

Gold-Nanoparticle Synthesization In Gum Arabic Solution By Pulsed Laser Ablation

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Abstract. Green synthesis of nanoparticles is crucial to effectively reduce the risk to the environment by eradicating hazardous components that are harmful to human health. The broad complications such as aggregation and oxidation of nanoparticles will potentially limit their usage. Gum Arabic (GA) has attained decent attention due to less toxicity and bio-compatibility with metals. Gold-nanoparticles (Au-NPs) have several applications in diagnosing cancer, targeted delivery of drugs and in cancer treatment. This project is conducted by synthesizing Au-NPs in GA solution via pulsed laser ablation in liquid (PLAL) technique at varied laser fluences. A Q-switched Nd:YAG laser with wavelength of 1064 nm was focused using a lens with a focal length of 80 mm to ablate a gold plate immersed in GA solution. Four different laser fluences were tested. The laser fluences were 0.203, 0.214, 0.250 and 0.272 J. The Au-NPs synthesized in the GA solution were then characterized using photoluminescence (PL) and UV-Visible double beam spectrometer (UV-Vis). The highest laser fluence has shown the highest intensity while the wavelength of all peaks is the same indicating the same nanomaterials being synthesized in each sample. The UV-Vis spectra indicated that the absorbance increases as the holding time is prolonged. It is believed that the formation of Au-NPs is a nucleating process and followed by a growing process.

1. Introduction

1.1. Nanoparticles and Gold-Nanoparticles

A nanoparticle is a microscopic particle of any shape with a dimension ranging from 1 nm to 100 nm. Different sizes and shapes of nanoparticle of the same material show differences in physical and chemical properties. Nanoparticles are used in almost all field of science. It has a wide variety of applications in industry such as textile, pharmaceutical and cosmetics.

Recently, metallic nanoparticle had been in the spotlight in biomedical sciences and engineering due to their huge potential in nanotechnology [1]. Gold-Nanoparticles (Au-NPs) has several applications in diagnosing cancer, targeted delivery of drugs and in cancer treatment. Au-NPs has numerous advantages over other nanomaterials due to non-toxicity and biocompatibility. Different drugs are available for the treatment of cancer but resulted in damaging both healthy and cancerous cells and this leads to necrosis. Instead, Au-NPs causes damage only to the cancerous cell. Due to its size smaller than human cells, gold-nanoparticles penetrate the tumor and destroy only the cancer cell. Due to photophysical properties, Au-NPs are useful for the diagnosis of cancer [2].



1.2. Pulsed Laser Ablation in Liquid Method

The laser ablating process of a target sample starts with the absorption of incoming photons, which can produce heating and photoionization in the irradiated area. The phase and the amount of the ablated material depend on the absorbed photon energy. The profile of absorbed energy is non-constant in time and non-uniform on the whole target area, which results in the large size distribution of metallic nanoparticles. The charging of the irradiated area due to the photoionization results in expulsion of material from the target. Due to the coexistence of all these different mechanisms in laser ablation process, PLAL is also called the explosive boiling ablation technique.

Figure 1 shows the various stages at different time sequences of producing nanoparticles using nanoseconds-laser ablation in liquid. The interaction of nanosecond pulsed laser of sufficient threshold energy with the interface between liquid and the metal target results in the formation of a microplasma layer. Once the laser beam strikes the sample, mass leaves the surface in the form of electrons, ions, atoms, molecules, vapours, liquid drops, clusters and particles as depicted in Figure 1 (A) and 1(B), where each of the processes like fragmentation, sublimation and atomization are separated in time and space.

Mechanisms like multiphoton absorption are associated with this materials removal process. Multiphoton absorption is when an electron is excited from the valence band to the conduction band by photon absorption. The multiphoton absorption mechanism is observed in the case of femtosecond pulses, whereas for nanosecond pulse duration, cascade ionization becomes dominant due to the wavelength-dependent inverse Bremsstrahlung (IB) process.

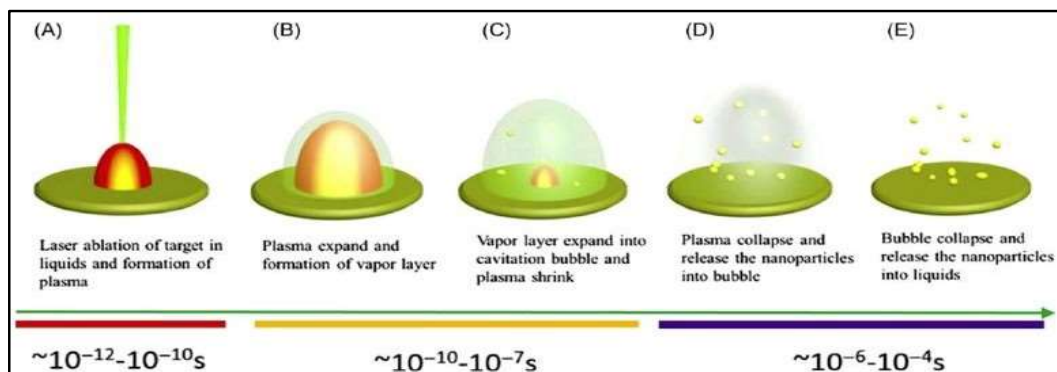


Figure 1. Mechanism of various stages of ns-laser ablation in liquid and time sequence [3].

During this process, the free electrons which gain sufficient energy release the bound electrons of metal atoms by frequent collisions with them, leaving more ions which results in cascade ionization through IB absorption. This process leads to the multiplication of free electrons to form a plasma plume, which is accompanied by the generation of shock waves, followed by cavitation bubbles, as shown in Figure 1(C).

The disturbances in the path of liquid because of shock waves create cavitation bubbles, and the frequent expansion and collapse of this bubble result in the formation of secondary shock waves. The detachment of the shock wavefront from the plasma takes place immediately after the plasma formation because its velocity is much larger than the particle velocity behind the front. Therefore, the plasma plume, once formed, starts absorbing a significant portion of the remaining part of the laser pulse through IB effect to increase plasma temperature. Plasma expansion takes place in thermal adiabatic conditions and finally as the plasma plume cools down, the solid particles nucleate and grow subsequently to form nanoparticles. This is shown in Figure 1(D) and 1(E).

1.3. Gum Arabic Solution

Gum Arabic (GA) is a derivative of excretion of Acacia Seyal or Acacia Senegal trees. It contains a mix of complex polysaccharides in addition to oligosaccharides and glycoproteins. However, the compositions will depend on the type of soil, source, and the type of climate.

GA had been used for many years apart from traditional medicine and daily application for certain diseases. In the Middle East, GA was used by the Egyptians as a pain reliever and glue. Doctors used GA to treat various health complications. In present days, GA is broadly used in the pharmaceutical and also food industries [4].

Figure 2(a) show the UV-Visible spectra of the GA-ZnO nanoparticles at an absorption peak of 354 nm. It was found that the lower absorption wavelength reflected a higher bandgap and a smaller nanoparticle size, which influence the UV light absorbance of ZnO nanoparticle. The sharp absorption of ZnO shows the monodispersed nanoparticle distribution. Figure 2(b) shows the functional groups of GA-ZnO nanoparticles using FTIR analysis. The peak in the region between 424 and 475 cm^{-1} agreed to Zn-O stretching. The presence of ZnO was also confirmed by the XRD pattern in Figure 2(c). Figure 2(d) shows the DLS narrow size distribution with a size averaging about 180 nm of GA-ZnO nanoparticles. This size was found to be smaller compared to ZnO nanoparticles that was not stabilized with GA which is 1020 nm [5].

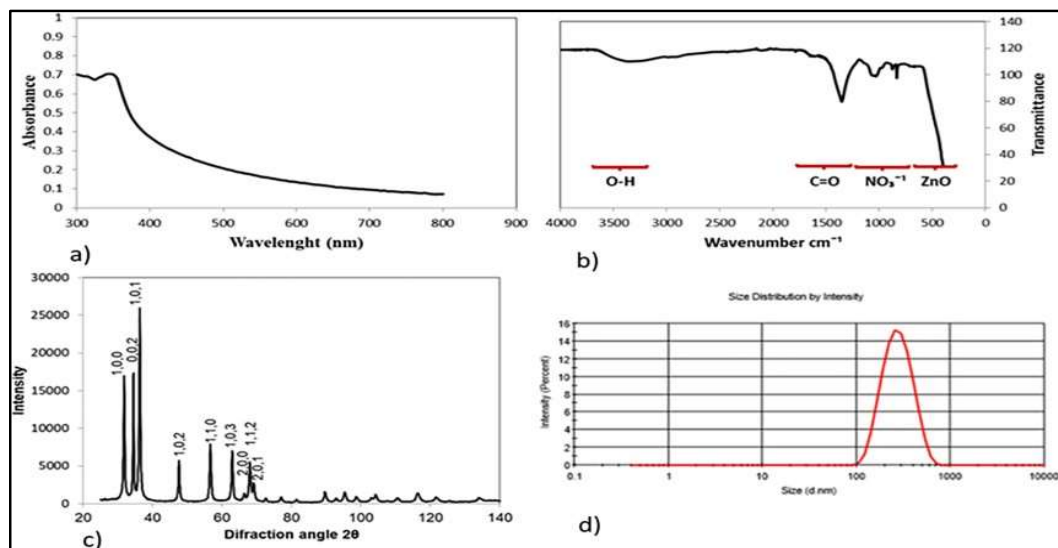


Figure 2. ZnO nanoparticles characterization a) UV-Vis spectra of ZnO nanoparticles; b) FTIR spectrum of ZnO nanoparticles; c) XRD spectrum of ZnO nanoparticle; d) size distribution by intensity of ZnO nanoparticles based on DLS analysis [5]

2. Experimental

2.1. Synthesis of Gold-Nanoparticle

The experimental set up is shown in Figure 3. A Q-switched Nd:YAG laser was used for ablation. It is operating at a fundamental wavelength of 1064 nm. A gold plate (99.99% purity) was immersed at the bottom of a cuvette which filled with 10 ml GA solution. The laser light of wavelength 1064 nm was focused onto the surface target using a convex lens of focal length 80 mm at different laser voltages; 850 V, 1000 V, 1050 V and 1150 V. The frequency used was 1 pulse per second (1 Hz) with 4000 pulses for each sample at room temperature (better state). The solution was rotated on a rotational platform at 90 rpm to achieve a homogenous mixture during the ablation process. The fabricated Au-NPs was characterized using photoluminescence (PL) and UV-visible double beam spectroscopy (UV-Vis).

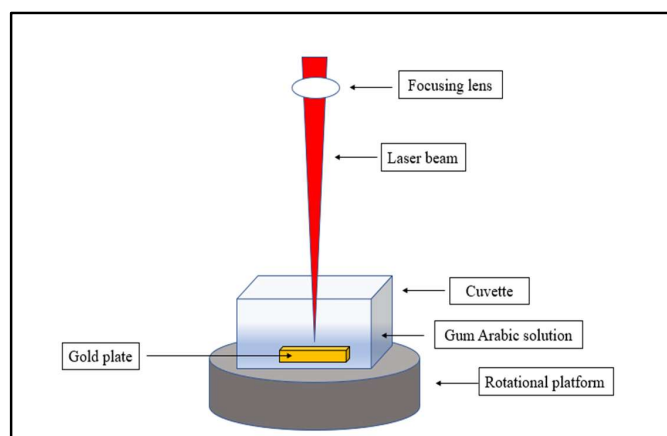


Figure 3. Experimental setup for Au-NPs synthesis using laser ablation in GA solution.

2.2. Analysis methods

2.2.1 Photoluminescence (PL). Photoluminescence spectrum obtained using Spectrofluorometer (PL), model: Fluoromax 4C (2015). The sample was filled into the cuvette then placed on the sample holder. Using Fluorescence V3.5 software, the excitation wavelength was selected at 350 nm in the range of initial and final emission and slit width was selected between 360-650 nm prior to running the instrument. After the instrument completed on sample scanning, the raw data can be obtained as well as the PL spectrum.

2.2.2 UV-Visible Double Beam Photo Spectrometer (UV-Vis). UV-Vis spectra were characterized using Shimadzu UV-1800 Double Beam UV/Visible scanning Spectrophotometer. At first, distilled water was filled in two plastic cuvettes and placed into the sample holder. Using UV Probe 2.34 software, the wavelength range was set in the range of 200 - 700 nm. After placing both cuvettes that were filled with distilled water, the baseline was recorded by clicking on the baseline button on the software interface (not necessary to explain using software). Next, the distilled water in one of the two cuvettes were replaced with samples and afterwards being characterized by running the instrument. After the instrument completed scanning the sample, raw data can be obtained as well as the UV-Vis spectra.

3. Results and Discussion

3.1. Photoluminescence (PL)

Figure 4 show the PL spectra of 4 samples recorded at different fluences with Au-NPs in GA solution. The PL intensity increases as laser fluence is increased. The central peak around 436 nm indicates the colour of the Au-NPs. As can be seen in Figure 4, the PL intensity has been changed randomly from lowest to highest laser fluence. The intensity of the peak may be intensively influenced by the increase of interactions between Au-NPs and excitation photons [6]. Generally, the increasing in the PL peak intensity reveals higher radiative recombination rate of the photogenerated electron-hole pairs. This could be caused by increasing in the concentration of the luminescent species [4]. In [6] it was confirmed that the number of NPs in the ablation environment increases with increasing laser fluence during the ablation process. However, for the case of our samples, the PL intensity shows a non-linear trend.

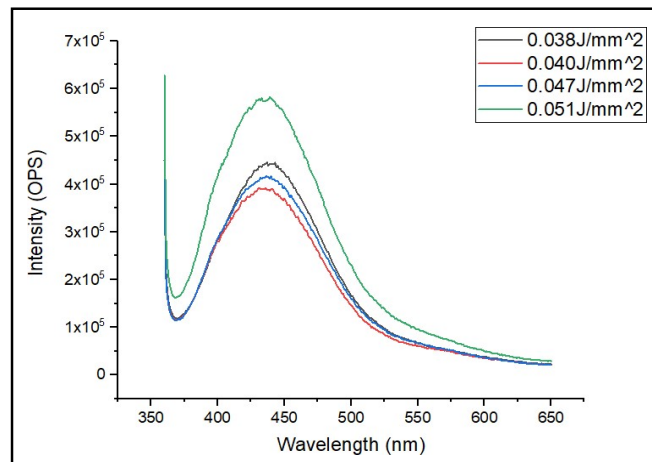


Figure 4. PL spectra obtained for different fluences.

3.2. UV-Visible Double Beam Photo Spectrometer (UV-Vis)

In Figure 5 (a), (b), (c) and (d), the absorption peak found to be increased without any significant changes in the shape of the spectrum, which corresponds to the plasmon absorption peaks of Au-NPs. To rule out interferences of the natural UV light, the solutions were kept in the dark container after irradiation. UV-Vis spectra indicated that the absorbance increases as the holding time is prolonged. It could be seen that the absorbance at the peaks increases in a linear fashion, holding on till 20 August 2020 and then the rate of increment has declined as it progressed.

Time evolution phenomenon had been reported in UV-induced nanoparticles synthesis. For example, Esumi et al. [7] investigated using sugar-per substituted poly(amidoamine) dendrimers as the reducing agent to produce gold and silver nanoparticles in aqueous solutions. They observed that the absorbance at 520 nm showed a similar evolution type as a function of time. It was thought that the formation of Au-NPs was a nucleating process followed by a growing process [8].

Our findings agreed well with the suggested nucleation-growth mechanism. More interestingly, we revealed that GA solution was special in that the particle growth reaction could continue. GA solution may have reduced Au-NPs into very tiny size nanoparticles. Due to high surface energy, they tend to aggregate to form larger Au-NPs. Once the ablation was completed, the nucleation and growth process could still happen [8].

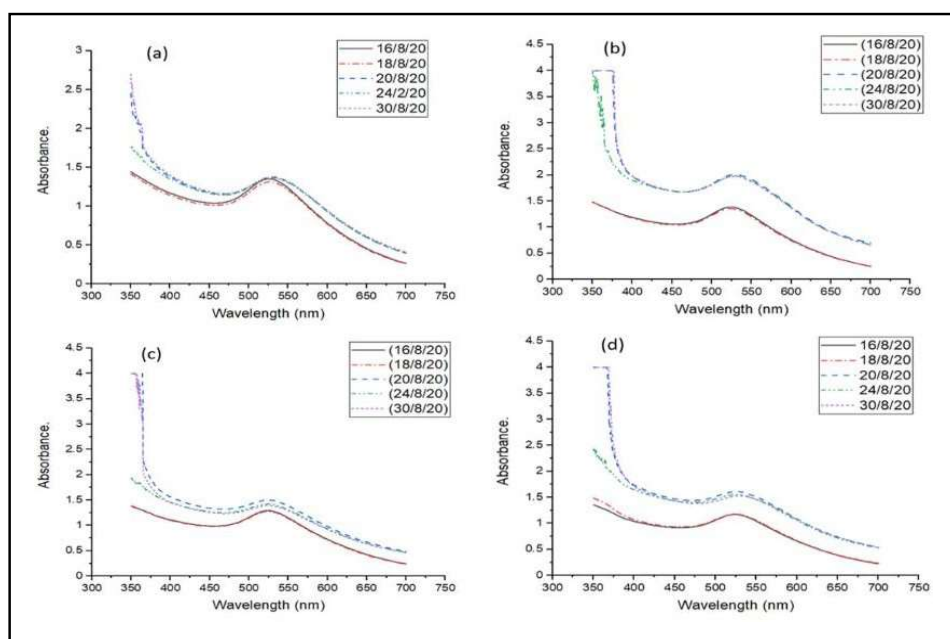


Figure 5. UV-Vis spectra comparison of the same fluence on different days of UV Vis characterization. (a) For fluence of 0.038 J/mm^{-2} . (b) For fluence of 0.040 J/mm^{-2} . (c) For fluence of 0.047 J/mm^{-2} . (d) For fluence of 0.051 J/mm^{-2} .

4. Conclusion

A pulsed laser ablation in liquid (PLAL) system was set up successfully, and the production of gold-nanoparticles (Au-NPs) were achieved. Au-NPs were successfully synthesized by varying the laser voltages by 850, 100, 1050 and 1150 V (better to mention on the term laser fluence). The synthesis of gold-nanoparticle (Au-NPs) in Gum Arabic (GA) solution by pulsed laser ablation in liquid (PLAL) also produced a sample with less contamination. Investigation on the properties of Au-NPs were done by photoluminescence (PL) and UV-Visible double beam photo spectrometer (UV-Vis) characterization.

The PL characterization revealed the intensity of Au-NPs in GA solution prepared by different laser fluences. The PL intensity shows a non-linear trend. UV-Visible double beam photo spectroscopy (UV-Vis) revealed the absorbance of each sample prepared by different laser fluence. It was found that the UV-Vis spectra indicated that the absorbance increased as the holding time prolonged. It was thought that the formation of Au-NPs was a nucleating process followed by a growing process.

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