

Three-dimensional model of quantum dots' self-assembly under the laser field action

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Abstract

This study considers the self-assembly process of quantum dots to nanostructures with the predefined geometry, which proceeds in the external resonant laser field within the three-dimensional model of Brownian dynamics. Average aggregation time of nanoparticles depending on the external field wavelength was calculated. The probability of such structures formation was estimated for the calculated average aggregation time and for the pulse duration of the laser used in the experiment.

Keywords: laser-induced self-assembly; nanotechnology; photostimulated aggregation; quantum dots

1. Introduction

Colloidal quantum dots as well as nanostructures based on them attract considerable interest of researchers due to their unique properties and possibilities of their numerous applications. [1-4]. Hindrance to wide applications of nanostructures composed of quantum dots is the absence of facile route for their production that would enable stable reproduction of the same topology of a nanostructure. The development of self-organization techniques for the formation of quantum dots' structures with pre-defined configuration are under way [5,6]. The authors of the present communication suggested an universal method of nanostructures' formation under action of external quasi-resonant field due to the self-organization of nanoparticles [7-9]. Topology and content of forming nanostructure depend on the wavelength and the polarization of external field. The first experiments [10] have shown the principal possibility of pairs' formation from an ensemble of chaotic colloidal quantum dots. It was demonstrated that if the wavelength is chosen to correspond the maximum of dipole-dipole attraction of a pair of particles then up to 50% of initially solitary particles become aggregated into pairs. However, 2D model calculations that were performed earlier do not allow ultimate analysis of the results obtained in the above cited experiment. Present communication reports on the results of 3D modeling of the quantum dots' self-assembly in the external field that allow complementing and generalizing its peculiarities.

2. Calculation Model

As it is known, important role in the process of quantum dots' aggregation is played by the shape of potential curve [11-12]. Herein, the cumulate potential of pair interaction includes van der Waals forces (responsible for attraction of particles) as well as forces preventing spontaneous aggregation of nanoparticles (electrostatic and elastic repulsion). [13]. Since spontaneous aggregation leads to formation of structures with uncontrolled geometry, it is necessary that repulsion between particles prevailed the attraction in the absence of laser field. On the other hand, the presence of external action, in our case, quasi-resonant laser field allows controllable reducing of the potential barrier height, and since the process is of resonant nature, the geometry and content of the forming structure can be controlled, too.

Preliminary modeling of this process allows estimating the optimal parameters of experiment and revealing the peculiarities of nanoparticles' self-assembly process.

2.1. Interaction potential of a pair of nanoparticles

Modeling of the process was done using Brownian dynamics approach. Potential energy of pair interaction included electrostatic repulsion, van der Waals interaction and induced dipole-dipole interaction. Potential of elastic repulsion was not accounted for since it arises only when stabilizing layers of two nanoparticles become overlapped, that is after electrostatic repulsion is overridden, which moment was considered by us as the moment of two-particle structure formation.

For describing van der Waals energy, let us employ the approximation of Hamaker - de Burgh theory, according to which the interaction energy of two spherical particles with the radius r_i made of the same material is expressed [14] as

$$W_v = \frac{-A_H}{6} \left(\frac{2r_i^2}{h^2 + 4r_i h} + \frac{2r_i^2}{h^2 + 4r_i h + 2r_i^2} + \ln \frac{h^2 + 4r_i h}{h^2 + 4r_i h + 2r_i^2} \right) \quad (1)$$

where A_H is effective Hamaker constant ($A_H \approx 50kT$, here $T = 300K$, k is Boltzmann constant), $h = r_{ij} - 2r_i$, is the interparticle spacing, and r_{ij} is the distance between particle centers.

General case of electrostatic interaction of two spherical nanoparticles is described on the base of DLVO theory. Every particle in a solution is surrounded by electric double layer (EDL). When spacing between particle surfaces exceeds the

thickness of these layers λ_0 (known also as Debye-Hückel radius or the size of diffuse part of antipolar ions layer), electrostatic interaction is practically absent, while at smaller distance the layers are overlapped.

Potential energy W_e of Coulomb interaction of overlapping EDLs is:

$$W_e = 2\pi\epsilon\epsilon_0 r_i \varphi_0^2 \ln[1 + \exp(-hk_0)] \quad (2)$$

where $k_0 = 1/\lambda_0$ is the screening constant; ϵ , ϵ_0 are the dielectric permeability of the medium and that of vacuum; φ_0 is the potential at the boundary of Helmholtz layer, the thickness of which δ does not exceed the size of hydrated ions constituting it.

The switch-over from 2D case [14] to 3D one requires essential modification of the equation system for calculation of dipole moments that will have the form:

$$\begin{bmatrix} 1/\chi_0 d_{1x} & -\frac{3r_x^2 - r^2}{r^5} d_{2x} & 0 & -\frac{3r_x r_y}{r^5} d_{2y} & 0 & -\frac{3r_x r_z}{r^5} d_{2z} \\ -\frac{3r_x^2 - r^2}{r^5} d_{1x} & 1/\chi_0 d_{2x} & -\frac{3r_x r_y}{r^5} d_{1y} & 0 & -\frac{3r_x r_z}{r^5} d_{1z} & 0 \\ 0 & -\frac{3r_x r_y}{r^5} d_{2x} & 1/\chi_0 d_{1y} & -\frac{3r_y^2 - r^2}{r^5} d_{2y} & 0 & -\frac{3r_y r_z}{r^5} d_{2z} \\ -\frac{3r_x r_y}{r^5} d_{1x} & 0 & -\frac{3r_y^2 - r^2}{r^5} d_{1y} & 1/\chi_0 d_{2y} & -\frac{3r_y r_z}{r^5} d_{1z} & 0 \\ 0 & -\frac{3r_x r_z}{r^5} d_{2x} & 0 & -\frac{3r_y r_z}{r^5} d_{2y} & 1/\chi_0 d_{1z} & -\frac{3r_z^2 - r^2}{r^5} d_{2z} \\ -\frac{3r_x r_z}{r^5} d_{1x} & 0 & -\frac{3r_y r_z}{r^5} d_{1y} & 0 & -\frac{3r_z^2 - r^2}{r^5} d_{1z} & 1/\chi_0 d_{2z} \end{bmatrix} \begin{bmatrix} E_{0x} \\ E_{0x} \\ E_{0y} \\ E_{0y} \\ E_{0z} \\ E_{0z} \end{bmatrix} \quad (3)$$

where $\chi_0 = |d_{12}|^2 / \hbar(\Omega + i\Gamma)$, Ω is the detuning of external field frequency from the resonance, \hbar is the Planck constant, and Γ is the homogeneous linewidth, $|d_{12}|^2$ electric dipole moment of the first excitonic transition; $r, r_{x,y,z}$ are the lengths of the vector connecting the particle, and of its projections; $d_{(1,2)(x,y,z)}$ are the projections of dipole moments of particles 1 and 2; $E_0, E_{0(x,y,z)}$ are the modulus of field strength of external field and its projections.

Expression for dipole-dipole interaction energy of two particles can be presented as:

$$W = \frac{\mathbf{d}_1 \mathbf{d}_2 r^2 - 3(\mathbf{d}_1 \mathbf{r})(\mathbf{d}_2 \mathbf{r})}{r^5} \quad (4)$$

from which the formula for dipole-dipole interaction force is obtained

$$F_{dd} = \frac{9(\mathbf{d}_1 \mathbf{r})(\mathbf{d}_2 \mathbf{r}) - 3\mathbf{d}_1 \mathbf{d}_2 r^2}{r^6} \quad (5)$$

Accounting all forces of pair interaction allows correct description of Brownian motion in the field of laser radiation and modeling of the self-assembly of nanoparticles into pre-defined structures.

3. Methods

Within the frame of above-described model, the interaction of two semiconductor nanoparticles suspended in water at limited distance under action of external laser radiation was considered.

The problem was investigated numerically by simple time-stepping technique. At the beginning of every pass the first particle was placed into the center of bounding cubic box while second particle was placed into a random point inside the box. The dimension of the box was chosen from the requirement that at the maximum initial distance between particles $L_{\max} = 21.7 \text{ nm}$ the energy of their attraction was equal to the thermal motion energy kT [14]; consequently, the cube edge is defined to be $a = 2L_{\max} / \sqrt{3} \approx 25 \text{ nm}$.

At every calculation step the dipole moments, cumulate forces acting on the particles, the velocities of particles and their renewed spatial coordinates were calculated. The viscous friction force, van der Waals force (1), electrostatic repulsion of surface potentials (2), and dipole-dipole interaction force (4) were accounted for. Besides, at every step the particle acquired additional random momentum in accordance with Brownian dynamics.

Calculations terminated either at the step when interparticle distance had become smaller than the sum of radii or when one of the particles leaved the bounding box. First case corresponds to particles' collision and pair formation while the second case

means the fail of aggregation. Final output values calculated at every pass are the successfulness of aggregation and the required time that corresponds to the number of steps. Based on 100 repetitions of modeling pass, the cumulate probability of aggregation, the probability of aggregation per time (10ns) and average aggregation time were determined. Every pass differed by random initial position of the second particle and by random action of Brownian forces.

Calculations were done for several values of wavelength in the vicinity of resonance, that for the particles under consideration was equal to $\lambda_r = 525\text{nm}$. Radius of particles including the absorbed layer was $r = 6\text{nm}$, the density $\rho = 5.81\text{g/cm}^3$, electric dipole moment of the first excitonic transition $|d_{12}|^2 = 2 \cdot 10^{-46}\text{J} \cdot \text{m}^3$. These particles' parameters corresponded to those of CdTe quantum dots used in the experimental study of the authors [10]. Water viscosity was taken to be $\eta = 8.9 \cdot 10^{-5}\text{P}$, dielectric constant $\epsilon = 81$; laser field strength in all calculations was taken to be $E_0 = 6 \cdot 10^6\text{V/m}$.

4. Results and Discussion

Fig.1 presents the dependence of aggregation probability on the laser wavelength.. The maximum of the probability is close to 100% at the wavelength $\lambda = 535.5\text{nm}$, somewhat redshifted with respect to the resonant value for isolated particle $\lambda_r = 525\text{nm}$. This redshift evidently is due to the corresponding redshift of the resonance of closely spaced interacting pair of particles. [7-9]. Probability of aggregation steadily diminishes with the increase of the wavelength above 545nm and approaches zero at 555nm.

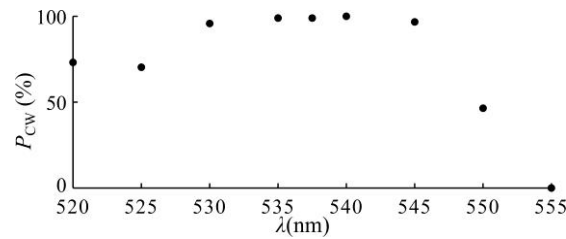


Fig.1. Dependence of aggregation probability on the laser wavelength.

Average aggregation time of a pair experiences minimum at the wavelengths close to the maximum aggregation probability and grows with the detuning off these wavelengths as plotted in Fig. 2. The aggregation wavelength is maximum this region and approaches 100%.

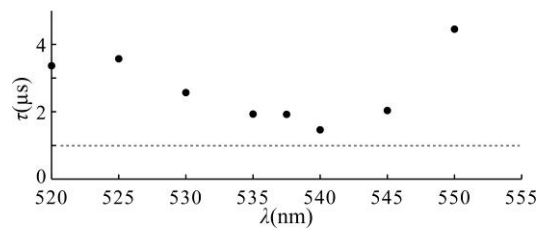


Fig.2. Dependence of average aggregation time for a pair of particles on the laser wavelength.

Average aggregation time is of order of microseconds for all studied wavelengths. Therefore, high aggregation probability can be obtained using cw laser or pulsed laser with the pulse duration of order of several microsecond. However, use of cw laser with the intensity necessary for aggregation of nanoparticles ($I = 10^6\text{W/cm}^2$) will lead to strong heating of both nanoparticles and local environment, and negative influence on the obtained structures must be expected. Pulsed lasers with microsecond pulse duration with the possibility of tuning in the broad wavelength range necessary for efficient assembly do not exist. Due to this fact, the experiments in [10] were conducted using tunable optical parametric oscillator with the required power and pulse duration 10ns. Therefore, it is worthy to estimate the probability of pair formation during a single 10ns pulse (Fig. 3).

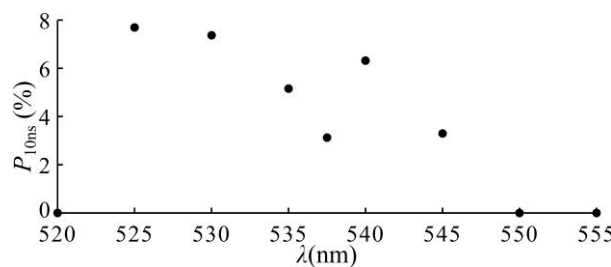


Fig.3. Wavelength dependence of aggregation probability during a single pulse with the 10ns duration.

Maximum probability is at $\lambda = 525\text{nm}$ and near to 8%. Therefore, using repeated pulsed action allows achieving formation of acceptable number of structures, which was observed in the experiment. [10] (after 3000 pulses approximately 40% of particles were assembled into pairs).

5. Conclusion

3D modeling of nanoparticles' self-assembly under the action of quasi-resonant laser field resulted in estimation of probability of this process and of characteristic time required. Maximum probability and shortest time required for self-assembly is achieved at the external field wavelength 535.5nm, which is redshifted with respect to the resonance of isolated nanoparticle, in accordance with earlier 2D calculations and 3D experiments. Average assembly time is as high as several microseconds. Since 10ns laser was used in the experiment, the probability of aggregation of a pair of nanoparticles during a single pulse was calculated, being near to 8%.

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