

Simulation of Conditions for Fabrication of Optical Nanowaveguides in the Form of Chains of Spherical Metal Nanoparticles by Electrostatic Functionalization of the Process Substrate

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Abstract—A method is proposed for electrostatic functionalization of substrates used to prepare ordered structures composed of closely spaced plasmon-resonant nanoparticles. The method ensures selective deposition of nanoparticles from the bulk of a colloidal system onto the substrates. This method is based on placing a metal nanotemplate of a required configuration at the opposite side of a substrate, with an electric potential being applied to the template. A mathematical model is developed to ensure that the system parameters responsible for the deposition of metal nanoparticles into ordered single-domain structures on the substrate from a bulk sol in a nonuniform electric field generated by the nanotemplate correspond to the real experimental conditions. Since the degree of imperfection of the synthesized chains governs the applicability of these structures to transmission of the optical excitation at the frequency of the surface plasmon of the particles, the dependence of the degree of imperfection on the physicochemical and electrical parameters of the system is studied using the Brownian-dynamics model. The calculations of the spectral and transmission properties of nanowaveguides of this type are exemplified.

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1. INTRODUCTION

Periodic chains composed of spherical metal nanoparticles may be applied as optical waveguides in which the energy of plasmon excitation is consecutively transmitted from one particle to another along a chain [1]. Exciting plasmon on one terminal particle, we may obtain an excitation signal at the opposite end of the chain with the help of a near-field optical probe. The excitation of a surface plasmon can be spatially limited by the size of one particle in the scales much smaller than the wavelength of an electromagnetic radiation. This circumstance makes it possible to handle light energy on the subwave scale [2, 3], miniaturize optical elements [4], and provide coherent time control at ultrashort times [5, 6]. In recent years, the effect of the propagation of a surface plasmon in ordered one-dimensional structures of nanoparticles has drawn great attention due to its possible numerous applications in nanoplasmonics [7–11] and spectroscopy [12–14], as well as for the elaboration of functional elements used in new-generation computing units in which modulated optical radiation plays the role of an electric current.

Development of methods and processes for the fabrication of one-dimensional (1D) and two-dimensional (2D) superlattices based on metal plasmon-resonant nanoparticles is an important and promising applied problem. At present, such units can primarily

be produced by placing a set of periodically arranged nanoparticles as structural elements on solid dielectric substrates. The study of the properties of nanoparticle aggregates of different configurations with regard to the influence of a substrate is of interest in connection with their practical application [15].

Such periodic structures composed of cylindrical nanoelements, each being on the order of 100 nm in size, may be obtained by nanolithography [16] and block copolymer lithography [17]. However, one of the most promising methods for producing ordered structures that do not require local physical actions is based on the ability of nanoparticles to self-organize in the course of random Brownian collisions in disperse systems with liquid dispersion media. In such a system, structural self-organization may be carried out on a process substrate brought into direct contact with a colloid. In this case, particles of a dispersed phase must be adsorbed in specified bounded regions of the substrate with the formation of a required 1D or 2D configuration of particles. It should be emphasized that a waveguide must be composed of monodisperse spherical nanoparticles, because any other shape of particles leads to substantial homogenous broadening or splitting of the plasmon absorption band of a single particle. Selective adsorption of nanoparticles on a substrate may be provided by functionalization of the

latter [18], which may be implemented by different methods.

In this work, we have proposed an electrostatic method for functionalization of a dielectric substrate. This method is promising for carrying out real experiments. It is based on the use of metal nanotemplates located at opposite sides of substrates, with an electric potential being applied to the templates.

The goal of this work was to determine the conditions under which metal spherical nanoparticles are selectively deposited to form ordered structures on a dielectric substrate equipped with a nanotemplate, as well as to study the imperfection of 1D chain structures synthesized under these conditions and find the methods of its minimization.

The data obtained make it possible to simulate a real experiment.

2. MODEL

The simulation was carried out by the Brownian-dynamics method [19]. This method enables one to reproduce natural conditions of structurization using realistic potentials of interparticle interaction in arbitrary disperse systems. The particle motion was calculated in a cell, in which, at an initial time moment, N particles are uniformly distributed. The sides of the cell may be larger than the particle sizes by, on average, two or three orders of magnitude. The cell walls are specular reflecting. At each iteration step, the following motion equations are solved for each particle:

$$\begin{cases} \frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \\ m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i - \mathbf{F}_f + \mathbf{F}_c + \mathbf{F}_p + \mathbf{F}_d \end{cases}, \quad (1)$$

where \mathbf{r}_i is the coordinate of a particle, \mathbf{v}_i is the particle velocity, m_i is the particle mass, \mathbf{F}_i is the resultant of potential forces applied to the i th particle (van der Waals and elastic interactions and gravity), \mathbf{F}_c is the stochastic hydrodynamic force, \mathbf{F}_f is the force of viscous friction, \mathbf{F}_p is the force of the interaction with the nanotemplate, and \mathbf{F}_d is the force of the dipole–dipole interparticle interaction. In this work, the motion equations were solved by the fifth-order Nordsieck–Gear predictor–corrector method.

One of the dominant factors that determine the positions of particles in a regular structure is the van der Waals dispersion attractive forces. Let us describe these forces using the approximation of the Hamaker–de Boer theory [20], according to which the potential energy of the interaction between two

spherical particles with radii a_i and a_j formed from the same material is described by the following relation:

$$U_v = -\frac{A}{6} \left(\frac{2a_i a_j}{h^2 + 2a_i h + 2a_j h} + \frac{2a_i a_j}{h^2 + 2a_i h + 2a_j h + 4a_i a_j} + \ln \frac{h^2 + 2a_i h + 2a_j h}{h^2 + 2a_i h + 2a_j h + 4a_i a_j} \right), \quad (2)$$

where $h = r_{ij} - (a_i + a_j)$ is the interparticle gap equal to the sum of the thicknesses of the adsorption layers (deformed in the region of the contact), r_{ij} is the distance between particle centers, and $A = 1.60 \times 10^{-19}$ J is the effective Hamaker constant for the interaction of two silver nanoparticles in water (see references in [19]).

Passing to the limit ($a_i \rightarrow \infty$), i.e., representing the substrate as a sphere with an infinite radius, we derive the following expression that describes the Van der Waals interaction between a particle and a dielectric substrate:

$$U_v = -\frac{A^* a_j}{6 h} \left[1 + \frac{h}{2a_j + h} + \frac{h}{a_j} \ln \frac{h}{2a_j + h} \right], \quad (3)$$

where h is the gap between the particle and the substrate and $A^* = 0.24 \times 10^{-19}$ J is the effective Hamaker constant for the interaction of a silver nanoparticle with a quartz substrate [21].

In order to prevent particles from rapid aggregation in colloids, before the formation of dispersed phase particles, a water-soluble polymer was added to the interparticle medium (as applied to hydrosols). In this case, each particle being formed appears to be surrounded with an adsorption layer, thickness h_i of which may be 1–3 nm. This layer weakens the van der Waals interaction and hinders the spontaneous coagulation of particles upon their collisions. In this work, a new approach is employed to describe elastic interactions of nanoparticles [19], this method being based on the solution of the Hertz contact problem [22] concerning deformation of two balls.

The energy of the elastic interaction between two contacting spherical particles with radii a_i and a_j and adsorption layers, which are deformed in the contact region, may be described as follows:

$$U_e = \frac{4}{15} (h_i + h_j - h)^{5/2} \times \left[\frac{(a_i + h_i)(a_j + h_j)}{(a_i + h_i) + (a_j + h_j)} \right]^{1/2} \left(\frac{E_e}{1 - \sigma_e^2} \right), \quad (4)$$

where h_i and h_j are the thicknesses of undeformed adsorption layers of the i th and j th particles, respectively; h is the interparticle gap with allowance for the deformation of the adsorption layers; E_e is the effective elasticity modulus of the polymer adsorption layers (which is assumed to be the same for both particles);

and σ_e is the Poisson ratio (characteristic values $\sigma_e = 0.15$).

The energy of the elastic interaction between a sphere with radius a_j and a substrate (at $a_i \rightarrow \infty$) may be described by the following equation:

$$U_e = \frac{4}{15}(h_i + h_j - h)^{5/2}(h_j + a_j)^{1/2} \left(\frac{E_e}{1 - \sigma_e^2} \right). \quad (5)$$

Allowance for dissipative forces is of fundamental importance for spontaneous ordering of dissipative systems. Moreover, in the absence of dissipative forces in a system, coagulation of particles becomes impossible because of their elastic (quasi-elastic) reflection from one another. For spherical particles with radius a_j , the viscous friction force, which is the main factor of kinetic energy dissipation, is determined by the Stokes formula

$$\mathbf{F}_f = 6\pi\eta(a_i + h_i)\mathbf{v}, \quad (6)$$

where η is the medium dynamic viscosity and \mathbf{v} is the particle velocity.

The interaction between particles and an ambient medium with fluctuating density results in a random change in the trajectories of the particle motion, which must compensate for the friction force and preserve the mobility of dispersed phase particles. In order to realize the Brownian motion, we assume that random force $\mathbf{F}_c(t)$ has the Gaussian distribution and is a δ -correlated random process [19]. During time step Δt , a particle is permanently subjected to the action of a random force (in our case, this is the hydrodynamic force). Before each integration step, the projections of random force $\mathbf{F}_{c,i}$ ($i = x, y, z$) onto coordinate axes are selected from the Gaussian distribution with the zero mean value and deviation as follows:

$$\langle \mathbf{F}_{c,i}^2 \rangle = \frac{12\pi\eta a_i k_B T}{\Delta t}. \quad (7)$$

An important role in the spontaneous ordering of colloids may be played by the forces of tangential friction that arise upon transverse relative displacement of particles in a chain (and their slip along the surfaces of each other) [19]. These displacements occur, in particular, upon the deformation of an aggregate interacting with a substrate or displacement of particles in the course of aggregate ordering. The direction of the tangential friction force is opposite to the projection of the velocity vector of the relative motion of particles onto the plane of the contact between their adsorption layers. The magnitude of friction force \mathbf{F}_f is determined by the product of effective friction coefficient μ and the value of elastic interaction force \mathbf{F}_e :

$$\mathbf{F}_f = \mu\mathbf{F}_e. \quad (8)$$

It may be derived in a simplified form as an analog of dry friction (although, it is actually not). In this case, the friction coefficient is an effective parameter that

characterizes the degree of the interaction between the adsorption layers of contacting particles.

Let us calculate the force of interaction between a thin charged metal filament (located at the opposite side of the substrate) and a metal spherical nanoparticle by the method of electrical images [23]. For this purpose, we divide the filament into elementary charges as follows:

$$q_j = f(x_j)\Lambda dl, \quad (9)$$

where Λ is the linear charge density of the filament, dl is the length of its element (which is assumed to be smaller than the particle radius by an order of magnitude), $f(x)$ is the longitudinal distribution function of the charge, and x_j is the coordinate of an elementary charge on the filament (in our case, the filament is oriented along the X axis). The $f(x)$ function is represented by a sixth-order polynomial and is introduced in order to arrange nanoparticles in the chain equidistantly rather than concentrate them at the center of the filament. In practice, this approach is implemented by, e.g., using substrates (or templates) with variable thicknesses. To be more specific, we shall assume that the filament is negatively charged. It should be taken into account that the elementary charge on the filament interacts with both the electrical image, which it induces on a spherical particle, but also with other images induced by other elementary charges (Fig. 1) [23]. In this case, the total force of the electrostatic interaction with the template is described by the following expression:

$$\mathbf{F}_p = \sum_{j=1}^n \sum_{i=1}^n \frac{1}{4\pi\epsilon\epsilon_0} \frac{q_i q_j}{|\mathbf{L}_j - \mathbf{I}_i|^2}, \quad (10)$$

where n is the number of elementary charges on the filament, $|\mathbf{L}_j|$ is the distance from the center of a sphere to an elementary charge on the filament, $|\mathbf{I}_i| = a^2/|\mathbf{L}_j|$ is the distance from the sphere center to the induced charge, $q_i = -aq_j/|\mathbf{L}_j|$ is the charge induced on the particle, ϵ is the dielectric permittivity of the ambient medium, and ϵ_0 is the electric constant.

As a whole, a metal particle is electrically neutral; therefore, the interaction with a charged filament causes rearrangement of the charges in the particle. The charges induced on the spherical particle are arranged along an arc (Fig. 1), while the compensating positive charge occurs in the particle center. To simplify the calculation of the interactions of the system of dipoles with the charges of filament elements, this system of dipoles may be replaced by one equivalent dipole moment.

Assume that the filament generates a nonuniform field with strength \mathbf{E} in the region of the particle location. Let us replace all elements of the filament by a single charge, which generates the same field strength in the region of the particle. For the dipole moment of

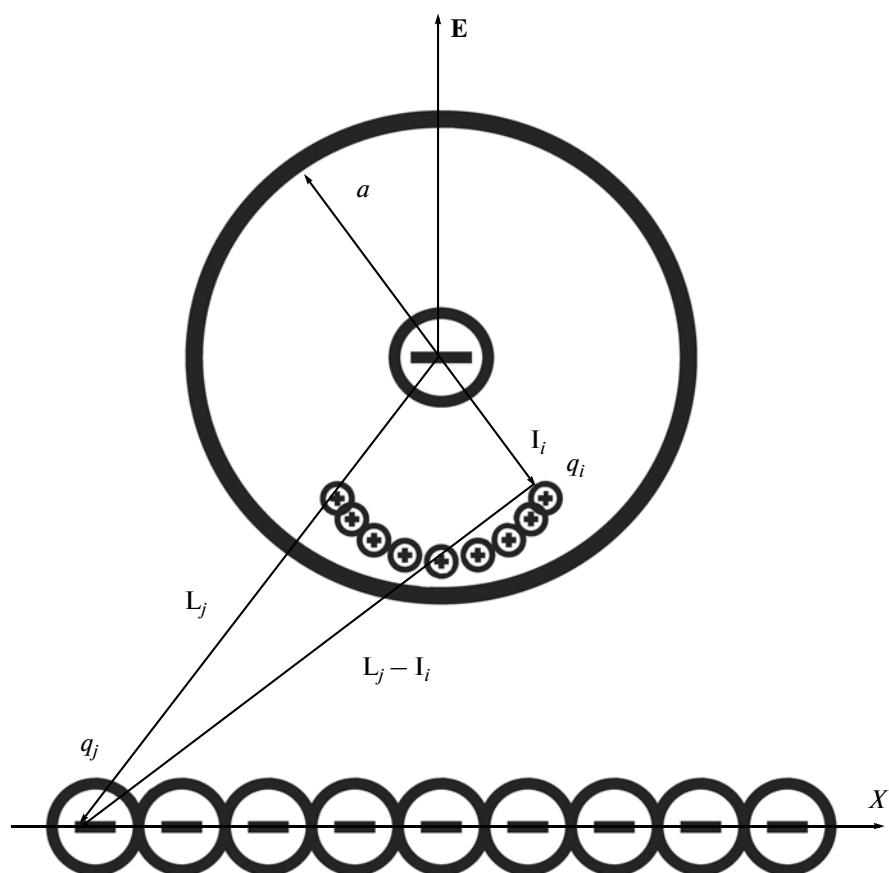


Fig. 1. Schematic representation of the distribution of induced image charges in a metal spherical particle.

a sphere, we have the expression $\mathbf{d} = 4\pi\epsilon\epsilon_0 a^3 \mathbf{E}$, while the energy of the dipole–dipole interaction between the i th and j th particles is described by the following expression [23]:

$$U_d = \frac{1}{4\pi\epsilon\epsilon_0} \frac{(\mathbf{d}_i \mathbf{d}_j) - 3(\mathbf{d}_i \mathbf{n})(\mathbf{d}_j \mathbf{n})}{r_{ij}^3}, \quad (11)$$

where $\mathbf{n} = \mathbf{r}_{ij}/r_{ij}$ is the direction vector between the centers of the interacting dipoles.

Allowance for these interactions is sufficient for describing the self-organization of nanoparticles on an electrostatically functionalized substrate.

3. RESULTS AND DISCUSSION

3.1. Study of the Imperfection of Synthesized Structures

To implement the self-organization of nanoparticles into a periodic structure, corresponding physico-chemical conditions must be created in a colloidal system. Primarily, the following parameters must be selected properly: (a) the type of the material of particles and their size-distribution function, (b) the properties of the adsorption layer on the particles (the layer

thickness and the polymer type), and (c) the properties of the interparticle medium (temperature, viscosity, ion concentration, and amount of dissolved polymer).

The discrete approach to the estimate of the electrostatic interaction force between particles and a functionalized substrate has demonstrated that, at a certain thickness of the polymer layer adsorbed on particles and magnitude of linear charge density, a narrow, rather ordered strand is formed from nanoparticles (Fig. 2a). The following main parameters were selected for the system: particle radius $a = 8$ nm, adsorption layer thickness $h = 2$ nm, linear charge density on the electrode $\Lambda = 3 \times 10^{-9}$ C/m, and substrate thickness $H = 30$ nm.

For describing the degree of imperfection of a single-stranded chain, a parameter is introduced that is, by analogy with the approach proposed in [25], determined as follows:

$$d = 1 - \frac{1}{N-1} \sum_{i=1}^N \sum_{j \neq i}^N \frac{k \cos^2 \varphi_j}{2}; \quad 0 \leq d \leq 1, \quad (12)$$

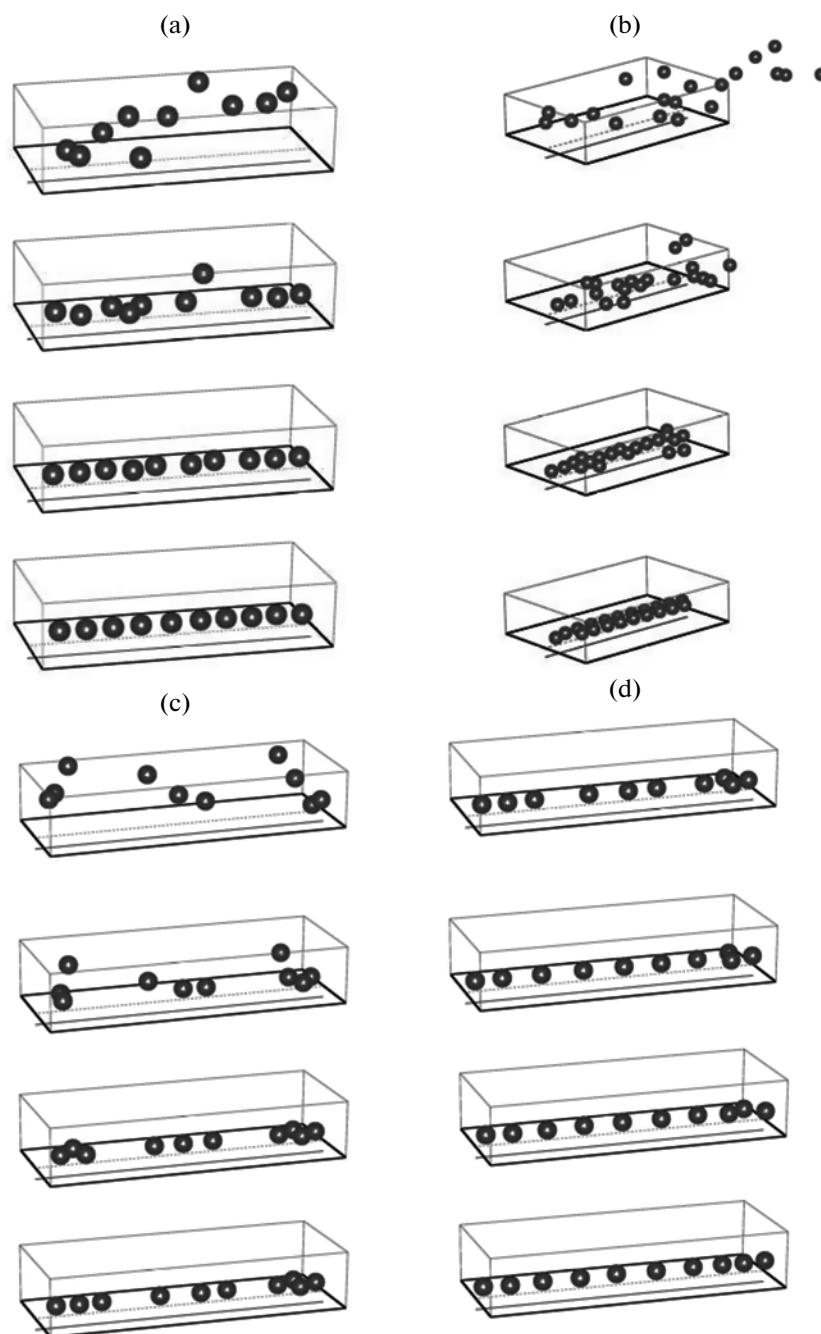


Fig. 2. Stages of chain structure formation on electrostatically functionalized dielectric substrate and possible methods of reducing imperfection: (a) formation of an ideal chain, (b) formation of a multi-stranded chain in a convective flow, (c) formation of a defective structure, and (d) reduction in the degree of imperfection by nanoparticle charging by UV radiation. The dashed line depicts the projection of the filament on the external plane of the substrate.

where N is the number of particles that compose a chain formed over the template and are located at a distance from the chain (r_{ij}) of no larger than the sum of the radii of adjacent particles (including the thicknesses of their adsorption layers); $k = 1$ and 0 for contacting particles (including the contact via the adsorp-

tion layers) and particles the adsorption layers of which are not contacting, respectively; and φ_j is the angle between the positive direction of the X axis along which the nanotemplate is oriented and radius vector \mathbf{r}_{ij} , which connects the i th and j th particles (Fig. 3a). The degree of imperfection is equal to zero for an

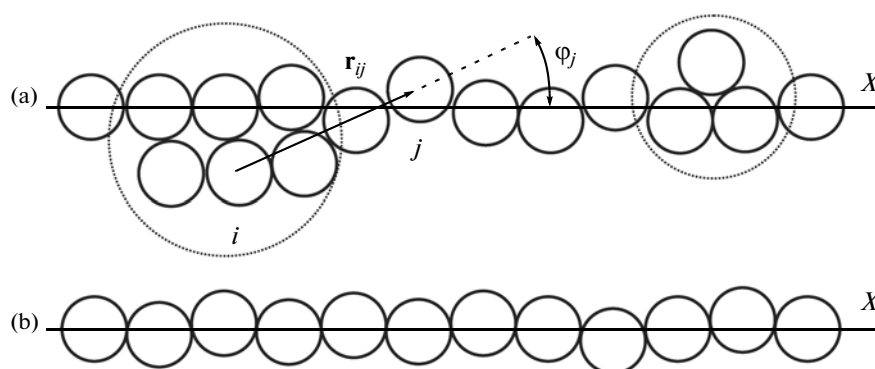


Fig. 3. Panel (a): characteristic types of defects in a chain and the determination of the degree of its imperfection and panel (b): a zigzag structure resulting from the chaotic thermal motion of particles.

ordered chain with an equidistant arrangement of particles (with no regard to the contribution of terminal particles), provided that the particle centers are located exactly along the X axis.

The dependences of the degree of imperfectness on the substrate thickness (Fig. 4), linear charge density of the electrode (Fig. 5), particle radius (Fig. 6), and adsorption-layer thickness (Fig. 7) have been plotted. It has been shown that chains composed of larger particles are more efficiently ordered. The kinetics of ordering has been found to weakly depend on the thickness of the adsorption layer; however, as the linear charge density increases and the substrate thickness decreases, the degree of imperfectness diminishes. Therewith, imperfect structures may be formed (see

Fig. 2c). Figure 3a illustrates the characteristic types of defects formed during particle deposition onto the substrate. Note that, under the described conditions, the degree of imperfectness of a formed single-stranded chain is not equal to zero, because, due to the chaotic thermal motion, particle centers lie on a weakly pronounced zigzag rather a straight line (Fig. 3b). Thus, the synthesized chains are two- rather than one-dimensional structures.

In order to reduce the degree of imperfectness of the synthesized chains, several methods have been analyzed. First, particles are deposited in a convective flow directed along the template at a bulk hydrosol velocity relative to the substrate of about 0.1 m/s. This condition facilitates the removal of unnecessary parti-

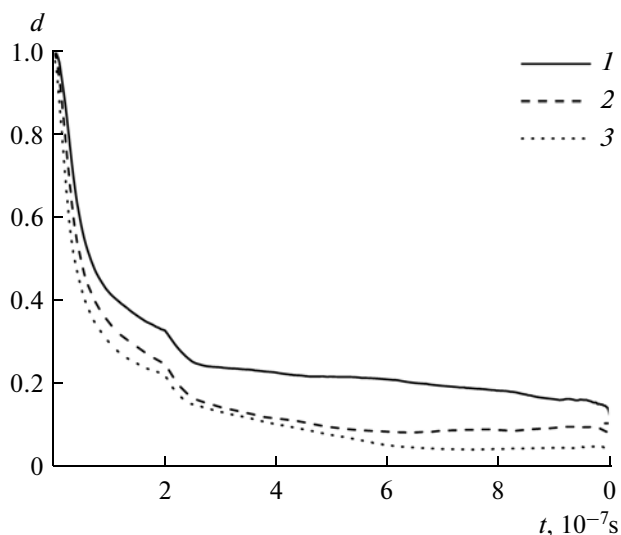


Fig. 4. Time dependences of the degree of imperfectness of a chain of particles in the course of its formation at different substrate thicknesses: (1) 40, (2) 30, and (3) 20 nm. See text for other parameters.

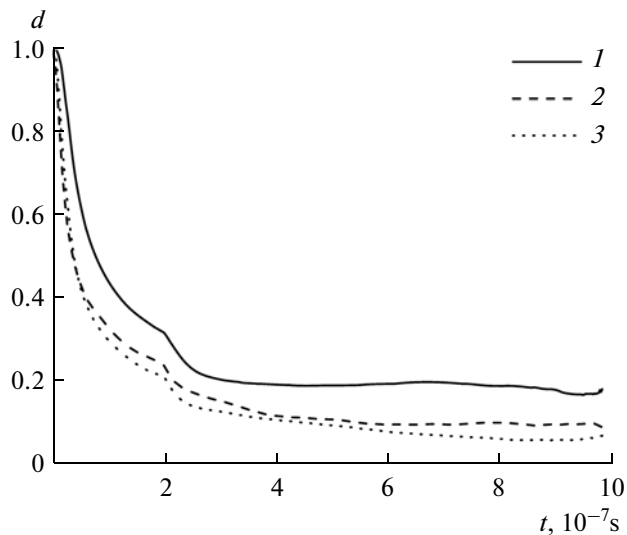


Fig. 5. Time dependences of the degree of imperfectness of a chain of particles in the course of its formation at different linear charge densities of nanotemplate: (1) 2×10^{-9} , (2) 3×10^{-9} , and (3) 4×10^{-9} C/m. See text for other parameters.

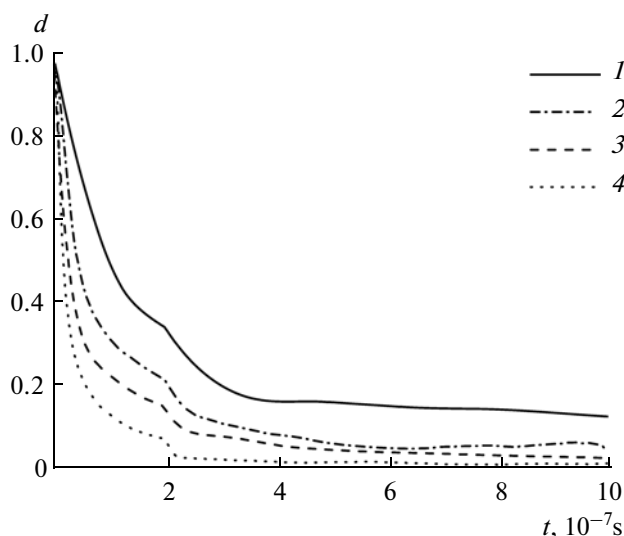


Fig. 6. Time dependences of the degree of imperfection of a chain of particles at different particle radii: (1) 4, (2) 6, (3) 8, and (4) 10 nm. See text for other parameters.

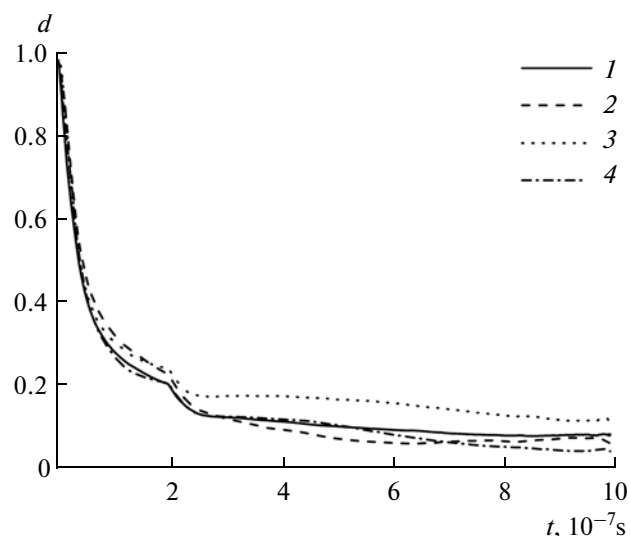


Fig. 7. Time dependences of the degree of imperfection of a chain of particles at different adsorption-layer thicknesses: (1) 1, (2) 2, (3) 3, (4) 4 nm. See text for other parameters.

cles. However, in this case, the most stable and rather ordered structure that is formed on the substrate is a two-dimensional two-stranded (or, even, multi-stranded) strip composed of nanoparticles, this strip being exemplified in Fig. 2b. As for chains of this type, it is necessary to additionally investigate their transmission and dispersion properties and compare them with those of an ideal single-stranded chain.

Second, in order to diminish the imperfection of the chain, the method of particle charging with the help of UV radiation using the electron photoeffect (Fig. 2d) was analyzed. Under these conditions, the additional electrostatic repulsion of positively charged particles increases their mobility in the process of selective deposition onto the substrate, destruction of defects, and ordering of the chain as a whole. Moreover, the charging of particles increases their attraction to the template bearing a negative potential. On average, the charge on the particles has a magnitude on the order of 1.6×10^{-18} C. However, this method of defect elimination increases the interparticle gap, thus degrading the optical and transmission properties of the chain.

Third, the possible action of mechanical vibrations with a frequency of 20 MHz excited in a quartz substrate using the piezoelectric effect was analyzed. Under these conditions, a fluctuating force directed normal to the substrate promotes periodic short-term detachment of particles from the substrate and, then, their more ordered arrangement over the template under the action of a random force.

In addition, in the case of excess particles deposited near a nanotemplate, the defects of the chain may be eliminated by combining this method of action on

particles with the development of a convective liquid flow directed normally to the template in the plane of the substrate. The detachment of particles weakly bonded to the substrate (outside the template) makes it possible, with the help of the convective flow, to remove undesired particles that create defects. Under these conditions, the degree of imperfection of the synthesized chain decreases (Fig. 8). Stage 3 in Fig. 8 corresponds to the gradual removal of unnecessary particles from the region located immediately over the template to the region outside the substrate. The strong oscillations of the imperfection in this region are due to the random character of the resultant of forces and random deformations of the substrate being formed. Final stage 4 describes the chain formation from the moment of the removal of unnecessary particles from it to the moment of its stabilization.

In addition, we have shown the possibility of using nanotemplates of different configurations to obtain more complex structures of nanoparticles—in particular, arc- and angle-shaped chains (Fig. 9).

3.2. Spectral and Transmission Properties of One-Dimensional Chain Structures Composed of Silver Nanoparticles

The application of periodic one-dimensional structures for the transmission of induced optical radiation in connection with the problems of nanophotonics is exemplified below by the results of calculating the optical properties of a quasi-periodic one-dimensional structure composed of spherical silver nanoparticles [26]. Figure 10a illustrates the plasmon absorption (extinction) spectra of a quasi-periodic chain

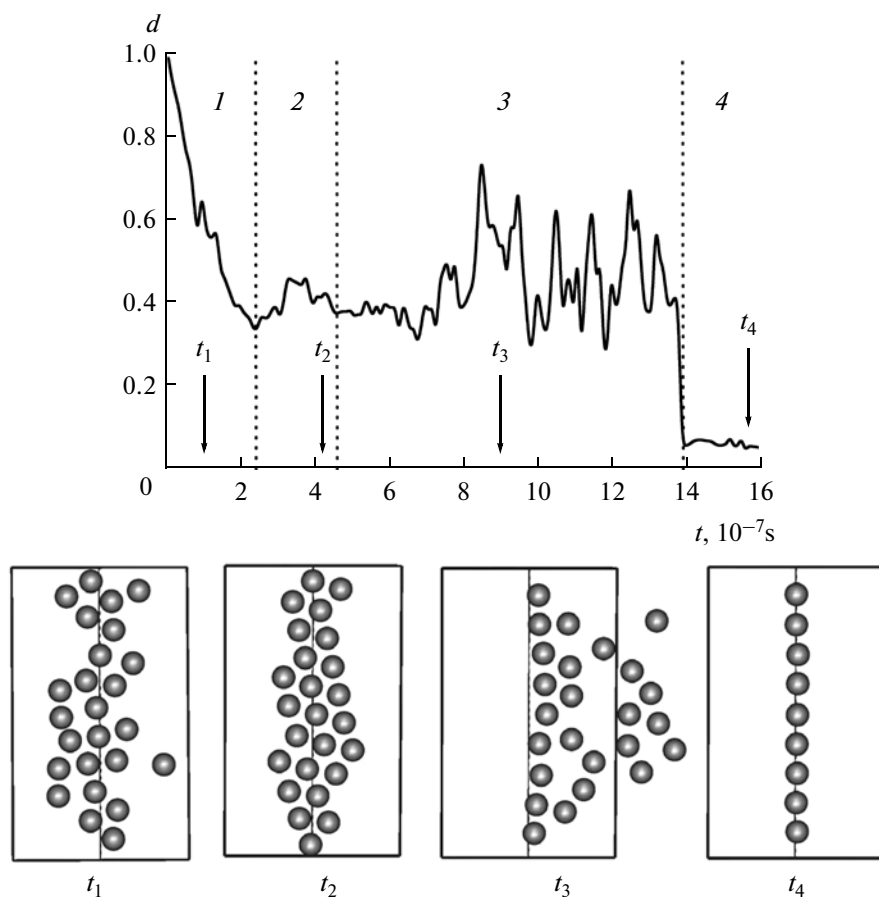


Fig. 8. Time dependences of the degree of imperfection of a chain of particles at different stages of its formation: (1) deposition of particles onto substrate, (2) formation of a stable imperfect structure on a substrate, (3) elimination of defects under the action of substrate vibrations in the vertical direction and a convective flow directed normal to the template in the substrate plane, and (4) formation of a stable single-stranded chain with a low degree of imperfection at the following system parameters: initial number of particles $N_0 = 25$, final number of particles in a single-stranded chain $N_1 = 9$, convective flow velocity $v = 0.25$ m/s, frequency of substrate mechanical vibrations $\nu = 20$ MHz, and average force at which substrate mechanical vibrations act on particles $F_s = 10^{-11}$ N. See text for other parameters.

structure composed of ten spherical silver nanoparticles at different polarizations of an exciting radiation. Extinction factor $Q_e(\lambda)$ was determined in [27]. The extinction spectra are similar to the spectra of the transmission of optical excitation through the waveguide. As can be seen from Fig. 10a, the transmission band strongly depends on the polarization of the exciting radiation and the interparticle distance.

The transmission properties of the same chain structure are characterized in Fig. 10b, in which they are defined by parameter $\mathbf{d}_i/\mathbf{d}_1$, which is the ratio of dipole moment \mathbf{d}_i of an i th particle to dipole moment \mathbf{d}_1 induced in a terminal particle of the chain. Here, parameter $\mathbf{d}_i/\mathbf{d}_1$ is presented as a function of the position (number) of particles in the chain. The methods for the calculation of transmission properties in terms of the dipole approximation are described in greater detail elsewhere [28–30].

The obtained dependence is strongly attenuating and sensitive to the polarization of the exciting radiation and interparticle distance. However, in the case of short chains, the extent of signal attenuation is admissible for their practical application.

CONCLUSIONS

It has been shown that periodic one-dimensional structures composed of metal nanoparticles can be obtained on dielectric substrates by the method of electrostatic functionalization of a substrate with the help of nanotemplates of different configurations. The magnitudes of electric parameters necessary for producing such structures are attainable under experimental conditions. Diverse spectral-selective nanophotonics elements applicable for the control of optical radiation in nanosized scales may be developed based on synthesized chains of plasmon-resonant particles and two-dimensional periodic structures. Possi-

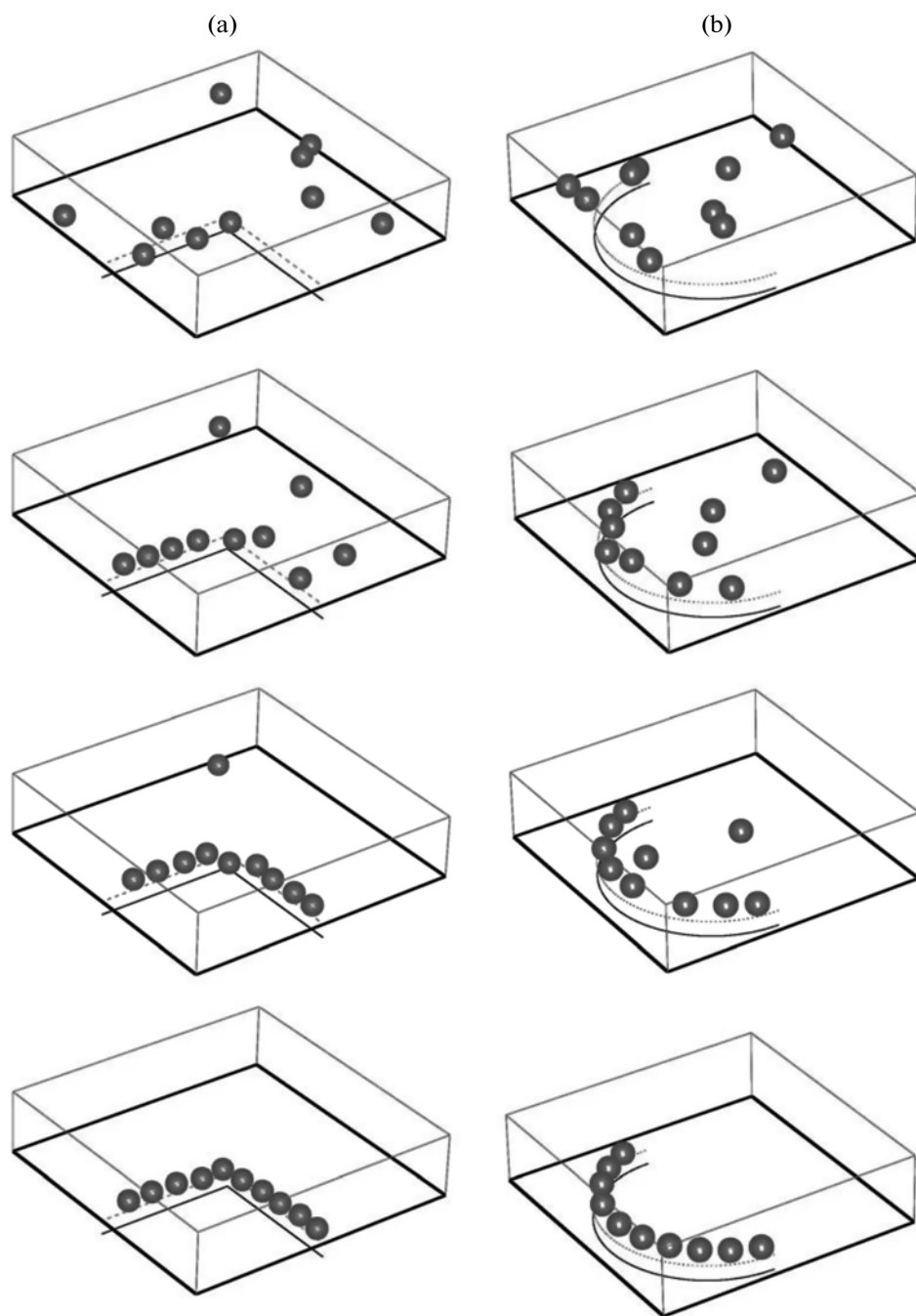


Fig. 9. Stages of the formation of chain structures with different configurations on electrostatically functionalized substrate: (a) angle-shaped chain and (b) arc-shaped chain.

ble types of defects that arise in the chains during their synthesis by the proposed method have been determined in this work. Allowance for the factor of imperfection in the calculations of the transmission, spectral, and dispersion properties will make it possible to determine the limits of applicability of imperfect chains composed of plasmon-resonant spherical particles as optical waveguides with nanosized cross sections.

The results of detailed studying the spectral, transmission, and dispersion properties of nanowaveguides of this type will be presented in a separate communication.

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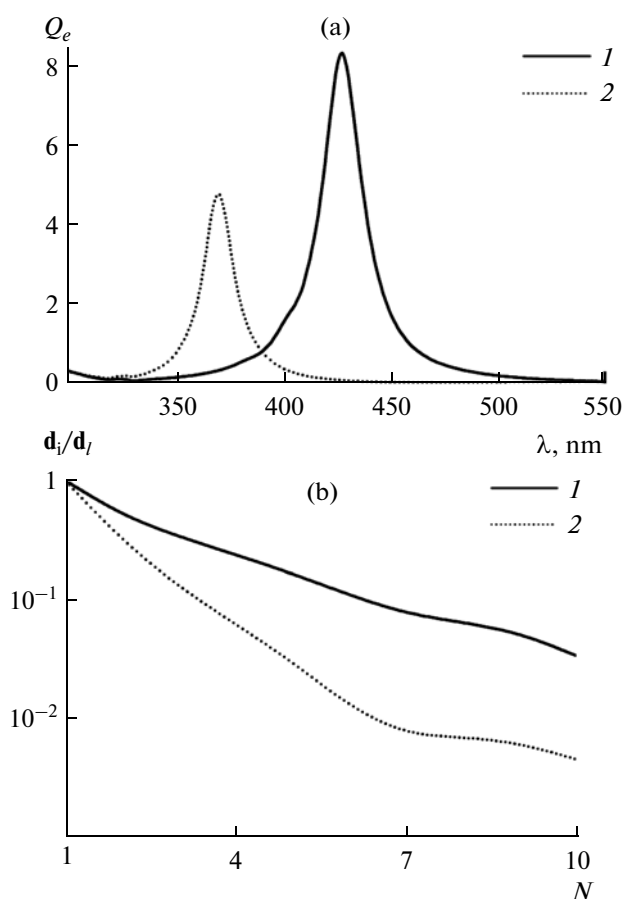


Fig. 10. Panel (a): Plasmon absorption (extinction) spectra of a quasi-periodic chain structure composed of spherical silver nanoparticles and panel (b): dependence of parameter d_i/d_l on particle position (number) in a chain. Exciting radiation is polarized (1) parallel to the chain and (2) orthogonally to the chain plane (particle radius is $a = 8$ nm and center-to-center distance is 20 nm).

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