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Self-Assembly of Nanoparticles Controlled by Resonant Laser Light

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The paper presents theoretical justification for the possibility of formation of nanoparticle structures with the predefined configuration. The process of formation is the self-organized aggregation of nanoparticles under the action of external resonant laser field. The formation of various nanostructures that contain metallic and semiconducting nanoparticles with resonances in the visible spectrum is considered in the dipole-dipole approximation.

Keywords: interaction of laser radiation with matter, dipole-dipole interaction, nanoparticles, nanostructures.

Introduction

Construction of nanoscale objects, study of their properties and application of these objects in electronics and photonics are presently among the main trends of both fundamental and applied research. The main disadvantage of using traditional technologies of microelectronics to produce nanostructures is the limit imposed by photolithographic copying. This makes cheap and mass production of nanostructures impossible [1]. It is worthwhile to mention here the review articles [2, 3]. They describe the methods of formation of nanoparticles and nanostructures with the use of laser radiation. However, these methods have disadvantages of photolithography mentioned above. Therefore, the use of self-organization phenomena is attractive because it can provide the basis for development of relatively cheap technology of complex nanoscale objects production. Self-organization phenomena that are based on intermolecular interactions are the

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most attractive. These phenomena allow the formation of extremely complicated structures without using any technological processes. One should note that the majority of studies devoted to self-organized nanostructures formation is based on the chemical interactions and employs selective interactions between molecules from which the nanostructures are to be formed [4–8]. It seems promising to use physical fields, laser radiation in particular, for controlled self-organization of nanoobjects into clusters. The shape and properties of clusters are imposed in the process of their formation. Under the action of laser radiation atoms, molecules and other microparticles become polarized and they interact with the laser radiation. This produces the so-called radiation forces. These forces allow one to control particles movement and to form structures with the size of order of radiation wavelength [9]. Laser induced polarization leads to the interparticle interaction if the average distance between particles is much smaller than the wavelength. This can be treated as the near field effect.

The use of laser irradiation of nanoparticles produces various effects that are known to turn the assembly of nanoparticles to either disordered or ordered structures. For instance, mesoscale filaments of carbon and gold nanoparticles are irreversibly obtained under laser irradiation with the use of optical trapping, hydro-thermal and chemical effects [10]. Light-controlled assembly of CdTe nanoparticles in helical structures [11] was ascribed to the production of photogenerated charges. Another prospective approach implies the modification of potential energy of the particles in the non-resonant electromagnetic field of the light wave due to particle interactions [12]. Self-assembly of nanoparticles under the action of non-resonant electromagnetic field in the wide frequency range was also investigated [13]. When nanoparticles resonantly interact with the electromagnetic field, this interaction gives new opportunities for selective manipulation of nanoparticles [14]. One should note that optical and spectral properties of silver nanoparticles with a surface plasmon resonance in the visible spectrum were extensively studied [15–22]. Nonlinear optical properties of fractal aggregates of such nanoparticles were experimentally studied [15, 16]. The influence of electromagnetic interaction between particles on spectral properties of their aggregates was also investigated [17–18]. Photochromic effects due to photostimulated aggregation were described [19–21] and the origin of these effects were discussed [22]. All these studies are devoted mainly to the study of spectral properties observed for weak electromagnetic field. The most interesting phenomena are expected in the case of action of strong laser field on the resonant particles. The energy of their electromagnetic interaction may exceed not only the energy of their thermal motion but also, in a number of cases, the energy of chemical bond.

It was theoretically shown that in the case of plasmon-resonant metallic and semiconductor nanoparticles the action of proper frequency electromagnetic field affects the geometry of the produced structures [23, 24]. It was found that interaction of particles in the laser field leads to the shift of their resonant frequencies. This shift depends on the distance between particles and particles orientation with respect to the laser field polarization. The given configuration of the aggregate of particles can be obtained only when laser field induces the attraction of particles. This is achieved by proper choice of the frequency and polarization of laser field.

The formation of one geometry of nanostructure or another strongly depends on the resonance linewidth of individual nanoparticle. Since plasmon resonances of metallic nanoparticles are rather wide it is interesting to consider the light-controlled aggregation of nanoparticles with narrower resonances. Such resonances can be found in semiconducting nanoparticles [25, 26] and in doped dielectric nanoparticles [27]. The formation of heterogeneous nanostructures that consist of different materials (dielectric, semiconducting and conducting nanoparticles) is also of great interest. A special feature of heterogeneous systems is the presence of several resonances with non-coinciding frequencies and linewidths. In the present paper we summarize the theoretical results obtained in dipole-dipole approximation on resonant light-controlled effects on formation of nanostructures that contain semiconducting and metal nanoparticles or just semiconducting nanoparticles. The influence of phases of induced dipoles on the interaction energy of particles is considered in detail.

1. Mathematical model of the process of interaction between nanoparticles

When metal or semiconductor nanoparticles in the state of Brownian motion interact with laser field then they acquire induced electric dipole moment due to polarization effect. Interaction of this dipole with laser field results in optical trapping in the regions with the dimensions of order of wavelength. Increased density of nanoparticles results in increased aggregation rate within an optical trap. The produced aggregates are disordered on the nanoscale but they can bear the signs of ordering on the sub-wavelength scale due to a variety of processes that depend on the medium containing nanoparicles [10, 28]. When several particles in the course of Brownian motion occasionally appear closely enough to each other then dipole-dipole interaction takes place. This is one of the manifestations of near-field effect. If the energy of electromagnetic interaction between nanoparticles exceeds the energy of thermal motion kT and the energy of a barrier preventing the aggregation then irreversible formation of nanostructures happens.

Let us consider an ensemble of N nanoparticles with coordinates r_i. The interaction between nanoparticles is dipole-dipole interaction and dipole moments of nanoparticles are induced by laser field. The size of the ensemble is supposed to be much less than the wavelength of laser radiation. Then external field strength can be considered homogeneous within the ensemble. It is assumed that electric field strength depends only on time: $\mathbf{E} = 1/2\mathbf{E_0}\exp(i\omega t)+c.c$. Local field acting on every nanoparticle is a sum of external field and the fields induced by all other particles. In the dipole-dipole interaction approximation the dipole moment vector induced on i-th particle at given frequency ω is

$$\mathbf{d_i} = \chi_0(\mathbf{E} + \sum_{\mathbf{j}\neq\mathbf{i}} \mathbf{E_j}). \tag{1}$$

Here $\chi_0 = |P_{12}|_i^2 / \hbar(\Omega + i\Gamma_i)$ is the linear polarizability of isolated nanoparticle, $|P_{12}|_i^2$ is the squared magnitude of electric dipole moment of the transition between ground (1) and excited (2) states for i-th particle, $\Omega = \omega_{0i} - \omega$ is the resonance detuning, $\hbar$ is the Planck constant, Γ_i is the homogeneous width of transition and $\mathbf{E_j}$ is the field produced by j-th nanoparticle in the position of i-th particle [29]:

$$\mathbf{E}_j = \frac{3(\mathbf{d}_j\mathbf{r}_{ij})\mathbf{r}_{ij} - \mathbf{d}_j r_{ij}^2}{r_{ij}^5}, \tag{2}$$

where $r_{ij} = r_i - r_j$ is the distance between particles. Interaction energy of i-th and j-th particles with excited dipole polarization is [12]

$$W_{d_{ij}} = -\mathbf{d}_i \cdot \frac{3(\mathbf{d}_j\mathbf{r}_{ij})\mathbf{r}_{ij} - \mathbf{r}_{ij}^2\mathbf{d}_j}{r_{ij}^5} = \frac{(\mathbf{d}_i\mathbf{d}_j)\mathbf{r}_{ij}^2 - 3(\mathbf{d}_i\mathbf{r}_{ij})(\mathbf{d}_j\mathbf{r}_{ij})}{r_{ij}^5}. \tag{3}$$

Therefore, calculation of interaction energy between particles requires solution of system of N equations with dipole moments of every particle $\bar{\chi}_i$ defined by expression (1). Renormalised linear polarizability of every particle can be also obtained. In general, it is a tensor that relates dipole moment vector induced on i-th particle to the vector of electric field strength: $\mathbf{d}_i = \bar{\chi}_i\mathbf{E}$. Imaginary part of renormalized polarizability is responsible for the absorption of light by i-th particle. Let us consider the binary interaction of two particles with different resonant frequencies in the dipole approximation. As an example let us choose silver nanoparticle [29] and semiconductor nanoparticle of CdSe [25, 26]. The optical properties of these nanoparticles are well studied.

Using relation (1) and introducing the frequency shift of i-th particle resonance due to interaction with neighbor particle $\omega_{si} = |P_{12}|_i^2 / \hbar r^3$, we obtain expressions for $d_{1x}(x||r_{12})$ and

$d_{1y}(y \perp r_{12})$ components of induced dipole moments of a pair of nanoparticles:

$$
\begin{aligned}
\mathrm{d_{1x}} &= r^3 E\omega_{s1}\cos\alpha\left[\frac{(\Omega_2+2\omega_{s2})(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})+\Gamma_2(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}+\right.\\
&\left.+i\frac{\Gamma_2(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})-(\Omega_2+2\omega_{s2})(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}\right]e^{i\omega t}+c.c,\\
\mathrm{d_{1y}} &= r^3 E\omega_{s1}\sin\alpha\left[\frac{(\Omega_2-\omega_{s2})(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})+\Gamma_2(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}+\right.\\
&\left.+i\frac{\Gamma_2(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})-(\Omega_2+2\omega_{s2})(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}\right]e^{i\omega t}+c.c,\\
\mathrm{d_{2x}} &= r^3 E\omega_{s1}\cos\alpha\left[\frac{(\Omega_1+2\omega_{s1})(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})+\Gamma_1(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}+\right.\\
&\left.+i\frac{\Gamma_1(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})-(\Omega_1+2\omega_{s1})(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-4\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}\right]e^{i\omega t}+c.c,\\
\mathrm{d_{2y}} &= r^3 E\omega_{s1}\sin\alpha\left[\frac{(\Omega_1-\omega_{s1})(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})+\Gamma_1(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}+\right.\\
&\left.+i\frac{\Gamma_1(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})-(\Omega_1+2\omega_{s1})(\Omega_1\Gamma_2+\Omega_2\Gamma_1)}{(\Omega_1\Omega_2-\Gamma_1\Gamma_2-\omega_{s1}\omega_{s2})^2+(\Omega_1\Gamma_2+\Omega_2\Gamma_1)^2}\right]e^{i\omega t}+c.c\,.
\end{aligned}
\tag{4}
$$

Here α is the angle between the line connecting the centers of nanoparticles and the vector **E** (Fig. 1).

It is convenient to present the expression for the energy of dipole-dipole interaction in terms of the amplitudes and phases of induced dipole moments of every particle. Then, after averaging over time, expression (3) takes the form

$$
W = \frac{|d_{1y}|\,|d_{2y}|\cos(\phi_{1y}-\phi_{2y})\sin^2\alpha - 2\,|d_{1x}|\,|d_{2x}|\cos(\phi_{1x}-\phi_{2x})\cos^2\alpha}{2r^3}, \tag{5}
$$

where $d_{1y}, d_{2y}, d_{1x}, d_{2x}$ are magnitudes and $\phi_{1y}, \phi_{2y}, \phi_{1x}, \phi_{2x}$ are phases of y and x components of time-averaged dipole moments of the first and the second particles.

2. Results and Discussion

2.1. One metallic and one semiconductor particles

The dependence of imaginary part of $(d_{1x} + d_{2x})/E\cos\alpha$ and $(d_{1y} + d_{2y})/E\sin\alpha$ on the external field wavelength is shown in Fig. 1 (solid line) for x (a) and y (b) components of electromagnetic field, respectively. This part is responsible for the absorption of the whole system consisting of two particles.

Dependencies of dipole-dipole interaction energy normalized by room temperature thermal energy kT on the laser wavelength are shown in Fig. 1 (dashed lines) for angles $\alpha = 0^0$ (Fig. 1a) and $\alpha = 90^0$ (Fig. 1b). The following parameters were used in the calculation. For semiconducting CdSe nanoparticle we take into account only most prominent long-wavelength exciton transition with resonant wavelength $\lambda_{01} = 590$ nm that corresponds to ω_{10}, the linewidth $\Delta\lambda_1 = 3$ nm, the radius $R_1 = 5$ nm and squared magnitude of electric dipole moment of the transition $|P_{12}|_1^2 = 1.91 \cdot 10^{-31}$erg·cm^3 [7, 8]. For silver nanoparticle corresponding values are $\lambda_{02} = 420$ nm, $\Delta\lambda_{12}$= 90 nm, $R_2 = 6$ nm and $|P_{12}|_2^2 = 3.12 \cdot 10^{-3}$erg·cm^3 [29]. The external

field strength is E = 200 ESU (10^6W/cm^2), temperature of the medium is T = 300 K and the distance between particles is r_{12} = 13 nm.

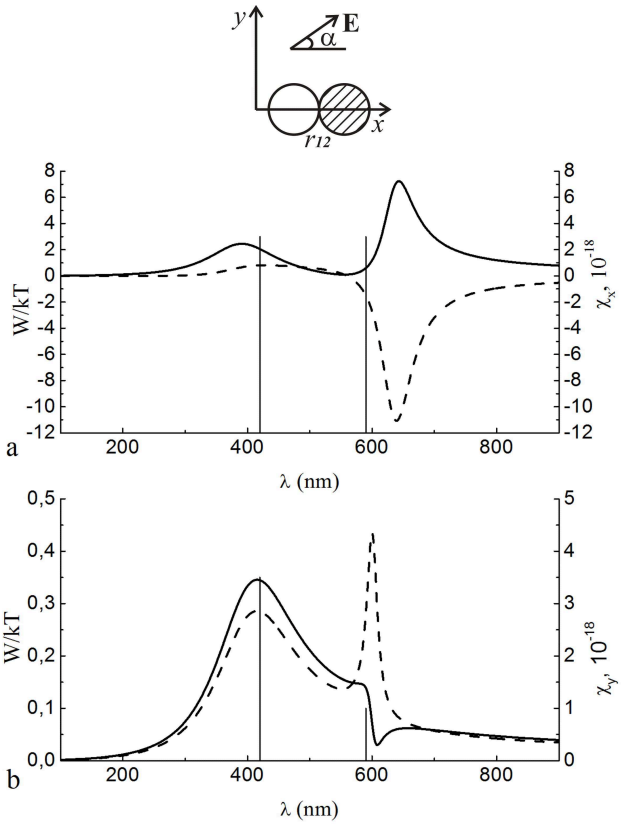

Fig. 1. Wavelength dependence of imaginary part of polarizability for pair of nanoparticles (solid line) χ and normalized dipole–dipole interaction energy of particles (dashed line). Vertical lines are resonant wavelengths of non-interacting nanoparticles. External field is directed at (a) $\alpha = 0^0$ and (b) $\alpha = 90^0$

As can be seen from expression (4) and Fig. 1, wavelength dependence of imaginary part of susceptibility responsible for the absorption noticeably differs from that for non-interacting particles for both field components x and y. One can see that x component has two prominent maxima with the positions shifted from the centers of non-perturbed resonances. This shift is due to the particle interaction and it depends on the resonances widths Γ_1, Γ_2, resonant frequencies of non-interacting particles and squared magnitudes of electric dipole moments $|P_{12}|_1^2$ and $|P_{12}|_2^2$. Characteristic feature is the existence of a dip in the area of 600 nm for imaginary part of polarizability for y field component (Fig. 1b). This dip is the Fano-like resonance and it reflects the interference nature of the particles pair interaction when particles have different resonant frequencies and linewidths [30, 31]. Spectral dependence of nanoparticles interaction energy at $\alpha = 0^0$ has the potential well (Fig. 1a dashed line) and the well depth considerably exceeds the energy of thermal motion. If the height of a potential barrier hindering the aggregation is smaller than this depth the formation of a stable pair of nanoparticles becomes possible. This pair of particles is oriented at the angle $\alpha = 0^0$ to the vector of electromagnetic field. The stability of the pair is sustained by either van der Waals or Coulomb forces. The latter are due to electron transfer between semiconductor quantum dot and metallic nanoparticle [32]. The dependence of

imaginary part of susceptibility at $\alpha = 90^0$ also has the minimum (Fig. 1b) but minimal energy remains positive in this case.

2.2. Three particles

Let us consider now the possibility to form such potential well that allows one to join a third particle at a given angle θ to a pair of particles. It can be accomplished by varying the radiation frequency and the angle α between the polarization plane of the radiation and the radius-vector r_{12} (see Fig. 2). Let us consider the case of formation of a structure consisting of 3 metallic particles. In this case, it is assumed that the pair of particles 1 and 2 acts as a single whole and that r_{12} can be oriented in space using auxiliary laser radiation. Analytical solution of Eqs. (1) and (2) for three particles is very cumbersome and it is not presented here. The distance between the particles of the pair is $r_{12} = 2R = 12$ nm. In Fig. 2, r_{23} is the distance between the second and third particles and θ is the angle between the straight lines r_{12} and r_{23}. The polarization of the external light field is directed at an angle α to the straight line that connects the centers of the first two particles and it is parallel to the x axis. Fig. 2 shows the dependence of the energy of the dipole–dipole interaction of the third particle with the two others on frequency and the angle α. The values of the particle radius, the external field strength and temperature are the same as in the above case with two interacting particles. The distance between the pair of aggregated particles and the third particle is $r_{23} = 15$ nm. The angle of arrangement of the third particle is equal to $\theta = 90^0$. It is seen from Fig. 2a that the minimum value of the dipole–dipole interaction energy is about –1.7 kT and it is attained at the angle of orientation of the external field polarization $\alpha \approx 65^0$ ° and at the radiation wavelength $\lambda \approx 500$ nm. Similarly to the above case of two interacting particles, when the particles approach each other the potential well becomes deeper and the resonance frequency is shifted toward the IR range. For example, for the particle arrangement shown in Fig. 2b, i.e., at $\theta = 120^0$ and $r_{23} = 12$ nm, the minimum of the potential well at $\lambda \approx 1600$ nm is about –6.9 kT. The field in this case should be oriented at the angle $\alpha = 90^0$. This is consistent with qualitative analysis. In addition, numerical calculation shows that a decrease in the angle θ also leads to the shift of the resonance frequency toward the IR range, to the small deepening of the potential well and to its shift towards smaller angles α. Thus, the calculated minimum is –2.2 kTat and it is observed at $r_{23} = 15$ nm, $\theta = 0^0$, $\lambda \approx 3500$ nm and $\alpha = 0^0$.

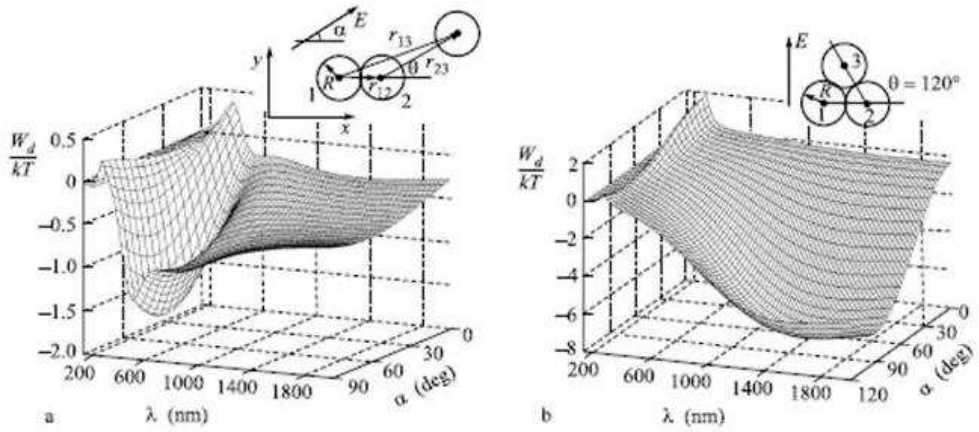

Fig. 2. Energy of interaction of a third particle with two other particles in electromagnetic field in relation to the orientation angle of the field polarization and the wavelength; the angle $\theta = 90^0$ (a) and $\theta = 120^0$ (b)

Calculations for various configurations of nanoparticles in a nanostructure, that is, for different values of angle θ , show that not all configurations are equally controllable through the change of wavelength, laser intensity and polarization. As one can see from figures, the potential well depth in the case of interaction of metal particles is of order of several kT at the field intensity close to $(10^6 \mathrm{W/cm}^2)$. Besides, the large spectral width of these wells attracts attention. This is because the large width of plasmon resonance of individual particles.

For comparison, let us compare results for heterogeneous structures with the case of homogeneous structure formation when semiconductor particle takes on a pair of already aggregated semiconductor particles. The resonance width of semiconductor particle is much smaller than that of metallic particle. Fig. 3 presents the dependence of interaction energy on the laser wavelength and angle α for $\theta = 120^0$.

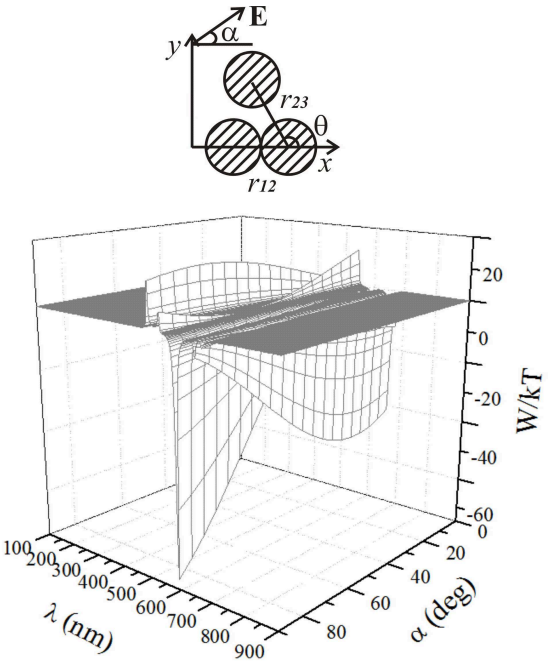

Fig. 3. The dependence of the energy of normalized dipole–dipole interaction between semiconducting particle and the pair of aggregated semiconducting particles on the laser wavelength and electric field direction angle

Individual resonant frequency of every aggregated particle is chosen to be corresponding to the wavelength 590 nm, while for the third particle it corresponds to 510 nm. The particle radius is $r_3 = 3$ nm. Linewidths of isolated nanoparticles and laser field strength are the same as in previous calculations. As can be seen from Fig. 3, two potential wells exist at $\alpha = 90^0$ and $\alpha = 20^0$. The well depths are 63 kT and 43 kT at wavelengths 595 nm and 655 nm. Figs. 4a and 4b show the dependence of interaction energy on wavelength at $\alpha = 0^0$ and $\alpha = 90^0$ for different angles θ. For $\alpha = 90^0$ configurations are possible either with $\theta = 120^0$ (the wavelength is 593 nm) or with $\theta = 90^0$ (the wavelength is 554 nm). While suitable potential wells for $\theta = 0^0$ and for $\theta = 45^0$ are absent.

When laser field polarization angle $\alpha = 0^0$, the formation of configurations with $\theta = 120^0, 90^0, 45^0, 0^0$ is possible since all of them have suitable potential wells at 655, 615, 685 and 710 nm, respectively. The accuracy of positioning the particle at the desired angle θ_0 can be found from the dependence of the energy of interaction between particle and two aggregated

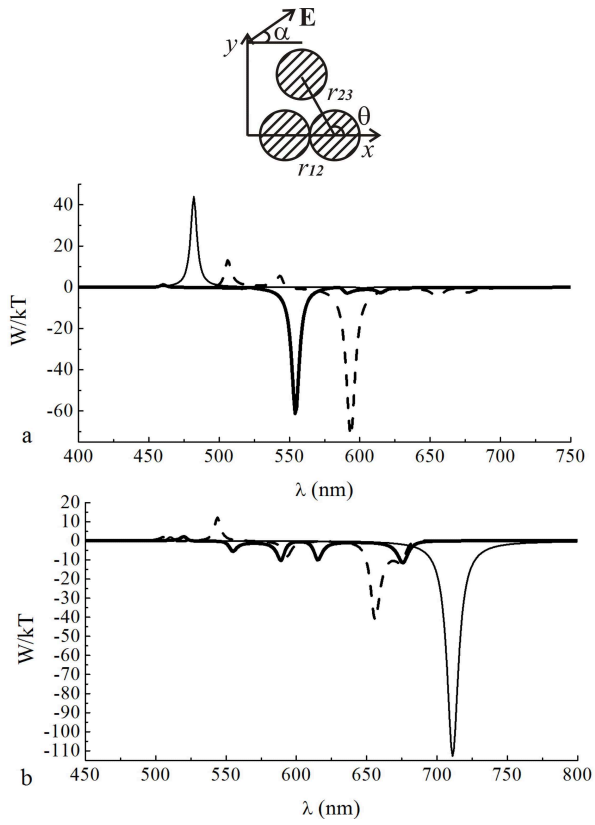

Fig. 4. The dependence of the normalized energy of dipole–dipole interaction between semiconductor particle and two aggregated semiconducting particles on the laser wavelength for different configurations of the nanostructure: $\theta = 120^0$ (dash), 90^0 (thick solid), and 0^0 (thin solid); (a) — $\alpha = 90^0$ and (b) — $\alpha = 0^0$

particles on the angle θ in the vicinity of θ_0. This dependence is presented in Fig. 5 for three different sets of particles.

The possibility to build structure with desired configuration (θ_0) can be quantitatively described by the angular width $\Delta\theta$ of the potential well on the level that is 1 kT higher than the value of potential well minimum. Evidently, $\Delta\theta$ can characterize the angular selectivity of desirable structure under conditions of thermodynamic equilibrium with the surrounding medium. As can be found from Fig. 5 for $\theta_0 = 90^0$, $\Delta\theta = 2.7^0$ for three semiconducting particles and $\alpha = 0^0$. While for $\alpha = 90^0$ and two semiconducting and one metallic particles $\Delta\theta = 16.9^0$. For the case of two metallic and one semiconductor particles the minimum at $\theta_0 = 90^0$ is absent, as it was already mentioned in the analysis of spectral dependencies. The highest selectivity ($\Delta\theta$ below 1^0) is expected for three semiconducting particles for both $\alpha = 90^0$ and $\alpha = 0^0$. The $\Delta\theta$ values and corresponding potential well depths $|W_{\min}|$ (in kT units) for two metallic and one semiconductor particles (mms), two semiconductor and one metallic particles (ssm) and three semiconductor particles (sss) are presented in Tab. 1 for laser intensity 10^6 W/cm^2. As can be seen, for ($\alpha = 90^0$) stable configurations with $\theta = 0^0$ are nonexistent for all particle sets because of the absence of potential wells for all considered wavelengths. For mms set, for both $\alpha = 90^0$ and $\alpha = 0^0$, and for ssm set and $\alpha = 0^0$ the configuration $\theta_0 = 90^0$ possesses potential wells, but stable configurations are absent as well as in the cases mms90 and ssm0 for $\theta_0 = 120^0$.

Of course, the $\Delta\theta$ values depend not only on the structure configuration but also on the

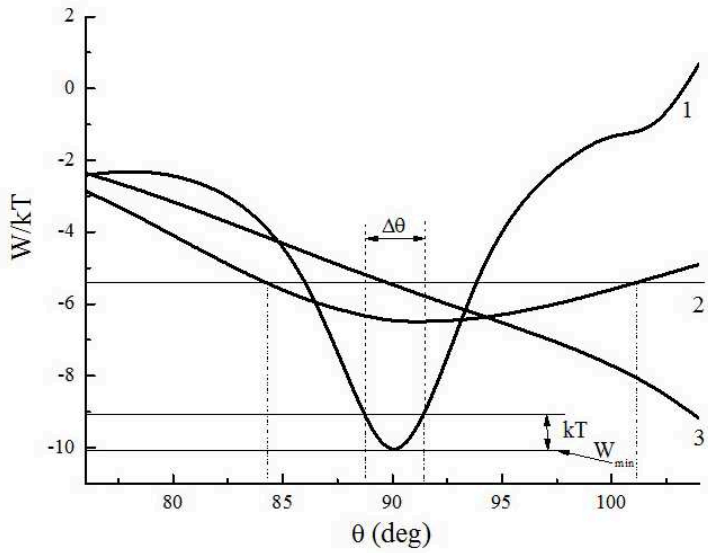

Fig. 5. Dependence of potential energy of interaction on the angle θ for $\alpha = 90^0$: 1 — three semiconducting nanoparticles, 2 — two semiconducting and one metallic nanoparticles, 3 — two metallic and one semiconducting nanoparticles

intensity of laser radiation. They decrease with the increase of the laser radiation. Joint consideration of spectral and angular widths of potential wells allows one to evaluate the possibility of light-controlled formation of nanostructures.

Table 1. Angular widths $\Delta\theta$ and potential well depths for various particle sets, particle configurations θ_0 and light polarizations α

θ_0		mms		ssm		sss	
		$\alpha = 0°$	$\alpha = 90°$	$\alpha = 0°$	$\alpha = 90°$	$\alpha = 0°$	$\alpha = 90°$
0°	$\Delta\theta$	7.38°	–	12.46°	–	4.718°	–
	$\lvert W_{min}\rvert$	4.117	–	20.84	–	112.7	–
90°	$\Delta\theta$	–	–	–	16.89°	2.739°	1.031°
	$\lvert W_{min}\rvert$	0.591	5.47	1.41	6.49	10.04	61.2
120°	$\Delta\theta$	3.44°	–	–	2.1°	0.19°	0.22°
	$\lvert W_{min}\rvert$	1.634	23.35	1.311	5.411	41.55	71.84

2.3. The influence of phases of induced dipole moments on the energy of dipole-dipole interaction

The results presented above indicate fundamental difference in the interaction between identical particles and between particles with different linewidths, resonant wavelengths and dipole moments. One can observe the occurrence of additional maxima and minima in the spectral dependence of interaction energy. For example, in distinction to a pair of metallic particles [23], calculations show (see Figs. 2 and 3) the occurrence of additional spectral minima in the interaction energy. This can be connected with phase relations of dipole moment oscillations induced on

individual particles. If electric dipole moments of transitions, linewidths or resonant frequencies of particles are different and the phases of induced dipole moment oscillations are different then situation may occur when phase difference is close to $\pi/2$ at the angle $\alpha = 90^0$. This results in occurrence of additional minima or maxima in the interaction energy [24]. Using (4), one can obtain the following expression for phases of dipole moment oscillations

$$\begin{aligned}
\phi_{1x} &= \text{arctg}\,\frac{\Gamma_2(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - 4\omega_{s1}\omega_{s2}) - (\Omega_2 + 2\omega_{s2})(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}{(\Omega_2 + 2\omega_{s2})(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - 4\omega_{s1}\omega_{s2}) + \Gamma_2(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}, \\
\phi_{12} &= \text{arctg}\,\frac{\Gamma_1(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - 4\omega_{s1}\omega_{s2}) - (\Omega_1 + 2\omega_{s1})(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}{(\Omega_1 + 2\omega_{s1})(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - 4\omega_{s1}\omega_{s2}) + \Gamma_1(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}, \\
\phi_{1y} &= \text{arctg}\,\frac{\Gamma_2(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - \omega_{s1}\omega_{s2}) - (\Omega_2 - \omega_{s2})(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}{(\Omega_2 - \omega_{s2})(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - \omega_{s1}\omega_{s2}) + \Gamma_2(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}, \\
\phi_{2y} &= \text{arctg}\,\frac{\Gamma_1(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - \omega_{s1}\omega_{s2}) - (\Omega_1 - \omega_{s1})(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}{(\Omega_1 - \omega_{s1})(\Omega_1\Omega_2 - \Gamma_1\Gamma_2 - \omega_{s1}\omega_{s2}) + \Gamma_1(\Omega_1\Gamma_2 + \Omega_2\Gamma_1)}.
\end{aligned} \tag{6}$$

As one can see from expression (5), the energy of dipole-dipole interaction for polarization angles $\alpha = 0^0$ (x component) and $\alpha = 90^0$ (y component) consists of just one term. Expression (6) shows how the phases of dipole moment oscillations depend on linewidths and resonant frequencies of interacting particles. Therefore, in the case of interaction of identical particles the phase difference in expression (6) is always zero and the cosine function in the expression (5) is always unity. One should note that in the case of stationary electric field the situation is completely the same. However, when parameters of individual interacting particles are different, cosine function can change its sign. This results in additional resonances mentioned above [24]. These resonances occur only in the case of oscillating polarization of particles.

The results of numerical calculations of phases of induced dipole moments oscillations and dipole-dipole interaction energy normalized to the energy of thermal motion are presented in Figs. 6 and 7 as a function of angle α and external field frequency. The following values of the quantities entering the equations are used: external field E=200 ESU (10^6W/cm^2), temperature T=300 K, distance between particles r_{12}=14 nm.

As one can see from Fig. 6b, induced dipole moments of metallic particles always oscillate with the same phase. The wavelength region around 800 nm corresponds to the interaction energy well and the well depth is equal to –6.6 kT. This means that stable aggregate of a pair of particles is formed. At the wavelengths from 400 to 550 nm the interaction energy of a pair of metallic and semiconducting particles experiences maximum of order of 0.6 kT that corresponds to particles repulsion (Fig. 6c) and the difference between oscillation phases of individual particles is close to π. In the region of 620 nm the potential well arises and the well depth is equal to –1 1.2 kT. This corresponds to attraction of particles and the phase difference equals zero.

For angle $\alpha = 90^0$ (y component of induced dipole moment) the dipole-dipole interaction energy of two identical particles (Fig. 7a) exhibits maximum at 350 nm that corresponds to repulsion of particles and phase oscillations of induced dipole moments are observed (Fig. 7b). The variation in phase of the value close to π takes place when wavelength is tuned over the resonance. More complicated situation occurs in the case of interaction of metallic and semiconducting particles. When phase difference of induced dipole moments oscillations becomes close to π (Fig. 7d), additional minimum in the energy of dipole-dipole interaction occurs. This minimum corresponds to weak attraction (the well depth equals –0.03 kT) and it lies in the region of 590 nm (Fig. 7c). Therefore, the occurrence of attraction between particles at $\alpha = 90^0$ is due to the phase shift of induced dipole moments of metal and semiconducting particles and the shift value is close to π.

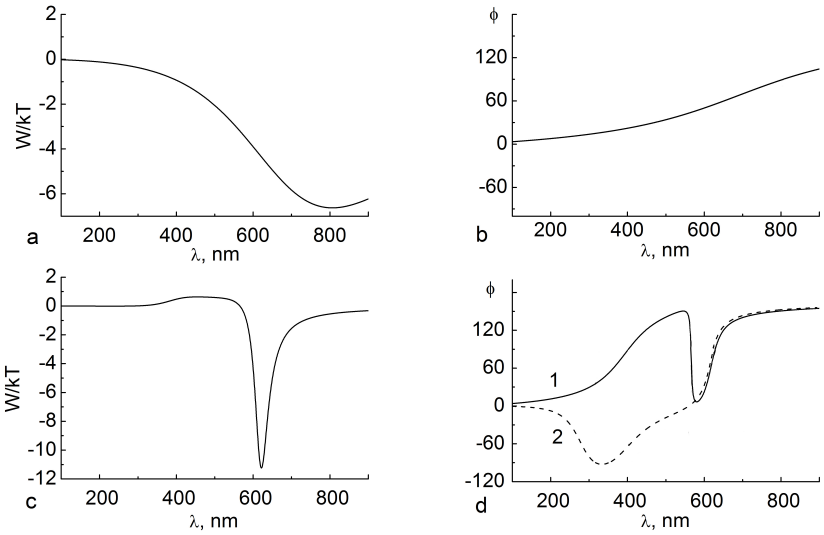

Fig. 6. The dipole-dipole interaction and phases of induced dipole moments: a, b are two metallic particles; c, d are metallic and semiconducting particles, angle $\alpha = 0^0$. 1 is the phase of induced dipole moment of metallic particle, 2 is the phase of induced dipole moment of semiconducting particle

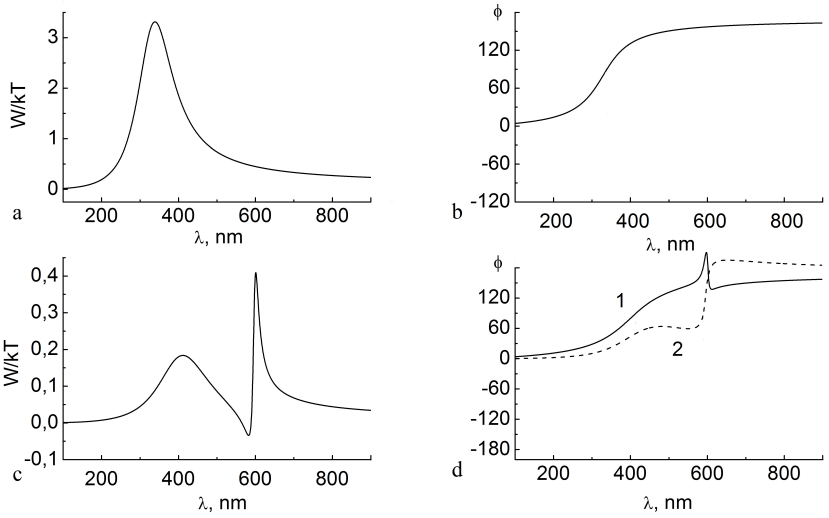

Fig. 7. The dipole-dipole interaction energy and phases of induced dipole moments: a,b are two metallic particles, c,d are metallic and semiconducting particles, angle $\alpha = 90^0$. 1 is the phase of induced dipole moment of metal particle, 2 is the phase of induced dipole moment of semiconducting particle

3. Conclusions

We theoretically show the possibility to control the self-organized aggregation of nanoparticles in order to form the structures with predefined geometry with the help of external resonant field of laser radiation. The basic idea of controllable aggregation is that interaction between particles

in a group under the action of external electromagnetic field depends on both the frequency and the polarization orientation of the field. As this takes place, either attraction or repulsion of particles is possible. If the potential well depth exceeds the threshold that prevents spontaneous aggregation then particles fall into the potential well. The formed structure is preserved due to action of van der Waals forces because the energy of interaction considerably exceeds the energy of thermal motion. The spatial configuration of the formed nanostructure can be predefined with the proper choice of frequency and polarization of the field. Nanostructures consisting of metallic and semiconducting nanoparticles with optical resonances in the visible spectrum are considered. The possibility of formation of such nanostructures is examined in dipole-dipole approximation. The choice of such nanostructures is dictated mainly by the fact that they form the basis for elements of micro- and nanoelectronics. In our study the following particles parameters are taken into account: resonant frequencies, resonance widths and electric dipole moments. Numerical analysis shows that for the commonly accepted values of the parameters the interaction energy between particles can achieve values comparable with the chemical bond energy in the laser field with the intensity below particle destruction threshold. The numerical algorithm is presented that allows one to choose the particles and field parameters that are necessary for formation of predefined nanostructures.

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References

[1] J.DeBoor, D.S.Kim, V.Schmidt, Sub-50 nm Patterning by Immersion Interference Lithography Using a Littrow Prism as a Lloyd's Interferometer, *Optics Letters*, **35**(2010), no. 20, 3450–3452.

[2] L.Li, M.H.Hong, M.Schmidt, M.L.Zhong, A.Malshe, H.B. in'tVeld, V.Kovalenko, Laser nano-manufacturing – State of the art and challenges, *CIRP Annals-Manufacturing Technology*, **60**(2011), no. 2, 735–755.

[3] S.Juodkazis, V.Mizeikis, S.Matsuo, K.Ueno, H.Misawa, Three-Dimensional Micro- and Nano-Structuring of Materials by Tightly Focused Laser Radiation, *Bulletin of the Chemical Society of Japan*, **81**(2008), no. 4, 411–448.

[4] M.M.Mahlambi, A.K.Mishra, S.B.Mishra, A.M.Raichur, B.B.Mamba, R.W.Krause, Layer-by-Layer Self-AssembledMetal-Ion- (Ag-, Co-, Ni-, and Pd-) Doped TiO2 Nanoparticles: Synthesis, Characterisation, and Visible Light Degradation of Rhodamine B, *Journal of Nanomaterials*, **2012**(2012), 302046.

[5] P.Akcora, H.Liu, S.K.Kumar, J.Moll, Y.Li, B.C.Benicewicz, L.S.Schadler, D.Acehan, A.Z.Panagiotopoulos, V.Pryamitsyn, V.Ganesan, J.Ilavsky, P.Thiyagarajan, R.H.Colby, J.F.Douglas, Anisotropic self-assembly of spherical polymer-grafted nanoparticles, *Nature Materials*, **8**(2009), no. 4, 354–359.

[6] A.K.Boal, F.Ilhan, J.E.DeRouchey, T.Thurn-Albrecht, T.P.Russell, V.M.Rotello, Self-assembly of nanoparticles into structured spherical and network aggregates, *Nature*, **404**(2000), no. 6779, 746–748.

[7] S.Kinge, M.Crego-Calama, D.N.Reinhoudt, Self-Assembling Nanoparticles at Surfaces and Interfaces, *Chemphyschem*, **9**(2008), no. 1, 20–42.

[8] Kyung-Jong Noh, Hyo-Jin Oh, Bo-Ra Kim, Sang-Chul Jung, Wooseung Kang, Sun-Jae Kim, Photoelectrochemical Properties of Fe2O3 Supported on TiO2-Based Thin Films Converted from Self-Assembled Hydrogen Titanate Nanotube Powders, *Journal of Nanomaterials*, **2012**(2012), 475430.

[9] Takuya Iida, Hajime Ishihara, Theoretical Study of the Optical Manipulation of Semiconductor Nanoparticles under an Excitonic Resonance Condition, *Physical Review Letters*, **90**(2003), no. 5, 057403.

[10] J.T.Bahns, S.K.R.S. Sankaranarayanan, S.K.Gray, L.Chen, Optically Directed Assembly of Continuous Mesoscale Filaments, *Physical Review Letters*, **106**(2011), no. 9, 095501.

[11] S.Srivastava, A.Santos, K.Critchley, K.Kim, P.Podsiadlo, K.Sun, J.Lee, C.Xu, G.D Lilly, S.C.Glotzer, N.A.Kotov, Light-Controlled Self-Assembly of Semiconductor Nanoparticles into Twisted Ribbons, *Science*, **327**(2010), no. 5971, 1355–1359.

[12] J.Rodriguez, L.C.DavilaRomero, D.L.Andrews, Optical binding in nanoparticle assembly: Potential energy landscapes, *Physical Review A*, **78**(2008), no. 4, 043805.

[13] J.Park, W.Lu, Self-assembly of nanoparticles into heterogeneous structures with gradient material properties, *Physical Review E*, **83**(2011), no. 3, 031402.

[14] T.Iida, H.Ishihara, Theory of resonant radiation force exerted on nanostructures by optical excitation of their quantum states: From microscopic to macroscopic descriptions, *Physical Review B*, **77**(2008), no. 24, 245319.

[15] A.V.Butenko, P.A.Chubakov, Y.E.Danilova, S.V.Karpov, A.K.Popov, S.G.Rautian, V.P.Safonov, V.V.Slabko, V.M.Shalaev, M.I.Stockman, Nonlinear optics of metal fractal clusters, *Zeitschrift Fur Physik D-Atoms Molecules and Cluster*, **17**(1990), no. 4, 283–289.

[16] S.V.Karpov, A. K.Popov, S.G.Rautian, V.P.Safonov, V.V.Slabko, V.M.Shalaev, M.I.Shtokman, Observation of a wavelength-selective and polarization-selective photomodification of silver clusters, *Jetp Letters*, **48**(1988), no. 10, 571–575.

[17] S.V.Karpov, A.L.Bas'ko, A.K.Popov, V.V. Slabko, Influence of electrodynamic interactions of particles on absorption spectra of silver sols during their aggregation, *Optics and Spectroscopy*, **9**(2003), no. 2, 230–240.

[18] S.V.Karpov, A.L.Bas'ko, A.K.Popov and V.V.Slabko, Specific features of absorption spectra of fractal-structured silver sols, *Optics and Spectroscopy*, **95**(2003), no. 2, 241–247.

[19] S.V.Karpov, A.K.Popov, V.V.Slabko, Photochromic reaction dynamics in metallic colloidal silver, *Izvestiya Akademii Nauk Seriya Fizicheskaya*, **60**(1996), no. 6, 43–50.

[20] S.V.Karpov, A.K.Popov, V.V.Slabko, Observation of the two-photon photoelectric effect in low-intensity optical fields during photostimulated fractal aggregation of colloidal silver, *Jetp Letters*, **66**(1997), no. 2, 106–110.

[21] S.V.Karpov, A.K.Popov, V.V.Slabko, Photochromic reactions in silver nanocomposites with a fractal structure and their comparative characteristics, *Technical Physics*, **48**(2003), no. 6, 749–756.

[22] S.V.Karpov, V.V.Slabko and G.A.Chiganova, Physical principles of the photostimulated aggregation of metal sols, *Colloid Journal*, **64**(2002), no. 4, 425–441.

[23] V.V. Slabko, G.G. Khachatryan, A.S. Aleksandrovsky, Self-organized aggregation of small metal particles controlled by an external light field, *JETP Letters*, **84**(2006), no. 6, 300–304.

[24] V.V.Slabko, A.S.Tsipotan, A.S.Aleksandrovsky, Resonant light-controlled self-assembly of ordered nanostructures, *Photonics and Nanostructures – Fundamentals and Applications*, **10**(2012), no. 4, 636–643.

[25] A.L.Rogach (Ed.), Semiconductor Nanocrystal Quantum Dots, Springer, Wien, NY, 2008.

[26] M.Alves-Santos, Rosa Di Felice, Guido Goldoni, Dielectric Functions of Semiconductor Nanoparticles from the Optical Absorption Spectrum: The Case of CdSe and CdS, *Journal of Physical Chemistry*, **114**(2010), no. 9, 3776–3780.

[27] N.E.Lyamkina, G.A.Chiganova, V.V.Slabko, A.M.Vorotynov, M.A.Taranova, Ultrafine Cr-Doped Al2O3 Prepared by Detonation Synthesis, *Inorganic Materials*, **41**(2005), no. 8, 830–835.

[28] Y.Zhang, C.Gu, A.M.Schwartzberg, S.Chen, J.Z.Zhang, Optical trapping and light-induced agglomeration of gold nanoparticle aggregates, *Physical Review B*, **73**(2006), no. 16, 165405.

[29] V.M.Shalaev, Electromagnetic Properties of Small-Particle Composites, *Phys. Reports*, **272**(1996), no. 2, 61–137.

[30] E.M.Averyanov, Mixing of molecular excitations in a uniaxial liquid crystal, *JETP*, **81**(1995), no. 1, 139–150.

[31] B.Lukyanchuk, N.I.Zheludev, S.A.Maier, N.J.Halas, P.Nordlander, H.Giessen, C.T.Chong, The Fano resonance in plasmonic nanostructures and metamaterials, *Nature Materials*, **9**(2010), no. 9, 707–715.

[32] J.Y.Yan, W.Zhang, S.Duan, X.G.Zhao, A.O.Govorov, Optical properties of coupled metal-semiconductor and metal-molecule nanocrystal complexes: Role of multipole effects, *Physical Review B*, **77**(2008), no. 16, 165301.

[33] N.N.Yanenko, On the weak approximation of the differential equations systems, *Siberian Math. J.*, **5**(1964), no. 6, 1431–1434 (in Russian).

[34] N.N.Yanenko, G.V.Demidov, The research of a Cauchy problem by method of weak approximation, *Dokl. Akad. Nauk SSSR*, **6**(1966), 1242–1244 (in Russian).

Самоорганизация наночастиц, контролируемая резонансным лазерным полем

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Теоретически показана возможность формирования структур из наночастиц с заранее заданной конфигурацией. Это возможно благодаря явлению самоорганизации наночастиц под действием внешнего резонансного поля лазерного излучения. Формирование различных наноструктур, содержащих металлические и полупроводниковые наночастицы с резонансной длиной волны в видимой области, считалось в диполь-дипольном приближении.

Ключевые слова: взаимодействие лазерного излучения с веществом, дипольное взаимодействие, наночастицы, наноструктуры.