Laser ablation of gold and titanium targets in heavy water

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Abstract. The synthesis of gold and titanium (OT₄-0) nanoparticles by laser ablation in D₂O and H₂O using the radiation of an Nd: YAG laser with a wavelength λ = 1064 nm is considered. The influence of a liquid absorption capacity in which laser radiation interacts with a target on laser ablation products is studied. In the case of ablation in heavy water, the optical density of nanoparticles colloids was increased in comparison with the optical density of colloids obtained with the same parameters, but in the H₂O medium. Also, when D₂O was used, the absorption bands of the particles were shifted to the long-wavelength region of the spectrum by ~ 15 nm. SEM - analysis of synthesized nanoparticles by laser ablation in H₂O and D₂O media revealed the formation of dense aggregates. SEM - surface analysis of targets after treatment in both heavy and H₂O water showed the formation of structures with a transverse dimension of the order 2 μm. Also, according to the energy dispersive analysis, when irradiating in H₂O and D₂O, an oxide layer of the same thickness was formed on the targets surface. The same morphology of laser-modified surfaces also leads to the equality of their conductive properties. The measurements of the current-voltage characteristics recorded the S-shaped behavior of the curves, which can be explained by the manifestation of the memristor properties of the modified titanium target surface coated with an oxide layer.

1. Introduction

At present, with the development of technologies, the need for the synthesis of functional materials is growing. Functional materials are understood to mean materials with enhanced or, conversely, suppressed properties compared to the properties of natural materials [1]. Functional materials include metallic micro and nanoparticles, as well as surface structures having a dimension from tens of nanometers to several microns. For example, metallic nanoparticles are characterized by a pronounced absorption band, a lowered melting point and ferromagnets or ferrimagnets demonstrate significant changes in the magnetic properties [2].

Methods for creating nanoparticles and surface structures can be divided into 4 main groups: chemical, physical, mechanical and biological [3]. The method of laser treatment of metals by subnanosecond pulses in a liquid, studied in this paper, combines the signs of both physical and chemical effects and allows obtaining nanoparticles and surface structures that are different in morphology and composition. The distinctive features of the laser ablation method are relative simplicity and the possibility of combining an almost unlimited number of targets and liquids. In this case, the shape, structure and composition of the ablation products depend on the parameters of the radiation, the target material, and the medium in which the processing takes place. Another feature of the method of laser ablation in a liquid is the possibility of repeated entry of synthesized particles into a laser beam. This can lead to fragmentation of nanoparticles and a decrease in the energy of the laser
radiation coming to the target surface [4]. Reduction of energy losses is possible when using a liquid medium that does not absorb or weakly absorb laser radiation at a wavelength.

In the present work, a comparison between laser ablation products synthesized by subnanosecond laser pulses of the near infrared range in liquid H$_2$O and D$_2$O media, similar in construction and properties [4], but with a different absorption capacity at a laser radiation wavelength of 1064 nm will be made. As targets, materials such as gold and titanium will be used. Laser treatment of titanium in water is a promising direction, because by this technique can be synthesized as nanoparticles of titanium dioxide, and developed surfaces covered with a layer of TiO$_2$. Titanium dioxide differs photocatalytic activity, which finds application in the organic pollutants decomposition [5]. Nanolayers of titanium dioxide can exhibit a memory effect [6] or can be used as an active element in pressure sensors. In order to reveal regularities and compare results, laser ablation of gold will also be performed, since gold is one of the most studied metals in papers devoted to pulsed laser ablation [7].

Early, in the paper Nishi T. et.al. [4] laser ablation of a palladium disc target immersed in heavy water or light water using second harmonic Nd:YAG laser was carried out. The authors investigated and compared the properties of palladium nanoparticles obtained in heavy water or light water. It was shown that liquid with smaller optical absorption coefficient improve the yield of nanoparticles. Also, particles obtained in heavy water were smaller and the changes in magnetic properties were observed. However, degree of aggregation and surface properties were not observed.

2. Experimental technique

For the synthesis of nanoparticles, an optical scheme, which is traditional for laser ablation in a liquid was used [7]. The source of laser radiation was Nd: YAG laser with parameters: wavelength 1064 nm, pulse duration 250 ps, pulse repetition rate 20 Hz, pulse energy 0.3 mJ, fluence on the target surface 0.2-1 J / cm$^2$. The gold (99.99%) 0.5 mm thick plate and titanium plate OT4-0 0.86 mm thick in H$_2$O and D$_2$O media were irradiated. The volume of the liquid was 1 ml, the thickness of the layer above the surface of the sample was 4 mm. The samples were cleaned with acetone before being placed in a cuvette. Near the titanium sample, a copper substrate in the cuvette, on which nanoparticle precipitation occurred during the irradiation, was placed.

In order to average the fluence on the sample surface of the, the laser action was carried out in a dynamic mode: the cuvette with the sample was moved by motorized Standa tables with respect to the focusing spot. The displacement parameters: the speed of the movement along the coordinate X is 100 μm / s, the step of the displacement along the Y coordinate is 9 μm, the processing area was 4 mm$^2$.

Schematic diagram of the installation is shown in Figure 1.

The obtained colloids were analyzed by optical spectrophotometry method. The spectrophotometer LOMO Spectrum SF-56 (Spectral range of measurements 190-1100 nm, spectral resolution from 0.3 nm) was used to record the absorption spectra. To analyze the particles deposited on the substrates, the electron microscope Carl Zeiss EVO 50, equipped with the X-Max 80 (EDX) energy-dispersive energy-dispersive detector, was used.
3. Results and discussion
Figures 2a, 3a show the optical absorption spectra of gold and titanium (respectively) nanoparticles obtained by pulsed laser ablation in H$_2$O and D$_2$O media. For comparison, the optical absorption spectra of gold and titanium nanoparticles, 10 nm in diameter, obtained in a medium with a refractive index equal to the refractive index of water (Figures 2b, 3b), theoretically calculated in Ref. [8], are also presented. It is important to note that the refractive indices of H$_2$O and D$_2$O at 20 °C differ by 0.00456, so we will consider them equal. Comparison of the experimental and theoretical absorption spectra of nanoparticles shows that the experimental curves are characterized by broadened and shifted absorption bands. This fact can be explained both by the particle size distribution and dipole-dipole interaction between each other in the colloid obtained by laser ablation in a liquid, and by the formation of oxide shells around particles [7].

![Figure 2](image1.png)

Figure 2. Optical absorption spectra of Au nanoparticles, a) obtained in D$_2$O and H$_2$O; b) For nanoparticles with diameter 10 nm in liquid with n = 1.33 (the result of calculations) [8].

![Figure 3](image2.png)

Figure 3. Optical absorption spectra of Ti nanoparticles, a) obtained in D$_2$O and H$_2$O; b) For nanoparticles with diameter 10 nm in liquid with n = 1.33 (the result of calculations) [8].

Gold particles are characterized by a wide absorption band in the wavelength range from 210 to 800 nm with two local maxima occurring at 325 nm and 550 nm. Two absorption bands associated with plasmon resonance (local maximum at 550 nm) and interband transitions (local maximum at 325 nm) are clearly visible [7].

Titanium particles are characterized by an absorption band in the wavelength range from 210 to 330 nm, and this band has two features that are clearly expressed in particles synthesized in heavy water.

When comparing the absorption spectra of titanium and gold particles synthesized in D$_2$O with the spectra of particles obtained in H$_2$O, a number of general laws were observed. The absorption spectra of particles obtained in heavy water were characterized by a higher optical density, which indicated the registration of a larger number of nanoparticles than in H$_2$O. In addition, despite the similarity in the structure of the molecules of heavy water and H$_2$O, the absorption bands of particles synthesized in D$_2$O are shifted to the long-wavelength region of the spectrum in comparison with the absorption
bands of particles obtained in $\text{H}_2\text{O}$. This behavior of the absorption spectra can be explained on the basis of an analysis of the absorption spectra of heavy water and $\text{H}_2\text{O}$ (Fig. 4).

Figure 4 shows that the wavelength of laser radiation $\lambda = 1064$ nm falls into the region of the $\text{H}_2\text{O}$ absorption band (900-1080 nm), and $\text{D}_2\text{O}$ in the indicated range practically does not absorb. Therefore, in the first stage of laser action in the $\text{D}_2\text{O}$ medium, a larger amount of energy will come to the target surface in comparison with the irradiation in the $\text{H}_2\text{O}$ medium. This, in turn, will lead to an increase in the concentration of particles in the volume of the liquid along the path of propagation of the laser beam and its attenuation. However, this attenuation of radiation will contribute only in the first minutes of laser action, after which the concentration of particles obtained in the volume of $\text{D}_2\text{O}$ and in the volume of $\text{H}_2\text{O}$ are equalized [4].

Study by scanning electron microscopy of copper substrates in a cuvette during the laser ablation of a titanium target in $\text{D}_2\text{O}$ and $\text{H}_2\text{O}$ revealed the formation of dense aggregates of titanium nanoparticles (Fig. 5). In this case, the particles obtained in heavy water (a) are characterized by a lower degree of aggregation in comparison with the particles synthesized in $\text{H}_2\text{O}$ (b). This fact agrees with the fact that a large number of nanoparticles are recorded by optical spectrophotometry in heavy water. Even with the same yield of nanoparticles in $\text{D}_2\text{O}$ and $\text{H}_2\text{O}$, the particles synthesized in $\text{H}_2\text{O}$ form so dense aggregates that it is practically impossible to distinguish individual particles in them (Fig. 5b).

The SEM images of the surfaces of titanium targets after irradiation can be considered as a proof of the identical yield of particles synthesized by laser ablation in heavy and distilled water (Figure 6).

It can be seen from the SEM images that, with an fluence on the surface of the samples of 0.8 J / cm², the structures, regardless of the chosen medium, have a similar morphology, the characteristic transverse dimension of which is $\sim 2$-$3$ μm.

Also, as a result of the action of subnanosecond infrared laser radiation on the titanium surface in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ media, a change in the surface color was observed in a dynamic mode at various fluencies, as in [9]. Since the formation of nanostructures on the SEM images, which could change the color of the surface due to the plasmon resonance effect, is not fixed, the staining of the sample
The surface can be explained by the fact that during the laser ablation in the D$_2$O and H$_2$O media, oxidative reactions occur.

![Figure 6](image)

**Figure 6.** SEM images of laser-induced structures on the surface of a titanium target. a) in distilled water, b) in heavy water.

Using an energy dispersive attachment for the SEM microanalysis, the percentage by weight of the oxygen content on the surface of irradiated targets was estimated as a laser radiation fluence function (Table 1).

| Q$_S$, J/cm$^2$ | H$_2$O O, % | D$_2$O O, % |
|----------------|-------------|-------------|
| 0.8            | 24.91       | 26.59       |
| 0.4            | 25.48       | 25.67       |
| 0.3            | 33.00       | 31.92       |

Elemental analysis showed that the maximum oxygen content in both samples was ~ 32-33%, regardless of the liquid. An increase in the fluence incident on the surface of the target led to a smooth decrease in the percentage of oxygen on the surface as a result of ablation processes.

In addition besides the study of morphology and elemental analysis of the surface, the conductive properties of the target before (Fig. 7a) and after irradiation in H$_2$O and D$_2$O media were measured (Fig. 7b). To do this, a signal of ± 2.5 V was applied to the modified Ti / Ti$_x$O$_y$ surface generator and the surface of the unirradiated titanium using a highly stable sawtooth signal generator. The oscillograms shown in Fig. 7 were taken from a resistor of 1.8 kOhm nominal value, connected in series with the sample under study. Since the resistor does not change the signal, all changes are related to the sample under study. Therefore, the presented oscillograms are the current-voltage characteristics of the samples under study. As expected from the similarity of the type of structures formed at a single energy density of laser radiation and the equality of the percentage of oxygen on the surface of titanium targets, the current-voltage characteristics of surfaces obtained in H$_2$O and D$_2$O are identical.

![Figure 7](image)

**Figure 7.** CVC of target Ti surface a) initial surface, b) Ti surface after laser processing in D$_2$O medium. The value of the division along the abscissa axis is 250 μs, along the ordinate axis - 500 mV (explanations in the text).

The observed S-shaped behavior of the curve of the CVC extracted from the irradiated surface is similar to the behavior of the curves characteristic of an electronic element such as a memristor.
The memristor effect occurs in nanoscale metal-insulator-metal structures due to charge transfer in the dielectric layer when an electric field is applied, for example, when oxygen vacancies are moving in the case of titanium dioxide. For the first time, the properties of the memristor layers were demonstrated in 2008 [6].

4. Conclusion

1. Colloidal gold nanoparticles were obtained by laser ablation in liquid D_{2}O and H_{2}O media. The following differences are recorded in the absorption spectra of synthesized nanoparticles: a colloid synthesized in heavy water is characterized by greater optical density and broadening of the absorption band compared to the colloid obtained in H_{2}O.

2. Titanium nanoparticles colloids were obtained by laser ablation in liquid D_{2}O and H_{2}O media. The absorption spectrum of particles obtained in the D_{2}O medium is characterized by two more pronounced features with local maxima at 234 nm and 285 nm.

3. SEM-analysis of the surface irradiated in the D_{2}O and H_{2}O media of the titanium target showed the formation of microstructures with a transverse size of 2 μm.

4. An energy dispersive analysis of irradiated titanium surfaces in D_{2}O and H_{2}O media has shown the formation of an oxide layer. The maximum oxygen content by weight was 33%.

5. Measurements of the current-voltage characteristics of surfaces of laser-modified titanium in H_{2}O and D_{2}O media have been carried out. The S-shaped behavior of the curves of the CVC is fixed, which can be explained by the manifestation of memristor properties in the structured surface of the titanium target.

The results of this study can be applied to optimize the production of nanoparticles by laser ablation in liquid media. Nanoparticles and structured surfaces of titanium oxide can be used as active elements of photocatalytic filters, and the detected memristor properties can be used in microelectronics and pressure sensors.

5. References

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