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Chapter 11

Metal Oxide Nanoparticle Preparation by Pulsed Laser Ablation of Metallic Targets in Liquid

Valery A. Svetlichnyi, Anastasiia V. Shabalina,
Ivan N. Lapin and Daria A. Goncharova

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Abstract

The basic mechanisms of pulsed laser ablation in liquids (PLAL) as a method for the synthesis of nanoparticles (NPs) were considered. Physical and chemical processes occurring during the PLAL that determine the formation, composition and structure of the nanoparticles obtained are described. The influence of the composition and properties of the target material, the solvent and the characteristics of the laser irradiation on the efficiency of the synthesis of nanoparticles is discussed. Separately, an influence of the absorption and scattering (including nonlinear) of laser radiation in the dispersion of nanoparticles on the primary synthetic processes and secondary transformations inside the colloidal solution is examined. The specificity of the characterization of the colloidal solutions of oxide particles produced by PLAL is highlighted. The most promising practical applications of nanomaterials obtained are identified and the examples of their successful use in catalytic research and biomedicine are provided.

Keywords: pulsed laser ablation, nanocolloids, chemical reactions, composition and structure of nanoparticles, metal oxide nanoparticles

1. Introduction

Interest in the study of fundamental processes of interaction of powerful optical radiation with matter and their practical applications arose simultaneously with the invention of lasers. Depending on the characteristics of the laser radiation (intensity, wavelength, pulse duration, polarization and coherence), the processes of interaction and the results of interaction may be

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different. At low intensities and high duration of the interaction of the radiation with the solid absorbing target, only heating of the target occurs. Increasing the intensity of the radiation can lead to the reaching of the melting temperature and to the further evaporation of the substance of the target. Under powerful pulse laser radiation, the evaporation of the substance occurs with the formation of plasma cloud that contains ions, clusters and small particles. For such an "explosive" evaporation, the term "laser ablation" (from Lat. "ablatio"—taking, removal) is used. Sometimes in the literature, the term "ablation" is interpreted more widely, covering the removal of substances from the surface as a result of any physical and chemical processes that occur under high-energy impact on the object. In the present chapter, the term "ablation" will be used only for the threshold process of explosive vaporization of material from a surface of solid targets with the formation of gas (vapor) plasma cloud via the rapid absorption of energy of high-power laser pulses in a limited volume.

First of all, the process of pulsed laser ablation (PLA), when micro-, nano- and later femtosecond pulses are exposed to the target, had found a successful application in laser materials processing for punching, marking and precise removal of layers of material in electronics [1]. Next, the PLA in gas phase and vacuum became successfully used for atomization of targets in mass spectrometry, obtaining thin films and ultrafine powders [2–4].

Using PLA of bulk targets in liquids to obtain nanoparticles (NPs) was initiated by the rapid development of nanotechnology in the 1990s of the twentieth century. The first deliberate use of this technique for the synthesis of nanocolloids took place in 1993 when the dispersions of Ag, Au, Pt, Pd and Cu nanoparticles in water and organic solvents for the surface-enhanced Raman scattering (SERS) spectroscopy were obtained [5].

Over the past two decades, pulsed laser ablation in liquids (PLAL) has become an effective and popular tool for obtaining nanosized materials. The absence of a mechanical interaction in the synthesis process and the ability to prepare "pure" nanoparticles without additional chemicals in the pure solvents straightaway in the form of stable colloids make this method very attractive for biological and medical applications. Catalysis, electronics and nonlinear optics are also the areas where the nanocolloids synthesized by the PLAL method and nanocrystalline powder obtained via further drying of the dispersions are used. The relatively simple experimental technique and the possibility of obtaining different types of nanoparticles (from metals to ceramics and polymers) on the same installation make this method a suitable tool for obtaining nanomaterials for the study of fundamental properties of substances in the nanostate. An opportunity to change the parameters of laser pulses and use various solvents with additives of precursors provides additional options to vary the composition, structure and dimensional characteristics of the nanoparticles obtained.

As of now, thousands of original research works, reviews and monographs on various aspects of the PLAL for the synthesis of nanostructures have been published [6–8]. They consider common mechanisms of PLAL and obtaining and characterization of specific nanomaterials as well. However, the interest in such research work continues unabated. On the one hand, this is due to the demand for nanomaterials with specific functional properties for various applications. On the other hand, there are three main aims that have not been achieved yet: effective control of structure and dimensional characteristics of nanoparticles obtained;

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obtaining of multicomponent particles and particles with complex structure, such as core shell; and initiation of the required chemical reactions in the synthesis process.

Another important point for PLAL as a synthesis method of nanoparticles is its low productivity caused by the physical mechanisms of the ablation process itself. It hinders the broad practical use of this technology. That is why the optimization of the experimental conditions to achieve maximum yield of nanoparticles in liquid is important. Individual factors that influence the productivity of particle synthesis via PLAL are, for example, the thermophysical characteristics of the target and its optical properties and secondary interaction of radiation with a plasma torch and with particles in a colloid. Developed theoretical models of the ablation process, to some extent, take into account the parameters of the medium and the characteristics of the laser irradiation. So far, however, focused systematic experimental investigation of the influence of the factors on the productivity of synthesis has not been carried out. In addition to solving a practical task of increasing the productivity of the method, these studies are important for obtaining new fundamental knowledge about the processes taking place in a reactor under the repetitively pulsed irradiation of the target in the presence of the concentrated colloids of particles with high chemical activity stimulated by laser radiation. Moreover, in addition to the changing of the effectiveness of the PLAL process, finite properties of nanomaterials may vary significantly.

In this section, the basic experimental aspects influencing the process of oxide nanoparticles obtaining under nanosecond-pulsed laser ablation of some reactive metals in liquids are discussed and the characteristics and some applications of such prepared nanoparticles are considered.

2. Preparation

2.1. Basics of laser ablation in liquids

In this section, the general processes occurring during PLAL of solid bulk targets are briefly described. A more detailed description can be found, for example, in Ref. [6].

Initially, laser ablation models that describe the process of absorption of the radiation by the target, its explosive vaporization with the formation and diffusion dynamics of plasma and the radiation interaction with plasma have been developed for the case of ablation in the gas phase. Our primary interest is in the description of the ablation process under the action of nanosecond laser pulses. In contrast to the very short (fs) pulses where the processes of excitation (isochoric heating) and further thermodynamic behavior of the system can be divided, more long (ns) pulses lead to the simultaneous course of these processes, making it difficult to describe them. In this case, the ablation is described well enough by the modern thermal model [9], which takes into account the absorption of radiation by plasma and uses a movable boundary of evaporation and evaporation obeying the Hertz-Knudsen law. This model works well not only near the ablation threshold but also when there is a large pumping over the threshold where a dense plasma plume appears.

The main differences between ablation in liquids and ablation in gas phase/vacuum are as follows. Firstly, ablation occurs at the boundary between the solid and liquid phase. Secondly, the formation and distribution of the plasma plume occurs in the liquid environment. Because the liquid has a much higher density and thermal conductivity than gas, this environment significantly affects the thermodynamic characteristics of the process. Thirdly, a large number of chemical transformations are possible in liquid. In characterization of the ablation in liquids, an approach described in Ref. [10] seems to be effective. It describes the process mechanisms, aggregate states and phase transitions depending on the pulse duration in temperature-density coordinates.

From the practical point of view, ablation in liquids leads to the following consequences. First of all, the threshold for ablation in liquids is higher than in gas and the material of the target removal rate, i.e., the productivity of obtaining nanoparticles, is much lower. Secondly, a vapor plasma plume that is much denser (up to 1023 cm^{-3}) is formed. At flame temperatures of 4000–5000 K, its pressure reaches 10 GPa and higher. This leads to efficient chemical transformations, as well as to the possible formation of metastable phases. Moreover, because the plasma is limited and is held by the dense liquid, its expansion occurs adiabatically at supersonic speed with the formation of a powerful shock wave.

In terms of practical use of PLAL in NPs synthesis, the use of ns excitation sources is the most promising. The greatest efficiency in the synthesis of large quantities of nanoparticles is observed exactly when nanosecond laser pulses are used. When short (femto- and picosecond) pulses are used, the productivity at the beginning of the process can be higher than for nanosecond pulses, but with the increasing of the particles' concentration in the solution, the efficiency of the process decreases sharply. This happens, for example, due to the secondary interaction of laser radiation with particles in solution that leads to its strong attenuation and scattering. In addition, the cost of a sufficiently powerful picosecond laser suitable for PLAL is several times higher and femtosecond (oscillator-amplifier) more than 10 times exceeds the cost of the usual nanosecond Q-switch Nd:YAG laser. In conjunction with the complexity of the operation and relatively low resources of such short-pulse lasers, the cost of synthesis of meaningful quantities of nanoparticles (except for scientific research and a number of high-tech biomedical applications) will not be justified.

The use of longer μs pulses significantly reduces the efficiency of the ablation process. This is connected with the higher threshold for ablation in liquids compared to gas/vacuum systems, as well as with the strong screening effect of the plasma for microsecond pulses. Besides, a large energy contribution to the media leads to the heating of the liquid that limits the power of lasers used. In addition, when long pulses (from several tens of ns to hundreds of μs) are used, other ablation mechanisms take place [11], which will not be covered in this chapter.

The scheme of the ablation process is presented in **Figure 1**. **Figure 1a** shows the formation of a plasma cloud, **Figure 1b** shows interaction of plasma with radiation, **Figure 1c** shows chemical processes in plasma and **Figure 1d** shows the result: nanoparticles in liquid and surface erosion.

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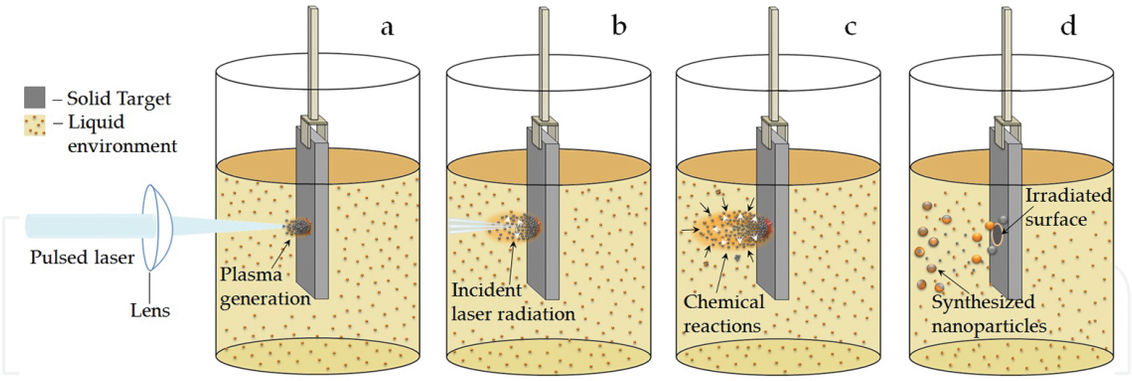


Figure 1. Nanosecond-pulsed laser ablation in liquids: (a) the formation of a plasma plume resulting from the absorption of laser pulse, (b) the evolution of the laser plasma in liquid during the nanosecond pulse and its interaction with radiation, (c) the further evolution of the plasma after the pulse and the chemical reactions inside the plume and at the border and (d) clusters (nanoparticles) in liquid and a crater on the surface of the target after the process.

There are three significant moments that should be noted:

— Interaction of a plasma cloud with the liquid that limits it and with laser radiation leads to the formation of powerful shock waves in the environment.

— Heated dense plasma cloud stimulates several types of chemical reactions inside the plasma and on the interface between three components: the target material, clusters (particles) that are formed and the solvent molecules.

— Generated particles remain in the liquid in the path of laser radiation and participate in a secondary interaction with the laser beam at long pulse-periodic irradiation of the target influencing the processes of plasma formation, diffusion dynamics and chemical reactions.

2.2. General experimental technique of PLAL

Experimental technique for nanosecond PLAL is simple; that makes this method attractive for laboratory applications. To start the process of ablation, it is enough to focus the radiation of a nanosecond laser source on the target surface submerged in the liquid. At the same time, to obtain high-quality nanocolloids with reproducible properties, a variety of experimental procedures are required.

There are two variants of introducing radiation into the reactor: from above, across the air/liquid border and sideways through the transparent window/side wall reactor. From the point of reproducibility of the experiment and control of the focus conditions, the second option is preferred. When the radiation is introduced to the reactor from above, there are difficulties related to the control of the liquid layer over the target and the formation of bubbles during ablation that leads to scattering and bad focusing. In addition, when the thickness of the layer of liquid above the target is small, the spraying of the liquid takes place and contamination of focusing elements and protective windows may occur. When the radiation is introduced through the side wall of the reactor, these obstacles do not appear. But in this case, the main

point is the radiation resistance of a window or transparent reactor wall that is affected by the laser beam. To minimize the power density of radiation in the window or wall of the reactor, one has to use short-focus lenses. In practice, the focal length of the lenses in such experiments is F = 25–50 mm.

As a result of the PLAL process, a thin layer of the material is removed from the surface of the target. After repeated multiple irradiation of the same place on the surface of the target, a crater appears and then a through-hole is formed. For uniform irradiation and to prevent crater formation, scanning of a laser beam on the surface of the target is used. To do this, one can either redirect the laser beam or move the target itself. There are two common methods for moving the target. For cylindrical targets, the rotation around their axis with a slow linear displacement is preferable. Most often, however, the target is a parallelepiped and in this case, scanning in the XY plane orthogonal laser beam is used.

The removal of the nanoparticles obtained by PLAL from the optical path of the radiation occurs either naturally through the convection or by the agitation of the liquid in a reactor, for example, using a magnetic stirrer. To produce large amounts of colloidal solutions with a concentration of nanoparticles of 10–50 mg/l, it is advisable to use flow reactors with the control of concentration in the synthesis process. Possible ways of technical implementation of such methods are considered, for example, in our work [12].

To obtain concentrated dispersions for further use and preparation of the nanocrystalline powders, it is better to carry out the optimization of synthesis conditions (considered below) instead of using flow reactors.

2.3. Effect of thermophysical parameters of the target on the PLAL process targets

One of the fundamental factors that determine the efficiency of ablation is a combination of thermophysical characteristics of the target material: melting point and evaporation temperature, heat capacity, heat of fusion and boiling and thermal conductivity. The dependence of ablation threshold and the thickness of the removed layer from the thermal characteristics of the target can be easily seen on the example of chemically inert materials, such as noble metals. For targets made of chemically active metals, this dependence may be more complicated. This is connected with the formation of oxides and other compounds on the surface of the target and these compounds' thermophysical characteristics differ from those of the target material. On the other hand, during the frequency pulse-periodic irradiation, the thickness of the modified layer on the surface is very thin and the thermodynamic characteristics of the PLAL are mainly determined by the properties of the target material. An additional factor, particularly for relatively refractory metals (Ti, Fe, etc.), is the decomposition of organic solvents on the surface of the target and formation of carbides, nitrides and other compounds.

Table 1 presents the basic thermophysical characteristics of the materials that were used as targets for nanosecond PLAL: T_{melt}, melting point; T_b, boiling point; H_{fus}, heat of fusion; H_{vap}, heat of vaporization; k, thermal conductivity; $E°$, standard electrode potential; W, pulsed power density of radiation on the surface of target; and v – rate of the target weight loss. Analyzing the table, one can establish the relationship between the thermophysical characteristics of the

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target, the power density that is used in the PLAL and the rate of nanoparticle production, which is estimated from the target weight loss per unit of time.

For example, the maximum productivity is observed for PLAL of cerium targets, which has a relatively low melting point and heat of fusion, as well as low thermal conductivity. This allows reaching high local temperatures easily and overcoming a high boiling point. It is interesting to note relatively low productivity for aluminum nanoparticles by PLAL. This is connected not only with the low weight of this metal but also with its high thermal conductivity that is ~15 times greater than for cerium. Low ablation productivity was found for magnetic 3d metals Fe, Ni and Co, as well as for Cu that has a very high thermal conductivity at a much lower boiling point. Despite the relatively low thermal conductivity, the rate for Ti nanoparticle production is not high; that is associated with large energy consumption due to high melting point and heat of fusion.

Target/ solution		T_{melt}, K	H_{fus}, kJ/mol	T_b, K	H_{vap}, kJ/mol	k, W/(m·K)	$E°$, V	W, MW/cm²	v, mg/h	Consist
Mg	DW	923	9.2	1363	131.8	171	−2.372	150	40	$Mg(OH)_2$
	Alc									$MgO@Mg(OH)_2$
Al	DW	933.5	10.75	2792	284.1	238	−1.700	200	25	$Al(OH)_3$
	Alc									Not determined
Ce	DW	1072	5.2	3699	398	10.9	−2.336	200	50	CeO_2
	Alc									CeO_2
Ti	DW	1935	18.8	3560	422.6	15.5	−1.63	800	10	TiO_2
	Alc						−1.19			$Ti@TiO_2$
Zn	DW	693	7.28	1179	114.8	113	−0.763	300	20	$ZnO/Zn(OH)_2$
	Alc									ZnO
Fe	DW	1812	13.8	3134	340	72.4	−0.441	600	12	Fe_3O_4
	Alc									$Fe@Fe_3O_4$
Co	DW	1768	15.48	3143	389.1	69	−0.28	600	12	$Co(OH)_2$
	Alc									Co_2O_3/Co_3O_4
Ni	DW	1726	17.61	3005	378.6	60.5	−0.234	600	12	Ni@NiO
	Alc									Ni
Sn	DW	505	7.07	3146	296	63	−0.14	300	30	Sn@SnO
	Alc									Sn
Bi	DW	545	11.3	1837	172	53.3	+0.317	250	40	Bi_2O
	Alc									$Bi@Bi_2O$
Cu	DW	1356	13.01	2840	304.6	398	+0.33	600	10	Cu_2O
	Alc						+0.522			$Cu@Cu_2O$

Q-switch Nd:YAG laser, λ = 1064 nm, t_{puls} = 7 ns, E_{puls} = 120 mJ, f = 20 Hz.

Table 1. Thermophysical and electrochemical characteristics of the targets, characteristics of the synthesis and composition of NPs obtained by PLAL.

2.4. Chemical transformations during PLAL

High temperature and pressure in plasma plume in PLAL stimulate various chemical reactions. Commonly, there are four types of chemical reactions [13] that are shown in **Figure 2**. The first two types of reactions occur within the plasma cloud. The first type is the interaction of ionized clusters of the target material with each other inside the plume. As a result of these interactions, metastable phases are often formed. The second type of chemical reactions occurs between the ionized molecules of the liquid and the target material. This is possible when the liquid is heated on the plasma/liquid boundary to the temperature of the plasma. Then so-called liquid plasma is formed and mixed with the main plasma cloud consisting of the target material. The third type of chemical reaction takes place on the plasma/liquid boundary at high pressure and temperature between the particles of the target material and molecules of the liquid, including the processes under the additional stimulation by the laser radiation. The fourth type of chemical reaction occurs after the collapse of the plasma plume directly in the liquid when the particles formed continue interacting with the molecules of the liquid environment.

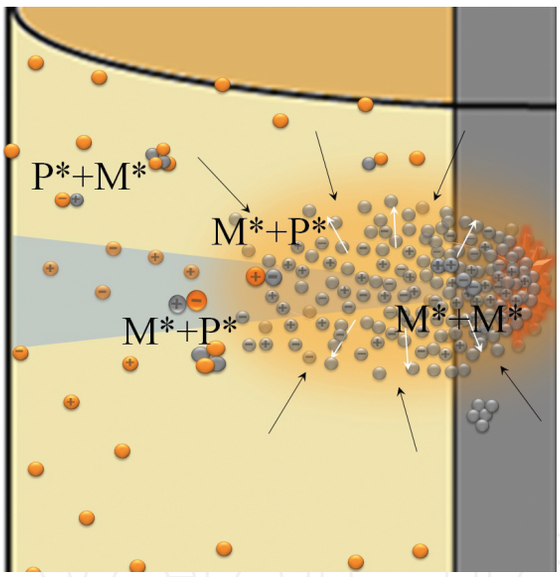


Figure 2. Types of chemical reactions that occur within PLAL.

Because the particles remain in solution, they can interact with the radiation when they appear on its path. This can lead to a significant change of particles' size distribution as a result of their melting and defragmenting under the influence of the laser beam. This also can effectively stimulate further chemical transformations of particles with different compositions and structures and molecules of the solvent. Secondary interaction is particularly strong when the high-energy photons of the visible and ultraviolet (UV) range of the spectrum are used. Moreover, these photons are better absorbed by the particles thanks to plasmon or exciton absorption in this wavelength range. Thus, the PLAL can be used to synthesize a large variety of compounds.

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In addition to the parameters of the plasma plume, the chemical interactions, obviously, depend on the chemical properties of the target material and the solvent. The most common chemical reactions are associated with the interaction with oxygen both in a free form and as part of the solvent molecules. **Table 1** shows the data on the chemical composition of the NPs obtained via ablation of different metals in distilled water and ethanol. Depending on the reactivity of the metal target that is characterized by a parameter $E°$ (standard electrode potential) and the type of the solvent, one can control the composition of the particles in the dispersion. The majority of metals react chemically during the PLAL in the water with the formation of oxides or hydroxides. Chemically active metals such as magnesium and aluminum hydrolyze during ablation in water (**Table 1**), while, for example, the PLAL of more inert Ni and Sn produces core-shell-type particles with the metal core and the oxide layer on the surface.

The use of different precursors provides additional opportunities to control the structure of the product particles. For example, adding different sulfur-containing precursors—thioacetamide (TAM) and hydrogen sulfide (H_2S)—to water during the ablation of metallic cadmium, CdS nanoparticles can be obtained [14].

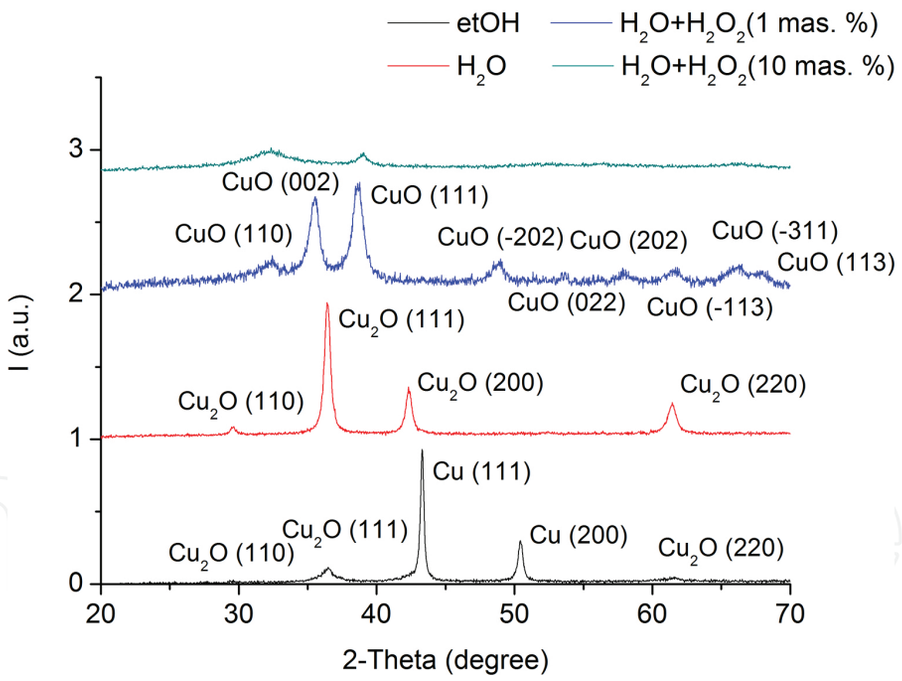


Figure 3. X-ray diffraction patterns of powders of NPs obtained via PLAL of metallic copper target in various solvents.

Figure 3 shows the X-ray diffraction (XRD) data for powders obtained by ablation of the copper metallic target. Using alcohol, water and additional oxidizer—hydrogen peroxide of various concentrations—as solvents, crystalline NPs of mostly metallic copper (I) oxide (Cu_2O), copper (II) oxide (CuO), as well as X-ray amorphous copper (I) hydroxide (CuOH) were obtained, respectively.

2.5. Influence of the secondary interaction of radiation with the NPs in solution on the productivity of the synthesis of nanoparticles and their composition

Because the ablated particles remain in the liquid after PLAL, secondary interaction of laser radiation with the synthesized particles has a significant impact, especially during the long process of synthesis of highly concentrated colloidal solution. Interaction of laser radiation with colloid NPs occurs in the liquid in front of the target. As a result of the absorption and scattering of the radiation, its intensity on the surface of the target can significantly decrease. To minimize these energy losses, the optimal layer thickness and focus radiation conditions have to be found.

Normally, the linear absorption and scattering of the dispersions can be measured and considered easily while selecting the conditions of PLAL. In our experiments, IR radiation of the fundamental harmonic of Nd:YAG laser with a wavelength of 1064 nm was used. It is known that metal targets have a large reflection in this range of the spectrum, compared to the radiation in the visible range and especially the UV range, which leads to the large energy losses. However, under the long pulse-periodic radiation, the reflectance of the material decreases up to several times [1]; that increases the efficiency of pumping. Additionally, due to minimizing of other losses, the use of IR radiation, especially for concentrated dispersions, can be evaluated. This is connected with the fact that almost all the metals do not have plasmon absorption in the near-IR range, plus there is no or minimal absorption of oxide particles and the contribution of linear scattering (compared to visible and UV ranges) is low.

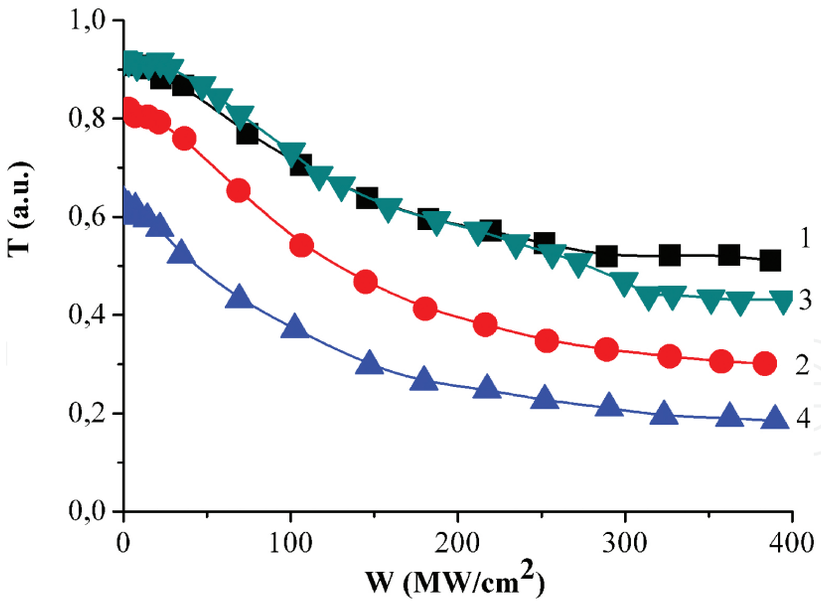


Figure 4. The dependence of transmittance of nanoparticle dispersions obtained by PLAL of zinc and copper targets in various solvents from the power density of ns laser radiation with the wavelength of 1064 nm.

In addition to the linear absorption, nonlinear processes of the interaction of radiation with the NPs have much greater influence on the productivity in the conditions of the powerful pulse excitation in colloidal solutions. These nonlinear processes show complicated depend-

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ence on/from the nature and concentration of the particles as well as the parameters of the laser pulses [15]. **Figure 4** shows the dependence of the deletion from the power density for fresh dispersions of nanoparticles obtained by PLAL of zinc targets (curves 1, 2) and copper (curves 3, 4) in water (curves 1, 3) and alcohol (curves 2, 4). Mass concentration of particles in solutions was about ~50 mg/l. From these figures, it is clearly seen that the nonlinear radiation limiting by the interaction with the NPs in the solution can significantly reduce the power density on the surface of the target and, therefore, the effectiveness of the PLAL even at the low concentrations and short optical length of the interaction.

Another important consequence of the interaction of colloidal NPs with pulsed laser radiation, as has been already noted in 2.4, is the initiation of chemical transformations and change of the dimensional characteristics of the particles. For inert metal particles, e.g., gold and silver, the processes of sintering, defragmentation and alloy particle formation are characteristic. For chemically active metals, chemical reactions are stimulated. For example, let us consider the changing of a spectrum of 2 ml of dispersion obtained by PLAL of metallic zinc target in alcohol (C = 0.1 g/l) after exposure to radiation of the fundamental harmonic of Nd:YAG laser (1.064 nm, 7 ns, 20 Hz) with the power density of 100 MW/cm^2 within 5 min. The formation of a characteristic band in the region of 300–350 nm for the irradiated solution points on the formation of ZnO oxide, whereas in the initial non-radiated solution, there is a significant portion of non-oxidized zinc metal phase (**Figure 5a**). Without irradiation, similar changes in the spectrum of the initial solution that is associated with the oxidation of metallic Zn particles in alcohol occur within a few hours.

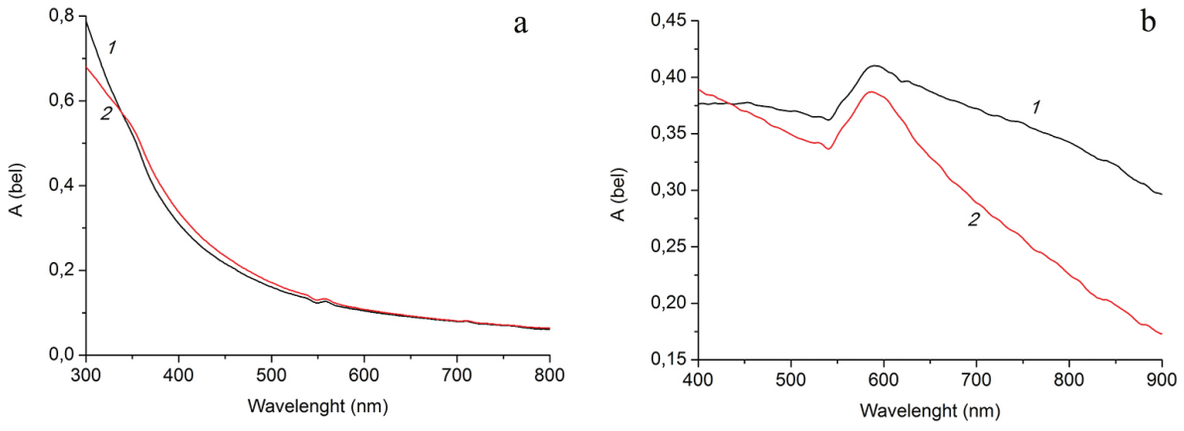


Figure 5. Absorption spectra of the dispersions of nanoparticles obtained by PLAL of zinc (a) and copper (b) targets in ethanol.

Figure 5b shows the spectra of colloidal solutions obtained by PLAL of copper in ethanol. The irradiation in the similar conditions as for zinc in **Figure 5a** does not lead to oxidation of more inert copper (a peak of a surface plasmon resonance of copper at 590 nm does not change), but scattering decreases and a wide band in the wavelength longer than 700 nm that belongs to the absorption of agglomerates disappears.

The examples show that in the process of colloidal solutions obtaining, especially under long-term irradiation and large concentrations, complex chemical processes in the dispersions occur. These processes are stimulated by the secondary interactions of NPs with the laser radiation. Thus, they can not only affect the composition and structure of the particles obtained, but significantly affect the optical properties of the environment and hence influence the PLAL process.

3. Characterization

When nanoparticles are characterized, it is often advisable to divide their properties into two classes. The first class consists of general physical-chemical properties that describe dimension parameters, composition and structure. The second class is presented by the functional properties that are closely linked/strongly connected with physical-chemical characteristics and define specific areas of NP practical application. For example, their fundamental characteristics—particle size, surface composition and charge parameters—determine their ability to penetrate into specific cells, i.e., their functional properties for therapy or diagnostics. Another example: The absorption spectrum connected with the nature of the particles and their size defines the functional ability to block UV radiation in the composition of protective sunscreen materials.

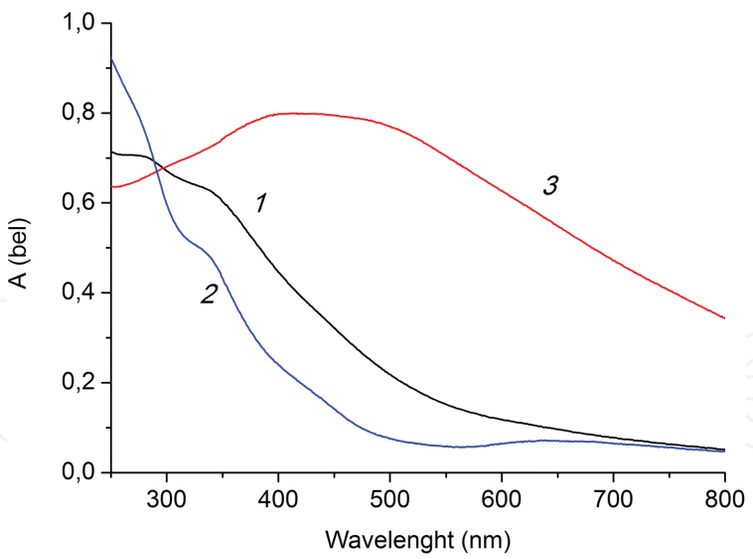


Figure 6. The dynamics of the absorption spectra of colloidal nanoparticles obtained by PLAL of metallic copper target in the water after synthesis (1), after 5 hours (2) and after 10 days (3).

The characterization of colloidal particles obtained by PLAL has numerous features related exactly to their condition. The state of the nanoparticles produced may be quite specific as a result of multiple chemical reactions that are initiated (even for relatively chemically inert materials) during high-power synthesis in the presence of a dense liquid phase. That is why

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the particles obtained have complicated structure with anisotropic composition, containing metastable phases and high defectiveness. Moreover, a unique solvate shell is formed around the particles and it can determine their properties in many respects. Colloid solution is often the dynamic non-stable system and continues to undergo significant changes at storage. Chemical reactions between active ablated particles, dissolved components of the target (ions) and gasses and molecules of solvent and impurities (or precursors) go on in the colloid. As an example, **Figure 6** shows the changes in the spectrum of colloidal nanoparticles' obtained PLAL of metal copper target in water during its storage. These changes are connected to the processes of oxidation and hydrolysis that occur in the colloid.

Drying of the dispersion is required to make tests of structure and composition of the nanoparticles by microscopic or X-ray methods. But even drying in the soft conditions without high temperature and oxygen can significantly transform the initial structure and composition of the nanomaterials, so it is important to be able to study the properties of NPs in their dispersions.

An effective tool to study the characteristics of NPs directly in colloids is modern optical methods (UV-Vis absorption and fluorescent spectroscopy, Raman spectroscopy, confocal fluorescent microscopy, photon correlation spectroscopy) that allow evaluation of the size and shape, as well as the composition and structure, of the nano-objects.

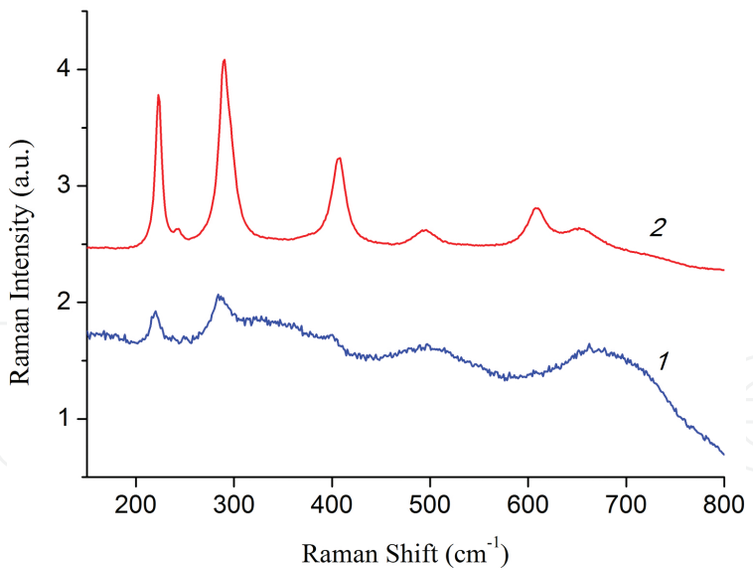


Figure 7. Raman spectra of iron oxide nanoparticles obtained by PLAL of metallic iron target in water: (1) powder after preparation and drying and (2) powder after laser irradiation.

So to determine the particles' size, apart from the widely used method of photon correlation spectroscopy based on the dynamic light scattering by the nanoparticles, there are empirical dependences between the diameter of NPs and the band gap in a certain range of sizes for a number of quantum dots including oxides [16, 17]. These dependences allow assessment of

the particles' size from the absorption spectra. UV-Vis absorption spectra are a simple, express method to study the formation of oxides in PLAL of a large number of metals (Ce, Ti, Cu, Zn, Mg, etc.), because a characteristic peak of exciton absorption appears in the spectrum.

Raman spectroscopy allows evaluation of the particles' structure both in powders and in dispersions. For example, this method makes it possible to distinguish between three iron oxide forms, magnetite, maghemite and hematite [18], that are difficult to recognize by other methods, including X-ray diffraction. **Figure 7** shows the Raman spectra of iron oxide nanoparticles obtained by PLAL of a metallic iron target in water. Freshly obtained magnetite with superparamagnetic properties (curve 1) during heating or irradiation by laser easily transforms into hematite (curve 2). Also, shifts and widening of bands in Raman spectra allow one to reveal the structure, including amorphous materials [19], defects and NP size [20, 21].

Fluorescence spectroscopy is used for the study of defective states of NPs of many oxides in dispersions and powders. For example, spectra and kinetics of fluorescence give information on different oxygen defects in zinc oxides [22], titanium oxide [23], tin oxide [24], etc.

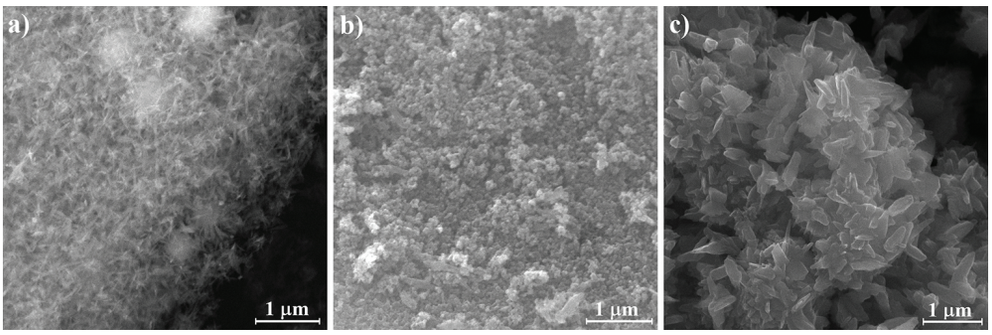


Figure 8. SEM images of CuO nanoparticles obtained at various conditions: drying of water dispersion with the subsequent annealing at 500°C (a), vacuum drying of water dispersion with addition of 1% (weight) hydrogen peroxide (b) and drying of water dispersion with addition of 0.01 M of nitric acid followed by annealing at 300°C (c).

Obviously, classic methods for determining particles' dimensional characteristics are important and are also used for the study of the NPs obtained by the PLAL method. A typical example of such a study is presented in **Figure 8**, which shows microphotographs of copper (II) oxide crystal powders. An important feature of using different solvents and precursors in PLAL is the ability to control not only the composition and structure of the particles but also their size and morphology. Additional treatments of the particles in the dispersions obtained by PLAL and different methods of nanopowder preparation from them (deposition, thermal and vacuum drying, subsequent annealing) allow, for example, synthesizing nanomaterials with different characteristics but the same chemical composition. Copper (II) oxide CuO powders in **Figure 8** are obtained in different experimental conditions of PLAL and further treatments: drying of water dispersion with the subsequent annealing at 500°C (a), vacuum drying of water dispersion with addition of 1% (weight) hydrogen peroxide (b) and drying of water dispersion with addition of 0.01 M of nitric acid followed by annealing at 300°C (c). In the first case, the oxidation of Cu_2O occurs; in the second case, CuO was obtained directly in the dispersion during the PLAL; in the last version, NPs of $Cu_2NO_3(OH)_3$ were a result of ablation and after

annealing, it transformed into copper (II) oxide. NPs of copper (II) oxide obtained by PLAL in water with additive of 1% (weight) of hydrogen peroxide exhibit needle-like shape. The average size of crystals is 10 nm and specific surface is sufficiently large—66 m^2/g (**Figure 8a**). The particles obtained by the annealing of copper (I) oxide are larger and faceted (**Figure 8b**) and the specific surface area is of 12 m^2/g (prior to annealing, BET surface area or specific surface area measured via BET method (S_{BET}) was 30 m^2/g). At the same time, the PLAL with the use of aqueous solutions of HNO_3 and subsequent annealing resulted in the formation of well-crystallized large particles (**Figure 8c**) with the specific surface area of ~2 m^2/g.

4. Application

The scope of application of metal oxide NPs is extremely wide and varied. However, for the oxide nanoparticles obtained by PLAL, there are two most promising applications: scientific research and biomedicine. In both cases, there is no demand for large quantities of nanomaterials and the disadvantage of the PLAL connected with the relatively low productivity is immaterial. Instead, the important advantages of PLAL are express preparation of a wide range of nanomaterials in laboratory conditions for scientific research and "pure" nanoparticles directly in the form of colloidal solutions for biomedicine.

Thus, in our laboratory, oxide nanoparticles obtained by PLAL are used in the study of catalytic processes for searching for the structure and composition of the most effective catalysts for various chemical and photochemical processes. In Ref. [25], the results of the study of catalytic CO oxidation reaction for CeO_2-Pd composites obtained by PLAL of Ce and Pd targets in various solvents are presented. The change of the synthesis parameters of PLAL allows control of the size, chemical composition and superficial properties of obtained particles and hence modification of the catalytic properties. In addition to the cerium dioxide, we used Al_2O_3, SnO, SnO_2, CuO and CuO obtained by PLAL as carriers and catalysts. Composites based on zinc oxide, titanium dioxide and copper oxide nanoparticles were used for the study of photocatalytic processes.

Nanocolloids obtained by PLAL are suitable material for the study of the influence of nanomaterials on the environment. On the one hand, inert enough particles of noble metals can be used to define their migration paths in different ecosystems and, on the other, to investigate the toxicity. Authors of Ref. [26] used several types of nanoparticles including particles obtained by PLAL to study their influence on different aquatic organisms.

Search for tools and methods of protection from antibiotic-resistant pathogenic bacteria strains is an actual problem of modern medicine. The use of nanoparticles as antibiotics that does not cause an adaptation effect among bacteria is one of the promising approaches. In this regard, a new area of research in biomedicine has appeared and the term "nano-antibiotics" [27] has been invented. Effects of zinc oxide nanoparticles obtained by PLAL on pathogenic bacteria were examined in Ref. [28] compared to silver nanoparticles and classic antibiotics. Then, we continued research using NPs of Cu_2O that are more movable and have the best antibacterial properties compared to NPs of ZnO. **Figure 9** shows a picture of cotton fabric samples with

ZnO and Cu_2O particles deposited from water dispersions obtained by PLAL; the composites obtained were covered by *Escherichia coli* bacteria. The figure illustrates the suppression of bacteria growth on fabrics with nanoparticles, while bacteria multiply on the test sample.

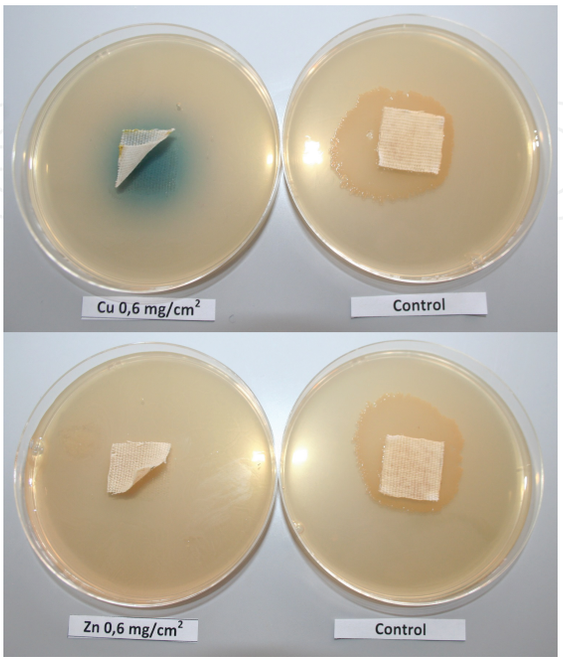


Figure 9. *E. coli* growth inhibition by zinc oxide and copper oxide nanoparticles.

Among other applications in biomedicine, the prospects of using CeO_2, TiO_2 and ZnO obtained by PLAL to protect the skin from UV radiation (sunscreen) are worth noting. Lately, CeO_2 has attracted more and more attention in this field [29] because its toxicity is much lower than standard TiO_2 and its photocatalytic effects are lower as well.

The new direction that has developed effectively in nanomedicine in the last decade is the use of magnetic nanoparticles for modern theranostics—to deliver drugs, for contrasting of pathological object and in magnetic therapy. The use of PLAL for obtaining nanoparticles with special magnetic properties based on oxides of 3d metals directly in the biologically compatible liquids, their functionalization by gold particles and biopolymers have great prospects for the applications mentioned above.

5. Conclusions

Pulsed laser ablation in liquids is a unique physical-chemical method of obtaining nanostructures in colloidal solutions. At the beginning of the process, physical high-energy pulsed laser irradiation stimulates the chain of both physical and chemical processes that lead to the formation of nanoparticles. Careful control of the process allows a large variety of nanostructures to be obtained. This method cannot be considered as the classic top-down approach of

nanomaterial synthesis, despite the fact that initially bulk targets are used. As a result of the PLAL process, a plasma cloud of ions and small clusters appears and nanoparticles are formed from it.

The potential use of PLAL for the synthesis of pure nanocolloids for high-tech applications in science, biomedicine and a number of other areas overlap with disadvantages associated with its relatively small productivity. The specific characteristics of nanosecond laser synthesis, including the factors influencing the effectiveness of PLAL; chemical transformations in the liquids; the specificity of nanodispersion characterization, including optical methods; and future areas of such prepared materials application discussed in the chapter using concrete examples are designed to help scientists and professionals who deal with synthesis, characterization and applications of the similar nanocolloids and powders in their studies.

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Author details

Valery A. Svetlichnyi*, Anastasiia V. Shabalina, Ivan N. Lapin and Daria A. Goncharova

*Address all correspondence to: v_svetlichnyi@bk.ru

Siberian Physical-Technical Institute of Tomsk State University, Tomsk, Russia

References

[1] Ready J.F. Industrial Applications of Lasers. 2nd ed. San Diego: Academic Press; 1997. 600 p.

[2] Miller J.C. editor. Laser Ablation: Principles and Applications. Berlin: Springer-Verlag; 1994. 197 p. DOI: 10.1007/978-3-642-78720-1

[3] Eason R. editor. Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials. Hoboken: John Wiley & Sons, Inc.; 2007. 707 p. DOI: 10.1002/0470052120

[4] Ullmann M., Friedlander S.K., Schmidt-Ott A. Nanoparticle formation by laser ablation. J. Nanopart. Res. 2002; 4: 499-509. DOI: 10.1023/A:1022840924336

[5] Neddersen J., Chumanov G., Cotton T.M. Laser Ablation of Metals: A New Method for Preparing SERS Active Colloids. Appl. Spectrosc. 1993; 47: 1959-1964. DOI: 10.1366/0003702934066460

[6] Yang G. editor. Laser Ablation in Liquids: Principles and Applications in the Preparation of Nanomaterials. Singapore: Pan Stanford Publishing Pt. Ltd.; 2012. 1164 p. DOI: 10.4032/9789814241526

[7] Zeng H., Du X.-W., Singh S.C., Kulinich S.A., Yang S., He J., Cai W. Nanomaterials via laser ablation/irradiation in liquid: A review. Adv. Funct. Mater. 2012; 22: 1333-1353. DOI: 10.1002/adfm.201102295

[8] Tan D., Zhou S., Qiu J., Khusro N. Preparation of functional nanomaterials with femtosecond laser ablation in solution. J. Photochem. Photobiol. C. 2013; 17: 50-68. DOI: 10.1016/j.jphotochemrev.2013.08.002

[9] Bulgakova N.M., Bulgakov A.V. Pulsed laser ablation of solids: Transition from normal vaporization to phase explosion. Appl. Phys. A. 2001; 73: 199-208. DOI: 10.1007/s003390000686

[10] Lorazo P., Lewis L.J., Meunier M. Short-pulse laser ablation of solids: From phase explosion to fragmentation. Phys. Rev. Lett. 2003; 91: 225502-1-225502-4. DOI: 10.1103/PhysRevLett.91.225502

[11] Leitz K.-H., Redlingshöfer B., Reg Y. Otto A., Schmidt M. Metal ablation with short and ultrashort laser pulses. Phys. Procedia. 2011; 12: 230-238. DOI: 10.1016/j.phpro.2011.03.128

[12] Lapin I.N., Svetlichnyi V.A. Features of the synthesis of nanocolloid oxides by laser ablation of bulk metal targets in solutions. Proc. of SPIE. 2015; 9810: 98100T1-7. DOI: 10.1117/12.2224699

[13] Yang G.W. Laser ablation in liquids: Applications in the synthesis of nanocrystals. Prog. Mater. Sci. 2007; 52: 648-698. DOI: 10.1016/j.pmatsci.2006.10.016

[14] Goncharova D., Lapin I., Svetlichnyi V. Synthesis of CdS nanoparticles by laser ablation of metallic cadmium target in presence different precursors. Adv. Mater. Res. 2015; 1085: 182-186. DOI: 10.4028/www.scientific.net/AMR.1085.182

[15] Sun Y.-P., Riggs J.E., Henbest K.B., Martin R.B. Nanomaterials as optical limiters. J. Nonlinear Opt. Phys. Mater. 2000; 9: 481-503. DOI: 10.1142/S0218863500000315

[16] Kippeny T., Swafford L.A., Rosenthal S.J. Semiconductor nanocrystals: A powerful visual aid for introducing the particle in a box. J. Chem. Educ. 2002; 79: 1094-1100. DOI: 10.1021/ed079p1094

[17] Zhang F., Jin Q., Chan S.-W.Ceria nanoparticles: Size, size distribution and shape. J. Appl. Phys. 2004; 95: 4319-4326. DOI: 10.1063/1.1667251

[18] Shebanova O.N., Lazor P. Raman study of magnetite (Fe_3O_4): Laser-induced thermal effects and oxidation. J. Raman Spectrosc. 2003; 34: 845-852. DOI: 10.1002/jrs.1056

[19] Yoshitake H., Abe D. Raman spectroscopic study of the framework structure of amorphous mesoporous titania. Micropor. Mesopor. Mater. 2009; 119: 267-275. DOI: 10.1016/j.micromeso.2008.10.027

[20] Spanier J.E., Robinson R.D., Zhang F., Chan S.-W., Herman I.P. Size-dependent properties of CeO_{2-y} nanoparticles as studied by Raman scattering. Physical Review B. 2001; 64: 245407-1-245407-8. DOI: 10.1103/PhysRevB.64.245407

[21] Choi H.C., Jung Y.M., Kim S.B. Size effects in the Raman spectra of TiO_2 nanoparticles. Vib. Spectrosco. 2005; 37: 33-38. DOI: 10.1016/j.vibspec.2004.05.006

[22] Svetlichnyi V.A., Lapin I.N. Structure and properties of nanoparticles fabricated by laser ablation of Zn metal targets in water and ethanol. Russ. Phys. J. 2013; 56: 581-587. DOI: 10.1007/s11182-013-0071-z

[23] Mathew S., Prasad A. K., Benoy T., Rakesh P.P., Hari M., Libish T.M., Radhakrishnan P., Nampoori V.P.N., Vallabhan C.P.G. UV-visible photoluminescence of TiO_2 nanoparticles prepared by hydrothermal method. J. Fluoresc. 2012; 22: 1563-1569. DOI: 10.1007/s10895-012-1096-3

[24] Gondal M.A., Drmosh Q.A., Saleh T.A. Preparation and characterization of SnO_2 nanoparticles using high power pulsed laser. Appl. Surf. Sci. 2010; 256: 7067-7070. DOI: 10.1016/j.apsusc.2010.05.027

[25] Slavinskaya E.M., Kardash T.Y., Gulyaev R.V., Stonkus O.A., Lapin I.N., Svetlichnyi V.A., Boronin A.I. Metal-support interaction in Pd/CeO_2 model catalysts for CO oxidation: From pulsed laser-ablated nanoparticles to highly-active state of the catalyst. Catal. Sci. Technol. 2016; 6 (17): 6650–6666. DOI: 10.1039/C6CY00319B

[26] Morgalev S., Morgaleva T., Gosteva I., Morgalev Y. Evaluation of the toxicity of superfine materials to change the physiological functions of aquatic organisms of different trophic levels. IOP Conf. Series. Mater. Sci. Eng. 2015; 98: 012006-1-012006-8. DOI: 10.1088/1757-899X/98/1/012006.

[27] Huh A.J., Kwon Y.J. "Nanoantibiotics": A new paradigm for treating infectious diseases using nanomaterials in the antibiotics resistant era. J. Control. Release. 2011; 156: 128-145. DOI: 10.1016/j.jconrel.2011.07.002

[28] Svetlichnyi V., Shabalina A., Lapin I., Goncharova D., Nemoykina A. ZnO nanoparticles obtained by pulsed laser ablation and their composite with cotton fabric: Preparation and study of antibacterial activity. Appl. Surf. Sci. 2016; 372: 20-29. DOI: 10.1016/j.apsusc.2016.03.043

[29] Yabe S., Sato T. Cerium oxide for sunscreen cosmetics. J. Solid State Chem. 2013; 171: 7-11. DOI: 10.1016/S0022-4596(02)00139-1

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