MONITORING OF DIAMETER OF GOLD NANOPARTICLES USING ULTRAVIOLET-VISIBLE SPECTROSCOPY

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DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

This research presents monitoring of average diameter and concentration of gold nanoparticles (NPs) using ultraviolet-visible (UV-Vis) spectroscopy. The reliability of the UV-Vis spectroscopy is verified by comparing it to the transmission electron microscopy (TEM) results. One of the main objectives of this study is to determine the gold nanoparticles' diameter and concentration evolution with ablation time. Also, the properties of gold NPs produced by using Pulsed Laser Ablation in Liquids (PLAL) in four different liquids were analyzed and compared. Deionized water, distilled water, ethanol mixture (70% ethanol, and 30 % deionized water), and polyvinyl alcohol (PVA) are used in the experiment as the liquid media. The laser source used is a Q-switched Nd: YAG laser with an energy of 315 mJ, a repetition rate of 1 Hz, and a wavelength of 1064 nm. The laser ablation was conducted for the duration of 60 minutes at room temperature to obtain the pure colloidal solution of gold NPs. The diameter of the gold NPs obtained from UV-Vis spectroscopy is 7.19 nm in deionized water. The diameter of gold NPs from TEM is 7.117 nm. The results between UV-Vis spectroscopy and TEM are relatively comparable. In the case of laser ablation in deionized water, the gold nanoparticle size does not change significantly with time. The average diameter over ablation time is 41.686 nm. The results also illustrate that the concentration of gold nanoparticles depends on ablation time. By increasing the ablation time, the concentration increased. The slope of concentration against ablation time is $2.11 \times 10^9\, cm^{-3}/min$. By comparing the gold NPs concentration and average diameter, the demonstration showed that distilled water has the smallest average diameter of $38.09\, nm$ and the highest concentration $3.67 \times 10^{11}\, cm^{-3}$. In contrast, ethanol mixture has the largest average diameter of 74.38 nm and the smallest concentration of $5.31 \times 10^9 cm^{-3}$. From these results, it is confirmed that UV-Vis spectroscopy is able to monitor the size and concentration of gold NPs by using PLAL in liquids.

ABSTRAK

Penyelidikan ini menunjukkan pemantauan purata diameter dan kepekatan zarah nano emas (AuNPs) menggunakan spektroskopi ultraunggu-nampak (UV-Vis). Kebergantungan spektroskopi UV-Vis adalah disahkan daripada keputusan perbandingan mikroskopi electron transmisi (TEM). Salah satu objektif utama dalam kajian ini adalah untuk menentukan perubahan diameter dan kepekatan AuNPs dengan masa ablasi. Juga, sifat AuNPs yang dihasilkan dengan menggunakan ablasi laser denyut (PLAL) dalam cecair yang berbeza turut dianalisis dan dibandingkan. Air nyahion, air suling, campuran etanol (70 % etanol, dan 30 % air nyahion) dan alkohol polivinil (PVA) digunakan dalam eksperimen sebagai medium cecair. Sumber laser yang digunakan adalah laser Nd:YAG pensuisan-Q dengan tenaga 315 mJ, kadar pengulangan 1 Hz, dan panjang gelombang 1064 nm. Ablasi laser dilakukan hingga 60 min pada suhu bilik untuk mendapatkan larutan koloid AuNPs yang tulen. Diameter AuNPs yang diperoleh dari UV-Vis adalah 7.19 nm dalam air nyahion. Manakala diameter AuNPs dari TEM pula adalah 7.117 nm. Keputusan antara spektroskopi UV-Vis dan TEM adalah sebanding. Untuk kes ablasi laser dalam air nyahion, saiz Au NP tidak berubah dengan ketara mengikut masa. Diameter purata sepanjang masa ablasi ialah 41.69 nm. Hasilnya juga menggambarkan bahawa kepekatan AuNPs bergantung kepada masa ablasi. Dengan meningkatkan masa ablasi, kepekatan juga akan meningkat. Cerun kepekatan terhadap masa ablasi adalah $2.11 \times 10^9 \frac{cm^{-3}}{\min}$. Dengan membandingkan kepekatan AuNPs dan purata diameter, demonstrasi ini menunjukkan bahawa air suling mempunyai diameter purata terkecil iaitu 38.09 nm dan kepekatan tertinggi $3.67 \times 10^{11}\ cm^{-3}$. Sebaliknya, campuran etanol mempunyai diameter purata terbesar iaitu 74.38 nm dan kepekatan terkecil $5.31 \times 10^9\ cm^{-3}$. Berdasarkan keputusan ini, ianya jelas bahawa spektroskopi UV-Vis mampu memantau saiz dan kepekatan yang diinginkan oleh AuNPs dengan menggunakan PLAL dalam cecair.

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LIST OF ABBREVIATIONS

PLAL	-	Pulsed Laser Ablation
Au	-	Gold
Ag	-	Silver
Cu	-	Copper
NPs	-	Nanoparticles
DLS	-	dynamic light dispersion
SEM	-	scanning electron microscopy
FT-IR	-	Fourier transforming infrared spectroscopy
XRD	-	X-ray diffraction
EDS	-	energy dispersive spectroscopy
TEM	-	transmission electron microscopy
UV-Vis	-	Ultraviolet-Visible
SPR	-	Surface Plasmon Resonance
OD	-	Optical Density

LIST OF SYMBOLS

D, d	-	Diameter
N	-	Concentration
λ_{spr}	-	SPR peak position
λ_0	-	theorical peak position
L_1, L_2	-	first and second theoretical electric dipoles
A_{abs}	-	surface plasmon resonance absorbance
A_{450}	-	is the absorbance at $\lambda = 450$ nm
B_1	-	the reverse of linear slope (m)

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the 21st century, nanotechnology has been one of the key technologies that have wide usage such as in optics, catalyst, biomedicine and etc. (Kalus *et al.*, 2019). Metal nanoparticles have gained tremendous attention in recent years because of their specific chemical, physical behaviour and surface plasmon behaviour (Khan et al., 2017). They provide a broad variety of electrical and optical properties which arise from the effects of quantum confinement. Gold (Au) nanoparticles (NPs) are promising materials for a wide variety of applications including sensors (Pérez *et al*, 2015), catalysis (Huang et al., 2012), systems for drug delivery (Masse *et al.*, 2019), cancer diagnosis and treatment (Suneetha *et al.*, 2014; Pérez *et al*.2015; Arachchige *et al.*, 2015).

AuNPs are the most stable and reliable metal nanoparticles, it can also be called Au colloids, which have been recognized for decades. AuNPs have been especially suggested as extremely useful synthesizing factors in phototherapy because of their specific shape and size of optical properties dependent, ease of synthesis, high coefficients of absorption, biocompatibility, and the capacity to sustain a large variety of functional ligands (Zhang *et al.*, 2017).

Since Roman times, the usage of AuNPs was used in glass coloring. Classical strategies for obtaining AuNPs are based on chemical salt reduction which Faraday discussed in the year of 1857(Faraday, 1857). Nowadays, it is still a prevalent issue as new reductant agents were introduced each year with a differing conditions and nature. The reagents act as reductants but also as stabilizers in such chemical synthesis methods. Then, for the first time in 1898, Richard Adolf Zsigmondy prepared colloidal Au in a diluted solution. Actual interest in work on nanoparticles started in 1959 after a popular talk by physicist Richard P. Feynman (Santhoshkumar *et al*., 2017; Feynman, 2009). Worldwide researchers and scientists who are well aware of AuNPs capabilities are seeking to discover new applications in a different science field.

To date, there are numerous nanoparticle synthesizing techniques available. These techniques, however, come in two specific approaches and can be described as either a bottom-up or a top-down approach. Presently, nanoparticles of various shapes, sizes, and compositions were developed through a wide variety of chemical and physical techniques. The Physical method involves techniques such as laser ablation (Santhoshkumar *et al*., 2017), high energy irradiation, and lithography (DeSimone et al., 2020). Whereas the chemical technique utilizes methods including photochemical reduction (John *et al*., 2018), electrochemical reduction (Haro-González *et al*., 2019), and chemical reduction (Faraday, 1857). These different techniques also have many drawbacks, including difficulties in managing the NPs sustainability, size and shape (morphology), reproducibility, and AuNPs separation. However, the isolation of chemical products and unreacted regents from the AuNPs often involves a purification stage. There are also several situations under which the existence of AuNPs-bound molecules is detrimental to the surface (Alluhaybi *et al*., 2019).

Non-chemical ways for forming metal NPs to avoid the existence of chemicals are very attractive in this regard. The method was defined as laser ablation synthesis in solution (LASIS) or as pulsed laser ablation in liquid (PLAL) is an effective process of producing AuNPs in liquid (Palazzo *et al*., 2017). Recently, PLAL has appeared as one of the most powerful green techniques for producing various NPs. Because of its usability, cost-effectiveness, reproducibility of contaminant-free samples, specific surface chemistry, and outstanding stability. This is also an environmentally friendly and adaptable method to produce NPs with optimal morphology and free from contaminants (Aso *et al*., 2019).

From the perspective of their tunable optical properties, the AuNPs are especially important, that significantly depending on both the particle shape and size. Au nanoparticles (AuNP) were a very significant and frequent resource in nanotechnology. Primarily it is because of their surface plasmon resonance. A distinctive characteristic of is the powerful vibrant color of the colloidal solution, caused by SPR or surface plasmon resonance absorption (Zeng *et al*., 2011). In colloidal solutions, spherical AuNPs show a variety of colors because of the core size growing from 1nm to 100 nm (Yeh *et al*., 2012).

AuNPs size and concentration can be described and characterized with Ultraviolet-Visible (UV-Vis) spectroscopy and transmission electron microscopy. The most popular technique for obtaining exact data on the average size distribution, AuNPs size, and shape is transmission electron microscopy (Khan *et al*., 2017). UV-vis spectroscopy is an extremely useful technique for estimating the concentration, size and aggregation of AuNPs (Aso *et al*., 2019).

1.2 Problem Statement

When the AuNPs is produced by using pulsed laser ablation (PLAL), the size of these AuNPs is determined through transmission electron microscopy (TEM). It is accurate but can be problematic because the results obtained are not on a real time basis. It is a local measurement. The result might not represent the whole of AuNPs colloid. Also, it might be expensive to characterize via TEM.

The monitoring of Au nanoparticles during production is important. The monitoring helps to identify the diameter and concentration of AuNPs. The process can assist in understanding how AuNPs concentration and its size changes as time varies. Furthermore, it can also provide the opportunity of manipulating the size distribution, size, and other properties of nanoparticles. To know about the size and concentration of Au nanoparticles, UV-Vis spectroscopy can be used instead of TEM. AuNPs exhibit surface plasmon resonance due to the interaction between light and electrons on the surface of the AuNPs. This results in scattering and absorption peak of AuNPs. So, it is extremely useful to characterize the AuNPs size and concentration.

Characterization of AuNPs through Ultraviolet-Visible spectroscopy has some advantages such as short time for measurement, simplicity, selectivity, and sensitivity to NPs. It means the UV-Vis spectroscopy method is a fast, easy, and a cheaper technique.

In addition, preparing AuNPs in monitoring with the desired size distribution, shape, diameter, and concentration is crucial. AuNPs' size distributions and shape in various liquid solutions are a very significant research field (Al-Azawi *et al*., 2015). The analysis indicates that the nanoparticles stability and their size distribution during laser ablation depends on the nature of the liquid ambience. In this research, by changing the liquids, the size of AuNPs will be different in specific liquids. This is because many applications in nano-biomedicine and biochemical such as anti-fungal, anti-diabetic, anti-bacterial, and anti-cancer require distribution of particles of a smaller size than that which was described before.

1.3 Objectives

The main aim of this research is to monitor the size and concentration of AuNPs produced in pulsed laser ablations. The following are specific the objectives of this work:

(a) To determine the gold nanoparticles diameter and concentration evolution with ablation time.

(b) To verify the reliability of UV-Vis method in determining the size and concentration of AuNPs by comparing it to TEM analysis results.

(c) To analyse and compare the properties of gold nanoparticles produced by using PLAL in four different liquids such as ethanol, deionized water, distilled water and polyvinyl alcohol.

1.4 Scope of Study

The AuNPs were prepared from an Au target by using PLAL. High purity of AuNPs with desirable morphology (shape and size) are needed in various applications. The laser used for this work is a Q-switched Nd: YAG laser. It has multiple laser parameters that can be changed, and the laser parameters can be used for the control of AuNPs characteristics. A nanosecond pulsed laser with a wavelength of 1064 nm; the energy of 315 mJ, 8 ns pulse duration and frequency of 1 Hz was used as a light source for the ablation process to produce 10 ml of colloidal Au solution. The ablation method was conducted for 60 min at room temperature. The liquids which were used in this experiment are deionized water, distilled water, ethanol (70% ethanol and 30% deionized water) and PVA.

During the 60 min of ablation by Nd: YAG laser, the UV-Vis spectra was used to monitor the Au colloidal solution by using Maya 2000 pro spectrometer. Transmission electron microscopy (TEM) is another effective available material imaging method that is used for characterizing the size of Au nanoparticles. In this research, the JEOL JEM-ARM 200F model of TEM with an acceleration voltage of 200 Kv was utilised.

1.5 Significance of Study

The significance of this study is to enhance and improve the current AuNPs characterization system by developing a real-time monitoring measurement system based on a UV-Vis spectroscopic technique. This technique analyses the size and concentration during the formation of AuNPs. This remarkable method will be an important effort to expand the potential resources of using PLAL process to achieve a high-quality and maximum quantity generation of AuNPs which are highly desired in some application fields. It is used to obtain a high quality and quantity generation of AuNPs which are desirable in some specific application.

The outcomes of this study will be a reference for researchers in the fields of biomedical, biological, and chemical sensing to generate AuNPs with specific properties for their applications.

1.6 The Outline and Organization of Dissertation

This research is divided into five chapters to thoroughly demonstrate the viability of using UV-Vis spectroscopy in identifying the diameter and concentration of AuNPs. A description of the study intent is provided in chapter one. It gives information about background of the study, research gap or problem statement, objectives of the study, scope, and significance of study.

Chapter 2 includes a detailed study of the literature about the properties, characterization, application, synthesis of AuNPs. It also discusses on pulsed laser ablation in liquid (PLAL), effect of laser pulse parameters on NPs preparation and determination of AuNPs size and concentration from UV-Vis spectra.

Chapter 3 explains the research methodology of this work. It includes the materials and instruments used, the detailed setup of the monitoring system, laser ablation system, generation of AuNPs, and experimental setup for PLAL Process.

Chapter 4 discusses about the experimental results. This includes the verification of UV-Vis method using TEM, monitoring of AuNPs size and concentration in the different liquids by using UV-Vis method, concentration and average diameter of AuNPs produced in liquids, and result of AuNPs ablation by using PLAL in different liquids.

chapter 5 concludes the whole research work with regard to the trend of the result. Besides that, it suggests other methods and additional resources for future study.

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