

PACS numbers: 79.20.Eb; 75.75.Fk; 78.67.Bf; 52.38.Mf; 81.16.–c
DOI: 10.1070/QE2015v045n12ABEH015864

Transport equation in the problem of the distribution function of nanoparticles in a colloidal solution exposed to laser pulses

N.A. Kirichenko, M.E. Shcherbina, A.A. Serkov, I.I. Rakov

Abstract. **The behaviour of a colloidal solution of gold nanoparticles irradiated by a repetitively pulsed laser with a pulse duration of a few nanoseconds is investigated theoretically and experimentally. A mathematical model is constructed, which allows the behaviour of the nanoparticle distribution function to be described. The model is based on the transport equation in the 'space' of particle sizes. The proposed model allows for a relatively simple study and makes it possible to establish some common patterns in the behaviour of an ensemble of nanoparticles under various conditions. The results obtained are in satisfactory agreement with the available experimental data.**

Keywords: *laser ablation, nanoparticles, fragmentation, mathematical model.*

1. Introduction

The behaviour of metal nanoparticles in different conditions is being actively investigated in a number of laboratories in the world due to considerable interest in connection with possible various applications of nanoparticles in physics, engineering, medicine, etc.

One of the directions is to study the behaviour of nanoparticles in a liquid under the action of laser radiation [1–8]. Under these conditions, particles are heated and subsequently ablated. In the experiments, the dynamics of the process can be monitored by measuring the absorption spectra of the solution and the distribution function of the particle size (or weight) at successive moments of time. However, the understanding of the properties governing the behaviour of particles requires the establishment of basic mechanisms and construction of mathematical models that allow for a fairly complete study. In addition, the model should be simply modified in view of the changing conditions, i.e., laser radiation parameters, solution concentration and use of other means of interaction.

The authors of Refs [8–10] proposed a model based on the integral-differential kinetic equation for the distribution function. This model, under some natural assumptions regarding the ablation mechanism, has allowed one to satisfactorily describe a number of experimentally observed common patterns in the behaviour of nanoparticles in a solution. It has been shown that the ablation dynamics of particles in a solution and in a vacuum (gas) at the same irradiation conditions varies considerably. In particular, in a liquid irradiated by pulses of duration of about 10 ns relatively large fragments are formed with a high probability, while in vacuum under the same conditions ablation products have dimensions close to monatomic. However, this model is not flexible enough to perform studies for a wider range of radiation and solution parameters, as well as to take into account other factors: transport processes, external fields, etc. In this regard, in this paper we propose a simplified but more flexible model which allows one to calculate the distribution function by solving the transport equation in the phase 'space' of sizes. Similar equations are used in solving various problems of the distribution of particles in a substance, for example in determining neutron fluxes in a reactor (the "age equation" [11]), thermal conductivity in gases and so on. On the basis of the developed model, we consider the ablation dynamics of nanoparticles in a solution exposed to repetitively pulsed radiation with duration of about 10 ns and compare the obtained results with the experimental data.

N.A. Kirichenko, M.E. Shcherbina, A.A. Serkov Wave Research Center, A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia; Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudnyi, Moscow region, Russia;
e-mail: kir@kapella.gpi.ru, mashkent@gmail.com;
I.I. Rakov Wave Research Center, A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia

Received 24 May 2015; revision received 8 July 2015
Kvantovaya Elektronika **45** (12) 1161–1165 (2015)
Translated by I.A. Ulitkin

2. Experimental

The initial colloidal solution of gold nanoparticles was obtained by laser ablation in a liquid [7]. As a radiation source we used an ytterbium fibre laser with a pulse width of 70 ns, repetition rate of 20 kHz and energy of 1 mJ at a wavelength of 1060–1070 nm. The laser beam was focused on the surface of a gold target by an F-Theta lens (focal length $f = 207$ mm). The working liquid was water purified by reverse osmosis. The laser fluence on the target surface was about 13 J cm^{-2} (according to the estimates based on the size of the melted surface region of the target). The laser beam was scanned with a galvo-optic system. The concentration of the resulting colloid of gold nanoparticles was 10^{14}–10^{15} cm^{-3}. This quantity was estimated based on a particle size distribution function with allowance for the target mass defect [8]. The typical rate of generation of nanoparticles (0.5 mg min^{-1}) decreased with time due to the increasing absorption and scattering of light by particles in a colloidal solution. To stabilise nanoparticles after their production in the colloidal solution we added a certain amount of polyvinylpyrrolidone (0.5 mg mL^{-1}).

Subsequent irradiation of the colloidal solution of gold nanoparticles in the absence of the target was conducted using a SOL Nd:YAG laser (Bright Solutions) as a laser radiation

source (wavelength of 1064 nm, pulse duration of 10 ns). The laser radiation was focused through the transparent bottom of the cooled cell by a lens with a focal length of 25 mm. The laser pulse repetition rate was 10 kHz, the pulse energy – 2 mJ, the energy density in the beam waist – about 6 J cm^{-2}. The volume of the irradiated portion of the colloidal solution was 2 mL. The experimental setup is shown in Fig. 1.

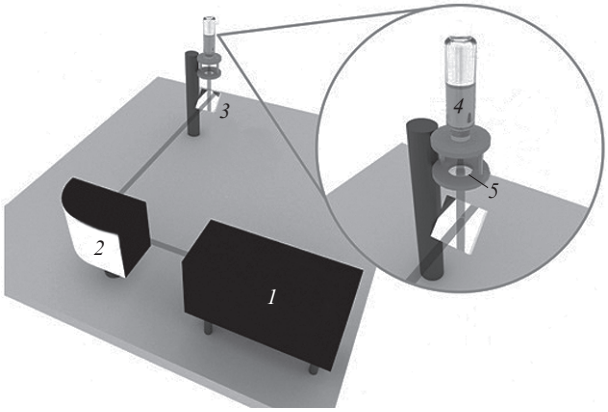

Figure 1. Experimental setup for the fragmentation of gold nanoparticles:
(*1*) laser light source; (*2*) galvo-optic scanning head; (*3*) dielectric mirror; (*4*) cell with a working substance; (*5*) focusing lens (f = 25 mm).

The morphology of the nanoparticles was studied by transmission electron microscopy (TEM). The nanoparticle size distribution was measured by using a CPS 24000 disc centrifuge.

3. Experimental results

Laser ablation of a gold target by nanosecond laser pulses in water usually produces nanoparticles having a wide size distribution. A TEM image of these nanoparticles is shown in Fig. 2.

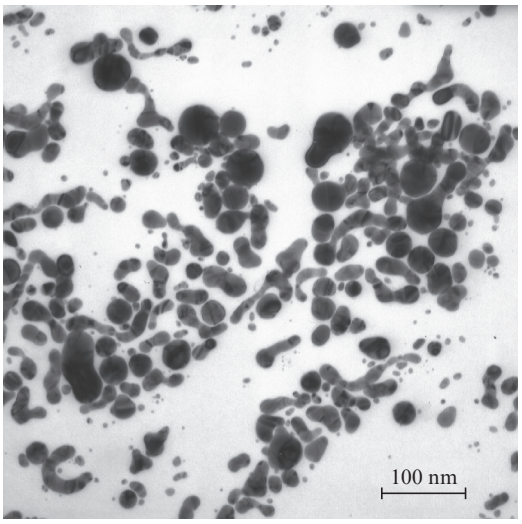

Figure 2. TEM image of initial gold nanoparticles obtained by laser ablation in water. The laser wavelength is 1060–1070 nm, the pulse duration is 70 ns and the fluence is 13 J cm^{-2}.

According to the TEM image, the transverse size of the nanoparticles can be up to 100 nm. To reduce the average nanoparticle size, as well as to narrow the maximum of their size distribution, the nanoparticles can be further subjected to laser irradiation in the absence of the target.

To study the process of fragmentation of gold nanoparticles under the action of nanosecond laser radiation, we performed a series of experiments in which the exposure time varied from 5 to 30 min. The evolution of the nanoparticle size distribution function is shown in Fig. 3.

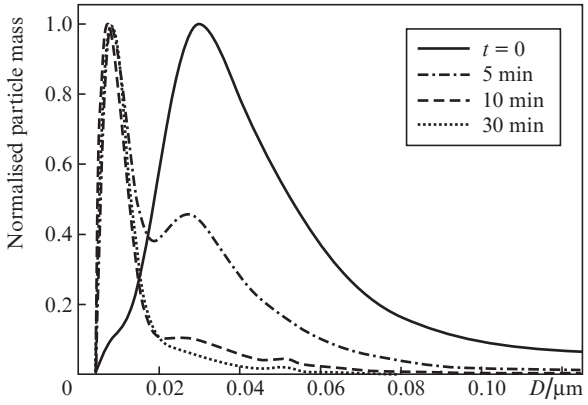

Figure 3. Evolution of the distribution function of gold nanoparticles by diameters D under the action of laser radiation with a wavelength of 1064 nm, a pulse duration of 10 ns and a fluence of about 6 J cm^{-2}.

In exposing the colloidal solution to laser radiation the maximum of the nanoparticle size distribution is shifted from 30 nm (initial position) to 7 nm. It should be noted that the final form of a smaller size maximum (its position and effective width) is achieved in 5 min after the onset of irradiation. Later on, there occurs only a decrease in the amplitude of the initial maximum.

4. Bifractional model of ablation of particles in a liquid

The results of theoretical and experimental studies [9, 10] performed under different conditions of irradiation of a colloidal solution of nanoparticles of some metals indicates that fragmentation in vacuum under typical experimental conditions mostly leads to the formation of monoatomic particles. In a liquid the size of emerging ablation products of nanoparticles is much greater. The reason is as follows.

The flux density of ablation products W according to the Clapeyron–Clausius law is given by the expression [9]

$$W \propto \exp[-mL_1/(k_B T)], \quad (1)$$

where L_1 is the specific heat of evaporation; m is the mass of the cluster separated from the particles; and T is the temperature. This relation can be rewritten in the form

$$W \propto \exp(-v/v_0), \quad v_0 = k_B T/(\rho L_1), \quad (2)$$

determining the probability of separation of a cluster of volume v. Here, ρ is the density of the particles. Estimates [9] show that, for example, in the case of gold at temperatures of

about 3000 K the characteristic size of separated particles is $v_0^{1/3} \approx 0.3$ nm. This means that the separation of the clusters containing many atoms is unlikely, and mainly atoms of the substance are transferred to the environment. In a liquid, the ablation dynamics is strongly affected by the environment, in particular the emerging vapour–gas shell. When a particle undergoes a transition into a completely or partially molten state, the movement of a dense medium facilitates separation of not only fine particles but also of relatively large fragments. According to the experimental data given in [9], the characteristic size of ablation products increases up to $v_2^{1/3} \approx 10$ nm. In this case, the size distribution is described by a relation similar to (2):

$$W \propto \exp(-v/v_2). \tag{3}$$

Due to this fact, Kirichenko et al. [9] proposed a mathematical model that allows one to calculate the time evolution of the particle size distribution.

We introduce the distribution function of particles by volume, n, such that $n(v,t)\mathrm{d}v$ is the number of particles of volume v in the range $\mathrm{d}v$ at time t. To describe the evolution of this function the authors of [8–10] used the kinetic equation

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{v}\int_v^\infty B(x,v)n(x,t)\mathrm{d}x - \frac{1}{v}\int_0^v B(v,x)n(v,t)\mathrm{d}x. \tag{4}$$

The first term in the right-hand side of (4) describes an increase in the number of particles of volume v in the process $(x) \to (v) + (x - v)$, and the second – a decrease in the number of particles in the process $(v) \to (x) + (v - x)$. The coefficients $B(v,x)$ determine the probabilities of the corresponding processes.

This approach faces difficulties both in determining the common properties of the process and in attempts to estimate either additional factors affecting the dynamics of the system. In this connection it is of interest to construct a more simple, convenient for different applications and generalisation, model.

Let the concentration of nanoparticles in the solution be small, so that the frequency of their collisions is small. Then, the main factor determining the evolution of the distribution function is the ablation of available particles. The number of particles can vary with time. However, if we neglect the processes of deposition of particles on the walls of the vessel, their total mass M per unit volume in a medium remains unchanged:

$$\rho\int_0^\infty n(v,t)v\mathrm{d}v = \mathrm{const} = M. \tag{5}$$

To set up the transport equation, we take into account the fact that according to Fig. 3, there are two groups of particles: 'small' and 'large'. The available experimental data and calculations based on equation (1) show [9] that in a wide range of laser radiation parameters and initial particles, 'small' fragments have a distribution function localised in the vicinity of a certain volume of diameter 5–10 nm. The specific value of this volume is close to the value v_2 in equation (3). There is also a scatter of 'small' particle in their size, which determines the width of the distribution function that varies slightly in the process. The latter factor can be considered separately.

Note also that, since the probability of formation of particles with the size on the order of atomic ones is nonzero, the number of the latter increases, resulting in a complete dissolution of particles in a liquid after a sufficiently long time; the reverse process – coagulation or agglomeration – is unlikely due to the low concentration of particles in the solution and low frequency of their collisions.

We denote the volume distribution function of 'large' particles by $n_1(v,t)$. This means that the number of 'large' particles having volumes in the range from v to $v + \mathrm{d}v$ is

$$\mathrm{d}N_1 = n_1(v)\mathrm{d}v. \tag{6}$$

The number of 'small' particles is denoted by $N_2(t)$. If during ablation, j_{abl} 'small' particles of volume v_2 each are separated per unit surface of a 'large' particle per unit time, the position of 'large' particles on the v axis over the same time is shifted in the direction of 'small' volumes by the value of $j_{\mathrm{abl}}Sv_2$, where $S = S(v) \propto v^{2/3}$ is the area of the particle surface. In other words, the specified value is the speed of motion $u_{\mathrm{abl}} = -j_{\mathrm{abl}}S(v)v_2$ along the v axis. Introducing the particle flux density $q_{\mathrm{abl}} = n_1u_{\mathrm{abl}}$, we write the law of conservation of mass (continuity equation):

$$\left(\frac{\partial n_1}{\partial t}\right)_{\mathrm{abl}} = -\frac{\partial q_{\mathrm{abl}}}{\partial v}, \text{ or } \left(\frac{\partial n_1}{\partial t}\right)_{\mathrm{abl}} = \frac{\partial}{\partial v}(j_{\mathrm{abl}}Sv_2n_1). \tag{7}$$

The sign of the derivative in the right-hand side of the equation is determined by the fact that the fragmentation leads to a shift in the direction of smaller values of the volumes.

The rate of change in the number of 'small' particles is given by the equation

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = \int_{v_2}^\infty j_{\mathrm{abl}}S(v)n_1(v,t)\mathrm{d}v + j_{\mathrm{abl}}S(v_2)n_1(v_2,t)v_2. \tag{8}$$

In equations (7) and (8) we formally assume that the function $n_1(v,t)$ is defined in the range $v_2 \leqslant v < \infty$. The second term in the right-hand side of (8) takes into account the fact that a particle of volume v_2 becomes a 'small' particle. The number of such particles is approximately $n_1(v_2,t)v_2$.

We define the boundary and initial conditions:

$$n_1(\infty,t) = 0, \quad n_1(v,0) = n_0(v), \quad N_2(0) = 0. \tag{9}$$

Equations (7) and (8), together with conditions (9), ensure the fulfilment of the law of conservation of total mass (5) of all particles in the system. Indeed, assuming

$$M_1 = \rho\int_{v_2}^\infty n_1(v,t)v\mathrm{d}v, \quad M_2 = \rho N_2(t)v_2, \tag{10}$$

from the transport equation (7) we have

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left[\rho\int_{v_2}^\infty n_1(v,t)v\mathrm{d}v\right] = \rho\int_{v_2}^\infty v\frac{\partial}{\partial v}[j_{\mathrm{abl}}S(v)v_2n_1]\mathrm{d}v$$

$$= -\rho v_2 j_{\mathrm{abl}}Sv_2n_1(v_2,t) - \rho\int_{v_2}^\infty j_{\mathrm{abl}}Sv_2n_1\mathrm{d}v$$

$$= -\rho v_2\frac{\mathrm{d}N_2}{\mathrm{d}t} = -\frac{\mathrm{d}M_2}{\mathrm{d}t},$$

which implies that $M = M_1 + M_2 = \mathrm{const}$.

Equation (7) has a general solution

$$n_1(v,t) = \frac{1}{u(v)} f_0\left(t + \int \frac{\mathrm{d}v}{u(v)}\right). \tag{11}$$

Here, $f_0(y)$ is a function, the type of which is determined from the initial condition.

Analysis of experimental data (Fig. 3) shows that the form of the distribution function of 'small' particles (position of the maximum and width) hardly changes during the process. Consequently, the ablation rate of some 'large' particles per unit area of their surface is almost constant. This allows us to conclude that

$$u(v) \equiv j_{\mathrm{abl}} S(v) v_2 = 3av^{2/3}, \tag{12}$$

where a is a constant. Then, the solution of (11) can be written as

$$n_1(v,t) = v^{-2/3}\varphi(at + v^{1/3}). \tag{13}$$

The specific form of the function $\varphi(z)$ is determined by the initial condition from (9), which gives

$$\varphi(z) = z^2 n_0(z^3). \tag{14}$$

Finally, we obtain

$$n_1(v,t) = \left(1 + \frac{at}{v^{1/3}}\right)^2 n_0((v^{1/3} + at)^3). \tag{15}$$

If we pass from the particle volume v to its diameter D, $v = \pi D^3/6$, then the solution can be rewritten in the form:

$$n_1(D,t) = \left(1 + \frac{\beta at}{D}\right)^2 n_0\left(\left(\frac{D}{\beta} + at\right)^3\right), \tag{16}$$

where $\beta = (6/\pi)^{1/3} \approx 1.24$.

In experiments we obtained size distribution functions μ of the mass m of the particles:

$$\mathrm{d}m(D,t) = \mu(D,t)\,\mathrm{d}D. \tag{17}$$

Therefore, instead of (16) we will use the distribution $\mu_1(D)$:

$$\mathrm{d}M_1 = \mu_1(D,t)\,\mathrm{d}D,$$
$$\mu_1(D,t) = \rho \frac{\pi D^3}{6} n_1(D,t) \frac{1}{2}\pi D^2 \equiv AD^5 n_1(D,t). \tag{18}$$

Accordingly, the initial distribution of the particles by volume $n_0(v)$ is expressed through $\mu_1(D,0)$:

$$n_0(v) = \frac{1}{A\beta^5 v^{5/3}} \mu_1(\beta v^{1/3}, 0). \tag{19}$$

To construct a complete distribution function that takes into account 'large' and 'small' particles, we can use a superposition composed of distribution functions of particles from each group. The first (μ_1) is described by formula (18). To construct the second one (μ_2), we take into account the fact that being produced in ablation 'small' particles have a standard distribution function $f_2(D)$. Considering that it is normalised by the condition

$$\int_0^\infty f_2(D)\,\mathrm{d}D = 1,$$

we assume

$$\mathrm{d}M_2(D,t) = \mu_2(D,t)\,\mathrm{d}D = M_2(t) f_2(D)\,\mathrm{d}D. \tag{20}$$

Here, $M_2(t)$ is the total mass of 'small' particles produced by the instant of time t. It can be found by using the constancy of the total mass M of all particles:

$$M_2(t) = M - M_1(t), \quad M_1(t) = \int_{D_2}^\infty \mu_1(D,t)\,\mathrm{d}D. \tag{21}$$

Here, $D_2 = (6v_2/\pi)^{1/3}$ is the diameter of a 'small' particle. Accordingly, the observed distribution can be written as

$$\mu(D,t) = \mu_1(D,t) + \mu_2(D,t). \tag{22}$$

5. Numerical modelling

In the calculations, we used an experimentally found initial distribution function $\mu(D,0)$, which, with the help of formula (19), was used to find the form of the function $n_0(v)$. Then, using relations (16) and (18) we found the distribution function of 'large' particles, $\mu_1(D,t)$.

To construct the distribution of 'small' particles, $\mu_2(D,t)$, we approximated the distribution function f_2 in the region of small sizes:

$$f_2(D) = A_2\left(\frac{D - D_{\min}}{D_2}\right)^q \exp\left[-\left(\frac{D}{D_2}\right)^\gamma\right], \tag{23}$$

where $q \approx 1.2$; $\gamma \approx 1.5$; and $D_2 \approx 10.5$ nm. The diameter $D_{\min} \approx 0.8$ nm determined the lower boundary of the distribution, when the particles become almost monoatomic and their further ablation terminates. The coefficient A_2 was found from the normalisation condition

$$\int_0^\infty f_2(D)\,\mathrm{d}D = 1.$$

For the selected points in time, we used formula (21) to determine the total mass of 'small' particles M_2, which made it possible to obtain the required distribution (20).

The problem contains the parameter a, introduced in (12) and associated with a single particle ablation rate: $a = (4\pi/3)^{1/3} j_{\mathrm{abl}} v_2$. It defines the time scale of the process. Figure 4 shows the theoretically calculated distribution functions for several moments of time. Their comparison with the experimental data (Fig. 3) yields $a \approx 5.5\times10^{-4}$ μm min^{-1}. Herewith, there is good agreement between the simulation results and the experiment. One can see from Fig. 4 that the maximum of the distribution in the region of small sizes is formed in about 5 min after the onset of irradiation, which is consistent with the experimental data.

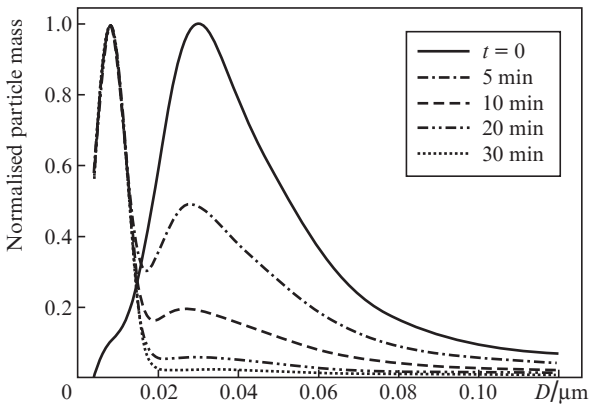

Figure 4. Distribution functions of gold nanoparticles by diameters D at different times, resulting from mathematical modelling.

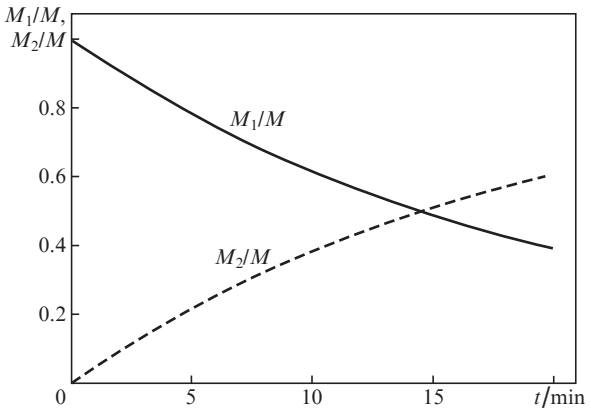

Figure 5. Time dependences of normalised total masses of 'large' and 'small' particles.

It is also interesting to see how the total mass of 'large' and 'small' particles changes with time. This is illustrated in Fig. 5, which shows that after about 15 min, half of the mass is concentrated in 'small' particles.

6. Conclusions

We have proposed an effective mathematical model for the investigation of the dynamics of the distribution function of irradiated nanoparticles. The model is based on the transport equation in the 'space' of particle sizes. Comparison of theoretical and experimental results (Figs 3 and 4) shows good agreement. The constructed model makes it possible to take into account various factors that could affect the dynamics of the process, such as the external field, spatial inhomogeneity of the field of laser exposure, etc.

Acknowledgements. This work was partially supported by the RF President's Scholarship Council (Scholarship No. SP-753.2015.2), by the RF President's Grants Council (State Support of Young Russian Scientists Programme, Grant No. MK-4194.2015.2) and by the Russian Foundation for Basic Research (Grant Nos 15-02-04510 and 15-32-20296).

References

1. Wagener P., Jakobi J., Barcikowski S. *J. Laser Micro/Nanoeng*., **6** (1), 59 (2011).
2. Wagener P., Barcikowski S. *Appl. Phys. A*, **101** (2), 435 (2010).
3. Mafune F., Kohno J., Takeda Y., Kondow T. *J. Phys. Chem. B*, **107**, 12589 (2003).
4. Akman E., Genc Oztoprak B., Gunes M., Kacar E., Demir A. *Photonic Nanostruct. Fundam. Appl*., **9**, 276 (2011).
5. Mohamed M.B., Volkov V., Link S., El-Sayed M.A. *Chem. Phys. Lett.*, **317**, 517 (2000).
6. Tsuji T., Iryo K., Watanabe N., Tsuji M. *Appl. Surf. Sci*., **80**, 202 (2002).
7. Shafeev G.A., in *Lasers in Chemistry. Vol. 2. Influencing Matter* (Weinheim: Wiley VCH, 2008) pp 713–741.
8. Bozon-Verduras F., Brayner R., Voronov V.V., Kirichenko N.A., Simakin A.V., Shafeev G.A. *Kvantovaya Elektron*., **33** (8), 714 (2003) [*Quantum Electron*., **33** (8), 714 (2003)].
9. Kirichenko N.A., Sukhov I.A., Shafeev G.A., Shcherbina M.E. *Kvantovaya Elektron*., **42** (2), 175 (2012) [*Quantum Electron*., **42** (2), 175 (2012)].
10. Kuzmin P.G., Shafeev G.A., Serkov A.A., Kirichenko N.A., Shcherbina M.E. *Appl. Surf. Sci.*, **294**, 14 (2014).
11. Smelov V.V. *Lektsii po teorii perenosa neitronov* (Lectures On Neutron Transport Theory) (Moscow: Atomizdat, 1978).