

***Ministry of Higher Education and  
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***University of Misan***

***College of Science***

***Department of Physics***



## **Study of Nanoparticles Synthesis by Pulse Laser Ablation**

**A research submitted to the College of Science - Department of Physics, in partial  
fulfillment of the requirements for obtaining a Bachelor of Science degree in  
Physics**

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**1446 A.H.**

بِسْمِ اللَّهِ  
الرَّحْمَنِ  
الرَّحِيمِ

{ يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ  
أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ

{ خَيْرٌ }

صدق الله العلي العظيم

## الإهداء

الحمد لله حباً وشكراً وامتنان على البدء والختام

( وَآخِرُ دَعْوَاهُمْ أَنِ الْحَمْدُ لِلَّهِ رَبِّ الْعَالَمِينَ )

لم تكن الرحلة قصيرة وإلا الطريق محفوفاً بالتسهيلات ، لكنني فعلتها، فالحمد لله الذي يسر البدايات وبلغن النهايات بفضلته وكرمه اهدي هذا النجاح لنفسي أولاً ، ثم الى كل من سعى معي إتمام هذه المسيرة، دمت لي سنداً لا عسر له ....

الى النور الذي أنار دربي والسراج الذي ال ينطفئ نوره والذي بذل جهد السنين من اجل ان اعتلي سلالم النجاح الى من احمل اسمه بكل فخر والى من حصد الأشواك عن دربي ليمهد لي طريق العلم لطالما عاهدته بهذا النجاح ها انا اتممت وعدي واهديته اليك " والدي العزيز "

الى من علمتني الخالق قبل الحروف إلى الجسر الصاعد بي الى الجنة الى اليد الخفية التي أزالته عن طريقي الأشواك ، ومن تحملت كل لحظة ألم مررت بها وساندتني عند ضعفي وهزلي والدتي العزيزة" وإلى من هم دائما الكتف والسند الذي لا يميل إلى أحبائي.... إخوتي وأخواتي.

وكذلك إلى زملائي ورفاق الدرب، الذين كانوا شركاء في المسيرة، كان لوجودكم أثر لا يُمحى، وكانت كلماتكم دافعاً يمضي بي نحو الأمام، فشكراً لكم جميعاً، وأسأل الله أن يكتب لكم التوفيق والنجاح في كل درب تسلكونه

واخيراً من قال أنا لها "نالها" وأنا لها إن أبت رغما عنها أتيت بها، ما كنت أفعل لولا توفيق من الله ها هو اليوم العظيم هنا، اليوم الذي أجريت سنوات الدراسة الشاقة حاملة فيها حتى تواتت بمنه وكرمه الفرحه التمام، الحمد لله الذي به خيراً واملأ واعرقتنا سروراً وفرحاً ينسيني مشقتي.

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***Sara & Zainab***

## **Abstract**

In this research, the pulsed laser ablation method was studied for preparing nanomaterials. Laser ablation involves the generation of NPs by laser ablating a solid target that lies in a gaseous or a liquid environment and collection of the NPs in the form of nanopowder or a colloidal solution. This method is considered one of the simplest and cheapest preparation methods, with a single step, a long stability period, low aggregation, it does not require the use of toxic, hazardous, or pyrophoric chemical precursors for nanomaterial synthesis and thus is an environmentally friendly (“green”) and laboratory safe method and a high ability to determine the properties of the prepared nanoparticles, the resulting NPs, colloidal solutions are ultrapure, (i.e., they do not contain any counter ions or reaction by- products), and this facilitates the use of the NPs in biological or biochemical in vivo applications.

The particles produced with PLAL tend to be electrically charged which leads to stable nanoparticle colloids after the initial coalescence.

During the study, it was found that in most of the research, Nd-YAG laser was used because of its distinctive properties. Several liquids can be used for preparation, such as (Deionized Water, Ethanol, Methanol, Acetone, and Ionic Liquids) according to application used.

After preparing the nanoparticles, these particles can be deposited as a thin film using several methods to perform the required measurements. The most important of these measurements are (UV-visible, X-ray diffraction, Field emission scanning electron microscopy, Atomic force microscopy, Transmission electron microscopy, Atomic Absorption spectroscopy, and Fourier transform infrared spectroscopy).

## Supervisor Certification

We certify that this thesis entitled "***Study of Nanoparticles Synthesis by Pulse Laser Ablation***" were prepared by (***Sara Khalaf Kadhim and Zainab Jasim Jabr***) under our supervision at the Physics department in the College of Science of the Misan University, in a partial fulfillment of the requirements for Bachelor of Science degree in Physics..

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*Date:     /     / 2025*

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## List of Abbreviation

Abbreviation	Full Name
AAS	Atomic Absorption Spectroscopy
AFM	Atomic Force Microscopy
EEW	Electro Exploding Wire
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
LAL	Laser Ablation in Liquid
Nd:YAG	Neodymium-doped Yttrium Aluminum Garnet
NPs	Nanoparticles
PLAL	Pulsed Laser Ablation in Liquid
SEM	Scanning Electron Microscopy
SHG	Second Harmonic Generation
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
UV-vis	Ultraviolet-Visible
XRD	X-ray Diffraction

# Chapter One

## 1.1 Introduction

Nanotechnology is a term that is used to describe the science and technology related to the control and manipulation of matter and devices on a scale less than 100 nm in dimension. It involves a multidisciplinary approach involving fields such as applied physics, materials science, chemistry, biology, surface science, robotics, engineering, electrical engineering and biomedical engineering. At this scale the properties of matter is dictated and there are few boundaries between scientific disciplines. Nanotechnology (sometimes shortened to nanotech") is the study of manipulating matter on an atomic and molecular scale. Generally, nanotechnology deals with developing materials, devices, or other structures with at least one dimension sized from 1 to 100 nanometres. Quantum mechanical effects are important at this Quantum-realm scale. Nanotechnology is considered a key technology for the future Nanotechnology is very diverse, Ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the Nanoscale to direct control of matter on the atomic scale. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication, etc. Scientists debate the future Implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterial and their potential effects on global economics, nanotechnology is ‘the art of manipulating materials on an atomic or molecular scale especially to build microscopic devices’[1].

Laser ablation is a green way for the creation of the NPs based on ablation of metal plate's [2]. Pulse laser ablation in liquids (PLAL) has a promising future as a rapid, unpretentious and the greater part versatile technique to prepare noble metal nanoparticles for analytical chemical as well as biological sensing applications. Metal nanoparticles could be prepared by laser ablation in clean liquids without pollution [3]. Pulse laser ablation in liquids (PLAL) has a promising advantage to control the size and the form of the NPs by adjusting the laser parameters such as laser fluence, wavelength, and pulse number. The interface between a laser beam and target substance is leading to the configuration of plasma and a cavitation bubble in which the ablated matter condenses [4].

## 1.2 Literature Survey

**Abdulrahman K. Ali. (2013)** [5] produced pure copper nanoparticles in fast and one-step method by Nd-YAG irradiation of copper target with a 1064 and 532 nm laser wavelengths in pure water. The particle size, shape and size distributions were measured using a transmission electron microscope TEM. The UV–VIS spectroscopy has been employed for the optical properties. Nanoparticles with diameters 30 nm were observed to be formed in the colloidal solution. The UV–VIS spectrum of the material shows weak plasmon peak around 620 nm, indicating the formation of copper oxide nanoparticles. A clear blue shift is observed in the direct band gap (4.3eV) of these nanoparticles presumably to the quantum confinement effects exerted by the nanosize.

**Kubiliute et al. (2013)** [6] prepared aqueous solutions of ultra-pure gold nanoparticles by methods of femtosecond laser ablation from a solid target and fragmentation from already formed colloids. New pathways of chemical functionalization of such nanoparticles can be envisaged as compared with chemically synthesized and stabilized Au colloids.

**Al-Haddad et al. (2014) [7]** formation Cu NPs by pulse laser ablation (PLA) in different solution (distill water DW, de-ionized water DI, (Ethylene glycol (EG) mixed with (DI)). The SPR of colloidal copper nanoparticles reported previously with a peak at 590-640 nm is in compatible with the present result, and see that when the pulsed laser increase the intensity of SPR increase and the particles size of Cu NPs increases, found that when the different solution and constant laser power and pulses the surface Plasmon resonance changes.

**Leena F.Hamza et al.(2014) [8]** Silver nanoparticles have been prepared by using pulsed laser ablation (Q-switched Nd:YAG) 1064nm pulse duration and( $E= 100\text{mJ}$  to  $400\text{mJ}$  ) of pure Ag metal plate immersed in de ionized water and ethelenglycol. The synthesized nanoparticles are characterized using transmittance electron microscopy (TEM) and UV-VIS spectrophotometer. The effect of the pulses energies and number of shots have been reported .The silver nanoparticles exhibited a surface Plasmon resonance effect with wave length ( $\lambda_{\text{spr}}=400\text{nm}$ ). It was noticed that the Plasmon absorption peak shifts toward longer wavelengths (red shift) as we increased ethelenglycol concentration, usually is associated with an increase in particle size.

**Nguyen The Binh et al. (2014) [9]** Used Nd:YAG laser to produced platinum nanoparticles (Pt NPs) by laser ablation method in solution of polyvinyl pyrrolidone ( $\text{C}_6\text{H}_9\text{NO}$ )<sub>n</sub> (PVP) . The influence of average laser power, laser wave length, laser irradiation time and concentration of PVP solution in water on morphology, size distribution of Pt NPs was investigated. The mean diameter of the Pt NPs in 0.01M PVP solution was of 9 nm.

**Gracia-Pinilla et al. (2014) [10]** synthesized Au and Cu nanoparticles (NPs) and clusters in aqueous media by nanosecond pulsed laser ablation (NPLA) through the irradiation of light of wavelength of 1064 nm produced by a Nd:YAG laser at a fluence of  $20 \text{ mJ/cm}^2$  per pulse and of pulses of 5 ns. The study of the effects of the polyethyleneimine (PEI) on the Au and Cu-NPs and clusters is performed. The

capping process was performed during the irradiation of the Au or Cu targets using the laser. The procedure allows for a remarkably low range of particle sizes on the sample between 0.5 nm and 10 nm, with an average of 5 nm. The addition of the polymer (PEI) in the aqueous media inhibits the formation of aggregates or the coalescence process of the NPs, and it also produces Au-PEI and Cu-PEI clusters with sizes smaller than 2 nm; in both cases, narrow size distributions were validated by HRTEM and zeta potential (ZP) analysis. Show the surface Plasmon resonance (SPR) decrease in PEI (capping) of Au and Cu. The high crystallinity (five-fold preferential orientation) of the Au-NPs-PEI (capping) compared with Au-NPs without PEI was also evidenced by microscopy analysis.

**Raúl Bola Sampol. (2014) [11]** obtained a solution of silver nanoparticles by laser ablation in order to analyze the effectivity of this method. The laser used was a Nd:YAG with 1064 nm of wavelength. Characterization of these particles was done using a transmission electron microscope and a spectrophotometer of double beam, in order to measure both the size and the absorption spectrum of these nanoparticles. The average diameter of the produced nanoparticles increases, from 9 to 22 nm, as the laser pulse energy increases from 9 to 13 mJ. These particles obtained in solution present a strong absorption due to plasmon resonance around 400 nm. It is observed that the peak absorbance of each sample is directly related with the concentration and the size of silver nanoparticles. The position and the maximum value of the peak absorbance variates when ablation time, energy density or laser energy are changed. Ablation efficiency is reduced as time progresses during the process due to the absorption and dispersion of laser light by the nanoparticle solution.

**Shukri et al. (2015) [12]** studies the effect of laser wavelength on gold nanoparticle fabrication. Colloidal solutions of gold nanoparticles were prepared by pulsed laser ablation technique in de-ionized water. A Q switched Nd:YAG laser with constant energy of 65mJ and operation at fundamental wavelength and second harmonic generation was utilized as a source of energy. Fabricated particles were characterized

by using Smart Nanoparticles Measurements (SNM) system. The average diameters of gold nanoparticles achieved as 19 nm and 12 nm corresponding to 1064 nm and 532 nm respectively, this means the surface Plasmon resonance in wavelength 532 nm is smaller than 1064 nm. The fragmentation of colloidal particles by self-absorption of laser pulses is the responsible mechanism to cause for reduction

### **1.3 Aim**

A theoretical study of the preparation of nanoparticles using pulsed laser ablation and a study of the most important devices used for nanoparticle examinations.

## Chapter Two

### 2.1 Introduction of Nanoparticles

Nanoparticles (NPs) are the fundamental component of Nanotechnology. Nanoparticles are the particulate matters with at Least one dimension less than 100 nm. They can be made up of Carbon, metal, metal oxides or organic matter. the nanoparticles (NPs) can exist in different shape, size and structure such as spherical, cylindrical, tubular, conical, hollow core, spiral, flat, wire etc. It can be also be irregular in shape. The surface of NPs can either be uniform or irregular. they can also exist in crystalline and amorphous forms which can be either single crystal solid or multi- crystal solid. Multi- crystal solid can either be loose or agglomerated. the physio- chemical properties of these NPs are mostly influenced by their variation in size & shapes. Owing to unique physical and chemical properties, NPs has achieved great success in wide variety of applications in different fields such as medicinal, environmental, energy-based research, imaging, chemical & biological sensing, gas sensing etc. Researchers are more inclined towards nanotechnology as it is considered as one of the important factors for a clean and sustainable future. [13]

Nanoparticles (NPs) have complex structure. they are comprised of two or three layers: (i) a surface layer: functionalized by a variety of small molecules, metal ions, surfactants or polymers (ii) The shell layer: can be purposely added and is chemically different from the core, and (iii) The core material: the central portion of NPs. The characteristic properties of NPs are generally due to the core material. Hence, NPs are often referred to by their core material only.

Nanoparticles exhibit unique physical and chemical properties Such as: electronic & optical properties, mechanical properties, Magnetic properties & thermal properties. This uniqueness has led to its application in different areas. Some of the significant Applications of NPs are discussed below:



Nanoparticles have made major contributions to clinical medicine in the areas of medical imaging and drug/gene delivery. Nanoparticles are commonly used for environmental remediation. Owing to excellent Young modulus, stress and strain properties, NPs find applications in mechanical industries especially in coating, lubricants. Nanoparticles have been increasingly incorporated into food packaging to control the ambient atmosphere around food, keeping it fresh and safe from microbial contamination [14]

## **2.2 The Unique Properties of Nanoparticles**

Nanotechnology relies on nanomaterials, which are gaining increasing attention due to their unique and novel properties. When a material is at a size of less than 100 nanometers, it exhibits new and often different properties compared to its known properties in its natural form. This difference in properties is primarily due to two main reasons:

### **2.2.1 Surface Area to Volume Ratio**

One of the most critical properties of nanoparticles is their high surface area to volume ratio. As the size of a material decreases, a larger proportion of its atoms or molecules are exposed on the surface, leading to an increase in surface energy and reactivity. This phenomenon results in several key advantages, including: enhanced reactivity: nanoparticles have a higher number of surface atoms, which makes them more reactive compared to bulk materials. Improved solubility and dispersion: due to their small size and high surface area, nanoparticles can disperse more easily in solutions. Increased mechanical strength: nanoparticles can enhance mechanical properties in composite materials by reinforcing their structure. [15,16]

### **2.2.2 Quantum Confinement Effect**

The quantum confinement effect occurs when the size of the nanoparticle becomes comparable to the de Broglie wavelength of electrons, leading to discrete

energy levels. This effect is especially prominent in semiconductor nanoparticles, such as quantum dots. Size-dependent optical properties: The bandgap energy of nanoparticles increases as their size decreases, leading to shifts in their absorption and emission spectra. Tunable Electronic Properties: Nanoparticles can exhibit unique electrical characteristics, useful in nanoscale transistors and memory devices. Increased efficiency in photonic applications: Quantum dots can absorb and emit photons with high efficiency [15,16]

## **2.3 Synthesis Nanoparticles**

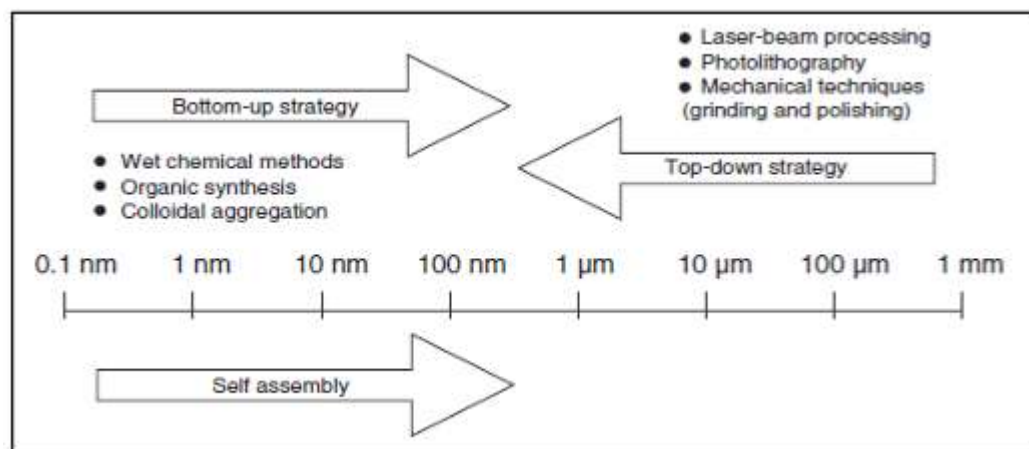
### **2.3.1 Top down approach**

It involves breaking down of large size bulk material into nano size particles, could be done by milling, attrition process and electro explosion wire technique. It is a quick manufacturing process but requires more energy, so it is not suitable for large scale production. Another drawback of top down approach is imperfections of surface structure such defects have a significant impact on the physical and other properties of Nano particles [17]. Cu Nano particles synthesized by the top down approach of electro exploding wire (EEW) technique [18] In this technique copper plate is kept inside suitable medium such as water, current approximately  $10^{10}$  A/m<sup>2</sup> is applied to the medium through the copper wire which leads to melting and evaporation of copper metal plate taken place. Evaporation of metal creates the plasma which readily dispersed in the media followed centrifugation to separate the particles [19] Similarly synthesized the silver Nano particles and analysis the structural properties such as XRD, SEM, UV-Vis spectroscopy. The top-down method is the method of breaking up a solid substance; it can be Sub-divided into dry and wet grinding. A characteristic of particles in grain refining Processes is that their surface energy increases, which causes the aggregation of particles to increase also. In the dry grinding method the solid substance is ground as a result of a shock, a compression, or by friction, using such popular methods as a jet mill, a hammer mill, a shearing mill, a roller mill, a

shock shearing mill, A ball mill, and a tumbling mill. Since condensation of small particles also takes place simultaneously with pulverization, it is difficult to obtain particle sizes of less than 3 $\mu\text{m}$  by grain refining. On the other hand, wet grinding of a solid substrate is carried out using a tumbling ball mill, or a vibratory ball mill, a planetary Ball mill, a centrifugal fluid mill, an agitating beads mill, a flow conduit beads mill,

### 2.3.2 Bottom up approach

Bottom approach refers to building of material from molecule by molecule, atom by atom and cluster by cluster. During the assembling process physical forces acting on the nanostructure used to combine the particles in to a larger one. For synthesis of complex nanostructures, nanotechnologist mostly prefer bottom up approach because the advantage of this approach is to precise control of particle size resulting good optical electronic and other properties [20]



**Figure (2.1):** Top Down and Bottom up Approach.

## 2.4 Surface Plasmon Resonance

Surface plasmon resonance (SPR) relies on the concept of total internal reflection. In this set-up, light passes through a prism and reflects off the sensor chip surface (typically gold) into a detector at a specific incident angle, known as the resonant angle. Light is absorbed by electrons in the sensor chip surface. The result is an

Intensity loss in the reflected beam which can be detected as a dip in the SPR reflection intensity curve. The shape And location of the dip can then be used to provide Information about the surface The binding of biomolecules results in changes in refractive index on the Sensor chip. When a ligand is immobilized on the sensor chip and the binding of the analyte is measured, there is an increase in mass associated with the binding event. The increase in mass causes a proportional increase in the refractive index,

Surface plasmon resonance (SPR) has emerged as a powerful optical detection technique for studying the binding behaviour of immobilized ligands and analytes in solution. The technique makes it possible to measure interactions in real time with high sensitivity. Over the past two decades, SPR has become the gold standard for studying biomolecular interactions in biomedical research and drug discovery. SPR allows researchers to determine which molecules interact, how strongly they bind and inform experiments using mutants, truncations or other variations to probe specificity [21]

## **2.5 Laser Ablation**

Laser ablation involves the generation of NPs by laser ablating a solid target that lies in a gaseous or a liquid environment and collection of the NPs in the form of nanopowder or a colloidal solution. It is an easy, fast and straightforward method for NPs synthesis/generation as compared to other methods. It does not require long reaction times, high temperatures, or multi-step chemical synthetic procedures. It can also produce a number of different types of NPs from metallic to semiconducting and polymeric, as well as NPs of complex multi-element metallic or semiconducting alloys. It does not require the use of toxic, hazardous, or pyrophoric chemical precursors for nanomaterial synthesis and thus is an environmentally friendly (“green”) and laboratory safe method. In the event that generation occurs in water, the resulting NPs, colloidal solutions are ultrapure, (i.e., they do not contain any counter

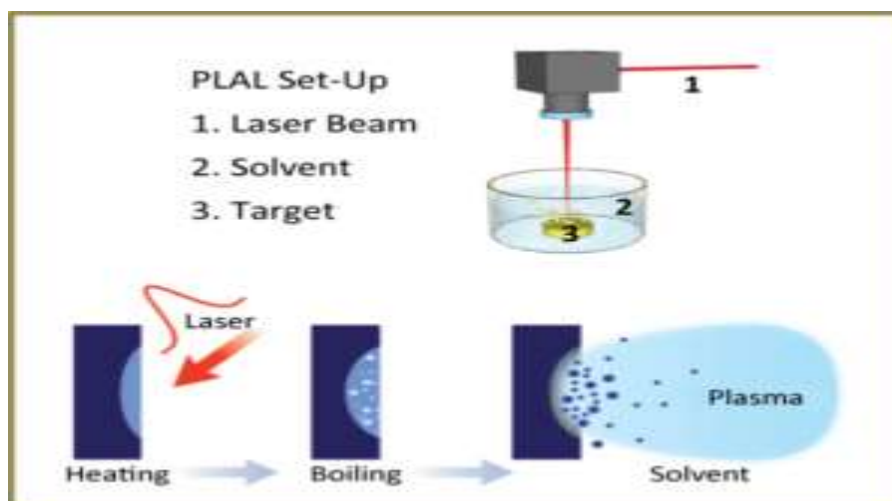
ions or reaction by-products), and this facilitates the use of the NPs in biological or biochemical in vivo applications. The produced NPs do not carry any insulating capping ligands on their surfaces, and this in turn facilitates their applications inorganic electronics. The produced NPs can easily be functionalized with a ligand of choice, through the subsequent addition of the ligand into the NPs' colloidal solution after its synthesis or in situ by performing the ablation in a suitable solvent. The method can be applied with an almost unlimited combination of target materials and liquids, leading to the direct synthesis of NPs in a medium of choice. The properties of the produced NPs such as shape, size, size distribution, composition, and structure for each target material depend on the choice of the laser parameters used for ablation such as wavelength, pulse repetition rate, pulse width, pulse energy, and fluence, as well as of the environment (vacuum, a controlled gas atmosphere or a liquid) in which generation occurs. Furthermore, generation of NPs in liquids offers the unique advantage of fine tuning the size distribution of the produced NPs simply by adjusting the ablation time duration or by a post-irradiation of the produced NPs' colloidal solution. Finally, synthesis of NPs by laser ablation offers the possibility for the formation of so-called "colloidal alloys," i.e., colloidal solutions that consist of alloy NPs or of a mixture of different types of NPs. To understand the mechanisms of NP formation by laser ablation, it is first important to review the mechanisms of interaction between a material and an intense laser beam, i.e., a laser beam whose fluence (energy per unit area) onto the material surface is greater than the so-called ablation threshold of the material (which is defined as the minimum fluence to cause material removal), which is incident on its surface. The interaction of an intense laser beam with a material, in terms of material removal (ablation), is determined mainly by the temporal width of the laser pulse in relation to the electron-phonon coupling time constant of the material.<sup>1</sup> The laser energy is first transferred to the carriers of the material, in the case of a metal to the free electrons, while in the case of semiconductors to the electrons in the valence band, which are then excited to the

conduction band. After a short time of carrier thermalization (usually on the order of 100 fs), the carriers start transferring their energy to the lattice via electron-phonon coupling (usually in a time scale of the order of 1 ps). During this period, if the pulse width is larger than the electron-phonon coupling time constant (as in the case of a nanosecond [ns] pulse) energy continues to pass into the material by the laser beam, even after the carriers have finished transferring their energy into the lattice. This results in laser energy being dissipated as heat, from the region where the laser beam is incident to the material's surface. This in turn results in melting of the material, formation of a pronounced heat affected zone, recast layers, surface debris, mechanical cracks, and other defects around the area where the laser beam is incident to the material's surface. The ablation of the material in this case, even for low fluences, is via melting and vaporization, i.e., a solid to liquid to vapor transition. On the other hand, when the temporal width of the laser pulse which is incident to the material's surface is shorter than the electron-phonon coupling time constant (as in the case of a femtosecond [fs] pulse) the laser energy is largely confined to the initial volume in which the irradiation was absorbed. In this case, there is no dissipation of laser energy into heat from the irradiated area, and due to the ultrashort pulse width, the surface enthalpy of the material is a few orders of magnitude higher than its sublimation enthalpy. This results in the ablation of the material at low fluences via sublimation, i.e., a direct solid to vapour transition. However, even in the case of a fs pulse, for fluences higher than a certain value, the energy penetration depth into the material is controlled by the heat penetration depth and ablation is dominated by the electron thermal diffusion length rather than by only the optical absorption length of the laser radiation into the material, leading to thermal diffusion from the volume defined by the focused [22]

## **2. 6 Properties of Liquid - Phase Laser Ablation**

In addition to the generation of NPs by laser ablation of a solid target in ambient air or a gas atmosphere, in case that the ablated target is immersed in a liquid

environment the NPs are generated within the liquid that surrounds the target, resulting in the formation of a colloidal solution the main difference between ablation in air and in liquid is that liquid produces a stronger confinement of the expanding plasma plume, and this can greatly affect the thermodynamic and kinetic properties of the evolution of the plasma plume. Ablation in a liquid environment also results in different environments where expansion, cooling, and condensation of the plasma plume species occurs. Due to the confinement effect of the liquid, the generated plasma plume has higher temperature, pressure, and density than it would under identical conditions of ablation but in air/vacuum. At the plasma-liquid interface, the liquid is heated at the same very high temperature as the plasma, resulting in the vaporization of the liquid and creation of a so-called “liquid” plasma. Eventually these two plasmas are mixed. Chemical reactions might take place between plume species and “liquid” plume species within the volume of the plume, at the plume-liquid interface, or inside the liquid. For instance, ablation of a metallic target in water results in the formation of metal oxide NPs, i.e., the NPs are oxidized as they are formed for example, ablation of iron in water results in the formation of iron oxide NPs [23] ablation of pure graphite in ammonia solution results in the synthesis of carbon nitride nanocrystals [24] and ablation of silver or gold in chloroform or carbon tetrachloride results in the formation of silver or gold chloride NPs [25] Another important difference between NP generation in air/vacuum/gas and liquid is that in liquid, due to the stronger confinement, the quenching time of the expanding plasma plume is shortened [26] and usually resulting in a distribution of NPs with a lower average diameter than in the case of air/vacuum/gas. The shorter quenching (cooling) time of the plasma plume also affects the “freezing” of metastable phases of the ablated material before the formation of the stable phases.



**Figure (2.2):** PLAL setup for nanoparticle growth.

## 2.7 Basic Mechanism of Pulse Laser Ablation in Liquid

Laser Ablation in Liquid (LAL) for the production of nanostructures is based on the ejection of material by a laser pulse irradiating a solid target immersed in liquid. The laser-matter interaction and the consequent ablation are strongly dependent on the irradiance and the duration of the pulse, on the background liquid, on the sample geometry and morphology as well as on the focusing condition.

Established, ns-PLAL is based on a sequence of different processes: laser ablation and plasma induction, energy exchange from plasma to the liquid and consequent generation of the cavitation bubble and release of particles from the bubble to the solution. Laser ablation and nanoparticle generation in liquids has proven to be a unique and efficient technique to generate, excite, fragment and conjugate a large variety of nanostructures in a scalable and clean way. Laser-matter interaction: The basic mechanisms inducing the laser ablation in liquid, as well as their dependence on laser pulse properties, do not differ notably, with respect of laser ablation in Gaseous environment. In the case of ns-laser ablation, just a portion of the laser pulse reaches directly the target surface, while most of the laser pulse is spent in electron heating by inverse Bremsstrahlung. This implies that the ablated material is converted to a plasma phase during the laser pulse irradiation. Differently to what can be observed in a gas

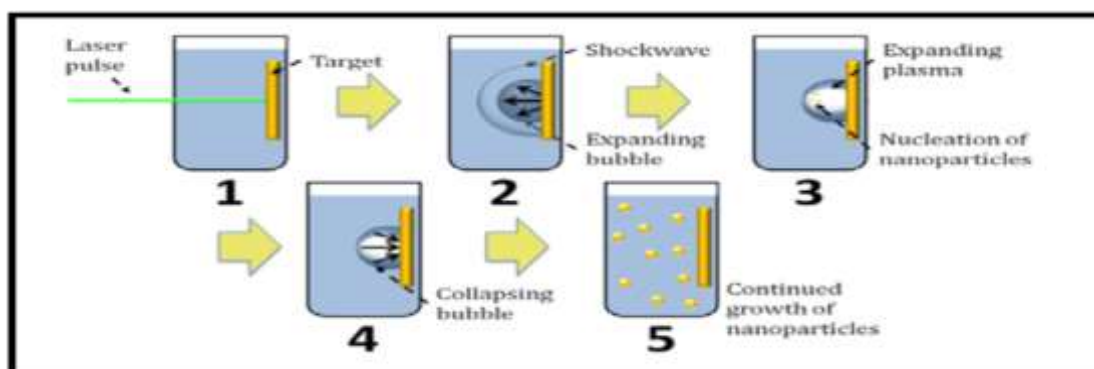


background environment, as a consequence of the water incompressibility, the ablated material is strongly confined and in turn reaches high density. This effect decreases the penetration of the laser through the plasma during the initial stage of expansion, inducing the propagation of gradient of temperature in the ejected material, i.e the plasma. For what concerns the type of target used, it should be considered that morphological, electrical and optical properties of the target [27].

## 2.8 Nanoparticles in the Solvent

After the nucleation and initial growth in the plasma and in the bubble, the nanoparticles are released into the liquid. As already mentioned, the particles can grow by condensation of atoms and coalescence of smaller clusters[28]. The particles produced with PLAL tend to be electrically charged which leads to stable nanoparticle colloids after the initial coalescence.

In a study of PLAL-produced gold nanoparticles in water it was found that the gold surfaces are partially oxidized, which can be the cause of the charge on the surface of the particles [29]. The addition of salts increases the amount of free charges in the solvent and it was found to decrease the initial coalescence, which led to considerably smaller nanoparticles. Stabilization through electrostatic repulsion leaves the surfaces of noble metal particles reactive, which enables functionalization by conjugation of molecules [30,31].



**Figure (2.3)** The step-wise nanoparticle formation process in pulsed laser ablation in liquid[32].

## Chapter Three

### 3.1 Introduction

In this chapter studies the most commonly used laser device for synthesizing nanoparticles using PLAL, the liquids used in this method, and how to prepare the nanoparticles after they have been prepared for the necessary examinations.

### 3.2 Nd-YAG laser

Nd:YAG (neodymium-doped yttrium aluminum garnet;  $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$ ) is a crystal that is used as a lasing medium for solid-state lasers. The dopant, triply ionized neodymium, typically replaces yttrium in the crystal structure of the yttrium aluminium garnet (YAG), since they are of similar size. Generally the crystalline host is doped with around 1% neodymium by atomic percent. [33]

Laser operation of Nd:YAG was first demonstrated by Geusic et al. at Bell Laboratories in 1964. [34]

Neodymium ions in various types of ionic crystals, and also in glasses, act as a laser gain medium, typically emitting 1064 nm light from a particular atomic transition in the neodymium ion, after being "pumped" into excitation from an external source.

Nd:YAG lasers are optically pumped using a flashlamp or laser diodes. They are one of the most common types of laser, and are used for many different applications. Nd:YAG lasers typically emit light with a wavelength of 1064 nm, in the infrared [35]. However, there are also transitions near 940, 1120, 1320, and 1440 nm. Nd:YAG lasers operate in both pulsed and continuous mode. Pulsed Nd:YAG lasers are typically operated in the so called Q-switching mode: An optical switch is inserted in the laser cavity waiting for a maximum population inversion in the neodymium ions before it opens. Then the light wave can run through the cavity, depopulating the excited laser medium at maximum population inversion. In this Q-switched mode, output powers of 250 megawatts and pulse durations of 10 to 25 nanoseconds have

been achieved the high-intensity pulses may be efficiently frequency doubled to generate laser light at 532 nm, or higher harmonics at 355 and 266 nm.

Nd:YAG absorbs mostly in the bands between 730–760 nm and 790–820 nm. At low current densities krypton flashlamps have higher output in those bands than do the more common xenon lamps, which produce more light at around 900 nm. The former are therefore more efficient for pumping Nd:YAG lasers[36].The fundamental specialized parameters are:

- Laser model: Q-switching Nd:YAG laser Second Harmonic Generation (SHG).
- Laser wavelength: (1064/532) nm.
- Power density: (0.8-1.8) J/cm<sup>2</sup>.
- Repetition frequency: (1-6) Hz.
- 10 ns pulse duration.
- Cooling unit: inner circulation water cooling power supply 220V.



**Figure (3.1):** Nd-YAG laser.

### **3.3 The Liquid Uses**

#### **3.3.1. Water (Deionized Water)**

Water is the most common liquid medium used in laser ablation. Deionized water, in particular, is often preferred due to its ability to minimize contamination during the process. Acts as a coolant, preventing overheating of the target material. Helps in minimizing plasma formation, reducing heat damage to the material surface. Enhances nanoparticle formation by providing a stable medium for the ablation process. Water is especially effective in applications like nanomaterial synthesis and laser cleaning. [37,38]

#### **3.3.2. Ethanol**

Ethanol is another popular choice in laser ablation, especially when organic compounds are being targeted. Ethanol can accelerate the formation of nanoparticles in comparison to water due to its lower boiling point. It improves the laser-material interaction, enhancing the ablation efficiency. Reduces the heat-affected zone, which is critical in certain sensitive material [37,38]

#### **3.3.3. Organic Solvents (Methanol, Acetone, etc.)**

Organic solvents such as methanol and acetone are used when there is a need for specific solubility characteristics, or when working with organic materials.

Organic solvents provide better absorption of laser energy than water, which leads to higher ablation efficiency. These solvents help in controlling the size and morphology of the nanoparticles produced. They are used when dealing with organometallic compounds or in cases where hydrophilic interactions must be avoided. [37,38]

#### **3.3.4. Ionic Liquids**

Ionic liquids are relatively new in the field of laser ablation. They are attractive due to their high thermal stability, non-volatility, and ability to dissolve both polar and

non-polar substances. Enhance the production of highly stable nanoparticles. Provide a chemically inert environment, which is crucial for delicate materials. Control the size and shape of the nanoparticles with better precision than traditional solvents.[37,38]

### **3.4 Material Preparation**

#### **3.4.1 Formation of Nanoparticles**

Evaporation-condensation and laser ablation are the most important physical approaches. The absence of solvent contamination in the prepared thin films and the uniformity of NPs distribution are the advantages of physical synthesis methods in comparison with chemical processes. Physical synthesis of NPs using a tube furnace at atmospheric pressure has some disadvantages, for example, tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability. Moreover, a typical tube furnace requires power consumption of more than several kilowatts and a preheating time of several tens of minutes to reach a stable operating temperature. It was demonstrated that NPs could be synthesized via a small ceramic heater with a local heating area. The small ceramic heater was used to evaporate source materials. The evaporated vapor can cool at a suitable rapid rate, because the temperature gradient in the vicinity of the heater surface is very steep in comparison with that of a tube furnace. This makes possible the formation of small NPs in high concentration. The particle generation is very stable, because the temperature of the heater surface does not fluctuate with time. This physical method can be useful as a nanoparticle generator for long-term experiments for inhalation toxicity studies, and as a calibration device for nanoparticle measurement equipment . The results showed that the geometric mean diameter, the geometric standard deviation and the total number concentration of NPs increase with heater surface temperature. Spherical NPs without agglomeration were observed, even at high concentration with high heater surface temperature [39]

### 3.4.2 Preparation of the Glass Substrate

Test glass slides cut to  $(2.5 \times 6) \text{ cm}^2$  for XRD measurement and cut to  $(1 \times 1) \text{ cm}^2$  were used as substrates for SEM measurement.

The cleaning procedure of the glass substrates could be summarized as follows:

Step (1) the glass substrates placed in a clean beaker containing pure alcohol and then rinsed in an ultrasonic unit for (15) minute.

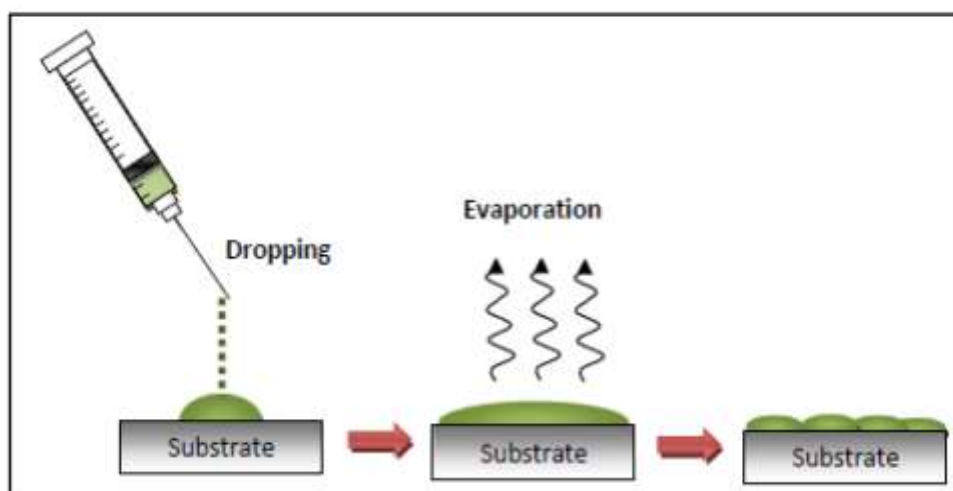
Step (2) repeat step (1) by replacing the pure alcohol with distilled water.

Step (3) silicon slides eventually are dried with soft paper.

### 3.5 Deposition Layer of Nanoparticles

#### 3.5.1 Drop-Casting Deposition

Drop-casting deposition is utilized to study the morphology of the metals NPs as shown in Figure (3.2). The colloidal solution was made to vibrate for 15 minutes before deposition by ultrasonic vibrator and stirrer in order to get homogeneity of the product. With this process, the thickness of the film is proportional to the concentricity of the liquid. A thin film of colloidal liquid was deposited on glass substrates. It is simply based on covering the substrate with 3 ml drops of the solution and left to dry at room temperature or in an oven at  $65^\circ \text{C}$  temperatures for 10 min under vacuum[40]



**Figure (3.2): Drop-casting procedure.**

### **3.5.2 Thin film deposition (Direct Spray)**

In recent years, spray coating has emerged as a viable approach for low-cost deposition of solution-processed thin films. Spray coating is a large area, high-throughput, inexpensive, and industrially scalable process that can be used to create thin films of material which conform to the shape of the substrate. Spray coating involves ejecting fine liquid particles of smart materials by a jet stream of carrier gas onto the substrate. Spray coating is a contact-free approach suitable for any substrate material and is particularly appropriate for low temperature processing[41] The dynamics of spray droplet impingement on a substrate surface is a complex fluid mechanics problem subjected to different details, such as spreading, splashing, rebounding, coalescence and interaction with other droplets, drying phenomena, Wetting/dewetting, and etc. Substrate properties such as roughness, Permeability and surface energy also contribute significantly towards the droplet spreading and surface wetting. Spray coating on a permeable and rough surface hinders droplet spreading and increases the chance of splashing. Solution absorption by the substrate may also slow down droplet spreading. Therefore, droplet impact dynamics, such as droplet size and velocity, requires adjustment to enhance spreading and surface coverage on rough and permeable surface. The functionality of deposited thin film has a direct dependence on structure, morphology, roughness, and integrity of the stacked thin solid films [42]

## Chapter Four

### 4.1 Introduction

In this chapter, the most important devices used in the examination of nanoparticles resulting from pulsed laser ablation were studied.

### 4.2 UV-visible

Ultraviolet-visible (UV-vis) spectroscopy is used to obtain the absorbance spectra of a compound in solution or as a solid. What is actually being observed spectroscopically is the absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state of the compound or material. The UV-vis region of energy for the electromagnetic spectrum covers 1.5 - 6.2 eV which relates to a wavelength range of 200 -1200 nm. The Beer-Lambert Law is the principle behind absorbance spectroscopy. For a single wavelength,  $A$  is absorbance (unitless, usually seen as arb. units or arbitrary units),  $\epsilon$  is the molar absorptivity of the compound or molecule in,  $b$  is the path length of the cuvette or sample holder (usually 1 cm), and  $c$  is the concentration of the solution

$$A = \epsilon bc \dots \dots \dots (4.1)$$

All of these instruments have a light source (usually a deuterium or tungsten lamp), a sample holder and a detector, but some have a filter for selecting one wavelength at a time. The single beam instrument has a filter or a monochromator between the source and the to analyze one wavelength at a time. The double beam instrument has a single source and a monochromator and then there is a splitter and a series of mirrors to get the beam to a reference sample and the sample to be analyzed, this allows for more accurate readings. In contrast, the simultaneous instrument does not have a monochromator between the sample and the source; instead, it has a diode array detector that allows the instrument to simultaneously detect the absorbance at all



wavelengths. The simultaneous instrument is usually much faster and more efficient, but all of these types of spectrometers work well.

UV-vis spectroscopy works well on liquids and solutions, but if the sample is more of a suspension of solid particles in liquid, the sample will scatter the light more than absorb the light and the data will be very skewed. Most UV-vis instruments can analyze solid samples or suspensions with a diffraction apparatus , but this is not common. UV-vis instruments generally analyze liquids and solutions most efficiently [43]

### 4.3 X-ray Diffraction Measurements

X-ray diffraction (XRD) is a versatile technique used commonly in the field of nanotechnology to characterize and acquire accurate information regarding the composition, crystal structure, and crystalline grain size of nanoparticles.

The working principle of the XRD method involves the scattering of X-rays due to the revolution of electrons in the atom's nucleus when the rays strike on the nanoparticles. The scattered X-rays are reflected in various directions, which cause interference patterns. These patterns are either destructive or constructive but only the scattered X-rays that undergo constructive interaction result in diffraction.

In a nanoparticle, constructive interference results when two waves are moving in phase with each other, and destructive interference results from out-of-phase movement. The atomic-scale arrangement and the diffraction are strongly and inversely correlated: atoms having shorter periodic arrangements show greater diffraction angles and vice versa

In an XRD technique, the interference occurs when the light of a designated wavelength illuminates a periodic structure having a predefined spacing. The XRD principle follows Bragg's law,

$$n * \lambda = 2 * d * \sin\theta \dots\dots\dots(4.2)$$

where  $\lambda$ ,  $n$ ,  $d$ , and  $\theta$  refers to X-ray wavelength, integer, atomic plane spacing, and diffraction half-angle, respectively. As a result, information regarding the sample's crystal defects, crystal size, crystalline phase, shape anisotropy, strain, texture can be obtained from the evaluation of the diffraction peaks' width, shape, and position [44,45]

#### **4.4 Field Emission Scanning Electron Microscopy (FESEM):**

Field Emission Scanning Electron Microscopy (FESEM) is an advanced analytical technique that provides both topographical and elemental information with extremely high resolution. It offers magnification levels ranging from 10X to 300,000X, with virtually unlimited depth of field. Compared to conventional Scanning Electron Microscopy (SEM), FESEM produces much clearer images with significantly reduced electrostatic distortion, achieving spatial resolution down to 1.5 nanometers three to six times better than traditional SEM. One of the major advantages of FESEM is its ability to investigate very small contamination spots using low electron accelerating voltages compatible with Energy dispersive X-ray spectroscopy (EDS). Additionally, the use of low-kinetic-energy electron beams minimizes penetration, enabling surface-level analysis with high accuracy. High-quality images can be obtained at low voltages (0.5 to 30 kV) with minimal charging effects, eliminating the need for conductive coatings on insulating materials. For ultra-high-magnification imaging, in-lens FESEM systems are employed to provide even greater spatial resolution and detailed surface visualization [46]

#### **4.5 Atomic Force Microscopy (AFM)**

Atomic force microscopy (AFM) is a technique that is used to map the topography and to study the properties of material on a nanoscale. AFM uses a probing tip at one end of a spring-like cantilever to interact with the material (sample). The interaction between the sample and the tip gives rise to either attractive or repulsive forces. These forces give information about the topography of the sample. If the tip and

the sample are close to each other, the attractive force deflects the cantilever towards the sample, and when the tip is brought into contact with the sample, the repulsive force deflects the cantilever away from the sample. This phenomena can be explained by the Pauli exclusion principle. The cantilever system acts as the force sensor. The cantilevers come in different shapes, the choice depends on the kind of measurements to be conducted. In order to have a small sensitivity to the force, a spring constant  $k$  is chosen in the range of 0.01 – 100 N/m (Meyer, 1992). For cases of vibrations of the cantilever, the cantilever is vibrated at the resonant frequency. Since the resonance frequency is independent on the force constant and the mass of the cantilever as in this means the mass of the cantilever has also to be minimised. This is done by reducing its dimensions. A laser beam detects these deflections. This happens when the incident laser beam is reflected off the surface of the cantilever, any deflection will cause changes of the direction of the reflected beam. A high resolution deflection detector (position sensitive detector) is used to register these change. The changes can either be large or small. The detector is sensitive enough that to amplify even the very small deflections.

The AFM operates in two general modes, the static mode also known as the contact mode and the dynamic mode (the non-contact mode and the tapping mode). In each of the modes, there is a dominant interaction forces. The repulsive forces are seen in the contact mode, the attractive forces are observed in the non-contact mode. In the tapping mode at high frequencies we can see both the repulsive and the attractive mode [47]

## **4.6 Transmission electron microscopy (TEM)**

Transmission electron microscopy (TEM) provides images obtained by a beam of electrons transmitted through a thin specimen, thus allowing the detailed visualization of the interior of the sample. This microscopy technique has widely been used in nanomedical research and is able to reveal the fine relationships between

nanoparticulates and cell/tissue components due to the unique information provided by its high resolution. Thanks to the very short wavelength of the electron beam (100,000-fold shorter than the photons in the visible spectrum), a sub-nanometer resolution can be achieved corresponding with approximately 0.2 nm in conventional TEM. However, biological samples need to be appropriately processed to be observed with a transmission electron microscope and this preparation may limit the resolution to approximately 2 nm. For example[48], resin embedding causes a noise, which becomes larger with the increasing section thickness whereas cryofixed and cryosectioned samples, where resin embedding is omitted, must be protected by a methylcellulose layer (Tokuyasu technique) that may decrease the image quality. Therefore, to observe biological samples in TEM, it is necessary to set up preparation procedures suitable to match the structural and/or molecular preservation with the resolution. Despite the sample processing limitations, the TEM resolution remains significantly higher in comparison with light microscopy; moreover, it may often allow the direct visualization of nanoconstructs and cell/tissue components without recourse to markers[49,50,51,52]. The TEM techniques also have their drawbacks; the microscope and the related equipment are more expensive than those required for light microscopy, the sample processing is time consuming and must be performed by skilled personnel and observations can only be made on small and very thin (usually 70–90 nm) sample slices. In addition, only “static” information can be obtained due to the physical/chemical fixation and resin embedding of the sample, which precludes dynamic studies. Despite these caveats, TEM remains the technique of choice to finely study the interactions of nanoconstructs with the biological environment.

#### **4.7 Atomic Absorption Spectroscopy (AAS)**

Atomic Absorption Spectrometry, or AAS, is an analytical technique commonly used for the quantitative and qualitative determination of elements in samples such as aqueous solutions, waters, sea-waters, metals and alloys, glass, drugs, food, environmental samples, industrial wastes, biological samples among others. This

technique is based on measuring the amount of electromagnetic energy of a particular wavelength (ultraviolet or visible region), which is absorbed as it passes through a cloud of atoms of a particular chemical element (the analyte) coming from samples and standards. An appropriate mathematical treatment allows relating the amount of absorbed energy to the number of absorbed atoms by providing a measurement of the element concentration in the sample. This technique is established, relatively quickly, economically affordable and allows to determine more than 60 chemical elements from a huge type of samples. [53]

#### **4.8 Fourier Transform Infrared Spectroscopy (FTIR)**

The measurement of infrared light absorption (or transmission) by a material as a function of wavelength is known as infrared (IR) spectroscopy (or frequency). The IR spectrum is produced as a plot of absorption (or transmission) versus wavelength (or frequency). The fundamental heat spectrum of materials, which is principally caused by molecular vibrations and their corresponding rotating absorption bands, is examined using infrared spectroscopy[54]. The IR spectroscopy was the first structural spectroscopic technique and is an analytical method which is used to characterize the bonding structure of atoms based on the interaction of the IR radiation at which the substance Absorbs and lead to the production of vibration in molecules. It gives the techniques for identification and characterization of chemical structures to obtain information from biological to composite materials, from liquidsTo gases[55]. The basic principle of IR is measurement of amount of IR radiation by absorption, emission or Reflection. It is also called as vibrational spectroscopy. It is widely used for structural elucidation of molecules. The Spectral regions can be divided into further 3 regions; the FARInfrared ( $400\text{-}10\text{ cm}^{-1}$ ), MID Infrared ( $4000\text{-}400\text{cm}^{-1}$ ), NIR ( $13000\text{-}4000\text{ cm}^{-1}$ ). It is based on the absorption pattern of other compoundsincluding isomers. When reference Spectra available, most compound can be obvious identified on the basis of spectra of IR[56]. Most widely used IR is MIR, but remaining both can also provide important information. FTIR is real time measurement analytical method

and Non-destructive technique, which is unable to identify the unknown compounds (quantitative determination) and their corresponding concentration (qualitative determination) from liquid, gas or solid samples. During vibrations, there is change in the dipole moment. In this case we can call as IR active substances and a radiation corresponds to a change in dipole moment. For IR inactive substances, the dipole moment is zero, there is no matter how long the bond is in the molecule (IR –Active; polar bonds, asymmetric molecules. IR inactive; non-polar bond, symmetrical molecule). In IR each chemical bond has a very specific vibrational frequency which is corresponding to an energy level.

#### **4.9 Conclusion:**

1. Nanoparticles are particles with dimensions between 1–100 nm, exhibiting size-dependent properties such as enhanced surface area, quantum effects, and unique optical and electronic behaviors, making them vital in various nanotechnology applications.
2. Laser ablation is an efficient and safe technique for nanoparticle synthesis. It is simple, fast, and does not require hazardous chemicals or high temperatures.
3. Nd:YAG laser is a common and efficient type of solid-state laser used in various applications. It can operate in both pulsed and continuous modes and is based on a YAG crystal doped with neodymium ions, which is optically pumped to produce light at a wavelength of 1064 nm.
4. Liquid used in laser ablation (such as water, ethanol, organic solvents, or ionic liquids) greatly affects the efficiency of the process, as these liquids differ in their ability to cool the target, absorb laser energy, and control the characteristics of the resulting nanoparticles, such as size and shape.
5. Evaporation-condensation and laser ablation are among the most important physical methods for synthesizing nanoparticles, characterized by the absence of chemical

contaminants and uniform particle distribution, unlike chemical methods. Techniques such as localized heating using a ceramic heater or laser ablation allow precise control over the size and shape of the produced particles with high efficiency.

6. Thin film deposition, methods like spray coating and drop-casting are simple and low-cost, but they are influenced by substrate properties and solvent behavior, which can lead to non-uniform thickness or internal structure in the film.
7. UV-Vis spectroscopy is used to analyze light absorption and electron excitation in materials. It is suitable for analyzing solutions and liquids but is less accurate for solid samples or suspensions due to light scattering.
8. XRD technique relies on X-ray diffraction to reveal the crystal structure. It is an effective tool for analyzing crystal size, atomic arrangement, and defects in solid and nanomaterials.
9. Advanced nanoscale imaging techniques such as FESEM, AFM, and TEM are essential tools for accurately analyzing and studying the physical and surface properties of nanoparticles.
10. Infrared (IR) spectroscopy is an analytical technique used to study the molecular structure of materials by their interaction with infrared light.

#### **4.10 Future works**

- 1- Study the effect of repetition rate, pulse duration, laser wavelength on the nanoparticles size.
- 2- Study of the preparation of nanoparticles by other methods.
- 3- Study and preparation of nanoparticles for specific metals.
- 4- The study used of these nanoparticles in the treatment of cancer cells and antibacterial.

## References

- [1] T. Singh, Introduction to Nanotechnology System, Technical Report, ResearchGate, Aug. 2020. [Online]. Available: <https://doi.org/10.13140/RG.2.2.12770.15049/1>
- [2] A.R. Sadrolhosseini and A.S. Bin Muhammad Noor “Laser ablation Synthesis and optical properties of copper nanoparticles” J. Mater. Res., Vol. 28, pp. 2629-2636, (2013).
- [3] T. B. Nguyen, T. D. Nguyen, Q. D. Nguyen and T. T. Nguyen, “Preparation of platinum nanoparticles in liquids by laser ablation Method,” Advances in Natural Sciences: Nanoscience and Nanotechnology, vol. 5, IOP Publishing, pp. 1–5, (2014).
- [4] A. A. Salim, N. Bidin, “Pulse Q-switched Nd:YAG laser ablation grown Cinnamon nanomorphologies: Influence of different liquid medium” Journal of Molecular Structure., vol. 1149, pp. 694-700, (2017).
- [5] Dr. Abdulrahman, “One-Step Synthesis of Copper Oxide Nanoparticles Using Pulsed Laser Ablation in Water: Influence of the Laser Wavelengths on Optical Properties,” J. Eng Tech., vol. 31, no. 7, pp. 894–902, 2013.
- [6] Kubiliute, R., Maximova, A., K., Lajevardipour, A., Yong, J., Hartley, J. S., Mohsin, A. S., and A. Kabashin, “Ultra-pure, water dispersed Au nanoparticles produced by femtosecond laser ablation and fragmentation,” Int. J. Nanomedicine, vol. 8, pp. 2601–261, 2013.
- [7] Al-Haddad, D. R. M. S, D. I. M. Ibrahim, and A. H. Khalid, “The Study of the Nonlinear Optical Properties of Copper Nanoparticle Prepared By Pulse Laser Ablation PLA .,” Int. J. Eng. Res. Appl., vol. 4, no. 5, pp. 89–96, 2014.
- [8] Leena F Hamza and D. I. M. Ibrahim, “Preparation of silver nanoparticles by pulsed laser ablation in liquid medium,” Int. J. Eng. Comput. Sci., vol. 3, no. 9, pp. 8261–8264, 2014.



- [9] Binh, N. The, Thanh, N. Dinh, Dong, N. Quang, Trinh, and N. Thi, “Preparation of Platinum Nanoparticles in Solution of Polyvinyl Pyrrolidone ( PVP ) by Laser Ablation Method,” J. Sci. Math. – Phys., vol. 30, no. 2, pp. 18–24, 2014.
- [10] Gracia-Pinilla, M. A., Villanueva, M., R. Delgado, N. R., Melendrez, M. F., and J. Menchaca-Arredondo, “Au and Cu Nanoparticles and Clusters Synthesized by Pulsed Laser Ablation: Effects of Polyethylenimine (PEI) Coating,” Dig. J. Nanomater. Biostructure(DJNB), vol. 9, no. 4, pp. 1389–1397, 2014.
- [11] Bola Sampol and Raúl, “Preparation of silver nanoparticles by laser ablation in water,” Facultat de Fisica, Universitat de Barcelona, p. 645, 2014.
- [12] Shukri, W. N. W., Bidin, N., Affandi, S., Bohari, and S. P., “Synthesize of Gold Nanoparticles with 532nm and 1064nm Pulse Laser Ablation,” J. Teknol., vol. 16, pp. 181–187, 2015.
- [13] Kumari, S., & Sarkar, L. (2021). A review on nanoparticles: Structure, classification, synthesis & applications. Journal of Scientific Research (Banaras Hindu University), 65(8), 42–46. <https://doi.org/10.37398/JSR.2021.650809>
- [14] Cao, Z., & Dobrynin, A. V. (2016). Nanoparticles as adhesives for soft polymeric materials. Macromolecules, 49(9), 3586-3592. Ealia S. A. M., & Saravanakumar M. P. (2019). A review on the classification, characterisation, synthesis of nanoparticles and their application IOP Conf. Ser.: Mater. Sci. Eng. 263 03]
- [15] B. H. Fain, Nanoparticle Technology Handbook, Elsevier, 2018. C. N. R. Rao, The Chemistry of Nanomaterials: Synthesis, Properties and Applications, Wiley, 2014.P.
- [16] Jain and T. K. Landy, Surface Area Effects in Nanomaterials, Journal of Materials Science, vol. 53, no. 2, pp.

- [17] 234-248, 2019.[9] A. P. Alivisatos, Semiconductor Clusters, Nanocrystals, and Quantum Dots, Science, Vol. 271, no. 5251, pp. 933-937, 1996. 2.2. Technique for
- [18]Thakkar K N; Mhatre S ; Parikh R. Y, Nanomedicine: Nanotechnology, Biology and Medicine, 2010, 6(2) ,257-262
- [19]Siwach O P; Sen P, Journal of Nanoparticle Research, 2008, 10(1), 107-114.[20]Alqudami A; Annapoorni S, Plasmonics, 2007, 2(1), 5-13.
- [21] Doyle M E; Glass K A, Comprehensive Reviews in Food Science and Food Safety, 2010, 9(1), 44-56.
- [22]B. B. Motsa and R. V. Stahelin, "A Beginner's Guide to Surface Plasmon Resonance," Portland Press Limited, Feb. 2023. [Online]. Available: [https://doi.org/10.1042/bio\\_2022\\_139](https://doi.org/10.1042/bio_2022_139)
- [23]N. G. Semaltianos, "Nanoparticles by laser ablation," Critical Reviews in Solid State and Materials Sciences, vol. 35, no. 2, pp. 105–124, 2010, doi: 10.1080/10408431003788233.
- [24] P. P. Patil, D. M. Phase, S. A. Kulkarni, S. V. Ghaisas, S. K.Kulkarni, S. M .Kanetkar, and S. B. Ogale, Pulsed-laser-induced reactive quenching at a Liquid-solid interface: aqueous oxidation Of iron, Phys. Rev. Lett., 58, 238 (1987).
- [25]L. Yang, P. W. May, L. Yin, J. A. Smith, and K. N. Rosser, Ultra-Fine carbon nitride nanocrystals synthesized by laser ablation in Liquid solution, J. Nanopart. Res., 9, 1181 (2007).
- [26]G. Compagnini, A. A. Scalisi, and O. Puglisi, Ablation of noble metals in liquids: a method to obtain nanoparticles in a thin polymeric film, Phys. Chem. Chem. Phys., 4, 2787 (2002).
- [27] G. W. Wang, Laser ablation in liquids: Applications in the synthesis Of nanocrystals, Prog. Mat. Sci., 52, 648–698, (2007) /

- [28] E. Fazio et al., "Nanoparticles Engineering by Pulsed Laser Ablation in Liquids: Concepts and Applications," *Nanomaterials*, vol. 10, no. 12, pp. 1–27, Nov. 2020, doi: 10.3390/nano10122480
- [29] Sylvestre et al., "Surface Chemistry of Gold Nanoparticles Produced by Laser Ablation in Aqueous Media," *J. Phys. Chem.*, vol. 108, pp. 16864–16869, 2004.
- [30] Y. Qian, W., Murakami, M., Ichikawa, Y., & Che, "Highly efficient and controllable PEGylation of gold nanoparticles prepared by femtosecond laser ablation in water," *J. Phys. Chem. C*, vol. 115(47), pp. 23293–23298, 2011.
- [31] S. Petersen, S., & Barcikowski, "In situ bioconjugation: Single step approach to tailored nanoparticle-bioconjugates by ultrashort pulsed laser ablation," *Adv. Funct. Mater.*, vol. 19(8), pp. 1167–1172, 2009.
- [32] A. Singh, "Green synthesis of TiO<sub>2</sub> nanoparticles and carbon nanotubes by pulsed laser ablation of titanium and graphite in deionised water," TAMPERE UNIVERSITY OF TECHNOLOGY, 2014
- [33] Science Resource Guide: An Introduction to Laser Technology and its Applications. (2019). United States Academic Decathlon. PDF file.
- [34] John F. Ready, *Industrial Applications of Lasers* (Second Edition), Academic Press, 1997, ISBN 9780125839617, <https://doi.org/10.1016/B978-012583961-7/50001-6>.
- [35] Koechner, Walter (1988). *Solid-State Laser Engineering* (2nd ed.). Springer-Verlag. ISBN 3-540-18747-2.
- [36] Yariv, Amnon (1989). *Quantum Electronics* (3rd ed.). Wiley. ISBN 0-471-609978
- [37] K. T. Lee, M. A. Kim, and W. S. Yoon, "Laser Ablation in Liquid Media: A Review ", *Journal of Nanoscience and Nanotechnology*, vol. 12, no. 1, pp. 40–50, 2022.

[38]X. Wang, et al., "Effects of Solvents on Laser Ablation Synthesis of Metal Nanoparticles," Journal of Materials Science, vol. 54, no. 12, pp. 7890–7899, 2021.

[39]<https://pmc.ncbi.nlm.nih.gov/articles/PMC4326978/>

[40]<https://nanocomposix.com/pages/depositing-monolayers-and-thin-films-of-nanoparticles>

[41].Carey, Tian, Chris Jones, Fred Le Moal, Davide Deganello, and Felice Torrisi. "Spray-Coating Thin Films on Three-Dimensional Surfaces for a Semitransparent Capacitive-Touch Device." ACS applied materials & interfaces 10, no. 23 (2018): 19948-19956.

[42].Zabihi, Fatemeh, and Morteza Eslamian. "Characteristics of thin films Fabricated by spray coating on rough and permeable paper substrates." Journal Of Coatings Technology and Research 12, no. 3 (2015): 489-503.

[43][https://chem.libretexts.org/Bookshelves/Analytical\\_Chemistry/Physical\\_Methods\\_in\\_Chemistry\\_and\\_Nano\\_Science\\_\(Barron\)/04%3A\\_Chemical\\_Speciation/4.04%3A\\_UV-Visible\\_Spectroscopy](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/04%3A_Chemical_Speciation/4.04%3A_UV-Visible_Spectroscopy)

[44]Fultz, B., & Howe, J. (2013). Transmission Electron Microscopy and Diffractometry of Materials. Springer. doi:10.1007/978-3-642-29761-8

[45]Widjonarko, N. (2016). Introduction to Advanced X-ray Diffraction Techniques for Polymeric Thin Films. Coatings. doi:10.3390/coatings6040054

[46][https://photometrics.net/field-emission-scanning-electron-microscopy-fesem /](https://photometrics.net/field-emission-scanning-electron-microscopy-fesem/)

[47]Kyeyune, B. (2017). Atomic Force Microscopy (Master's thesis, African Institute For Mathematical Sciences, Tanzania). Retrieved from <https://www.researchgate.net/publication/322294428>

[48]Hayat M.A. Principles and Techniques of Electron Microscopy: Biological Applications. 4th ed. Cambridge University Press; Cambridge, UK: 2000. [Google Scholar]

[49]Margus H., Padari K., Pooga M. Insights into cell entry and intracellular trafficking of peptide and protein drugs provided by electron microscopy. *Adv. DrugDeliv. Rev.* 2013;65:1031–1038. doi: 10.1016/j.addr.2013.04.013. [DOI] [PubMed] [Google Scholar] 10(12),

[50]Malatesta M. Transmission electron microscopy for nanomedicine: Novel Applications for long-established techniques. *Eur. J. Histochem.* 2016;60:2751. Doi: 10.4081/ejh.2016.2751. [DOI] [PMC free article] [PubMed] [Google Scholar]

[51]Reifarh M., Hoeppener S., Schubert U.S. Uptake and Intracellular Fate of Engineered Nanoparticles in Mammalian Cells: Capabilities and Limitations of Transmission Electron Microscopy-Polymer-Based Nanoparticles. *Adv. Mater.* 2018;30:1703704. Doi: 10.1002/adma.201703704. [DOI] [PubMed] [Google Scholar]

[52]Fatima N., Gromnicova R., Loughlin J., Sharrack B., Male D. Gold nanocarriers For transport of oligonucleotides across brain endothelial cells. *PloS ONE.* 2020;15:e0236611. Doi: 10.1371/journal.pone.0236611. [DOI] [PMC free article] [PubMed] [Google Scholar]

[53]H. J. I. Filho, R. F. dos S. Salazar, M. da R. Capri, and Â. C. Neto, "State-of-the-Art and Trends in Atomic Absorption Spectrometry," in *Atomic Absorption Spectroscopy*, InTech, Jan. 2012. [Online]. Available: <https://www.researchgate.net/publication/221922577>

[54] JEFFREY S. GAFFNEY, NANCY A. MARLEY, AND DARIN E. JONESUniversity ofArkansas atLittle Rock, Little Rock, AR, US FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

[55] Andrei A. Bunaciu , Hassan Y. Aboul-Enein & Serban Fleschin (2010): Application of Fourier Transform Infrared Spectrophotometry in Pharmaceutical Drugs Analysis, Applied Spectroscopy Reviews, 45:3, 206-219

[56] Vasilica Tucureanu, Alina Matei& Andrei Marius Avram (2016): FTIR spectroscopy for carbon family study, Critical Reviews in Analytical Chemistry, DOI: 10.1080/10408347.2016.1157013

## الخلاصة

في هذا البحث، دُرست طريقة الاستئصال بالليزر النبضي لتحضير المواد النانوية. تتضمن هذه الطريقة توليد جسيمات نانوية عن طريق استئصال هدف صلب في بيئة غازية أو سائلة بالليزر، وجمعها على شكل مسحوق نانوي أو محلول غرواني. تُعدّ هذه الطريقة من أبسط وأرخص طرق التحضير، بخطوة واحدة، وفترة استقرار طويلة، وتجمع منخفض، ولا تتطلب استخدام مواد كيميائية سامة أو خطرة أو سريعة الاشتعال لتخليق المواد النانوية، وبالتالي فهي طريقة صديقة للبيئة ("خضراء") وآمنة مختبريًا، وتتميز بقدرة عالية على تحديد خصائص الجسيمات النانوية المُحضرة. تتميز الجسيمات النانوية الناتجة، والمحاليل الغروانية، بأنها فائقة النقاء (أي أنها لا تحتوي على أيونات مضادة أو نواتج ثانوية للتفاعل)، مما يُسهّل استخدامها في التطبيقات البيولوجية أو الكيميائية الحيوية داخل الجسم الحي. تميل الجسيمات المنتجة باستخدام PLAL إلى أن تكون مشحونة كهربائيًا، مما يؤدي إلى تكوين جسيمات نانوية غروانية مستقرة بعد الاندماج الأولي..

خلال الدراسة، وُجد أنه في معظم الأبحاث، استُخدم ليزر Nd-YAG نظرًا لخصائصه المميزة. يمكن استخدام العديد من السوائل للتحضير، مثل (الماء منزوع الأيونات، والإيثانول، والميثانول، والأسيتون، والسوائل الأيونية) وفقًا للتطبيق المستخدم.

بعد تحضير الجسيمات النانوية، يمكن ترسيب هذه الجسيمات كغشاء رقيق باستخدام عدة طرق لإجراء القياسات المطلوبة. من أهم هذه القياسات (مطياف الأشعة فوق البنفسجية المرئية، حيود الأشعة السينية، المجهر الإلكتروني الماسح، مجهر القوة الذرية، مجهر الإلكترون النافذ، مطيافية الامتصاص الذري، ومطيافية الأشعة تحت الحمراء باستخدام تحويل فورييه).



جمهورية العراق  
وزارة التعليم العالي والبحث العلمي  
جامعة ميسان  
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## دراسة تحضير الجسيمات النانوية بطريقة الاستئصال بالليزر النبضي

بحث مقدم الى كلية العلوم-قسم الفيزياء وهو جزء من متطلبات نيل شهادة  
البكالوريوس علوم في علوم الفيزياء

من قبل

سارة خلف كاظم & زينب جاسم جبر

بإشراف

الدكتورة داليا خالد ناصر

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