The development of a mathematical model of the propagation of radiation in metal nanoclusters in order to determine the possibility of controlling their properties by the SBS method

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**Abstract.** The choice of material for nanoclusters and for coating directly affects the properties of superpower capacitors. There are serious difficulties in the experimental assessment of their effect. It is of interest to adapt the method developed by authors to control these parameters. The article focuses on the theoretical analysis of the influence of the material on the properties of coatings, as well as the possibility of using the SBS method for various types of materials.

1. Introduction

For a number of years the authors have been developing SBS based method for controlling nanoparticles in colloidal solutions [1]. The essence of this method can be simply explained. The SBS spectrum has an intensity peak with a maximum at the stimulated emission wavelength and an intensity distribution in the form of one or more peaks in the Stokes or anti-Stokes region. We have successfully used it to control objects containing DNA, because DNA is a typical nanostructure. Nonlinear effects, such as SBS, arise at sufficiently low densities of radiation propagating through the solution. [2]. A similar density of radiation can be achieved by combining the fields of luminescence and laser radiation [3] giving the characteristic peak. Similar peaks are well interpreted by methods of the theory of image recognition [3-4].

The advantage of that method is in obtaining the Stokes or the anti-Stokes component of the spectrum only from particles providing high degree of coherence. [2]. Study carried out by authors has shown that such properties are present in the nanostructures of certain materials, in the DNA, and in the nano-markers for PCR or oncology [3]. We are not getting the information about the composition and about impurities of large size and tall concentration, and that enable for an easy processing and application of the method for a complex monitoring of the presence and the concentration of nanoparticles.

Currently, roll-based electro-pulse technology is analyzed to be very promising for doping the surface of electrode materials with metal nano-clusters. In the essence, that technology is carrying out physical and chemical processes that ensure the formation of a metal layer out of a colloidal solution of nano-clusters in the pore space of the electrode materials.

Particles of silver, nickel and other metals in a form of their colloidal solutions are deposited on a busophyte coating. That technology has been tested in the laboratory conditions [5].

The application of the method developed by authors enable for predicting of the properties of coatings at the stage of colloidal solution, since the uniform formation of filaments and the strength of their adhesion to the busophyte are functions of the field around the particles. However, in contrast to
the solutions considered for other applications, in this case the nanoclusters have a significant anisotropy. The analysis of the absorption spectra of anisotropic nanoclusters is complicated by the manifestation of several plasmon oscillations, each corresponding to a certain characteristic size.

On the one hand, it is of interest the study of the influence of the material on the properties of nanocoatings. On the other hand, an experimental study of the influence of dimensions on the optical properties of metal containing nano-systems is complicated. This is because the accuracy of determining the cluster size, by electron microscopy is controlled by the contrast. The latter, in turn, depends on the atomic number. The silver-containing nanocomposites is only system that has been studied to date experimentally by authors and by other researchers is. Therefore, the theoretical evaluation of the distribution of the field around the clusters into the thread for different types of metals is of considerable practical interest. For that purpose, on the basis of the COMSOL 5.5 software has been developed a mathematical model and performed calculations for three types of materials.

2. Model
The model is presented in a two-dimensional approximation, in the coordinate plane $x, y$ (figure 1). It is also assumed that the nanoclusters are stretched into a straight thread with a constant diameter and a length significantly exceeding the diameter of the cluster. Environment is the air, (figure 1; region 1 $(z > 0)$), since nano-threads are touching busofit only by their surface (figures 1, 2; region 2 $(z < 0)$). Thus, the laser radiation described in the Gauss approximation is an electromagnetic wave that falls on a dense array of very thin wires (or rods). The distance between the rods and therefore also the diameter of the rod are much smaller than the wavelength. Under these conditions, the rod matrix does not function as a diffraction grating. Instead, for light polarized along the rods, the rod matrix behaves as if it were a solid sheet of metal. Whereas, for light polarized perpendicular to the rods, the matrix is almost transparent to the electromagnetic wave. However, in the latter case, a dipole bond is created between the rods, thereby linking the electromagnetic excitation between the rods beyond the illuminated area.

![Figure 1. A coordinate plane x, y, z.](image1)

![Figure 2. Modified by nanoclusters silver busophyt thread.](image2)

The electric field model in the Drood-Lorentz approximation for the field dispersion was chosen for the calculation [6]. Electric field model is (1-3):

$$\varepsilon_r = (n - ik)^2,$$

$$\sigma = 0,$$
\[ \mu_r = 1^2, \]

where \( n \) is the actual refractive index, \( k \) is the imaginary part of the refractive index, and \( \varepsilon_r \) is the complex refractive index (4):

\[ \varepsilon_r = \varepsilon_r^0 + \sum_{j=1}^{N} \frac{f_j \omega_p^2}{\omega_j^2 - \omega^2 + i\Gamma_j \omega}, \]

\[ B = \mu_0 \mu_r H. \]

Gaussian two-dimensional beam is in the equation [6] (paraxial approximation):

\[ E_G(x, y) = E_0 \sqrt{\frac{\omega_0}{\omega_r(y)}} \cdot e^{-\left( \frac{(x-\eta(y))^2}{2R(y)} \right)} \cdot \exp(-i(ky - \eta(y) + \frac{kx^2}{2R(y)}) e \]

is approximated by the expansion of the plane wave (7):

\[ E_{pw} = \sum_{j=M_{1,0}}^{M} \sum_{j'=M_{1,0}}^{M} \alpha_{jk} \hat{u}(k_j) \cdot \exp(-i(k_j \cdot r)). \]

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}, \]

where the angular frequency is determined by the \( \omega_p \) – frequency of the plasma (9):

\[ \omega = \frac{2\pi c}{\lambda}. \]

The simplest is the case of homogeneous spherical clusters, for which there is only one surface Plasmon with a depolarization coefficient of \( 1/3 \) and a weight of 1. In this case, the expression for the absorption coefficient is greatly simplified [6] (10):

\[ p = D^2 \frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h} E_{exc}. \]

The frequency of oscillations of that surface plasmon is determined by the values of the dielectric constants of the particle and the matrix. In the case of metallic inclusions, the real part of the permittivity is negative, which can lead to resonance absorption:

\[ \alpha(\omega) = f \cdot \frac{\varepsilon}{\mu^2} \cdot \frac{\varepsilon}{c} \cdot 9 \left( -\text{Im} \left\{ \frac{1}{2\varepsilon_h + \varepsilon} \right\} \right). \]

\[ 2\varepsilon_h + \varepsilon(\omega) = 0. \]

The data for the calculations were taken from the work [7, 8].

3. Results and Discussion

Three types of materials were selected to analyze the results. They are silver, since the properties of nano-silver have been studied to some extent; and also nickel and aluminum. Aluminum was chosen because, as a result of its availability, this material might be of practical interest. A significant influence of the chemical nature of the metal on the intensity and half-width of the maximum resonant absorption is known. Figure 3 shows the typical experimental spectrum for nano-silver in colloidal solution obtained by the above method. It can be seen that spectrum has three pronounced maxima. With good accuracy such spectra can be decomposed into three Lorentzian curves, that is, three hypersonic waves are arising in the medium [9]. Most likely this suggests that silver nanoparticles have an elongated shape. That has been indirectly confirmed by an electron microscope photograph (figure 2).
Figure 3. Spectrum silver nanoclusters.

Figures 4, 5 show the distribution of the electromagnetic field strength along and across the nanoclusters. It can be seen that for silver and nickel conditions creating a plasmon resonance are observed on the interface. Thus, a narrow resonance band is observed for silver clusters, which is confirmed by both these experiments and those of other authors [10]; while only a blurred peak is present in the nickel spectrum.

An increase in the intensity of the electric field near the surface when the surface plasmon is excited, leads to an increase in the intensity of the fluorescence spectra in silver, as well as in nickel.

However, in silver the intensity of the electromagnetic field at the maximum is almost three times higher, which will certainly lead to a significant improvement in the capacitance characteristics of the capacitor. This is because when an external electric field is applied (irradiating a nanocluster with light or using a coated busophyte in a super-powerful capacitor), positively and negatively charged regions of space are created as a result of the displacement of the conduction electrons. Near these regions, the electric field strength (1) is many times greater than the field strength (2) of the light wave incident on a particle. For nickel that intensity is less. And the Stokes component, most likely, will have a lower intensity resulting in a lower power of such capacitor. However, exact comparison is not possible, because the power is greatly affected by other technological parameters. At the same time, for aluminum such resonance condition does not exist, and part of the field moves away from the surface. Obviously, this is the result of high conductivity of aluminum. We may not be able to control aluminum nanoparticles by using these methods.

Figure 4. The x-component of the electric field (1) and Gaussian beam (2): (a) in the silver nanoclusters; (b) in the nickel nanoclusters.
Figure 5. The x-component of the electric field (line 2) and the Gaussian beam background field (line 1) in the aluminum nanoclusters.

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Figure 6 shows the typical experimental spectrum for nano-nickel cluster in colloidal solution. It seems that two waves are excited for nickel in the Stokes and anti-Stokes regions. The photograph of nickel nanoclusters has been shows in the paper [5]. Nanoclusters settle not in the form of threads, but in the form of particles of various shapes. This is because nickel adhesion on the surface of carbon materials is higher than silver adhesion. Despite this, our calculations have been indirectly confirmed to experimental results.

Figure 6. Spectrum nickel nanoclusters.

The Stokes and anti-Stokes waves are stable even at low nickel concentrations only if they are excited by a laser with a wavelength in the red region of the spectrum. Obviously, this is due to a decrease in
luminescence intensity with increasing wavelength. At the same time, for silver, the Stokes wave exists in the IR region up to concentrations of $10^{-3}$ mg/L.

Experiments have shown that an increase in the size of nanoparticles from the initial 5–30 nm to 1–2 μm occurs in a colloidal solution. Evolution of the shapes of nanoparticles from spherical to spherical particles of larger diameter, crystalline and lamellar is observed. The growth of spherical particles occurs due to the fusion of small nanoparticles and their “dissolution” in larger nanoparticles. The rate of evolution depends on the parameters of the process of creating a colloidal solution. We used our method to control the dynamics and stability of such compounds. A study of the dynamics of the spectra showed that the transition from spherical to lamellar particles is accompanied by the appearance of a stable additional maximum in the region of the Stokes component. The value of the logarithm of the intensity at each of the maxima remains a linear function of the concentration of nanoparticles. The process of sharp fusion of nanoparticles into clusters leads to the appearance of several maxima at once in the Stokes or anti-Stokes region, while the linearity of the above characteristics is violated.

4. Conclusions

1. The model was developed for the distribution of the electromagnetic field of constant intensity by coherent radiation for wavelengths of 670-1017 nm.

2. Calculations were made with the COMSOL software package. The results allow authors to highlight the influence of the type of material on the properties of the coating.

3. It is shown that the best material for coating the busophyte substrate in terms of improving the capacitance characteristics is silver due to the formation of resonance at the cluster surfaces. The same phenomena, but of lesser intensity, can be observed at the surface of nickel. Aluminum does not create conditions for the formation of plasmon resonance, and, as a consequence, the increase in the capacity of the condenser can be achieved only by increasing the surface of the product.

4. It is shown that the developed method for monitoring the presence and the concentration of metal nanoparticles in colloidal solutions is not applicable to all materials.

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