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PULSED LASER ABLATION OF THE SOLID TARGETS IN A LIQUID ENVIRONMENT

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Article Info	Abstract
Received: 26.09.2017 *Accepted: 06.10.2017* **Keywords:** Pulsed Laser, ablation, nanoparticles	In this paper, the viability of laser ablation of gold target immersed in medical distillated water used to produce nanoparticles having morphological, structural and compositional properties for medical applications is explored. The morphological properties were investigated by means of scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDX) analysis was used to reveal the composition of resulting particles. The absorbance in the wavelengths range of 300-800 nm can be assigned to the small gold nanoparticles.

1. Introduction.

During the last years special attention has been given for synthesis of metal nanoparticles, especially for noble metals such as gold, knowing their physical and chemical properties that made them attractive for practical applications in biotechnology, for medical applications when the laser irradiation is guided inside the human body to ablate the “soft” tissue and chemical catalysis [1, 2]. Metal nanoparticles are performed in liquid laser ablation with various solvent because of the advantages of this method over chemical synthesis being its simply and clean procedure [1-3]. It has been explored the laser ablation of gold in medical distilled water and gold nanoparticles have been obtained using the laser ablation at nanoseconds pulses with wavelength of 532nm. The size control of gold nanoparticles has been achieved by changing the wavelengths [4-6], pulse duration and supplementary laser irradiation [7-9].

2. Experimental Technique

The experimental setup for laser ablation in liquid environment consists of Nd:YAG laser operating at the second harmonic 523nm with 7ns time pulse duration and 10Hz repetition frequency, irradiating the surface of a gold target placed in a distillated medical water cell (solvent). The laser radiation is focused on the target surface by a lens with 30cm focal length and the cell is filled with 20ml solvent. The laser fluence at the target surface was varied in the range of 2–6.75J/cm^2. The medical distillated water was purchased from pharmacy.

The laser ablation of gold target in water was accompanied by the presence of a small plasma plume above the target surface. The plasma plume intensity depends on the laser energy and light focusing conditions. For the gold target, a visible pink coloration of the solution indicating nanoparticles formation has been noticed several minutes after the beginning of the ablation experiment.

After the ablation experiment was performed, the optical absorption spectra of gold nanoparticles were measured with the spectrophotometer Ocean Optics. The quartz cell having a length of 1cm was used for absorption measurements. The gold nanoparticles were placed and evaporated on a glass substrate.

3. Results and Discussions

The figures 1a-1d show the typical absorption spectra of gold nanoparticles solution obtained by the 532nm laser ablation of gold target at various fluences and laser ablation times. It is easy to observe that the optical absorption spectra of gold nanoparticles have a characteristic peak of surface plasmon resonance. The plasmon peak position was around 519nm, indicating the formation of particles with dimensions around 50nm in medical distillated water used.

The presence of the single surface plasmon peak indicates that the formed nanoparticles were nearly spherical. In the case of two plasmon peaks in the absorption spectrum, the particles have an ellipsoidal shape [10]. At small laser fluences of 2-3.24J/cm^2 the medical distilled water has a pink coloration and by increasing the fluence at 6.75J/cm^2, a light violet coloration appears. At higher laser fluence and laser ablation time, an increase of the nanoparticles concentration is observed.

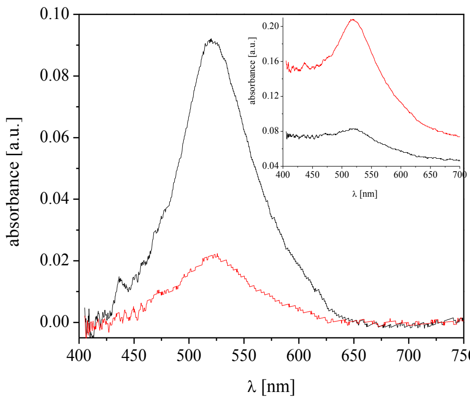


Figure 1a. The plasmon peak of the optical absorption spectra of gold nanoparticles at two fluences, black 6.75J/cm^2 and red 2J/cm^2, respectively. The time laser ablation was 15min. Inset is presented the recorded optical spectra.

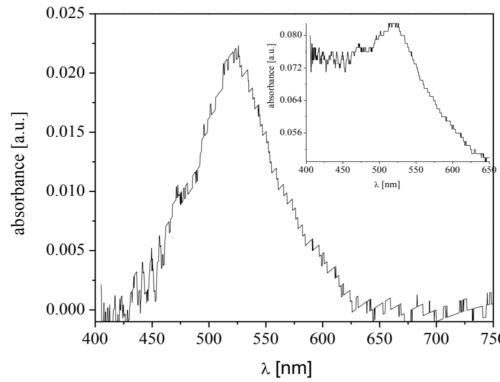


Figure 1b. The plasmon peak of the optical absorption spectra of gold nanoparticles at fluence 2J/cm^2. The time laser ablation was 30min.

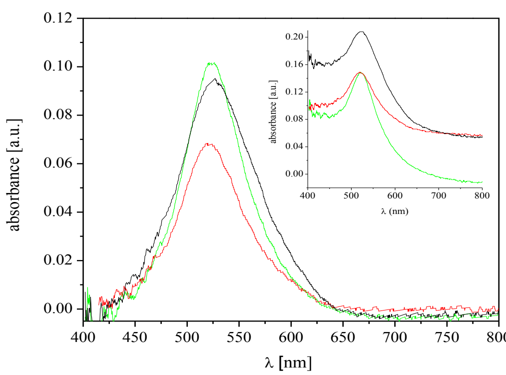


Figure 1c. The plasmon peak of the optical absorption spectra of gold nanoparticles at three fluencies, black 2.54J/cm^2, red 2J/cm^2, and green 3,24J/cm^2, respectively. The time laser ablation was 60min.

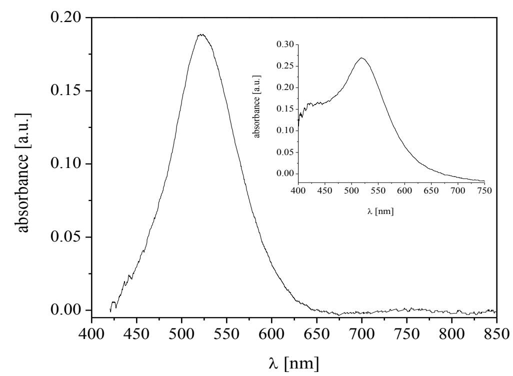


Figure 1d. The plasmon peak of the optical absorption spectra of gold nanoparticles at fluence 2J/cm^2. The time laser ablation was 90min.

In figure 1a are presented the absorption spectra of gold nanoparticles at various fluences and a constant time of laser ablation. To find the height of the plasmon peak, the background of the recorded optical absorption spectra were eliminated. From figure 1a, it is observed that an increase in the fluences starting from 2J/cm^2 to 6.75J/cm^2, the absorption peak is growing at high value. Moreover, in figure 1b increasing twice the laser ablation time from 15-30min and keeping constant the laser fluence at 2J/cm^2, a small increase of the plasmon peak is observed. The figure 1c presented the absorption spectra of nanoparticles at three fluences of the laser ablation. The laser ablation time onto the target was 60min. An increase of the plasmon peak is noticed. A high increase of the plasmon peak can be seen in figure 1d, where the laser fluence is 2J/cm^2 and the laser ablation time was 90min.

An evaluation between figures 1a - 1d shows that keeping a constant fluence at a certain value, in our case 2J/cm^2, and increasing the laser ablation time, the plasmon peak growths almost exponentially. This effect is observed in figure 2a, where the absorbance of the resonance plasmon peak increases fast, this being associated to an increase of the nanoparticles concentration.

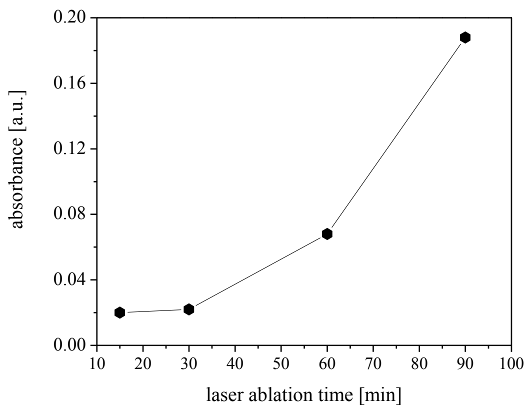


Figure 2a. The relative absorbance of gold nanoparticles at various laser ablation times on the target: 15min, 30min, 60 min and 90 min respectively. The laser fluence was 2J/cm^2.

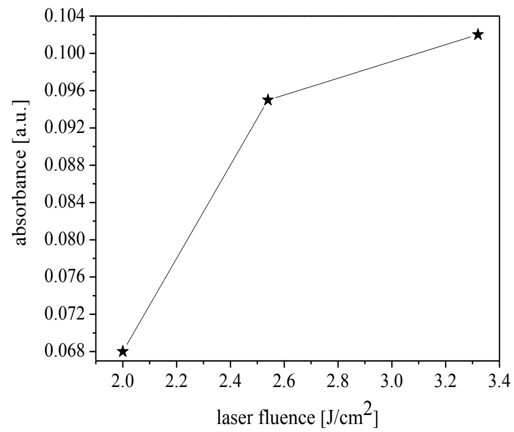


Figure 2b. The relative absorbance of gold nanoparticles for various laser fluences 2J/cm^2, 2.5J/cm^2 and 3.24J/cm^2, respectively. The laser ablation time was 60min.

In figure 2b, it is presented the absorbance for three laser fluences: 2J/cm^2, 2.5J/cm^2 and 3.24J/cm^2, respectively. The time laser ablation onto the target was 60min. The resonance plasmon peak absorbance shows an increase that leads to nanoparticles concentration growth. In the case of laser fluence increase, the absorbance of the nanoparticles is also intensified and seems to reach a threshold, meaning that the nanoparticles join themselves and conglomerates are being formed.

A small drop of the sample solution was then placed onto the glass and dried at room temperature. The parameters of the solution are the fluence of 6.75J/cm^2 and the ablation time of 15min. In figure 3, it is presented the X-ray diffraction pattern of the gold nanoparticles solution. By means of X-ray diffraction it is possible to estimate the size of the nanoparticles using Scherrer's formula [11], the gold nanoparticles dimensions being in the range of 50-100nm.

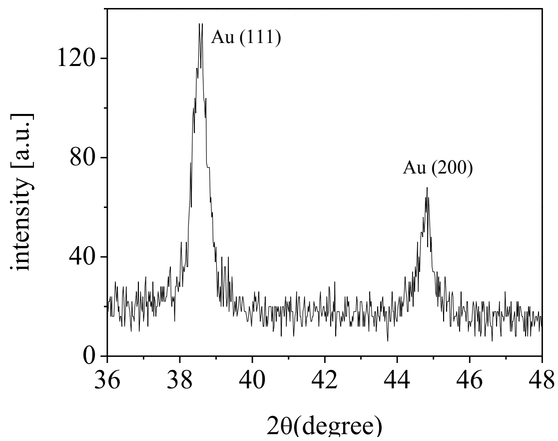
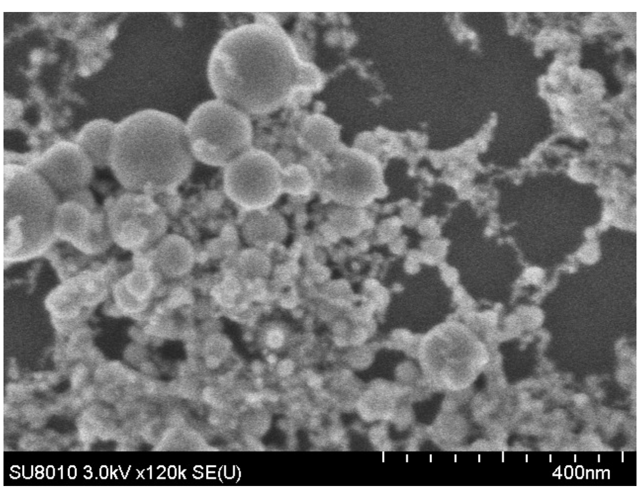
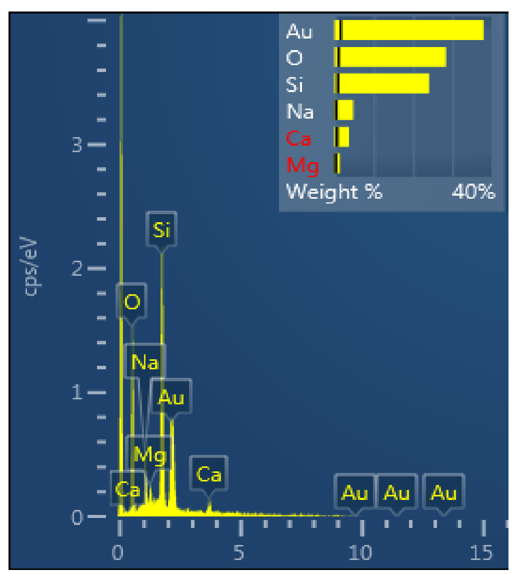


Figure 3. X-ray diffraction of gold nanoparticles solution prepared by pulsed laser ablation in medical distillated water placed on the glass substrate and dried at room temperature. The laser fluence is 6.75J/cm^2 and laser ablation time was 15min.

The SEM image of one sample of the gold nanoparticles in medical distillated water is illustrated in figure 4a. The laser fluence of the obtained gold nanoparticles was 3.24J/cm^2. An EDX mapping of sample synthesized from gold targets identified spherical particles observed in SEM image as containing gold.

Figure 4b represents an example of the EDX. Others species as Na, Ca, Si and Mg represent some impurities coming from the glass substrate.





(a) (b)

Figure 4. (a) Typical SEM image of gold nanoparticles obtained from gold target at a fluence of 3.24J/cm^2; (b) The EDX image of the sample presented in figure 4a.

Conclusions

Gold nanoparticles were obtained using the laser ablation at nanoseconds pulses with wavelength of 532nm. Different techniques (XRD, SEM coupled with EDX optical absorption spectroscopy) were applied for the characterization of synthesized gold nanoparticles. EDX and X-ray measurements confirmed the presence of gold in nanoparticles dried at room temperature on the glass sample. A faster growth in the gold nanoparticles concentration by increasing the laser ablation time than by raising the laser fluence was presented.

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