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Optical properties of Platonic clusters of plasmonic nanoparticles

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Abstract. **In the framework of the dipole approximation, we have developed a model of optical properties of a meta-atom consisting of spherical nanoparticles located at the vertices of Platonic solids. Based on the model, we have found and analysed the dynamics of changes in the optical spectra with a change in the length of the edge of a polyhedron. We have observed strong hybridisation and splitting of initially degenerate modes of individual nanoparticles. The obtained results can be used as the basis for the development of an optical nanosensor, which can determine the change in the chemical and biological composition of the environment.**

Keywords: *DNA origami, plasmons, nanoparticles, meta-atoms, oligonucleotides, DNA, biosensors, Platonic clusters, optical spectra.*

1. Introduction

The development of optical nanodevices is extremely important for many applications. These are biosensors [1, 2], nanolasers [3], interconnectors for computer chips, nanomodulators of light, nanodevices for drug delivery and tumour treatment (theranostics) [4, 5], etc.

The development of such optical nanodevices requires new approaches, and in the present work we propose for the first time to use for these purposes plasmon nanostructures produced using the rapidly developing DNA origami technology [6–22].

This technology is very promising, because it allows one to position nanoparticles in a nanostructure with greater accuracy than that of modern electronic or optical lithography. The fabrication of complex three-dimensional nanostructures from nanoparticles using DNA bonds is possible on the basis of canonical Watson–Crick base pairing in DNA [6]. This approach opens up unprecedented opportunities for controlling three-dimensional macromolecular structures on a large scale. Figure 1a shows a scheme of the formation of DNA-origami structures using closed single-stranded DNA (scaffold, usually DNA of bacteriophage M13 with a length of 7249 base pairs). Certain sections of the scaffold (highlighted in red) are brought together using a short 'staple' oligonucleotide (30–100 base pairs), the ends of which are complementary to those sections that need to be brought together. Using several staple crossovers makes it possible to shape an originally shapeless closed DNA like origami figures from a sheet of paper.

Since DNA has a spiral structure, one can set contact points between the strands by changing the position of the transition of the staple from one strand to another (although this is one strand, but for clarity, its individual sections are depicted as separate strands in the form of cylinders). This makes it possible to assemble the strands in flat structures (2D origami) or in three-dimensional bundles of several strands (3D origami), as well as in all kinds of three-dimensional figures (3D wireframe origami) (Fig. 1b).

Using this technology, nanoparticle nanostructures have been constructed in the form of arrays [9], chains [16–17], spirals [10] and nanorings [18]. Stein et al. [19] produced nanochains from dye molecules, while Sharma et al [20] and Fu et al. [21] generated chains of quantum dots. Recently, the feasibility of transmitting low-loss information through a waveguide made using DNA-origami technology has been demonstrated [22].

In this work, we have studied the optical properties of clusters consisting of plasmonic nanoparticles with a diameter of 10–20 nm, which are located at the vertices of Platonic polyhedra (Fig. 2). Such clusters, due to their sensitivity to the

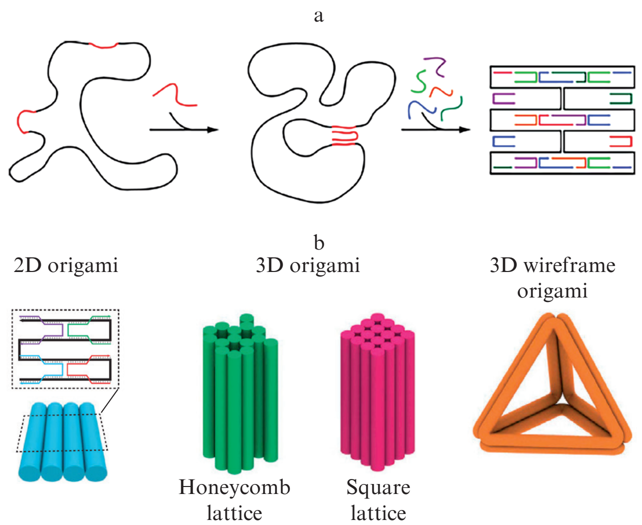

Figure 1. (Colour online) Scheme of assembly of two- and three-dimensional structures using DNA origami technology: (a) schematic [23] and (b) variants of multidimensional structures [24].

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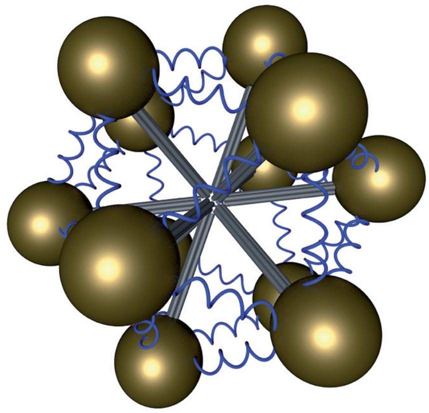

Figure 2. Scheme of an optical biosensor based on a plasmon nanostructure. Cylinders depict rigid DNA structures, and spirals represent flexible single-stranded DNA, which will 'pull together' nanoparticles and regulate their distribution over the sphere.

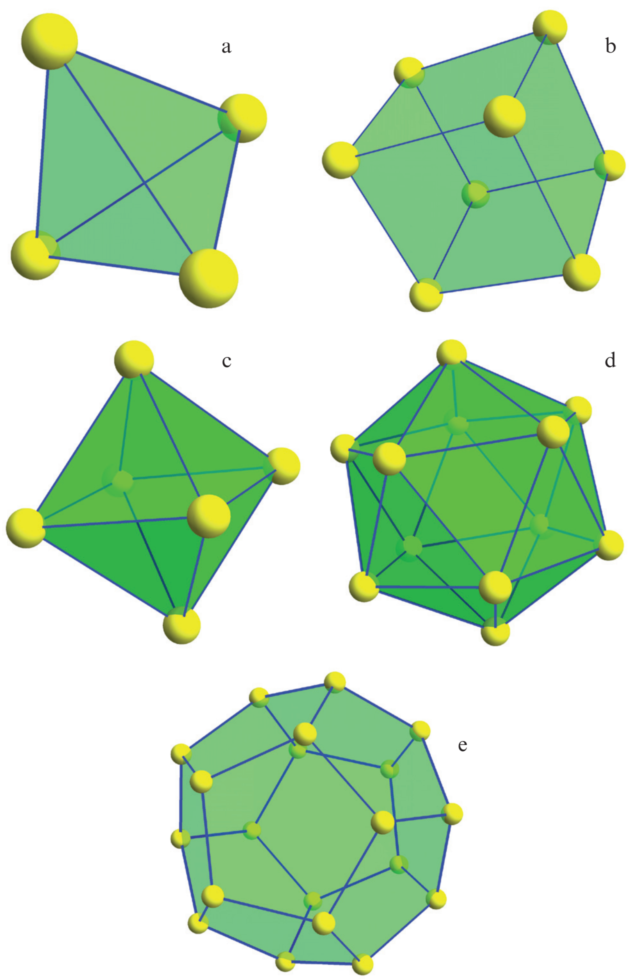

Figure 3. Clusters of nanoparticles (meta-atoms), the optical properties of which are considered in this work.

chemical and biological environment, can be used as sensors of the properties of this environment.

The radial position of plasmonic nanoparticles will be determined by rigid DNA structures (resembling a hedgehog), and the distribution of particles over the sphere will be determined by soft DNA bonds (helices), which ensure the contraction of nanoparticles with a force of the order of several piconewtons and the corresponding self-assembly. The resulting structures will change their shapes and, consequently, the optical and mechanical properties (absorption and scattering spectra) when placed on the surface of a living cell or in other biological objects with other refractive indices; therefore, by changing the spectra, it will be possible to judge the properties of these biological objects, i. e., these structures can act as a sensor.

In this work, we have examined the optical properties of Platonic clusters as functions of their topology and size. Figure 3 shows the shapes of the clusters in question.

Section 2 of this work presents a theoretical model that allows one to calculate the optical properties of meta-atoms. In Section 3, we consider the spectra of various Platonic clusters and analyse their changes as functions of size.

2. Theory of the interaction of Platonic clusters with light

An exact solution to the problem for calculating the optical properties of arbitrary clusters of spherical nanoparticles can be found using the T-matrix method [25–31]. Within the framework of the T-matrix method, Yannopapas et al. [32] considered the optical properties of clusters of six nanoparticles (linear chain, hexagon and octahedron) excited by radiation of a single molecule.

In principle, clusters with a large number of nanoparticles can also be analysed within the T-matrix method; however, such calculations require significant computational resources and, in terms of complexity, do not virtually differ from direct numerical calculations, for example, within the framework of the finite element analysis provided in Comsol Multiphasics [33].

In this regard, we consider here a model in which only the dipole moments of nanoparticles are taken into account, and the interaction between the higher multipole moments of individual nanoparticles is neglected [34]. The higher multipole moments of the meta-atom as a whole will be naturally nonzero. This model fully describes the physics of the phenomenon, is valid up to very small distances between individual particles, and can easily be implemented, for example, using the Wolfram Mathematica analytical system [35]. We have already successfully used this approach to describe the properties of three interacting dipoles [36], three nanocylinders [37], and three nanoholes [38].

To construct this theory, we suggested that nanoparticles forming a meta-atom can be represented as dipoles with isotropic polarisability

$$\alpha = R_0^3 \frac{(\varepsilon - 1)[1 - (k_0 R_0)^2/10]}{\varepsilon + 2 - (7\varepsilon/10 - 1)(k_0 R_0)^2 - (2i/3)(\varepsilon - 1)(k_0 R_0)^3}, \quad (1)$$

the expression for which is obtained by expanding the Mie coefficients [39, 40]. In formula (1), R_0 is the radius of a spherical nanoparticle; ε is its permittivity, which was taken in the form

$$\varepsilon(\lambda) = 3.7 - \frac{\lambda}{\lambda_{Pl}(\lambda_{Pl}/\lambda + 0.002i)}, \quad \lambda_{Pl} = 136 \text{ nm}, \quad (2)$$

which corresponds to the analytical approximation for silver [41]; and k_0 is the wavenumber of radiation.

If the coordinates of the meta-atom vertices are denoted by $\boldsymbol{r}_\mu$ ($\mu = 1, ..., N$), then the dipole moment $\boldsymbol{d}_\mu$ of each particle can be found by solving the system of self-consistent equations:

$$\boldsymbol{d}_{\mu i} = \alpha\left[\boldsymbol{E}_{\text{in}i}(\boldsymbol{r}_\mu) + \sum_{\nu \neq \mu}\sum_{j=1}^{3} \ddot{G}_{ij}(\boldsymbol{r}_\mu - \boldsymbol{r}_\nu)\boldsymbol{d}_{\nu j}\right], \tag{3}$$

where $\boldsymbol{E}_{\text{in}}(\boldsymbol{r}) = E_0(1, \mathrm{i}, 0)\exp(\mathrm{i}k_0 z)$ is the external electric field; and

$$\ddot{G}_{ij}(\boldsymbol{r}) = \left\{\delta_{ij}\left[\frac{(k_0 r)^2 - 1 + \mathrm{i}k_0 r}{r^3}\right] + r_i r_j\left[\frac{3 - 3\mathrm{i}k_0 r + (k_0 r)^2}{r^5}\right]\right\}\exp(\mathrm{i}k_0 r) \tag{4}$$

is the retarded Green's function of Maxwell's vector equations. System (3) consists of $3N$ linear equations (60 equations for a dodecahedron), which we solved using the Mathematica code.

If the external field in equations (3) is set equal to zero, then we can find the eigenmodes of meta-atoms. The found modes will have complex frequencies, because the system of nanoparticles in question radiates. Due to the high symmetry of the clusters under study, the total dipole moment of many modes is zero, but this does not mean that the modes do not interact with light, because even a plane electromagnetic wave excites higher (than dipole) multipole oscillations of meta-atoms. This conclusion is also confirmed by specific calculations, which will be presented in the next section.

Knowing the solutions of equations (3), we can find the meta-atom extinction coefficient $\boldsymbol{S}_{\text{ext}}$ normalised to the area $\pi R_0^2 N$ of all nanoparticles. The coefficient is found from the formula

$$\boldsymbol{S}_{\text{ext}} = \frac{4k_0\,\mathrm{Im}\left[\sum_\mu \boldsymbol{E}^*_{in}(\boldsymbol{r}_\mu)\boldsymbol{d}_\mu\right]}{2E_0^2 N R_0^2}. \tag{5}$$

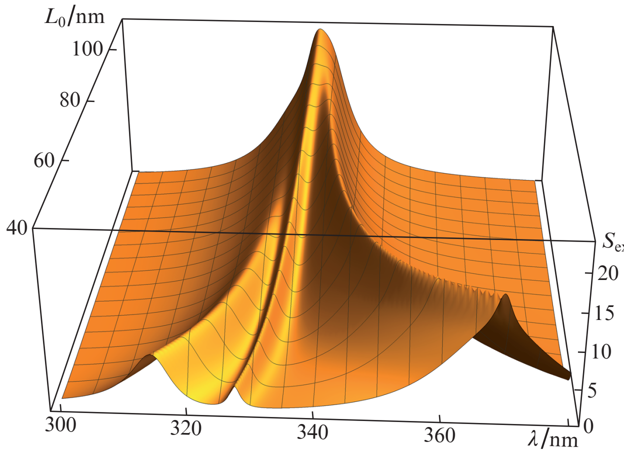

Figure 4. Extinction coefficient of a meta-atom in the form of a tetrahedron as a function of wavelength λ and tetrahedron edge length L_0; the radius of silver nanospheres forming a meta-atom is 20 nm.

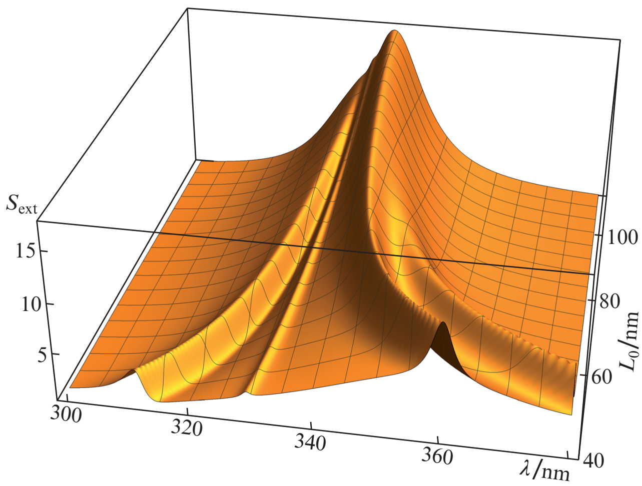

Figure 5. Extinction coefficient of a meta-atom in the form of a cube as a function of wavelength λ and cube edge length L_0; the radius of silver nanospheres forming a meta-atom is 20 nm.

3. Graphic illustrations and their analysis

3.1. Optical properties of a tetrahedron-shaped meta-atom

A tetrahedron-shaped meta-atom (Fig. 3a) has three triply degenerate, one doubly degenerate and one nondegenerate modes, $3N = 12$ modes in all, which have only five different resonant wavelengths. One of these modes is dark, i. e., it has a small dipole moment and weakly interacts with a plane electromagnetic wave.

An example of calculation results for the extinction coefficient of a tetrahedron-shaped meta-atom using expressions (3) and (5) is shown in Fig. 4 (see also Fig. 10). One can see that in the case of a tetrahedron there are three bright modes, the distance between which increases when the nanoparticles approach each other.

3.2. Optical properties of a cube-shaped meta-atom

A cube-shaped meta-atom (see Fig. 3b) has six triply degenerate, two doubly degenerate and two nondegenerate modes, $3N = 24$ modes in all, which have only 10 different resonant wavelengths. Five of these modes are dark, i. e., they have a small dipole moment and weakly interact with a plane electromagnetic wave.

An example of the calculation results of the extinction coefficient of a cube-shaped meta-atom using expressions (3) and (5) is shown in Fig. 5 (see also Fig. 10). One can see that in the case of a cube there are four bright modes, the distance between which increases when the nanoparticles approach each other.

3.3. Optical properties of an octahedron-shaped meta-atom

An octahedron-shaped meta-atom (see Fig. 3c) has five triply degenerate, one doubly degenerate and one nondegenerate modes, $3N = 18$ modes in all, which have only seven different resonant wavelengths. Two of these modes are dark, i. e., they have a small dipole moment.

An example of the calculation results of the extinction coefficient of an octahedron-shaped meta-atom using expres-

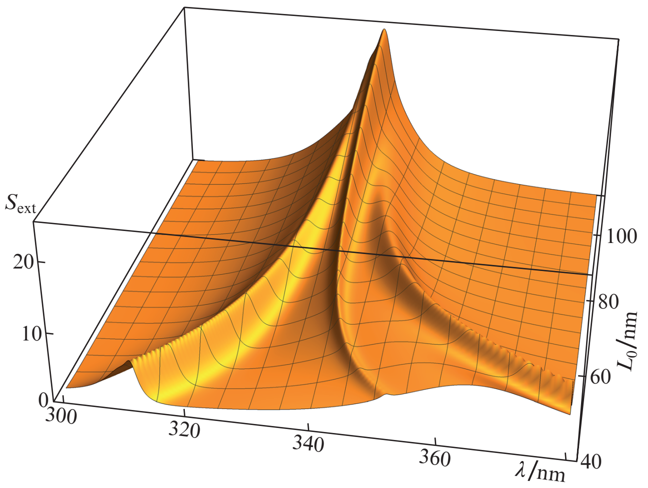

Figure 6. Extinction coefficient of a meta-atom in the form of an octahedron as a function of wavelength λ and octahedron edge length L_0; the radius of silver nanospheres forming a meta-atom is 20 nm.

sions (3) and (5) is shown in Fig. 6 (see also Fig. 10). One can see that in the case of an octahedron, as in the case of a cube, there are four bright modes, the distance between which increases when the nanoparticles approach each other.

3.4. Optical properties of an icosahedrons-shaped meta-atom

An icosahedrons-shaped meta-atom (see Fig. 3d) has three fivefold degenerate, two fourfold degenerate, four threefold degenerate and one nondegenerate modes, $3N = 36$ modes in all, which have only 10 different resonant wavelengths. Four of these modes are dark, i.e., they have a small dipole moment.

An example of the results of calculating the extinction coefficient of an icosahedrons-shaped meta-atom using expressions (3) and (5) is shown in Fig. 7 (see also Fig. 10). One can see that with decreasing edge length, the interaction between nanospheres increases, and the number of resonances increases to four.

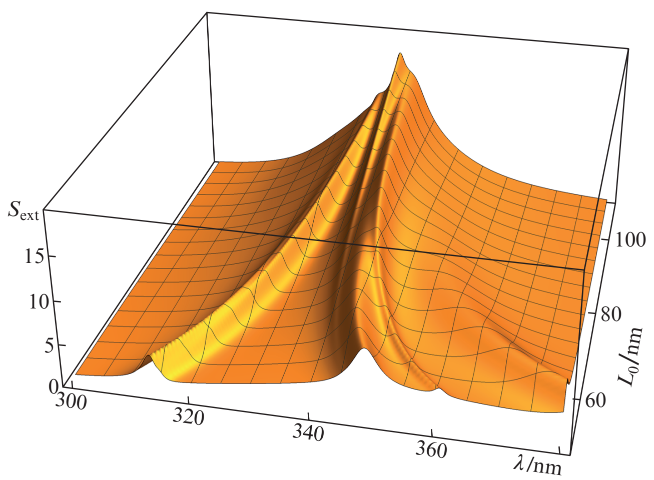

Figure 7. Extinction coefficient of a meta-atom in the form of an icosahedron as a function of wavelength λ and icosahedron edge length L_0; the radius of silver nanospheres forming a meta-atom is 20 nm.

3.5. Optical properties of a dodecahedron-shaped meta-atom

A dodecahedron-shaped meta-atom (see Fig. 3e) has five fivefold degenerate, four fourfold degenerate, six threefold degenerate and one nondegenerate modes, $3N = 60$ modes in all, which have only 16 different resonant wavelengths. Seven of these modes are dark, i.e., they have a small dipole moment.

An example of the calculation results of the extinction coefficient of a dodecahedron-shaped meta-atom using expressions (3) and (5) is shown in Fig. 8. One can see that with decreasing edge length, the interaction between the nanospheres intensifies, and the number of resonances increases to six.

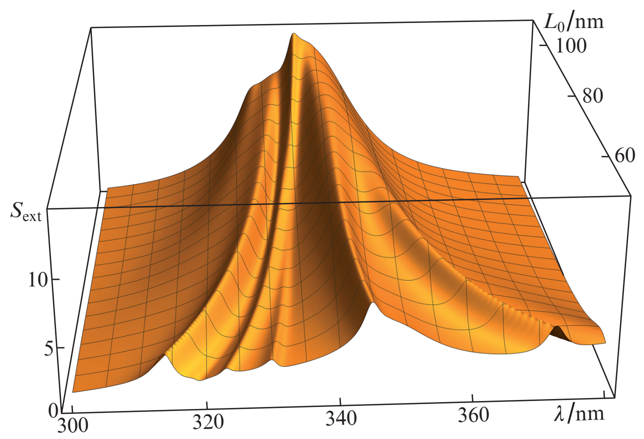

Figure 8. Extinction coefficient of a meta-atom in the form of a dodecahedron as a function of wavelength λ and dodecahedron edge length L_0; the radius of silver nanospheres forming a meta-atom is 20 nm.

3.6. Comparison of the optical properties of meta-atoms in the form of Platonic clusters

In Sections 3.1 – 3.5, we presented the dependences that describe the dynamics of the spectra of meta-atoms of a given topology with changes in the length of their edges under the influence of the environment. In this Section, we compare the spectra for the same edge length and particle radius of 20 nm, but for different topologies (Fig. 9).

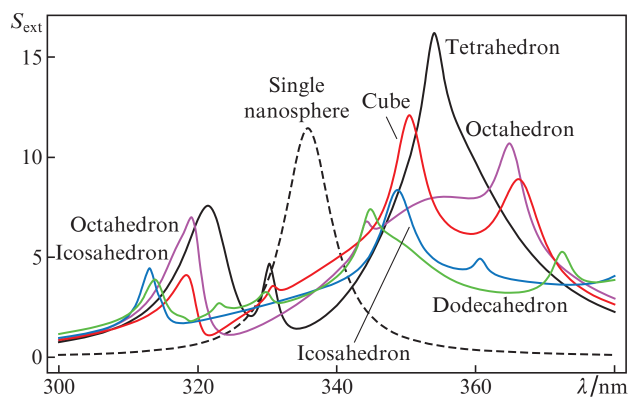

Figure 9. (Colour online) Comparison of the spectra of meta-atoms in the form of Platonic clusters with an edge length of $L_0 = 50$ nm and a particle radius of 20 nm.

With such parameters, the system exhibits large attenuation caused by both Joule and radiation losses, and some modes remain unresolved. To clarify the degree of influence of losses on the spectra, Fig. 10 shows the spectra of Platonic clusters with a nanoparticle radius of 10 nm and an edge length of 25 nm. A decrease in the overall cluster size leads to a decrease in radiation losses. In addition, when calculating the dependences shown in Fig. 10, the Joule losses in the metal are artificially reduced by 20 times compared to real ones.

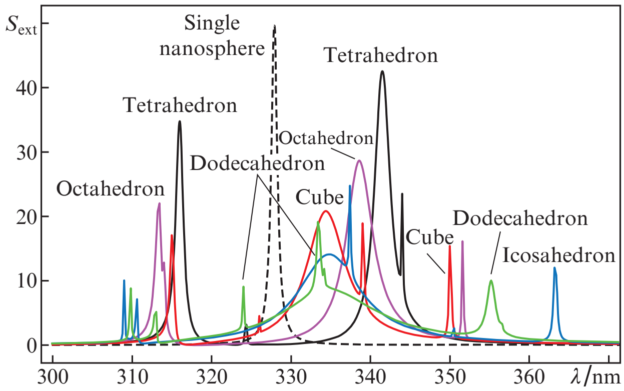

Figure 10. (Colour online) Comparison of the spectra of meta-atoms in the form of Platonic clusters with an edge length of $L_0 = 25$ nm and a particle radius of 10 nm.

A comparison of Figs 9 and 10 shows that the number of observed modes of Platonic clusters effectively increases with decreasing radiation and Joule losses. In this regard, Fig. 10 can serve as a good guide for understanding the optical properties of meta-atoms in the form of Platonic clusters and interpreting experimental data.

4. Conclusions

Thus, we have studied the optical properties of Platonic clusters, i. e., clusters whose nanoparticles are located at the vertices of Platonic polyhedra. It is shown that the extinction spectra substantially depend both on the topology of the cluster and on the length of its edge. The obtained results can be useful in the development of a new type of optical sensors, the observation of the spectra of which will allow one to study the dynamics of chemical and biological processes in a cell.

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