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# Laser Ablation Technique for Synthesis of Metal Nanoparticle in Liquid

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Additional information is available at the end of the chapter

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## Abstract

Recently, the synthesis and application of metal and ceramic nanoparticle are significant subject in science and engineering. The metal nanoparticles such as silver, gold, and copper nanoparticles have more application in material science, nanomedicine, electronic, photonic, and art. One of the green methods for preparation of metal nanoparticles is laser ablation technique that offers a unique tool for nanofabrication of nanoparticles. In this technique, the high-power laser ablates the metal plate and the nanoparticles are formed in the liquid. The properties of nanoparticles using laser ablation are unique, and they are not reproducible by any other method such as chemical methods. The important parameters to produce the metal nanoparticles are energy, wavelength, repetition rate of laser, ablation time, and absorption of an aqueous solution. Laser ablation is a simple method for fabricating the metal nanoparticles without surfactant or chemical addition. In this chapter, the mechanism of formation of metal nanoparticles in liquid, significant parameters for using the laser ablation technique to prepare the metal nanoparticles, and the preparation of silver, gold and copper nanoparticles will be reviewed.

**Keywords:** laser ablation, silver nanoparticles, gold nanoparticles, copper nanoparticles, mechanism of laser ablation in liquid, effect of wavelength in laser ablation, effect of temperature in laser ablation, laser ablation setup

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## 1. Introduction

Green synthesis of metal nanoparticles in liquid solution is the regard issue in the nanotechnology and nanomedicine research. Gold, silver, and copper nanoparticles were prepared using physical and chemical methods based on chemical reaction or interaction of gamma-ray,

X-ray, or UV-ray with chemical material. Gold, silver, and copper nanoparticles have significant chemical, biological, and physical properties. They are anti-cancer, anti-bacterial, and anti-inflammatory, and can improve the fluorescence properties of polymer composites. They are used to enhance the sensitivity and selectivity of biosensors based on conducting polymer. Hence, the green synthesis of metal nanoparticles is considerable in medicine and nanotechnology research. Laser ablation is a green and simple method for fabricating the metal nanoparticles without surfactant or chemical addition. Advantages of laser ablation technique are simplicity, the high purity of the nanoparticles, the ability to prepare variety metals and ceramics, and the in-situ dispersion of the nanoparticles in a variety of liquids [1]. Because the liquids have cooling effect and confinement effect and they cause the oxidation or reduction [2, 3] of particles. Metal nanoparticles have the plasmonic effect in the green and red part of the UV-visible spectrum due to scattering and absorb the photon. This effect depends on scattering cross section of metal nanoparticles which is higher than organic chromophores [4]. Some organic material can cap the metal nanoparticles [5]. Moreover, they have stable chemical and physical properties including high-temperature resistance, photo-irradiation, high acids or oxidation resistance [6–8], and catalytic properties [9, 10]. Therefore, the metal nanoparticles were used to enhance the response of biomaterial or organic material. Numerous methods including solution phase [11], photochemical [12], sonochemical [13], electrochemical synthesis [14], photolytic reduction [15], radiolytic reduction [16], solvent extraction reduction [17], microemulsion technique [18], polyol method [19], and microwave irradiation [20] were used to synthesize and disperse gold, silver, and copper nanoparticles in various mediums. These methods are based on chemical reaction or interaction of material with external field. Briefly, the photochemical method is based on absorption of light for conducting the chemical reaction. The sonochemical and microwave methods are based on concerned with application of ultrasound and microwave, respectively, for initiation of chemical reaction in liquid. Other methods, such as electrochemical synthesis photolytic reduction radiolytic reduction, solvent extraction reduction, microemulsion technique, and polyol methods, are based on chemical reaction in the liquids and reduction of another form of salted metals. But, laser ablation method is based on interaction of laser with metal plate and the nanoparticle formed and dispersed in the liquid.

Moreover, metal nanoparticles were dispersed into inorganic and organic materials including water [21], acetone [22], oil [23–26], chitosan [27], and PVA [28].

In this chapter, the significance of metal nanoparticle in art and life, the mechanism of laser ablation technique to form the nanoparticle in liquid, laser ablation setup, and the significant parameters of laser ablation for fabrication of metal nanoparticles are presented.

## 2. Nanomaterial influence in art and life

Nanomaterials and nanoparticles are involved in various applications such as sensor, catalysis, electronics, and plasmonic devices [5, 7]. The application of gold, silver, and copper nanoparticles is swiftly growing in biotechnology [5–8] to detect and recognize DNA and proteins [29]. They want to achieve the particular instrument and sensor for cancer diagnosis and cancer therapy [30].

Nanomaterials and nanoparticles have more application in medicine, industry, and art. The interface of art, science, and technology is nanotechnology. The effects of nanotechnology on art has been proven during Medieval perfectly, when artists unaware of this technology. The recent achievements of nanoparticles in the field of art have examined, and the techniques employed in the creation of works of art have been identified. These techniques include Medieval artisans were the first nanotechnologists. They made coloured glass or stained glass that are an important element in the ancient history and architecture [31]. The stained glass is attractive and multifunctional. On the other hand, Roman glass cage cup shows a verity of colors which are related to the direction of the light. When the light comes out from the back, it shows a red color, and it illustrates green color when the lighth reflects to different angle. Those stained glass and Roman glass cage cup [32] are attractive and multifunctional. They are good suggestion for dramatics phenomenon which have almost died, and there are no longer practices on the traditional theater stage. Artistic may give advantage to change modern performance of puppet show, which has been very popular in Malaysia as Wayang Kulit Kelantan. In addition, the stain glass windows may impact on the principle of performing the iconography, the visual images, and symbols used in the ceramic works of art and for interpretation of storytelling. Those traditional stories on ceramic works of art derived on the 'pictorial curtain' as a traditional Iranian play provided an opportunity for dramatizing situations that give way to mourning. Therefore, nanoparticles not only are able to revival some rituals but also can make a modern stage for those forgotten traditions.

The discussion on how to improve nanotechnology in science cannot be held without a general discussion on the impact of nanomaterial on human life. The impact of nano is felt in different areas, including music, particularly in the manufacturing of musical instrument, and visual art (Nanoforart), performing arts in specie in set design. More so, modern lifestyle has also experienced the introduction of nanotechnology in the production and supply of clothing and foods. Nanotechnology is regarded as a new, edge-cutting, and emerging technology with promising scientific advancement for the production of exceptional compact electronic devices, enhancing of food shelf life, medical advancement, and the production of unique cosmetics. More so, nanotechnology is a technology that is capable of enhancing the production of quality clothing, energy saving devices, and quality packaging that are capable of impacting daily living. It involves manipulating matter on near atomic scale for the production of new structures, systems, and devices [33]. Through this, healthy, efficient and sustainable systems can be created by combining science, art, and technology. In fact, the emergence of nanotechnology can be seen as the introduction of newer and more relevant topics than the ones that have gained much attention in time past, such as the techniques which were discovered by the Medieval artisans. The first nanotechnologists were the Medieval artisans who produced stained glass windows, which are significant elements of ancient history [34]. Recently, the field of art has experienced the use of nanoparticles for the production of nanowires for musical instruments such as photonic guitar. Reference to *materials by design*: the integration of proteins and music exposes the manner in which fiber rotation from proteins can be changed into music. Nanoparticles have properties that are important for use as biomaterials, for drug delivery, as composites of lightweight, and as functional coatings. Constructing hierarchical assemblies of less complex building blocks into architectures that are complex with superior properties is one of the emerging areas in the design of such materials. This approach is reviewed using a case study of silk, which is regarded as a

biomaterial that can be genetically processed and programmed. Silk inherently functions as a multipurpose protein fiber with hierarchical organization for the purpose of providing structural support, for eggs protection, and prey procurement. In addition, knowledge abstraction from the physical system enables the conversion of silk to a mathematical model through the use of category theory. This allows the translation of the mechanism of spinning fibers from protein into music, using a process which allocates a set of rules governing the system construction. The structure, properties, and mechanisms of the materials can be expressed in an entirely different domain, which is music. Science and art can be combined through the classification of structure-property relationships as a new way of creating new bioinspired materials by means of translating the mechanisms and structures from unique hierarchical systems within the framework of the integration of science and art through categorization of structure-property relationships presents a novel paradigm to create new bioinspired materials, through the translation of structures and mechanisms from distinct hierarchical systems and in the context of the inadequate number of building blocks that generally rules these systems [35]. The prototyped use of fiber strain sensors has been experienced in the area of music recording. Using this finding, a new use of low noise fiber optic strain sensors in music, especially in constructing a photonic guitar, is described in this article [36].

On the other hand, a novel category of nano-based products was developed by the FP7 projects known as MEMORI (Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets—Innovative Research for Market Transfer) and NANOFORART (nanomaterials for the conservation and preservation of movable and immovable artworks); the European Union funded this project which are aimed at creating greener and safer protection from regular products. According to the EU, the beauty of artworks can be manifested through the cleaning and preservation of art, but the environment, in the long run, should not be damaged by the products and chemicals which will be used. The purpose of this project was to develop and protect cultural assets that are environmentally friendly, through the use of advanced materials and methods [37].

In order to safely clean and preserve art works, the various materials used in their creation must be uniquely adapted products of conservation. There are a number of limitations associated with the use of traditional products, and they include relying on hard-matter solvents, toxic materials, layers of incompatible coatings, or even causing damage to materials such as leather or paper, which are water-sensitive. According to the Baglioni, who is the project manager of EU, money could be saved through the use of Nanoforart's products. The project manager added that such works have longer lifespan than those developed using conventional materials and are safe enough for tourist sites not to be shut down during the work [38]. By modifying nanotechnology, the discovery of some techniques which can be used in cleaning products was made; all the methods had their own unique protection advantages which are described below:

1. Nanocontainers and micellar solutions, when compared to the conventional methods which are based on pure solvents, are better with faster performance and less health risk as well as ecotoxicity. This is as result of the use of pure organic solvents which make up less than 5% of the formulations with water being the major (95%) solvent component



of these formulations. The reduction of penetration into the immovable artwork's matrix of porosity with regard to that occurring with organic solvents is another advantage of systems that are water-based. This causes the avoidance of redissolution of polymer into the artifact. The NANOFORART project has progressed above the state-of-the-art and developed into a technique for the production of new nanoparticle-based substance which can be used for plastering, stones, stucco, and wall paintings [39].

2. According to Giorgi et al. [40], it has been found that the acidity of paper can be neutralized using alcoholic dispersions of calcium and magnesium hydroxide nanoparticles. More so, this alcoholic dispersion can be used in generating carbonate alkaline reserve (after the reaction of the hydroxide with  $\text{CO}_2$  from air) through which further degradation is prevented. There has been a positive response to this method. One of the major advantages of this method is that the penetration of nanosized particles into the paper fibers is enhanced alongside a rapid carbonation as a result of their high surface reactivity. Again, with this method, the stabilization of alkaline nanoparticles requires no surfactants. There is minimal catalytic activity of iron and copper when pH is close to being neutral. The implication of this is that a definite control of the acidity/alkalinity of paper can enhance the reduction in the rate of oxidation degradation by means of Fenton reactions (as cited in Baglioni et al. [37], p. 317) [40].
3. In addition, the toxicity and effect of the cleaning methods can appear through the use of pure organic solvents. The use of solvent gels, which was first advocated for in the 1990s, permits the solvent localization and, in some case, the decrease in penetration of solvent into underlying layers of paint. However, the removal of solvent gels as well as their residues from a paint surface is often difficult. This is one of the problems which will be addressed in the current proposal. They use precise quantities of clean liquid control directly, without damaging the image or leaving residues [41].

### 3. Laser ablation mechanism and metal nanoparticles formation

The mechanism of laser ablation depends on physical properties of metals and environment medium. Therefore, the ablation of metals is an intricate subject [42–44]. Ablation of metal target commences with the sorption of laser beam energy. When the laser beam interacts with the metal target, the heat can generate and the photoionization of the metal target can occur. After that, metal nanoparticles will be released from the metal plate as the different phase that depends on the absorbed energy  $E$  [42], and plasma plume expands [43–45]. Hence, if the duration of laser ablation is much higher than the laser pulse duration, the ablation depth ( $L_a$ ) could be obtained as follows:

$$L_a \approx E^{\frac{2}{3}}, \quad t_a \approx E^{\frac{1}{2}}, \quad (1)$$

Where  $t_a$ ,  $T_e$  and  $t_1$  are the time of the ablation process, the electronic temperature during the ablation process, and the laser pulse duration, respectively [6, 42].

In accordance prior report, when the energy of laser beam is high enough to generate a plasma plume, an acceptable ablation rate can be obtained. During laser ablation of metal plates, the plasma plume can be formed with the generation of photon and sound [46, 47]. This phenomenon is confined near the metal plate [44, 46, 47]. The face of the metal plate face in the plasma plume remains at high temperature and high pressure during the ablation of the metal plate [44, 46–48]. During the laser ablation of the metal plate, some thermodynamic phenomena occur near the metal target. Therefore, a face of the target in the plasma plume observes energy and the physical parameters are not constant on the whole target area [44, 49, 50]. Moreover, sometimes the deportation of particles from the metal targets due to photoionization [51]. So, the concentration and distribution of metal nanoparticles become large in the liquids by using the laser ablation of the metal plate [50]. The formation of metal nanoparticles based on laser ablation of the metal plate can be explained as bubbling of metal molecules [43, 44, 49]. Some physical properties including of size and concentration of nanoparticles in the liquid are a function of the phase homogeneity of the material released into the liquid during the irradiation of metal target. In accordance with the literature, the changes of morphology were observed around the ablated area on the surface of Au or Ag plates, when the high-power laser (110 fs to 800 nm) was used to ablate the gold and silver plate at different fluences [52]. The high-power laser with the fluence of 60 and 1000 J cm<sup>-2</sup> can generate sharp and irregular craters [52]. Therefore, the variety of particle size and concentration of nanoparticles were achieved with different fluences [6, 50, 52, 53]. For example, the metal nanoparticles with small size have regular craters and low fluences [6, 50, 52]. The nanoparticles with the average size larger than 10 nm can generate the irregular craters and high fluences that related to boiling of metal plates [6].

The energy transfer to the electron on the surface of metal plates depends on the time duration of high power lasers such as femtosecond, picosecond, and nanosecond. It is time duration of laser ablation, and it is a significant factor for synthesis of nanoparticles. Hence, femtosecond laser pulses can release the electron from the metal plates faster than the thermal action of electron-photon phenomena. But, picosecond and nanosecond laser pulses can transfer the energy on a time scale longer than femtosecond laser pulse, so the thermal relaxation processes of the target [42, 54] can appear, and photothermal or photomechanical phenomena can be observed during the laser ablation of the metal plate. Hence, the ablation of the metal target will commence between 10 and 80 ps and plasma plume will form after 10 ns [42, 44, 46, 52], and the plasma appears after twice the pulse duration time [44, 46]. Therefore, when the metal plates are ablated with an ultra-short pulse laser (10<sup>-15</sup> and 10<sup>-12</sup> s), the delay between ejection of nanoparticles and interaction of laser beam with the metal target is not observable [42]. The concept of this delay is significant for the ablation mechanism [43, 46]. The plasma plume can absorb part of the incoming laser energy when the long laser pulse will be used for ablation of the metal target. The absorption of laser beam increases the temperature of the plasma and favors the atomization of the material contained in the plume [6, 44, 46]. Consequently, the phase materials released from the metal target are homogenized [6]. On the other hand, the laser energy absorbed by the target decreases due to the optical shielding of the plasma plume, while target ablation by interaction with the plasma plume is enhanced due to the increased plasma temperature [6, 44] and the absorption cross section of bulk metals is increased with a decreased laser wavelength [49]. Nevertheless, the ablation efficiency depends on absorption effects or the irradiation at short wavelengths. Metal nanoparticles usually have strong

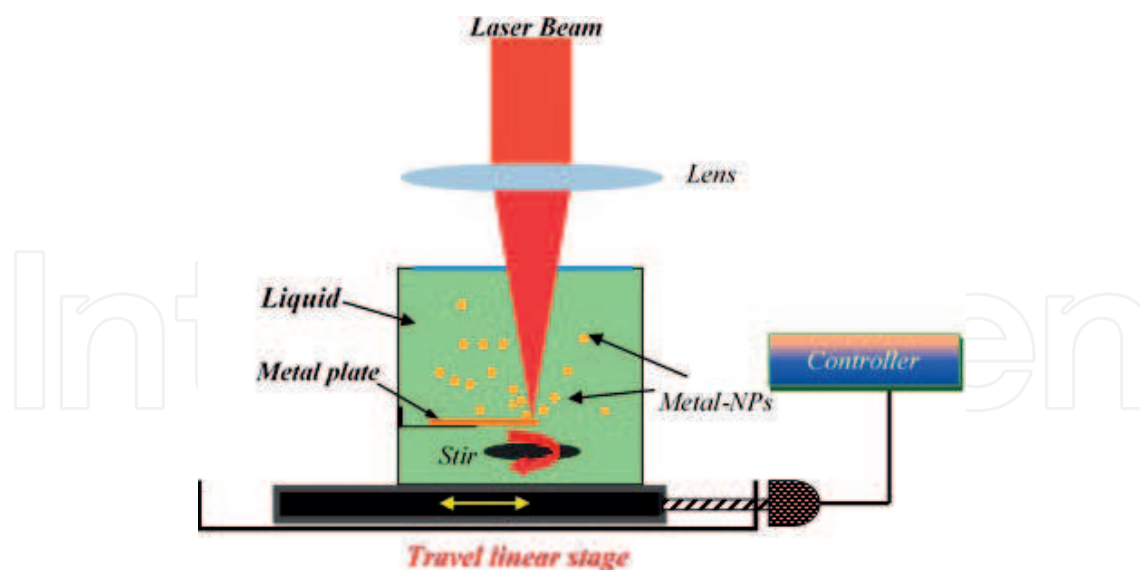
plasmon resonance or inter band transitions in the UV-visible spectrum; hence, the laser beam can be interacted and absorbed by metal nanoparticles which were generated in liquid. This phenomenon occurred with two negative effects including the damping of ablation rate and altering the concentration and distribution of particle size [54]. Plasma plume has the tendency to absorb the laser beam at short wavelengths during the ablation process [44]. Therefore, the relation between the absorption coefficient and ablation efficiency appear in nonlinear, and these phenomena are minimum when the laser beam wavelength in the infrared range [54].

The nucleation of nanoparticles is formed during the plasma plume cooling. The nuclei growth and coalescence are the predominant mechanisms in the formation of metal nanoparticles using laser ablation technique [44, 55]. This procedure was confirmed with microscopy image of the polycrystalline structure of metal nanoparticles [56–59]. Consequently, during the formation of particles, ion metal and nanoparticles that formed in the liquid have interaction [44, 54, 55]. The nanoparticles can grow without any agent and ligand for some day after preparation in liquid because metal ions remain in an aqueous solution few days, and the formation of metal nanoparticles such as Pt and Ag continue with high affinity with the liquid such as water [55, 60]. As mention above, the size of metal nanoparticles depends on the density of metal atoms and temperature [44, 55], and sometimes, the atomic density and the temperature are not homogeneous in the plasma plume since two boundary regions exist with the surrounding liquid and the metal target [44, 46]. Many researchers reported that an energy threshold exists for the formation of nanoparticles using laser ablation technique [48, 50, 52, 54, 55]. The preparation of metal nanoparticle using laser ablation of metal target requires the presence of a plasma plume, and the minimum metal atom density should be provided to form the metal nanoparticles in the solvent [49, 50, 54, 55, 61]. The evidence of strong reactivity between metal and solvent in the plasma plume are consequences of the extreme pressure and temperature conditions [44]. Consequently, the plasma plume is quenched one order of magnitude faster in liquids than in gas or vacuum and the cooling process may not be considered an adiabatic process [44, 62]. This is useful for out-of-equilibrium reactions and the synthesis of metastable phases formed at high pressures and temperatures [44].

#### 4. Laser ablation setups

Many researchers have used the laser ablation setup in different forms to syntheses the metal nanoparticles in a liquid. Basically, the laser ablation setup contains a lens, a high power pulsed laser, a liquid container, a stirrer, and a linear positioner. The metal targets such as gold, silver, or copper (99.99%) were submersed in liquid. A Nd:YAG pulsed laser beam of 532 nm or 1064 nm ablated the metal plate. **Figure 1** shows the laser ablation setup, which contains a Q-switched Nd:YAG laser, a solution container, a metal plate, a lens ( $f = 30$  cm), a travel linear stage, and a stirrer. The duration of pulse and the laser ablation time can change from 10 to 60 Hz and 5–60 min, respectively. To prevent the absorption of energy of laser beam in the liquid solution, the path length which the laser beam passes through the liquid must be adjusted to shortest length. So, the distance between the target and entrance windows is a significant factor to achieve the best energy of laser beam on the surface of the target. In order to make sure the metal nanoparticles disperse evenly in the liquid solution, stirring of





**Figure 1.** Laser ablation setup for the preparation of metal nanoparticles contains a travel linear stage, a high-power laser, a metal plate, and a liquid tank.

the solution is carried out during the ablation of the metal plate, and the solution container moves horizontally using travel linear stage for providing the fresh area to ablate the target.

## 5. The effect of thermal properties in laser ablation of metal plate

Normally, the metal nanoparticles are generated using high energy laser pulsed inside an aqueous solution with pico, nano, and femtosecond pulsed laser. Pulsed laser should be melted the target to generate the nanoparticles. If the femtosecond or nanosecond pulses are used to prepare metal nanoparticles, the main problem is the generation of heat in the sample, and the calculation of temperature is difficult. This problem can be significantly simplified based on diffusion length. Indeed, the heat diffusion length is smaller than laser spot size. Hence, the temperature can be controlled during the laser ablation of the metal plate. For example, in some typical experiments, the spot size is about  $10\ \mu\text{m}$ , and it is larger than diffusion length. Moreover, the laser beam has a flat-top profile, and the absorbed energy of laser beam causes the increasing of temperature in the target layer. The area of the layer that covers with the laser beam is equal to the spot size of the laser, and it surrounds by liquid that absorbs the heat and decreases the temperature of the layer. In the presence of liquid, the average temperature increases, and from thermal equilibrium, the relationship temperature and other thermodynamic parameter are obtained as follows [63, 64]:

$$T \cong \frac{Aj}{c\rho h} \quad (2)$$

where  $A$  ( $A = 1 - R$ , where  $R$  is the reflectivity coefficient at the laser wavelength) is the absorptivity of the metal plate at the particular wavelength, and  $c$ ,  $\rho$ , and  $h$  are the heat capacity of the target material, the density of the metal target, and the thermal diffusion length in

the metal plate, respectively. The temperature has the relationship with the energy density of the laser beam, or it is fluence  $j$ . The thermal diffusion length  $h$  depends on the thermal diffusivity of the target materials [65]:

$$h \propto \sqrt{a t_p} \quad (3)$$

where  $a$  ( $k/c\rho$ ,  $k$  is the thermal conductivity of the metal plate) and  $t_p$  are thermal diffusivity and the laser pulse duration, respectively, and the increasing of temperature ( $T$ ) depends on absorption of laser radiation in particular wavelength as follows:

$$\alpha^{-1} \ll h, \quad (4)$$

Some part of laser power is converted to heat and it is the consequence of the evaporation of a solution near the laser beam, and this power is very weak.

## 6. The effect of wavelength in laser ablation of metal plate

When the laser ablation of the metals plate is considered, the wavelength of laser beam is a significant parameter. Because the optical constants of the material depend on wavelength; hence, the metal nanoparticles and metal targets can absorb the energy of laser beam at the particular wavelength. Metal clusters release in the nano-size from the metal plate and they can provide the condition for absorption of laser energy at each pulse, so the metal target can melt and the generation of nanoparticles becomes faster. Consequently, the higher repetition rate of laser pulses can provide the higher rate of generation of nanoparticles [66].

Jeon and Yeh were reported about the wavelength dependence of particle size and the formation efficiency in laser ablation [67]. They prepared the silver nanoparticle in inorganic (water) and organic solution (isopropanol) using green laser and infrared laser at nanosecond pulse. They achieved that the particle size using the green laser is larger than the particle size using the infrared laser. Hence, the formation efficiency of nanoparticles using infrared laser was lower than that using the green laser. Moreover, the laser fluence can change the size of the nanoparticle as a function of laser wavelength [65]. Hence, the fragmentation of nanoparticles can improve with enhancement of fluence. The dimension of nanoparticles prepared using infrared photon increases when the laser fluence increases. Consequently, when the wavelength of laser beam decreases, the ablation efficiency increases with the energy of laser beam.

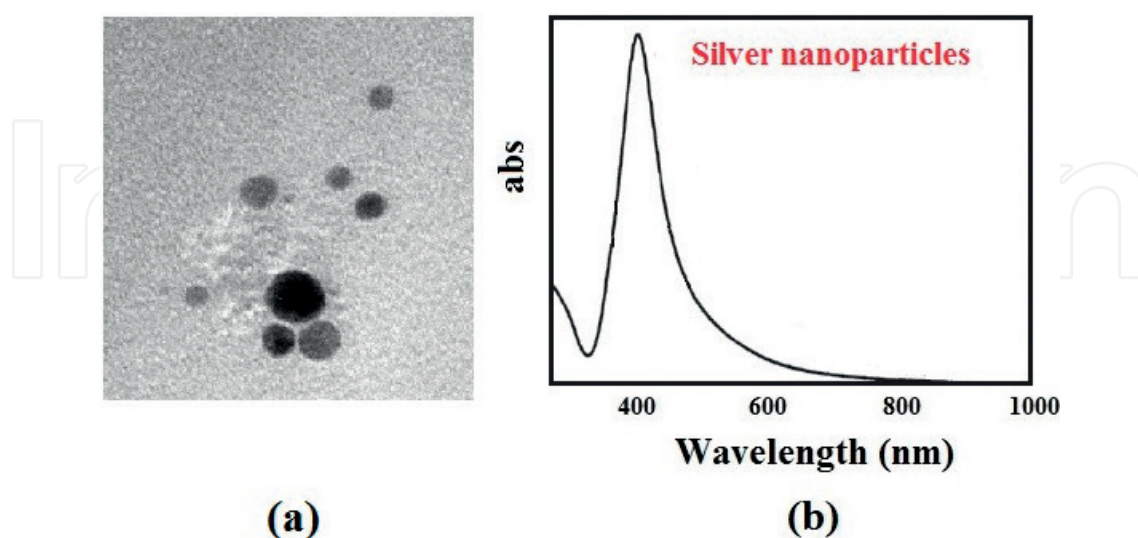
## 7. The effect of light absorption with nanoparticles in laser ablation method

The absorption of laser beam with nanoparticles is the effective factor of the laser ablation process at high laser fluence to prepare the nanoparticles in an aqueous solution. When the prepared nanoparticles have not high mobility in liquid, they are aggregated near the target.

Hence, they can absorb the energy of laser beam. This effect increases with increasing laser fluence because of the increase in the number of produced nanoparticles. Therefore, the intensity of laser beam that can reach the metal target is decreased. In addition, the size of the nanoparticles that absorb the incident laser beam decreases because of the laser-induced fragmentation occurs [68, 69]. This phenomenon was reported by Prochazka et al. [9]. They achieved the size of nanoparticles decreased when the laser beam interacted with the colloids during ablation of the metal target [70]. Consequently, the colloidal absorption causes the decreasing of the formation efficiency and the size of nanoparticles. This phenomenon called secondary effect. It can produce the high concentration nanoparticles and can control the formation process, and the size of nanoparticles and especially suppression of the ablation efficiency are undesired. Another considerable parameter is a flow-cell system, which is necessary for suppressing the colloidal absorption. Two colloidal absorption processes can be considered for preparation of metal nanoparticles. One is “interpulse” absorption and other is “intrapulse” absorption. The interpulse absorption related to the generation of nanoparticles by the earlier pulses stays in the laser beam path and absorbs the latterly coming pulses. The intrapulse absorption related to particles produced by the earlier part of one pulse immediately absorbs the later part of the same pulse.

## 8. Laser ablation of silver nanoparticle in liquids

Many researchers reported the preparation of silver nanoparticles in organic and inorganic solutions. Silver nanoparticles have biological, thermal, optical, and electrical properties. Hence, the synthesis of silver nanoparticles was presented using chemical and physical methods. Laser ablation of silver plate is an alternative and green method to prepare the



**Figure 2.** (a) TEM image of silver nanoparticle in oil and (b) UV-visible spectrum of silver nanoparticles produced using laser ablation.

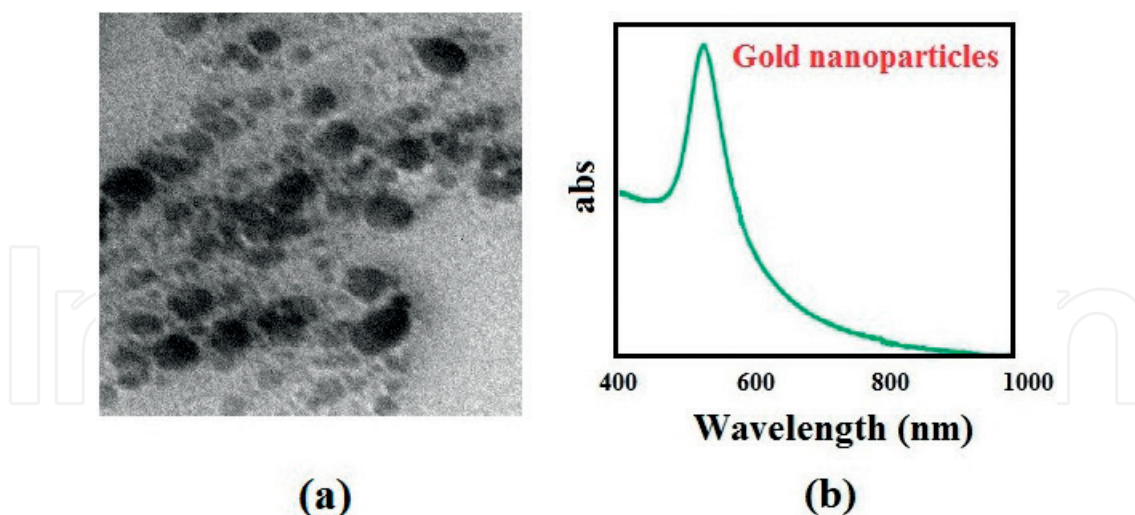
silver nanoparticles, and nanoparticles grow in the unique form of organic and inorganic solutions without any agglomeration and collapsing. Silver nanoparticles were prepared in water, methanol, palm oil [22], coconut oil [71], pomegranate seed oil [72], polyvinyl alcohol (PVA) [28], and graphene oxide solution [73]. Silver nanoparticles were capped by chain fatty acid of oils, and the particle size was about 10 nm. When the ablation time increases, the size of particles decreases. Nanoparticles formed in the spherical shape that was obtained using transmission electron microscope image (**Figure 2a**). The efficiency of the colloidal absorption by silver nanoparticles for 355, 532, and 1064 nm laser beam depends on localized surface plasmon resonance or the plasmon band around 400 nm (**Figure 2b**). Hence, the maximum and minimum efficiency occurred in 355 and 1064 nm. Thus, the influence of the colloidal absorption was more prominent for shorter wavelength laser beam, leading to the conclusion that the formation efficiency and the size of nanoparticles decrease with decreasing laser wavelength.

## 9. Laser ablation of gold nanoparticles in liquid

Gold nanoparticles (Au-NPs) have more applications for electronics [74], photodynamic therapy [75], therapeutic agent delivery [76], tumor therapy [77], sensors [78], drugs carriers [79], and medical diagnoses [80]. High activity and high sensitivity of Au-NPs have been fabricated using laser ablation in water [81]. The final product was used to reclaim the area of glassy graphite electrode for detection of Hg, Pb, Cu, and Co in the low concentration [81]. Gold nanoparticles can absorb and interact with the electrical field of laser beam [79], and Au-NPs generate localized surface plasmon absorption in the range of 400–900 nm [82]. The coherent excitation of free electrons causes the surface plasmon band in a colloidal nanoparticle [83]. The response of the Au-NPs to an interaction of laser beam depends on particle size, the surrounding material, and nanoparticle concentration [84]. Hence, the investigation and consideration of green synthesis of gold nanoparticles are intense interest subject in nanomedicine and nanotechnology area. Laser ablation technique is an alternative method for preparation of gold nanoparticles in an aqueous solution. Recently, gold nanoparticles were prepared in graphene oxide and vegetable oils such as pomegranate seed oil [25]. When gold nanoparticles were fabricated using laser ablation of the gold target, the nanoparticles were formed in the spherical shape (**Figure 3a**) that was investigated using transmission electron microscopy. The particle size was in the range of 20–5 nm, and the UV-visible absorption peak appeared about 530 nm (**Figure 3b**). In accordance with Mie theory, when the particle size decreases, the blue shift ( $\Delta\lambda$ ) occurs in the localized surface plasmon absorption peak as follows:

$$\Delta\lambda = \lambda_0 \times 0.18 \times \exp\left(\frac{-s}{0.23 \times D}\right) \quad (5)$$

where  $\lambda_0$ ,  $s$ , and  $D$  are central wavelength, interparticle gap, and particle size in the central wavelength [85, 86].



**Figure 3.** (a) TEM image of gold nanoparticles in oil and (b) UV-visible spectrum of gold nanoparticles produced using laser ablation.

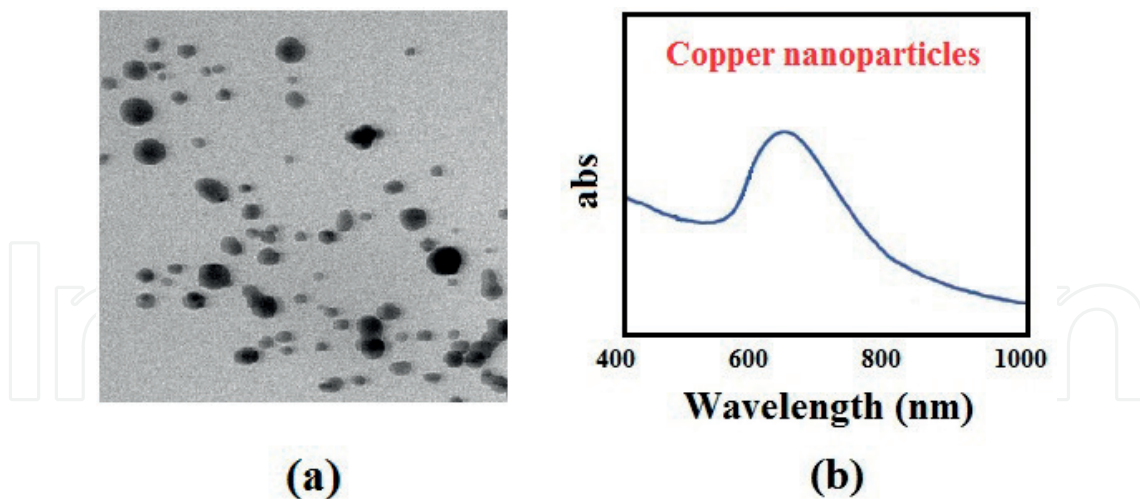
## 10. Laser ablation of copper nanoparticles

Copper nanoparticles (Cu-NPs) have more application conductive coatings, lubricants, sintering additives [87], and biosensors [88]. Copper nanoparticles are anti-inflammatory [89], reduce gastrointestinal mucosa [90], antioxidative [91], anti-ulcer [92], and are useful in preventing skin photosensitivity [93]. The copper nanoparticles strongly absorb the light beams about 600 nm, arising from the localized surface plasmon resonance (LSPR).

Recently, the application of vegetable oils such as palm oil [22], coconut oil [71], walnut oil [23], and castor oil [31] for dispersing the nanoparticles was considered for the preparation of nanometals [94]. These natural compounds contain triglycerides and non-polar long carbon chains that prevent nanoparticles agglomeration through steric repulsion [71].

Many methods based on the reaction of metal ions were presented to prepare copper nanoparticles. For example, solution phase [95], photochemical [96], sonochemical [97], and electrochemical synthesis methods [14] are the famous methods that are utilized for preparation of Cu-NPs in an aqueous solution. Laser ablation [98] is a green technique for the synthesis of copper nanoparticles. In the literature, the preparation of copper nanoparticles in distilled water, acetone, and ethanol [99] was reported using laser ablation. Malyavantham et al. [100] utilized the laser ablation technique to fabricate the Au-Cu NPs alloy. Copper nanoparticles were formed in the spherical shape (**Figure 4a**) in an aqueous solution. The UV-visible peak arose the localized surface plasmon resonance about 630 nm (**Figure 4b**). The influence of the colloidal absorption on the formation efficiency of copper nanoparticles was also the significant parameter to prepare copper nanoparticles. The formation efficiencies of Cu-NPs using 532 and 1064 nm laser beam were much closer than those of silver nanoparticles because the absorption at 532 nm in copper colloids was lower than that in silver colloids.





**Figure 4.** (a) TEM image of copper nanoparticle in oil and (b) UV-visible spectrum of copper nanoparticles produced using laser ablation.

## 11. Compression of silver, gold, and copper nanoparticles

The silver, gold, and copper nanoparticles formed in the liquid solution in the spherical shape using pulsed laser ablation of plate, and they have the localized surface plasmon resonance peaks in the visible range; but the copper nanoparticle has tendency to convert copper oxide sooner than gold and silver nanoparticles. According to the literature, the gold nanoparticle was formed in the liquids faster than silver and copper nanoparticles [101]. Gold, silver, and copper nanoparticles have the different biological and medical applications. Gold nanoparticles were used as an antibiotic, anti-fungal, and anti-microbial agent. Gold nanoparticles were used for drug delivery and anti-cancer. Silver and copper nanoparticles are a strong anti-bacterial and anti-inflammatory. Gold and silver nanoparticles were used as optical probes, sensor, and catalyst.

## 12. Conclusion

Laser ablation is a green and simple method for fabrication of the metal nanoparticles without surfactant or chemical addition, and the properties of nanoparticles are unique. The wavelength of laser and laser intensity are the significant parameters for production of metal nanoparticles; hence, the formation efficiency of nanoparticles using infrared laser was lower than that using the green laser, and the thermal effect strongly appeared in the case of laser with nanosecond pulse. The particle size was in the range of 5–20 nm, and the nanoparticles were formed in the spherical shape in an aqueous solution using laser ablation technique.

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