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Preparation of Silver Nanoparticles Dispersed in Almond Oil Using Laser Ablation Technique

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Abstract. Nanoparticle production by pulsed laser ablation (PLA) is a process that can generate pure nanoparticles (NPs) straight from a varied range of bulk substances and compounds. Silver nanoparticles (Ag NPs) are probably one of the most attractive noble metal nanostructures because of their unique and interesting physical and chemical properties. In this study, laser ablation of pure silver plate immersed in almond oil was carried out for Ag NPs production. Nd: Yag laser of wavelength 1064 nm, was used for the ablation of the Ag plate at different laser energies and ablation times. The almond oil permitted the formation of Ag NPs with a stable and homogeneity particle diameter in a reasonable time. The size distribution of the NPs was examined by High-Resolution Transmission Electron Microscopy (HRTEM). The particle sizes of the produced Ag NPs at laser energy 200 mJ in the solution at 10,15 and 20-min ablation times were 4.82, 3.11 and 1.82 nm respectively. The particle sizes of Ag NPs produced at different laser energies 150,200 and 250 mJ and at ablation time 10 min inside the solution were 5.39,4.82 and 1.92 nm respectively. The absorption peaks of the produced nanoparticles have been characterized using a UV-Vis spectrophotometer.

Keyword: Laser ablation, metal nanoparticle, almond oil

1. Introduction

Nanoparticles (NPs) formed by conventional chemical synthesis methods often include undesirable residues from the reactants. These residues can be toxic and unfavorable for applications. Production of NPs by pulsed laser ablation in liquid medium (PLAL) has received much attention as a novel NPs production method. The most important advantages of NPs prepared by the PLAL method are its high stability, the relative simplicity of the procedure and the absence of chemical reagents in the final preparation [1][2][3]. Due to their fascinating optical, catalytic, electronic and magnetic properties, which are particularly different from bulk samples, noble-metal NPs have seen spectacular growth in recent years. Silver NPs are probably the most attractive nanostructures for noble metals[4].

In this study, we prepared silver NPs in almond oil of different sizes. The main problem of the production of Ag NPs is the agglomeration of Ag nanoparticles in liquid due to thermodynamics, so recently some fatty acids or vegetable oils were used as a stabilizer[5] Hence, we have used almond oil in this study as a stabilizing agent in the preparation of Ag nanoparticles. Sweet almond oil has been described as unsaturated oil, with oleic acid (O, C18:1) being the main fatty acid (65%) with β – sitosterol as the most representative sterol and α – tocopherol as the major tocopherol[6][7][8]. We were able to control the size of produced Ag nanoparticles in almond oil by changing the laser parameters to obtain Ag NPs of the size required for a cosmetic application[9][10]. The size distribution of the NPs was determined by High-Resolution Transmission Electron Microscopy (HRTEM).

2. Experimental setup

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The experimental setup is shown schematically in Fig. 1. The beam from a Pulsed Q-Switched Nd: YAG (Quanta - Ray) laser of wavelength 1064 nm, pulse duration 8 ns and repetition rate 10 Hz was focused by a lens of focal length (f = 20 cm) on the surface of the silver target (purity: 99.99 % from Sigma Aldrich). The target was of a thickness (0.5 mm) and dimensions (2.5*2.5 cm^2) placed at the bottom of a glass vessel containing (20 ml) of almond oil (from FLUKA). The metal plate was washed first using the ultrasonic bath for 30 min and cleaned with ethanol and distilled water to get rid of organic contamination and then fixed at 18 mm below the almond oil surface.

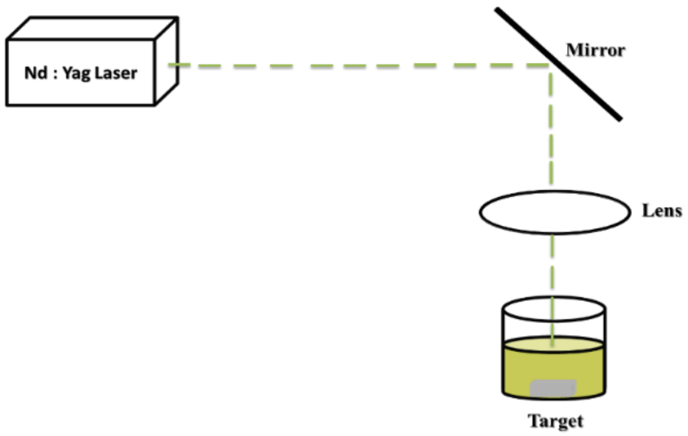

Fig 1. Schematic diagram of the experimental setup

The energy of the incident laser pulse was measured using (COHERENT- LASERMATE/D) power meter. The effective spot size of the laser beams on the surface of the target was 7 mm without the lens and is calculated to be 2mm on the surface of the target for wavelength (1064 nm). Ablation was carried out at room temperature and the formation of nanoparticles in the almond oil could be confirmed by the change of its color during ablation. During the ablation procedure, the solution was magnetically stirred to disperse the generated NPs[11]. The absorption spectra of the Ag nanoparticles in the almond oil were measured immediately after the ablation process using a UV-Vis double-beam spectrometer type (JASCO V-670). High-Resolution Transmission Electron Microscope (HRTEM)(JEM-2100) was used to determine the shape and the size distribution of the nanoparticles[12].

3. Results and Discussion

Through the laser ablation of silver plate in the almond oil, the almond oil firstly appeared colorless but after a small period of time, it began to change to yellow, then finally to brown. The darker color for solutions suggests a higher concentration of Ag NPs and this was confirmed by a UV-Vis absorption spectrum.
The FT-IR spectra of pure almond oil and of silver NPs in almond oil are shown in Fig.2 where the peaks corresponding to bands of olefinic double bonds (3002 cm-1), methylene group (2922, 2851, 1464 and 722 cm-1), methyl group (1464 and 1377 cm-1) and triglyceride ester group (1743, 1237, 1159 and 1097 cm-1)[13]. Actually, the peaks are sharper in the case of Ag NPs in almond oil due to the plasmonic effect of the nanoparticles[14][15]. We can say that the almond oil component can be used as a capping agent of Ag NPs.

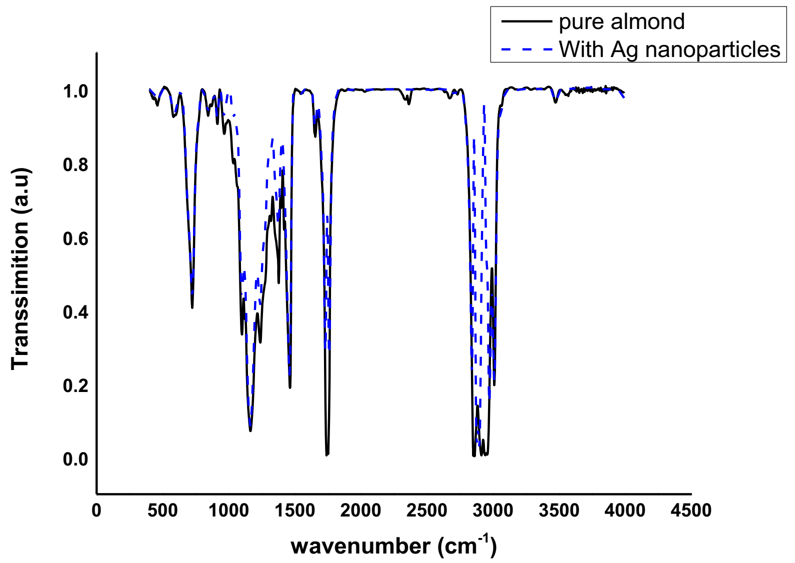

Figure 2. The FT-IR spectrum of pure almond oil and Ag nanoparticles in almond oil

3.1 Effect of ablation time

The optical absorbance spectra of silver colloids prepared by laser ablation in almond oil solution at different ablation times ranged from (5 to 20) min are shown in fig. 3.

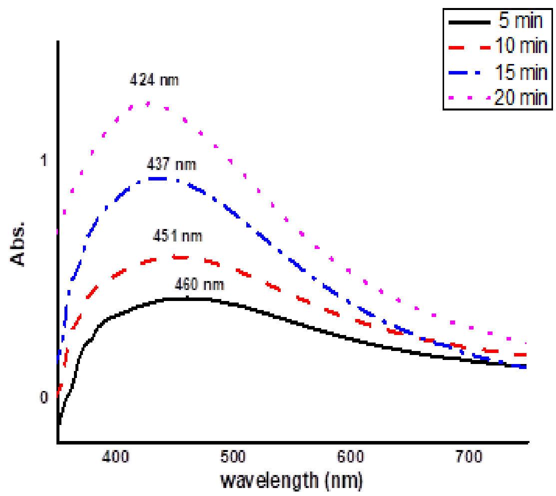

Figure 3. UV-Vis results show the intensity peaks having a blue shift with Increasing ablation time at laser energy 200 mJ

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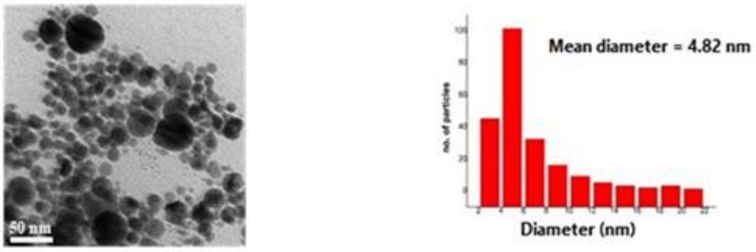
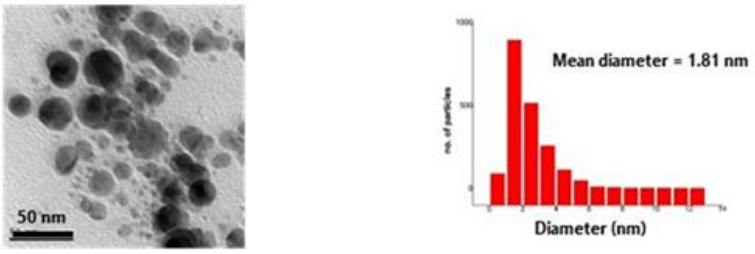
It is noticeable in fig.3 that, increasing the time of ablation from 5 to 20 minutes cause the absorption peaks to increase and shift to lower wavelength (blue shift). The absorption peaks arise from surface plasma resonance of silver nanoparticles. The increase in the peak intensity of the spectra is due to the increase in the concentration and volume fraction of the Ag nanoparticles inside the liquid. Conferring to Mie theory, the blue shift in spectra is due to the decreases in particle size[16][17]. This decrease in particle size was due to the interaction between produced Ag NPs and laser light for longer ablation times[18]. On the path of incident laser light, many Ag NPs were produced. Due to the interaction of the laser light and produced Ag NPs, large particles break down and get smaller. Fragmentation quality improves with increasing removal time; so, the obtained particles at longer ablation times are smaller and significant aggregation is not seen, which is expressed by the narrower particle distribution.



a) TEM micrograph and histogram for silver nanoparticle with time (10 min)
(average diameter = 4.82 nm)



b) TEM micrograph and histogram for silver nanoparticle with time (20 min)
(average diameter = 1.81 nm)

Figure 4. TEM micrograph and histogram for Silver nanoparticles in almond oil with times (10 and 20 min)

The TEM micrograph and size distribution of silver nanoparticles produced by laser for ablation time 10 and 20 min in almond oil solution at laser energy 200 mJ are shown in fig. 4. The corresponding average size of the produced NPs with 10 min ablation time was 4.82 nm and with increasing the ablation time to 20 min the size decreased to 1.81 nm.

3.2 Effect of the energy of the laser beam (150 -250 mj)

The absorption spectra of Ag NPs in almond oil at different laser energies ranged from (150 to 250) are shown in fig. 5. It is observed that the absorption peak position is slightly shifted towards the shorter wavelength with an increase in laser energy (blue shift). This finding suggests a reduction in particle size of the Ag NPs prepared with an increase in laser energy. In fact, higher laser energy leads to greater kinetic energy which increases collision between initially formed large nanoparticles in the condensation process which further reduces the size[19]. It is observed that the absorption peak intensity increases with the increase of laser energy. This attributed to the increase in the concentration and volume fraction of the Ag NPs produced in the almond oil.

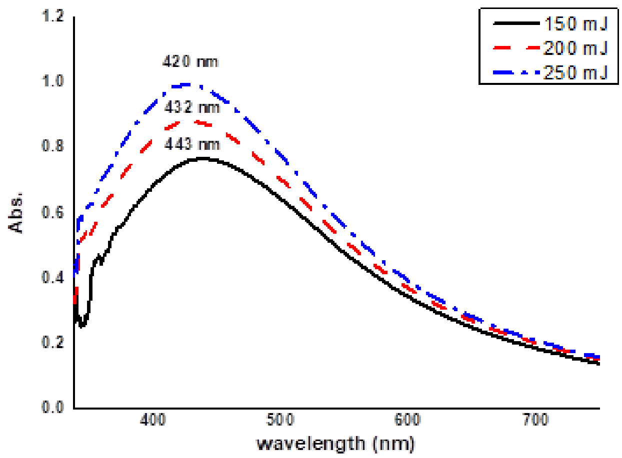
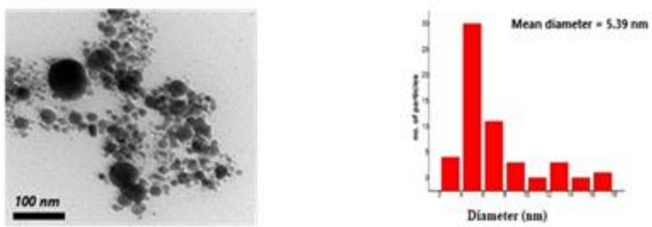
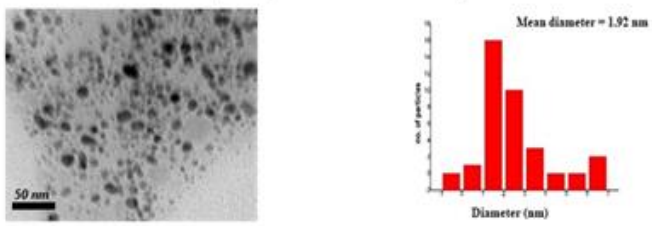


***Figure 5. UV-Vis results show the intensity peaks having a blue shift with increasing laser energy from 150 to 250 mJ* at 10 min ablation time**

The TEM micrographs and size distribution of Ag NPs produced by laser ablation for energy 150 and 250 mj at ablation time 10 min in almond oil solution. The average size decreases from 5.39 nm to 1.92 nm with increasing laser energy from 150 to 250 Mj are shown in fig 6.



a) TEM micrograph and histogram for silver nanoparticle with energy (150 mJ)
(average diameter = 5.39 nm)



a) TEM micrograph and histogram for silver nanoparticle with energy (250 mJ)
(average diameter = 1.92 nm)

Figure 6. TEM micrograph and histogram for Silver nanoparticles in almond oil generated with energy (150 and 250 mJ)

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3.3 Effect of aging

The absorption spectra of fresh (Ag/almond oil) and (Ag/almond oil) measured after 2 weeks and 4 weeks are shown in fig7. All samples display a little shift in peak position and a small increase in the full width of the half maximum (FWHM). This indicates minute aggregation of the ablated Ag NPs in almond oil.

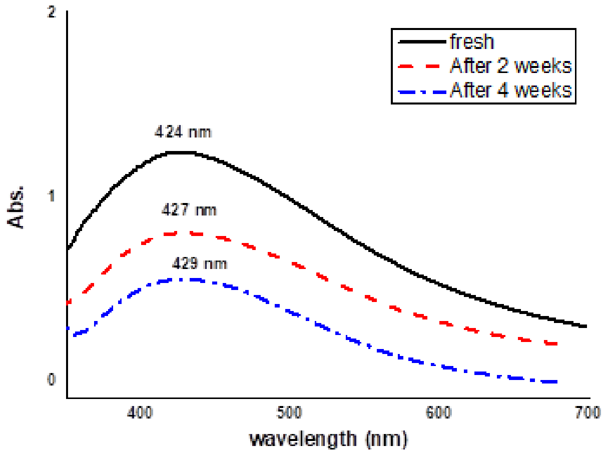

Figure 7 .UV-VIS for fresh and after several weeks

This observation shows the reasonable stability of the samples and also confirms the ability of almond oil as a stabilizer and size controller. These effects are due to the rivalry between the rapid formation of initial silver nanoparticles and the consequent growth of the particle due to the almond oil molecules capping the particle[20]. We can say that at the beginning of the ablation of the silver plate, A thick cloud of silver atoms over the ablation spot is produced. Silver atoms interact much stronger than silver atoms and almond oil molecules[21]. Therefore, a very slow agglomeration of the silver atoms occurs.

4. Conclusion

Laser ablation of a silver plate in almond oil was employed to prepare size-controlled silver nanoparticles using, fixed laser energy with increasing ablation time period and increasing laser energy for a fixed time period. The size of the ablated Ag NPs decrease in both cases, furthermore, the almond oil proved to be a good stabilizer for Ag NPs. Such as a simplified method for generating Ag nanoparticles in almond oil is relevant importance for the cosmetic industry.

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