜM[1], Hamdi Şükür KILIÇ[2, 3,4]

Received: 13.11.2024

Accepted: 27.12.2024

[1*]Dicle University, Faculty of Science, Department of Physics, Diyarbakır, Türkiye; ilhan.candan@dicle.edu.tr*, hbudakg@gmail.com
[2]Selcuk University, Faculty of Science, Department of Physics, Konya, Türkiye; serap.gezgin@selcuk.edu.tr
[3]Selcuk University, High Technology Research and Development Center (ILTEK), Konya, Türkiye
[4] Selcuk University, Directorate of Laser Induced Proton Therapy Application and Research Center, Konya, Türkiye
*Corresponding author

Abstract: Plasmonic gold nanoparticles exhibit exceptional optical properties, particularly Localised Surface Plasmon Resonance, which makes them ideal candidates for sensor applications. These nanoparticles are highly sensitive to changes in their surrounding environment, allowing for precise detection of molecular interactions and environmental shifts. In this study, we investigate the sensor properties of gold nanoparticles produced *via* Pulsed Laser Deposition, a clean and versatile method that allows for precise control over particle size, morphology, and distribution without the need for chemical reagents. Pulsed Laser Deposition process was optimized by adjusting laser fluence, pulse duration, and deposition time to produce gold nanoparticles with tunable plasmonic properties. The structural and optical characteristics of gold nanoparticles were analyzed using scanning electron microscopy, and UV-Vis spectroscopy, confirming that the size and morphology of the particles were controllable through the deposition parameters. The sensor performance of gold nanoparticles was evaluated through localised surface plasmon resonance measurements, which demonstrated their sensitivity to small changes in the refractive index of the surrounding medium. Specifically, the shift in localised surface plasmon resonance peak was measured upon exposure to different analytes, including protein A where a wavelength shift of 50 nm measured, indicating the high sensitivity of these nanoparticles for biosensing applications. The results suggest that Pulsed Laser Deposition-produced gold nanoparticles possess promising sensor properties for real-time detection and environmental monitoring, offering an efficient and reproducible platform for a wide range of sensing applications.

Keywords: Au nanoparticles; LSPR; plasmonics; PLD

Puls Lazer Depozisyonu Yöntemiyle Üretilen Plazmonik Altın Nanoparçacıkların Sensör Özelliklerinin Araştırılması

Özet: Plazmonik altın nanoparçacıklar (Au NP'ler), özellikle Lokalize Yüzey Plazmon Rezonansı (LSPR) sayesinde, sensör uygulamaları için ideal adaylar olarak öne çıkan üstün optik özelliklere sahiptir. Bu nanoparçacıklar, çevrelerindeki ortamdaki değişimlere karşı yüksek hassasiyet gösterir ve bu sayede moleküler etkileşimlerin ve çevresel değişimlerin hassas bir şekilde tespit edilmesini sağlar. Bu çalışmada, kimyasal reaktiflere ihtiyaç duyulmadan parçacık boyutu, morfolojisi ve dağılımı üzerinde hassas kontrol imkânı tanıyan temiz ve çok yönlü bir yöntem olan Puls Lazer Depozisyonu (PLD) ile üretilen altın nanoparçacıkların sensör özellikleri incelenmiştir. PLD işlemi, ayarlanabilir plazmonik özelliklere sahip altın nanoparçacıklar üretmek için lazer akısı, puls süresi ve biriktirme süresi ayarlanarak optimize edilmiştir. Altın nanoparçacıkların yapısal ve optik özellikleri, taramalı elektron mikroskobu (SEM) ve UV-Vis spektroskopisi kullanılarak analiz edilmiş ve parçacık boyutu ile morfolojisinin biriktirme parametreleri ile kontrol edilebildiği doğrulanmıştır. Altın nanoparçacıkların sensör performansı, çevrelerindeki ortamın kırılma indisi değişimlerine duyarlılıklarını gösteren LSPR ölçümleri ile değerlendirilmiştir. Özellikle, LSPR piki, protein A dâhil çeşitli analizlere maruz bırakıldığında 50 nm dalga boyu kayması ile ölçülmüş ve bu nanoparçacıkların biyosensör uygulamaları için yüksek hassasiyete sahip olduğunu göstermiştir. Sonuçlar, PLD ile üretilen altın nanoparçacıkların gerçek zamanlı algılama ve çevresel izleme için umut vadeden sensör özelliklerine sahip olduğunu ve geniş bir sensör uygulama yelpazesi için verimli ve yeniden üretilebilir bir platform sunduğunu göstermektedir.

Anahtar Kelimeler: Au nanoparçacıklar; LSPR; plazmonik; PLD

1. Introduction

Gold NPs (Au NPs) have attracted significant attention in recent years due to their unique plasmonic properties, which make them highly sensitive to changes in their surrounding environment [1-3]. These properties stem from surface plasmon resonance (SPR), a phenomenon where conduction electrons on the NP's surface resonate with incident light, leading to enhanced optical absorption and scattering [4-6]. This feature enables Au NPs to be applied in various fields, including chemical and biological sensing, catalysis, and photothermal therapies [7-10]. Among these applications, the use of Au NPs as sensors has been particularly notable for detecting molecular interactions and environmental changes with remarkable sensitivity and precision [11-13].

Producing Au NPs with well-defined plasmonic properties is essential for optimization of their performance as sensors. Numerous fabrication methods, such as chemical reduction and seed-mediated growth, have been used to synthesize Au NPs with controlled size and shape [13, 14]. However, these techniques can involve chemical residues and lack uniformity, posing challenges for

reproducibility and stability in sensing applications. To overcome these limitations, physical deposition techniques such as Pulsed Laser Deposition (PLD) have emerged as promising alternatives. PLD offers a highly controllable and clean approach for producing metal NPs (NPs) without chemical reagents, which is advantageous for maintaining purity and reducing environmental impact [15-18]. In addition, PLD enables precise control over particle morphology and distribution by adjusting parameters such as laser fluence, substrate temperature, and deposition atmosphere [19], making it possible to tailor the plasmonic properties of Au NPs for specific applications [20, 21].

In this study, we investigate the sensor properties of plasmonic Au NPs produced by PLD technique. Unlike traditional methods, PLD provides a unique approach to NPNP fabrication by allowing direct deposition of NPs onto various substrates under controlled conditions. This can potentially enhance the sensitivity and stability of Au NPs-based sensors by ensuring strong particle-substrate adhesion and minimizing surface contamination. Additionally, PLD can facilitate the production of Au NPs with highly tunable plasmonic characteristics, as the particle size, density, and distribution can be modified in situ. By exploring these attributes, we aim to optimize the performance of Au NPs as plasmonic sensors for detecting minute changes in the surrounding medium, particularly for applications requiring high sensitivity and rapid response times.

This paper focuses on the fabrication, characterization, and analysis of plasmonic Au NPs produced by PLD. We examine the effects of various deposition parameters on the morphology, optical properties, and sensor performance of NPs. Through advanced characterization techniques, including Scanning Electron Microscopy (SEM), and UV-Vis spectroscopy, we evaluate the relationship between NP structure and sensor efficiency. Our results provide insights into how controlled fabrication *via* PLD can enhance the plasmonic response and sensing capabilities of Au NPs, opening new possibilities for their application in real-time sensing and diagnostics. This study not only contributes to the understanding of the fundamental properties of plasmonic Au NPs produced by PLD but also presents a pathway toward scalable, reproducible, and environmentally friendly fabrication of NP-based sensors.

2. Materials and Methods

Au NPs were produced using a PLD system. The Nd:YAG laser (Continuum, Minilite II) was operated in pulsed mode with a 5 ns duration and a 10 Hz repetition rate at a fundamental wavelength of 1064 nm. This laser can also produce second, third, and fourth harmonics at wavelengths of 532, 355, and 266 nm, respectively, although only 1064 nm wavelength was used in this study. While shorter harmonics of the Nd:YAG laser are effective for certain materials, they are less efficient and practical for gold targets due to reduced absorption, increased surface damage, and interference from denser plasmas. The 1064 nm laser provides optimal energy coupling and ablation conditions for gold, making it the preferred choice for PLD applications involving gold targets. Using a 1064 nm laser for ablation of a gold target in PLD offers advantages in terms of material absorption efficiency, reduced thermal and photochemical effects, cost-effectiveness, and compatibility with standard deposition systems. It ensures effective and controlled ablation, resulting in high-quality thin films without causing significant damage to the target or undesirable plasma interactions. Laser pulse power was controlled using a neutral density filter, with measurements taken before the focusing lens (Figure 1). A glass microscope slide served as the substrate for depositing Au NPs. For substrate preparation, the

slide was initially cleaned with alkaline detergent, then immersed in isopropyl alcohol and acetone baths for 15 minutes each, and finally placed in an ultrasonic bath to complete the cleaning process. The ultrasonic bath uses high-frequency sound waves (typically 20–40 kHz) generated by a transducer in a liquid cleaning solution. These sound waves create microscopic cavitation bubbles in the liquid. When the bubbles collapse, they produce localized high-energy jets that effectively dislodge contaminants from the surface of the glass, including tiny crevices and irregularities. The slides were then dried using a nitrogen gas flow. The cleaned glass is dried, often using nitrogen gas or air to prevent streaks and water spots. The gold sputtering target used was a commercially available, high-purity (99.99%) sample from Plasmaterials, USA. To prevent any damage during deposition, the target and substrate were mounted on independently rotating holders. This setup ensured that each laser pulse impacted a different area of the target, achieving a uniform coating of Au NPs after laser ablation (Figure 1). The laser fluence in PLD must be carefully controlled to ensure efficient target ablation, proper plume formation, and high-quality thin-film deposition while avoiding damage to the target or defects in the film.

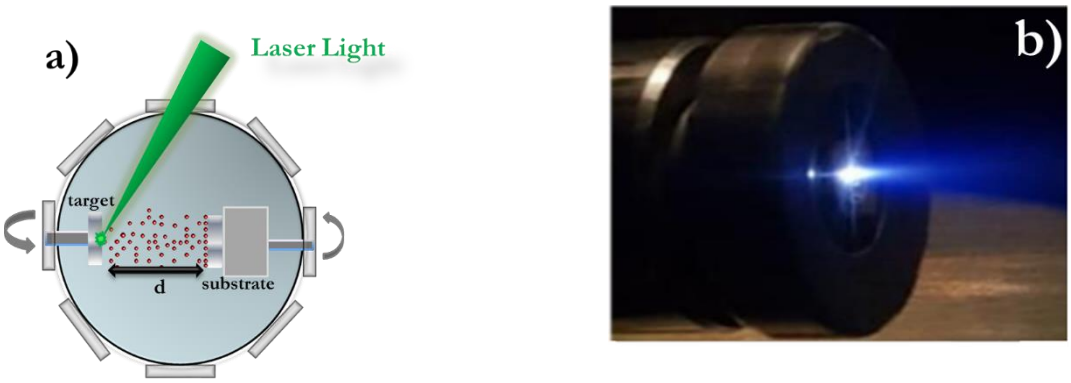

Figure 1. a) A schematic representation of the PLD system, which was designed, b) Plasma generated from the ablation of the Au target material using the PLD system [22].

A fixed distance of 5 cm was maintained between the target and substrate. The laser deposition process was conducted at room temperature for all films, with the laser energy set to 35 mJ per pulse. A 50 cm focal length lens used to focus the laser beam onto the Au target, with the beam angled at 45° to the target surface. All experiments took place under ultrahigh vacuum conditions, approximately 5×10^{-7} mbar. The gold sputtering target was ablated with 12.600 and 14.400 laser pulses to produce different NP morphologies. SEM image was used to analyze the morphology of the resulting Au NPs, while energy-dispersive X-ray (EDX) spectroscopy performed to determine the elemental composition of the thin film. The absorption spectra of Au NPs were measured using a UV-Vis spectrometer (V-670 Jasco, USA). To evaluate the sensor properties of the plasmonic NPs, a 1 ppm solution of protein A (Sigma-Aldrich) was prepared in ultrapure water as a solvent. Localized Surface Plasmon Resonance (LSPR) peak shifts of the plasmonic Au NPs were recorded using UV-Vis spectrometer.

3. Results and Discussion

Considering plasma production and NP formation scheme in the inserted in the figure 2a, Au NPs vaporized by ablating the Au sputtering target laser light form a plasma plume. These ablated Au

NPs are deposited on the microscopic slide substrate with high kinetic energy. Due to their high kinetic energy, Au NPs combine with each other and become large particles as shown in figure by being deposited on top of each other [23-25]. Figure 2 shows SEM images of Au NPs produced with 30 minutes of deposition (18.000 laser pulses). The images are magnified 50.000, 10.000, and 2.000 times, respectively. The size of Au NPs produced is approximately 370 nm at 50.000x magnification. In Figure 2b, three Au NPs are visible. As seen in Figure 2c, the number and size of NPs have increased. This is due to the increased deposition time, meaning the number of laser pulses was higher. Additionally, the particle density has also increased.

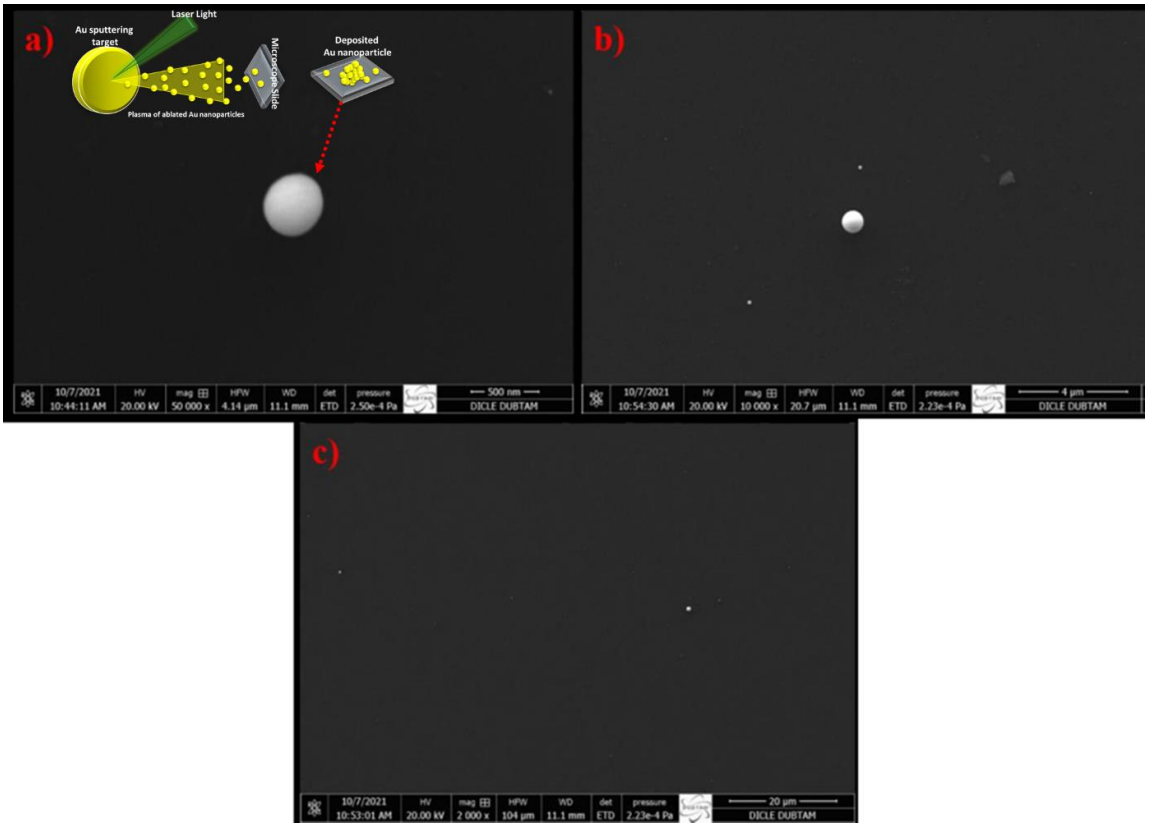

Figure 2. SEM images of Au NPs produced with 30 minutes of deposition time (18.000 laser pulses). Image magnified, a) 50.000 b) 10.000 c) 2.000 times.

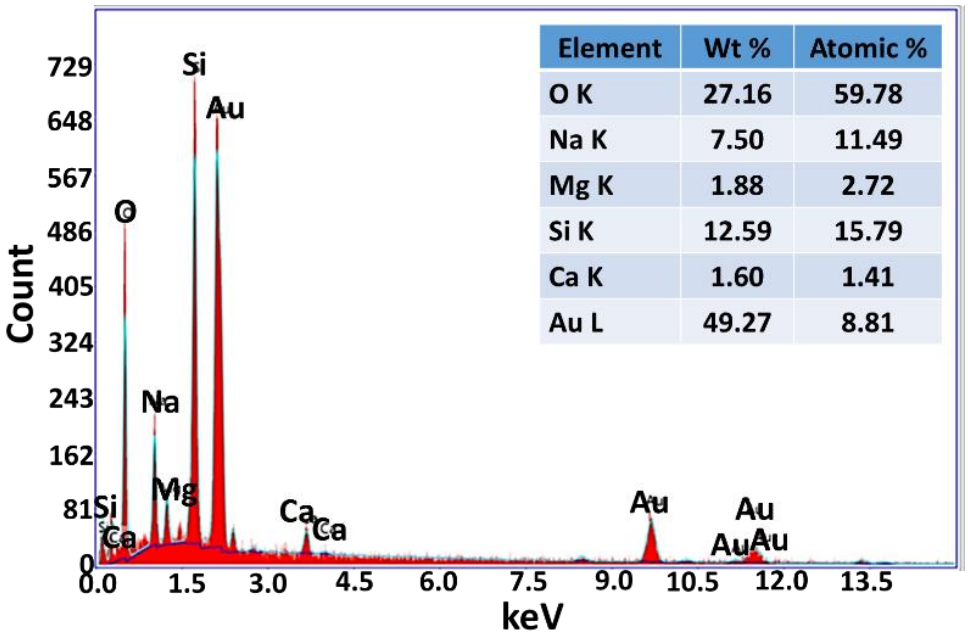

Figure 3. EDX spectrum of the produced Au NPs.

The elements present in the thin films are Au, Si, O, Na, Ca, and Mg. The presence of Au in the composition confirms the use of an Au target in the experiment, along with other components, as NPs are deposited on glass microscope substrates. The weight percentages of the elements are provided in the inset of Figure 3. EDX spectrum of Au NPs produced with 12.000 laser pulses is shown in Figure 3. The thin film composition includes Au, Si, O, Na, Ca, and Mg. Au NPs are deposited onto glass microscope substrates, and EDX findings align with the experimental setup.

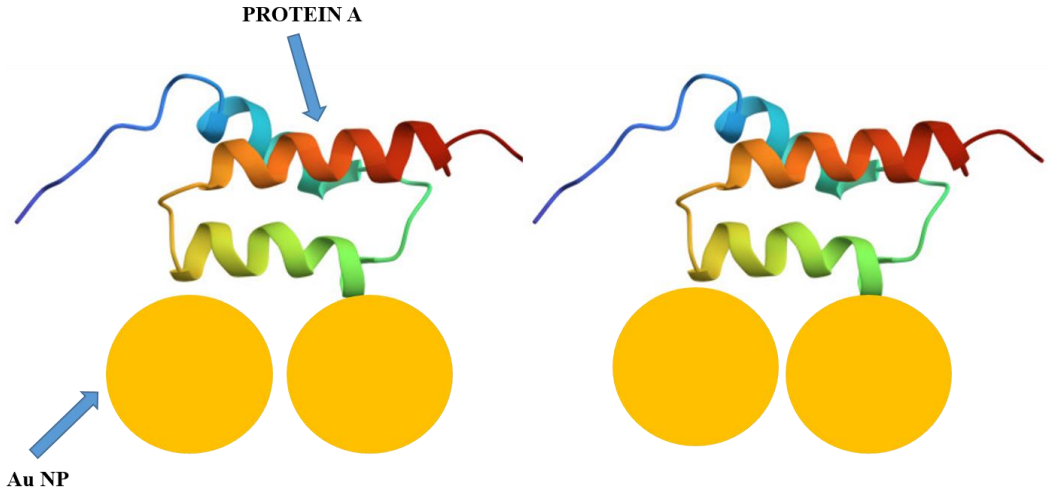

Figure 4. The illustration shows Au NPs binding to Protein A molecules.

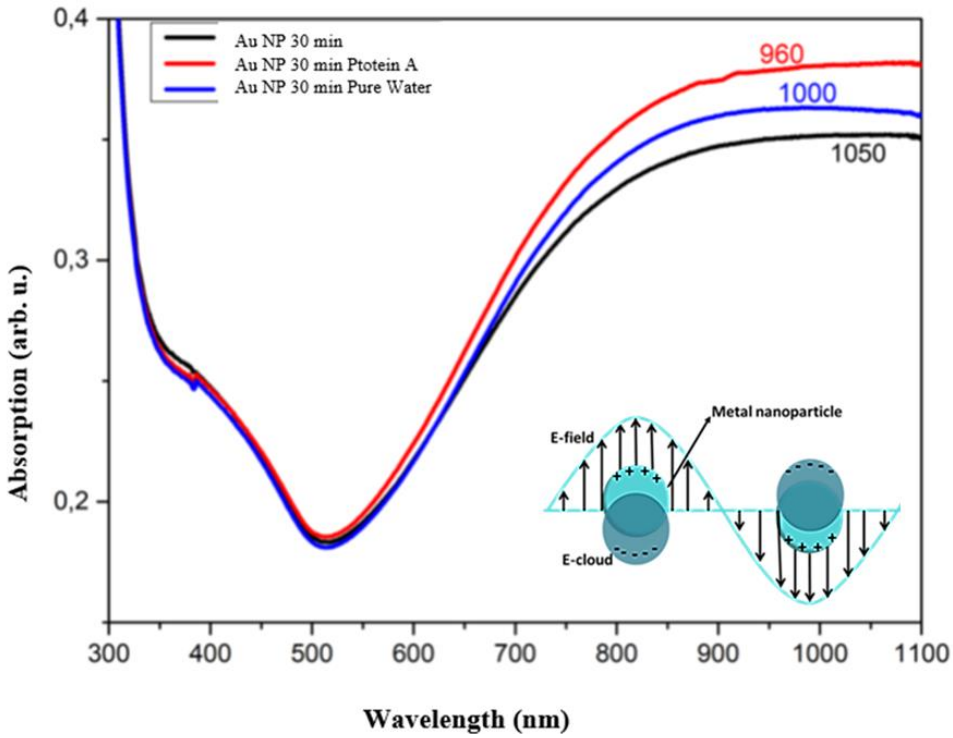

Figure 5. UV-Vis-NIR spectra of Au NPs produced by PLD for 30 minutes (18.000 laser pulses), as well as for pure water and protein A binding NPs. For pure water and protein A binding NPs, blue shifts of 50 nm and 40 nm are observed, respectively.

Plasmonic Au NP thin films were produced using PLD technique. Au NPs binds to Protein A molecules as shown in Figure 4. The synthesized Au NPs were analyzed *via* UV-Vis-NIR spectroscopy, and the results are displayed in Figure 5. As shown in the figure, LSPR peaks of Au NPs, produced with 18.000 laser pulses (30-minute deposition time), are located at 1050, 1000, and 960 nm, respectively. First, LSPR peak of pure Au NPs was measured and found to be positioned in the infrared region at 1050 nm. The large size of Au NP causes the restoring force on the electron oscillations (plasmon) within the particle (in the inset image in Fig 5) to decrease, and the electron oscillations to become distorted, decreasing their frequency, thus shifting LSPR wavelength to the infrared region.

The size of Au plasmonic NPs can be calculated by the following equation:

$$d = \frac{ln\left(\frac{\lambda_{spr} - \lambda_o}{L_1}\right)}{L_2} \quad \textbf{(3.1)}$$

Where, $\lambda_o = 532$ nm; $L_1 = 6.53$ nm; $L_2 = 0.0216\, nm^{-1}$ [26]. Using Eq (3.1), the NP size was theoretically calculated to be 202 nm for LSPR peak of 1050 nm. Its value is smaller than NP size obtained in SEM image. Next, a thin layer of ultrapure water was added to the produced Au NP film. The UV-Vis-NIR spectrum showed a blue shift of approximately 50 nm in LSPR peak, positioning it

at 1000 nm. Finally, a solution of protein A, prepared at a concentration of 1 ppm and diluted in pure water, was added onto Au NP film, and UV-Vis-NIR spectrum was recorded. LSPR peak of Au NPs with protein A shifted to 960 nm. Therefore, it was determined that the binding of protein A shifted LSPR peak of Au NPs by 40 nm to a shorter wavelength. Additionally, when considering the shift relative to the refractive index, LSPR peak of Au NPs measured in air (n=1) was at 1050 nm, while in pure water (n=1.33) it shifted to 1000 nm, resulting in a 50 nm wavelength shift, corresponding to approximately 152 nm/RIU in refractive index units.

4. Conclusion and Suggestions

This study has demonstrated the potential of PLD as a highly effective and controllable method for producing plasmonic Au NPs tailored for sensor applications. Through careful tuning of deposition parameters, including laser fluence, pulse duration, and deposition time, we were able to fabricate Au NPs with well-defined morphology and LSPR characteristics. SEM imaging, coupled with UV-Vis spectroscopy, confirmed that PLD-produced Au NPs exhibited uniform size and distribution, crucial factors in achieving reliable sensor performance. Our findings show that SPR peak of Au NPs responded sensitively to change in the refractive index of the surrounding medium, with measurable shifts upon exposure to various analytes. This sensitivity underscores the suitability of these NPs for real-time detection and molecular sensing. Additionally, the environmentally friendly, chemical-free nature of PLD production offers an advantage in reducing contamination and enhancing the reproducibility of Au NP-based sensors, making this approach especially promising for biosensing applications. The observed sensor properties highlight that PLD-produced Au NPs could be effectively utilized in applications requiring precise and rapid detection, such as in environmental monitoring and medical diagnostics. The relationship between deposition conditions and LSPR response provides valuable insights into tuning the performance of plasmonic nanomaterials. Future work could further explore PLD's capabilities for multi-metallic or alloy NP production, aiming to expand the range of detectable substances and increase sensor selectivity. In conclusion, this study contributes to advancing the fabrication and application of plasmonic nanomaterials, demonstrating that PLD is a viable, scalable, and efficient technique for producing high-performance sensors based on Au NPs.

Conflict of Interest

The Authors report no conflict of interest relevant to this article

Research and Publication Ethics Statement

The authors declare that this study complies with research and publication ethics.

References

[1] Bai, X. et al. (2020). The basic properties of gold nanoparticles and their applications in tumor diagnosis and treatment. *International journal of molecular sciences*, 21(7), 2480.

[2] Zhou, W. et al. (2015). Gold nanoparticles for in vitro diagnostics. *Chemical reviews*, 115(19), 10575-10636.

[3] Ramachandran, T. et al. (2024). Gold on the horizon: unveiling the chemistry, applications and future prospects of 2D monolayers of gold nanoparticles (Au-NPs). *Nanoscale Advance.*

[4] Ghosh, S.K. and Pal, T. (2007). Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications. *Chemical reviews*, 107(11), 4797-4862.

[5] Amendola, V. et al. (2017). Surface plasmon resonance in gold nanoparticles: a review. *Journal of physics: Condensed matter*, 29(20), 203002.

[6] Gezgin, S.Y., A. Kepceoğlu, and Kılıç, H.Ş. (2017). An investigation of localised surface plasmon resonance (LSPR) of Ag nanoparticles produced by pulsed laser deposition (PLD) technique. in *AIP Conference Proceedings*. AIP Publishing LLC.

[7] Falahati, M. et al. (2020). Gold nanomaterials as key suppliers in biological and chemical sensing, catalysis, and medicine. *Biochimica et Biophysica Acta (BBA)-General Subjects*, 1864(1), 129435.

[8] Hang, Y., A. Wang, and N. Wu, (2024). Plasmonic silver and gold nanoparticles: shape-and structure-modulated plasmonic functionality for point-of-caring sensing, bio-imaging and medical therapy. *Chemical Society Reviews.*

[9] Candan, I. et al. (2024). Sensor properties of plasmonic silver and gold nanoparticles produced by pulsed laser deposition. *Journal of Optoelectronics and Advanced Materials*, 26(5-6), 186-198.

[10] Gezgin, S.Y., A. Kepceoğlu, and H.Ş. Kılıç. (2017). An experimental investigation of localised surface plasmon resonance (LSPR) for Cu nanoparticles depending as a function of laser pulse number in Pulsed Laser Deposition. in *AIP Conference Proceedings*. AIP Publishing LLC.

[11] Priyadarshini, E. and N. Pradhan. (2017). Gold nanoparticles as efficient sensors in colorimetric detection of toxic metal ions: a review. *Sensors and Actuators B: Chemical*, 238, 888-902.

[12] Candan, İ. (2022). *Plazmonik soy metal (Au, Ag) nanoparçacıklara dayalı sensör üretimi ve analizi*. Dicle Üniversitesi Fen Bilimleri Enstitüsü.

[13] Sadiq, Z. et al. (2024). Gold nanoparticles-based colorimetric assays for environmental monitoring and food safety evaluation. *Critical Reviews in Analytical Chemistry*, 54(7), 2209-2244.

[14] Qiao, J. and L. Qi. (2021). Recent progress in plant-gold nanoparticles fabrication methods and bio-applications. *Talanta*, 223, 121396.

[15] Escorcia-Díaz, D. et al. (2023). Advancements in nanoparticle deposition techniques for diverse substrates: a review. *Nanomaterials*, 13(18), 2586.

[16] Gezgin, S.Y. et al. (2020). Effect of Ar gas pressure on lspr property of Au nanoparticles: comparison of experimental and theoretical studies. *Nanomaterials*, 10(6), 1071.

[17] Gezgin, S.Y.ğ.t. and H.Ş. Kılıç. (2020). An improvement on the conversion efficiency of Si/CZTS solar cells by LSPR effect of embedded plasmonic Au nanoparticles. *Optical Materials*, 101, 109760.

[18] Jamkhande, P.G. et al. (2019). Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. *Journal of drug delivery science and technology*, 53, 101174.

[19] Kepceoğlu, A. et al. (2019). Nonlinear optical properties of zinc oxide thin films produced by pulsed laser deposition. *Materials Today: Proceedings*, 18, 1819-1825.

[20] Haider, A.J. et al. (2022). A comprehensive review on pulsed laser deposition technique to effective nanostructure production: Trends and challenges. *Optical and Quantum Electronics*, 54(8), 488.

[21] Goncalves, M.R., *Plasmonic nanoparticles: fabrication, simulation and experiments.* Journal of Physics D: Applied Physics, 2014. **47**(21): p. 213001.

[22] Candan, İ. et al. (2021). Biosensor Properties Of Plasmonic Silver Nanoparticles Produced By Pld. *Middle East Journal of Science*, 7(2), 112-122.

[23] Gezgin, S.Y. A. Kepceoğlu, and H.Ş. Kılıç. (2017). An investigation of localised surface plasmon resonance (LSPR) of Ag nanoparticles produced by pulsed laser deposition (PLD) technique. in *AIP Conference Proceedings*. AIP Publishing.

[24] Gezgin, S.Y. et al. (2016). Plasmonic tuning of gold doped thin films for layers of photovoltaic devices. in *AIP Conference Proceedings*. AIP Publishing.

[25] Gezgin, S.Y. A. Kepceoğlu, and H.Ş. Kılıç. (2017). An experimental investigation of localised surface plasmon resonance (LSPR) for Cu nanoparticles depending as a function of laser pulse number in Pulsed Laser Deposition. in *AIP Conference Proceedings*. AIP Publishing.

[26] Haiss, W. et al. (2007). Determination of size and concentration of gold nanoparticles from UV− Vis spectra. *Analytical chemistry,* 79(11), 4215-4221.