Features of the synthesis of nanocolloid oxides by laser ablation of bulk metal targets in solutions

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ABSTRACT

Laser ablation of bulk targets in a fluid – a promising new method for the synthesis of "pure" nanocolloids. Nanocrystalline materials produced by laser ablation are widely used in biology, medicine, and catalysis. High local temperature during ablation and large surface area of the particles promote chemical reactions and the formation of a complex composition of nanoparticles.

In this paper the characteristics of the process of ablation and the obtaining of nanoparticles in a liquid by laser ablation of active materials (Zn, Ce, Ti, Si) were studied. Ways of increasing the productivity of laser ablation were discussed. Characterization of nanocolloids and nanocrystalline powders were performed.

Keywords: pulse laser ablation (PLA), «pure» nancolloids, oxides nanoparticles, optimization of the PLA process

1. INTRODUCTION

An interest to the development of methods for synthesis of ultra-dispersed colloids and nanocrystalline powders is connected with high potential capabilities of their application in medicine, optoelectronics, and other areas. Such materials are also a convenient object for fundamental study of size effects. Pulsed laser ablation of bulk targets in liquids is a unique technique that allows obtaining nanoparticles of different chemical composition using the same general-purpose equipment[1-3]. An absence of mechanical contact and additional chemical reagents allows preparing "pure" nanoparticles straight in the form of colloids. Despite the low productivity that depends on the physical mechanisms of ablation process, the method has large prospects. This is connected with the unique properties of the nanocolloids obtained. The main of them are the lack of impurities, high defectiveness and good charge stabilization of the solution. Such materials can be effectively used in areas that do not require high concentrations, for example in biology, electronics, catalysis, and scientific research[3-5].

The mechanism of the synthesis of nanoparticles by laser ablation is as follows. Under the influence of powerful laser pulse, a rapid local heating of the target to the temperatures greatly exceeding the melting point takes place. As a result, the explosive vaporization of the target material from its surface occurs. The substance is vaporized in the form of free molecules, atoms, ions and clusters. This means that in front of the irradiated surface in liquid the vapor-plasma cloud is formed, which upon cooling forms a colloidal solution[1-3].

In regard to the synthesis of nanoparticles, there are two types of ablation – reactional and non-reactional. The preparation of chemically inert nanoparticles, such as noble metals, can be attributed to the non-reactional type of ablation[6-9]. Reactional ablation occurs when the evaporated material reacts chemically with the medium, including on account of high chemical activity of nanoparticles due to their high specific surface area and high temperature of the process. One of the processes that occur under such conditions is an oxidation. Thus the ablation of target of reactive metal in oxygenated liquids results in formation of oxides nanoparticles, hydroxides, and more complex structures[10-12]. The study of the properties and application of such nanomaterials is of a great interest.

The present article presents the results of study of the processes of oxides nanocolloids synthesis at the ablation of reactive metals targets – Zn, Ti, Ce – and Si semiconductor in liquid, and study of their properties that are important for practical application.

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2. THE FEATURES OF THE SYNTHESIS OF NANOPARTICLES BY NANOSECOND PLA METHOD

The process of pulsed laser ablation is studied in several research works[13-15]. Depending on the duration of the pulse different mechanisms of interaction of high-power pulsed radiation with matter are considered[13,15]. Nanosecond laser ablation is well described in the framework of one-temperature thermal model, while for femtosecond pulses more complex models have to be used. From the practical point of view it is important to know that ablation is a threshold process. In the curve of the dependence between the thickness of the evaporated layer of the material at the ablation and the intensity of the laser radiation three sections can be seen. In the subthreshold region the removal of the material is slight. Then, after the threshold, there is a linear section of the plot. For large excitation above the threshold the saturation occurs. The efficiency of the ablation process, the rate of particles accumulation, and their size characteristics for a fixed pulse width and a wavelength are substantially determined by the intensity of the radiation on the target surface.

The main parameters determining the effectiveness of the ablation are thermal characteristics of the target material – melting point, the temperature of evaporation, heat capacity and heat of fusion. The dependence of the threshold of ablation and the thickness of the surficial evaporating layer from the thermal characteristics of the target is well enough traced for chemically inert materials, such as noble metals. For targets made from reactive metals this dependence is more complicated. This is connected with the formation of surface oxides and other compounds. An additional factor, especially for refractory metals, is the solvent decomposition and the formation of surface carbides, nitrides and other compounds. The Table 1 shows the thermal characteristics of the materials that we used as targets in the nanosecond PLA, the ablation process conditions, and characteristics of the nanoparticles obtained. From the Table 1 the dependence of the rate of the particles accumulation from the complex of the above mentioned thermal parameters is clearly observed.

Table 1. Thermal characteristics of targets, parameters of the ablation and characteristics of the nanoparticles obtained by PLA (Nd:YAG laser, $\lambda = 1064$ nm, $t_{puls} = 7$ ns, $E_{puls} = 120$ mJ, $f = 20$ Hz)

Target	Ce	Zn	Ti	Si
$T_{melting}$, °C	797	419	1668	1423
Specific heat capacity, J(g·K)	0,205	0,388	0,52	0,705
Heat of fusion J/g	36,96	107,5	323,59	1655,63
Pulsed power density on the target, MW/cm^2	200	300	800	1000
Nanoparticle/structure	CeO_2 cubic	ZnO wurtzite	TiO_2 anatase+brookite	SiO_2 amorphous
The rate of the nanoparticles accumulation (target weight loss), mg/h	50	20	10	5
Average size, nm	19	15	10	7
S_{BET}, m^2/g	53	25	124	429

An important parameter of PLA is also a wavelength of the laser radiation. It is known that most materials absorb more in the UV range. Additionally, is it is well known that there is the large reflection coefficient of metal surfaces in a wide spectral range from visible to infrared. At the same time it is experimentally established that prolonged exposure to the target can considerably reduce its reflection coefficient on account of heating, changing the chemical composition and the roughness of the surface. The wavelength of the laser radiation apart from the influence on the efficiency of interaction with the target, greatly affects the process of secondary interaction with the nanoparticles formed. The layer of colloidal solution in front of the target absorbs and scatters laser radiation blocking its access to the target. The degree of attenuation of the radiation depends on the linear and nonlinear optical properties of nanoparticles, their concentration and the thickness of the layer[16]. Due to the fact that the absorption and scattering of the particles are typically greater in the short wave region, it is preferable to use the long-wavelength lasers, e.g. the fundamental harmonic Nd: YAG laser.

Even though initially the PLA efficiency at short wavelength is higher, with the increasing of the concentration of nanoparticles in solution this advantage disappears.

Fig. 1 schematically shows the process of synthesis of nanoparticles by laser ablation in liquid. There are two basic optical circuit for input radiation at the PLA in liquid. In one case, the radiation is introduced from the top through the liquid/air boarder, in the other case – through the transparent wall of the vessel in which ablation occurs (Fig. 1). The second scheme has the advantage for manufacturability, productivity and focusing control. Its main drawback is the pollution and destruction of the windows of the reactor that is why the selection of the optimal conditions for the radiation power on the target surface is required[16]. This selection is individual for each target material and solvent. To prevent the destruction of the windows the rotation of the reactor and liquid circulation are also help.

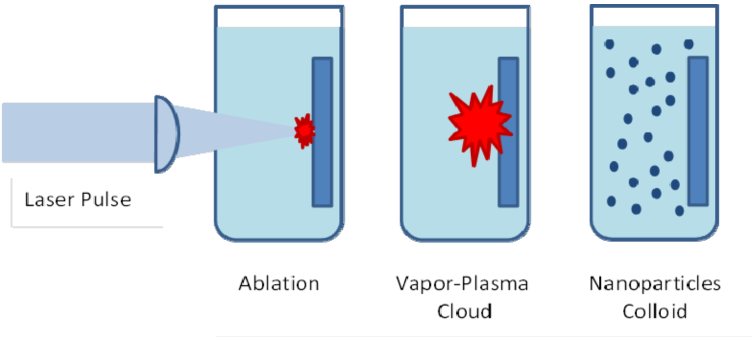


Figure 1. Scheme of the process of PLA.

3. INCREASE OF THE PRODUCTIVITY OF NANOPARTICLES SYNTHESIS BY NANOSECOND PLA

Low productivity of the synthesis of nanoparticles by PLA stimulates the search for ways to improve it. In the literature, there is only one work where the authors declare the possibility to obtain gram quantities of nanoparticles by the PLA in liquid[17]. There are two main directions to increase the productivity: optimization of the PLA process and scaling.

Optimization of the process firstly involves the selection of the optical circuit and the excitation parameters, depending on the properties of the target, the solvent and the particles obtained. This issue was discussed in the previous section. There are also additional optimization procedures for the efficient use of the target, changing the solution, etc. For the synthesis of nanoparticles in small concentrations we proposed a flow setting for PLA with automatically controlled concentration of nanoparticles in solution (Fig. 2, 3)

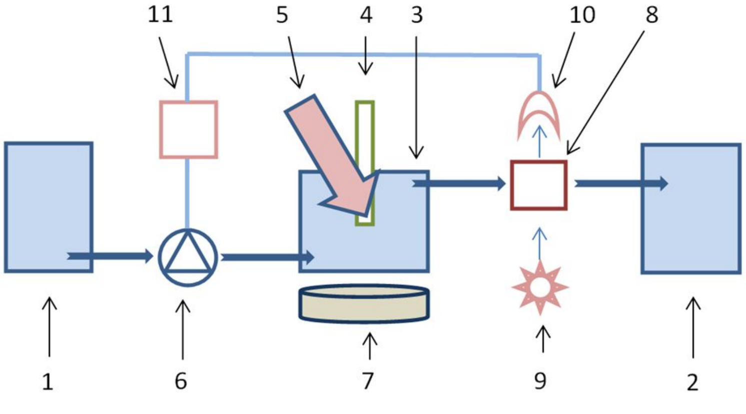


Figure 2. Scheme of flow setting for PLA with automatically controlled concentration of nanoparticles in solution: 1 – capacity for the initial solution, 2 – capacity for the final colloidal solution, 3 – ablation reactor, 4 – target, 5 – laser radiation, 6 – pump, 7 – magnetic mixer, 8 – flow cell, 9 – light-emitting diode, 10 – photodiode, 11 – pump control unit.

Fig. 2 presents a diagram illustrating the principle of the setting functioning. Its originality lies in the feedback control of the optical concentration of nanoparticles during the PLA. The concentration is controlled by measuring the change of transmittance of the solution due to absorption or scattering. The unit provides a constant productivity and repeatability of characteristics of the colloidal solution of nanoparticles. Setting capacity is 2-3 times higher in comparison with PLA without pumping and concentrations control.

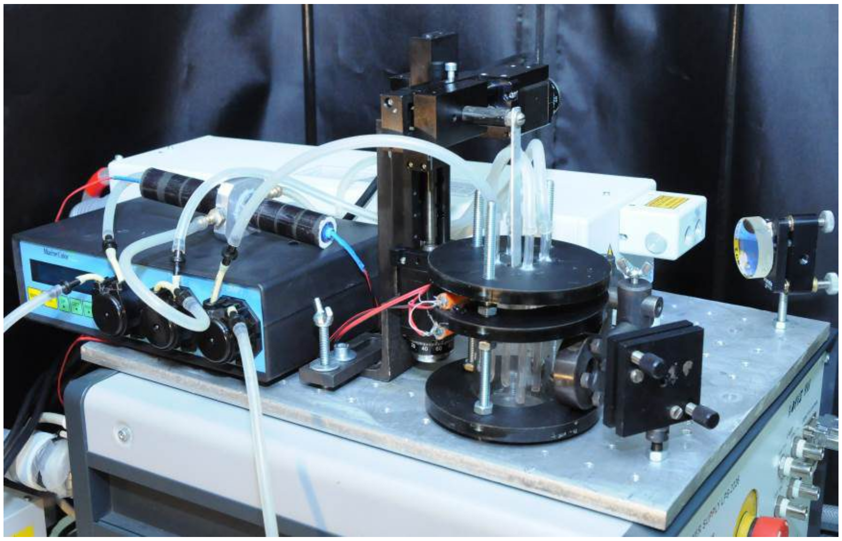
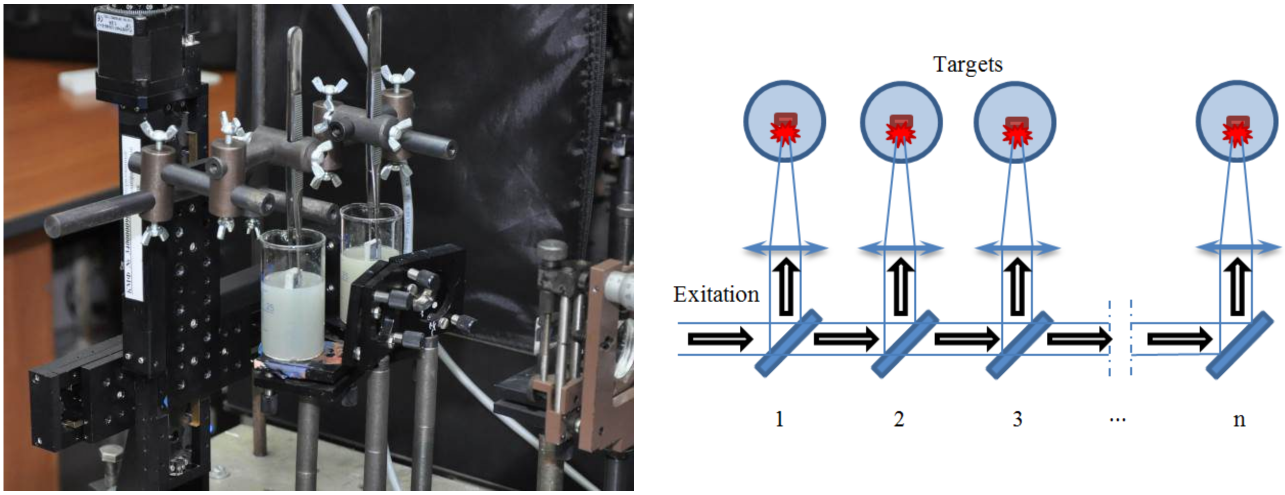


Figure 3. Photograph of the laboratory model of flow setting for PLA with automatically controlled concentration of nanoparticles in solution.

Additionally it is possible to increase the productivity of PLA by scaling. High-power lasers with pulse energy Joule and more can be used when the laser light is divided into multiple channels. In a single-channel system, the introduction of such energy in the reactor leads to overheating of the solution, and the destruction of the optical elements. On Fig. 4a there is a photograph of a two-channel system created in our laboratory in the process of PLA of cerium target by radiation of fundamental harmonic Nd: YAG laser with a pulse energy of up to 300 mJ. Laser beam is divided into two channels by means of a prism. Further, in each channel PLA of targets occurs independently. This setting allows 1.5 times increasing of productivity of PLA compared to a single channel.



a

b

Figure 4. Photograph of two-channel (a) and an optical circuit of multi-channel (b) settings for PLA in liquids.

For systems with a large number of channels, a system with a semi-transparent mirror is suggested (Fig. 4b). Apart from increased productivity, multi-channel setting for PLA at the same time allows obtaining nanoparticles of various compositions in various solvents independently.

4. THE FEATURES OF OXIDES SYNTHESIS

At ablation of chemically active materials, due to the high temperature and high surface area of nanoparticles, various chemical reactions occur effectively between the particles, liquid, gases dissolved therein and impurities. One of the most common reactions is oxidation. Metals under investigation – Ce, Ti, and Zn – have an electrochemical potential φ^0 from –2.363 to –0.763 V and effectively interact with water molecules. Si particles are easily oxidized in water as well. In addition to the particles under the ablation the target surface starts reacting.

As a result of oxidation nanoparticles with other optical properties are formed from the initial particles of metal. Thus plasmon absorption peaks of Ce, Ti, and Zn are in the range of shorter than 230 nm, whereas the oxides formed absorb in the range of 300-400 nm. The change of absorption and scattering of solutions in time should be also considered when selecting modes of PLA. Fig. 5a shows the spectra of the colloidal solution obtained by ablation of zinc for 5 minutes. Initially colloid shows a peak of the plasmon absorption of metal zinc at 230 nm. Over time, this peak disappears and only the edge of the exciton absorption band of zinc oxide can be seen at ~ 370 nm. Visually it is accompanied by a significant enlightenment of the solution (Fig. 5b). Additional purging the solution with oxygen or air accelerates the oxidation and prevents the formation of zinc hydroxide, especially at small concentrations of nanoparticles. Similar results were obtained with the ablation of Ce, Ti, and Si targets.

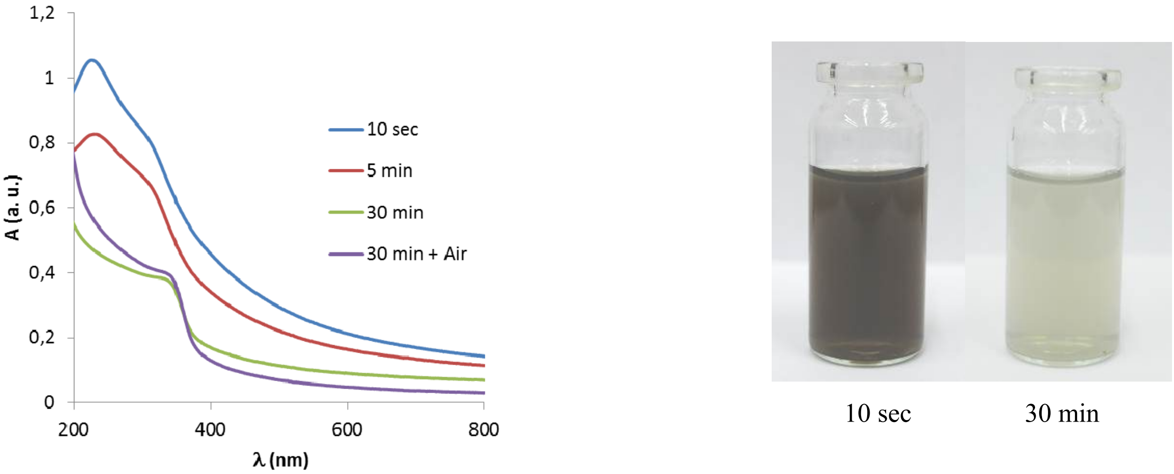


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Fig. 5. Absorbance spectra and a photograph of the colloids obtained by PLA of metal targets of Zn.

Figure 6. (a) the spectra of the nanoparticles of zinc, cerium and titanium oxides obtained at the ablation of metal the respective targets; (b) a photograph of the appearance of these colloids.

For the efficient production of colloidal solutions of oxide nanoparticles with controlled concentrations we have developed a flow unit with additional oxidation. The system is an upgrade of the setting shown in fig. 2. Setting diagram illustrating the principle of its operation is shown in fig. 7. A system for saturation of the solution with gas and the second stage controls of the optical properties of the solution, controlling the degree of oxidation of initial metal nanoparticles, are added. On the basis of this unit obtaining of other types of nanoparticles, e.g., sulfide, is possible[18].

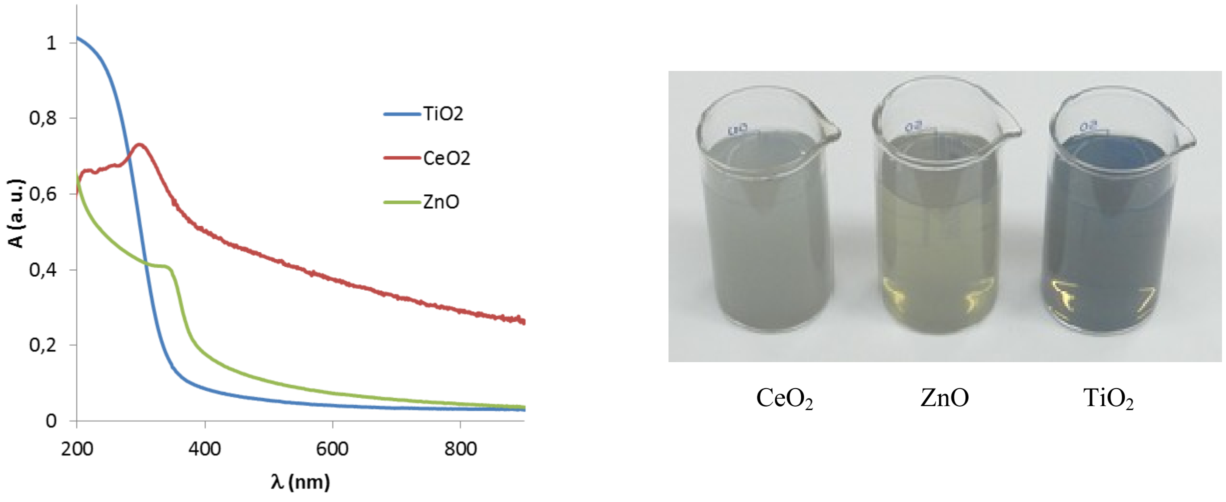

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Figure 6. (a) Absorbance spectra and (b) a photograph of the colloids obtained by PLA of metal targets of Ti, Ce, and Zn.

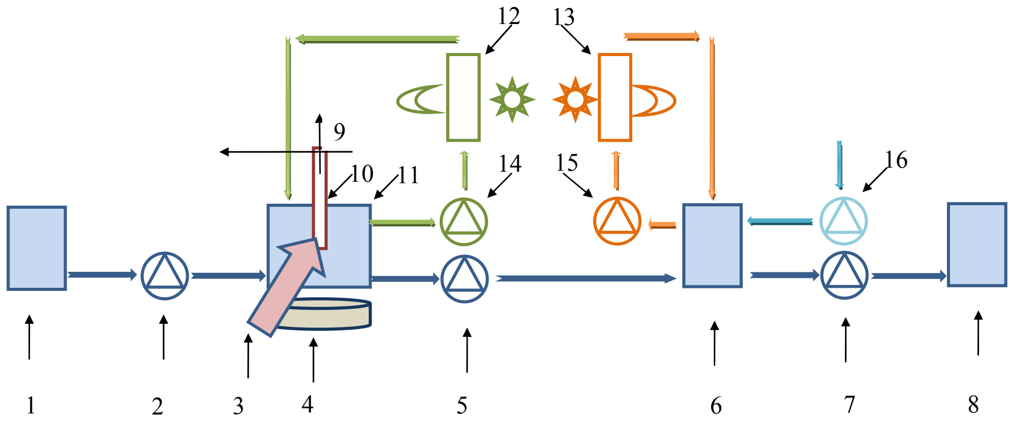

Figure 7. Scheme of flow setting for PLA with automatically controlled concentration of nanoparticles in solution and the system of additional oxidation: 1 – capacity for the initial solution, 2, 5, 7, 14, 15 – pump, 3 – laser radiation, 4 – magnetic mixer, 6 – intermediate capacity, 8 – capacity for the final colloidal solution, 9 – scanning of target, 10 – target, 11 - ablation reactor, 12 – optical system for concentration control, 13 – optical system for oxidation control, 16 – air compressor

5. CONCLUSION

The results of the work indicate that the pulsed laser ablation in a liquid is an effective and versatile method for the synthesis of «pure» nanocolloids of oxides nanoparticles. Depending on the thermal parameters of the target the productivity of the method varies under identical conditions of the process on used in laboratory PLA unit from 5 mg/h for Si and 50 mg/h for Ce. The use of multi-channel circuits and more powerful laser sources potentially enhances the productivity on the order, and more. The resulting nanomaterials are of a great interest in conducting research in the field of biomedicine and catalysis.

6. ACKNOWLEDGMENTS

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