The method of structural study of aggregates of plasmonic gold nanoparticles by UV/visible spectroscopy

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Abstract. The problem of obtaining nanostructured silicate glasses containing silver or gold particles and their agglomerates in recent years is one of the topical directions of photonics. The main advantage of gold in glass nanoparticles is the localized surface plasmon resonance (SPR). Due to their unique optical properties, these objects are used for optoelectronics devices as nano-antennas and biosensors. The position and shape of the SPR can be tuned to the desired wavelength in the visible and near infrared regions, varying the size, interparticle distances, and the dielectric medium in which the particles are located. The aim of this work is to analyze the optical spectra of gold nanoparticles implanted in silicate glass by irradiation with an ultraviolet laser and subsequent purification, and to determine of interparticle distances and particle sizes from the SPR spectra. For the theoretical description of optical spectra, the T-matrix approach was used, which allows to model the scattering of an electromagnetic wave by agglomerates of spheres, which correspond to studied agglomerates of nanoparticles. The application of this approach allowed to determine the structural parameters of aggregates, including averaged size of particles, average interparticle distance, statistical distributions over sizes and interparticle distances.

Keywords: nanophotonics, T-matrix method, surface plasmon resonance, gold nanoparticles.

1. Introduction

Nano- and meso-photonics is one of the most perspective directions of development in the digital technologies, in which photons from the visible spectral range play the role of electrons in semiconductor technology. The potential advantage of photon technology is high speed data transfer and processing, as well as miniature size of devices and high energy efficiency. One of the key problems in the creation of nanophotonics devices is the problem of localizing the light energy at the scale of nanometers. One of the possible solutions is usage of noble metal nanoparticles, in particular, silver or gold or their alloys. The these chemical elements are chosen since their frequencies of collective electron oscillations (called plasmon oscillations or plasmons) are in visible light regions and are well separated from inter-band transitions, which opens the possibility of the effective localization of the energy of light wave on a nanoscale scale due to the strong coupling between electrons and photons in a plasmon resonance state. At the same time, the tuning of the position and bandwidth of SPR spectrum can be performed by variation of atomic structure, size of nanoprticles and degree their agglomeration, system dimensions. Due to the possibility of the light wave localization, gold nanoparticles have great perspective for use in medicine [1], optoelectronic devices [2] and the creation of elements for the solar energy

conversion [3]. For the effective development of new applications of plasmonic nanoparticles is vital to be able to predict the optical properties of the material before synthesis. To achieve this goal, a method of modeling optical spectra based on the T-matrix method is proposed in this study.

Another important feature of this work is the method of obtaining plasmon gold nanoparticles and their arrays in near-surface region of glass, based on the use of UV laser irradiation with energy below the ablation threshold to minimize the damage of the matrix. This method allows to obtain plasmonic nanoparticle arrays with tunable resonance characteristics by variation of laser irradiation parameters. In this approach the region of nano-modification of the glass can be determined by the laser template, which is more precise then the spot size of the heating element [4]. which is very important for the construction of nano- and meso-photonic and plasmonic devices, such as nano-antennes, waveguides and nano-detectors.

2. Experiment details

In this work, a silicate glass of the composition was used:75.4 % SiO_2, 4.2 % Na_2O, 7.1 % B_2O_3, 4.3 % MgO, 8.2 % CaO, 0.7 % Al_2O_3, 0.3 % K_2O, 0.02 % SnO_2. The surface of the glass was previously coated with a gold film thickness of 70 nm (Sputter coater EMITECH K550; current: 20 mA, Ar pressure: 10^{-1} mbar), which was exposed to an ultraviolet laser (Lambda Physik LPX 315, wavelength: 193 nm, pulse duration: 20 ns, intensity of laser radiation is 140 mJ/cm^2). The paper [5] shows that the thickness of the film after irradiation with the first laser pulse depends on the laser beam intensity. Thus, the laser irradiation intensity was chosen so that, on the one hand, the gold film thickness was minimal after the first laser pulse, and on the other hand did not exceed the ablation threshold. The first laser pulse breaks the film, and the subsequent contribute to the gold particles penetration into the near-surface layers of glass. Figure 1 shows shots of the scanning electron microscope of the film surface before irradiation with a laser and after exposure to 50 laser pulses, which show the destruction of the film as a result of laser action. To obtain information on the particles formed in the near-surface layer of glass after irradiating the film with 50 laser pulses, the film remains were removed from the glass surface by acetone.

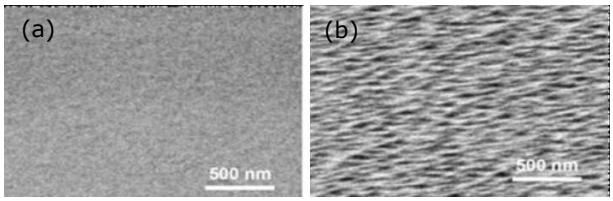

Figure 1. SEM images (tilt angle 80°) of the surface of gold coated float glass (a) before laser irradiation; (b) after 50 laser pulses.

Optical spectra were measured in extinction mode using a UV/vis/NIR spectrometer (Perkin Elmer, Lambda 900) in the wavelength range from 300 to 800 nm. To reduce the spot size to the areas irradiated by the laser, we used a circular aperture 3 mm in diameter. The optical density was calculated as $OD = \log_{10}\left(\frac{I_0}{I}\right)$, where I_0 and I are intensities of incident and transmitted light. The residual optical densities considered in the following is obtained after subtracting from the observed OD the optical density of basic glass, which does not contain nanoparticles.

3. Theoretical methods

The surface plasmon resonance (SPR) strongly depends on the type of metal, the dielectric properties of the surrounding medium, and the geometric characteristics of the nanoparticles. The latter includes not only the shape or size of individual nanoparticles, but also the local the nanoparticles position that can form nanoparticle agglomerates. The size effect has been thoroughly investigated and has many applications [6, 7], in contrast to the effects of agglomeration of nanoparticles. The physics of interaction between the particles is well established [8], and the relationship between the experimentally observed spectrum and the arrangement of nanoparticles in agglomerates has not yet been studied at the quantitative level. The theoretical description of the SPR spectra can be performed at different levels: from the quantum calculation of collective oscillations of electrons to the analytical description constructed within the framework of the Mie theory. The first mentioned approach is based on the time-dependent theory of the density functional (DFT). However, the calculated load of such an approach is great. In most cases, less demanding approaches to computing are used [9], based on the continuum models of nanoparticles. All material properties are accounted for by a frequency-dependent macroscopic dielectric constant. The method of discrete dipole approximation (DDA) [9], the Mie theory and the T-matrix method describe the SPR spectrum in the framework of classical representations and are based on solving the Maxwell equations [10]. The structure of the approach of the DDA method assumes a numerical solution of the equations and requires a huge amount of time resources even when using high-performance technique in comparison with the Mie theory and the T-matrix method, which assume the expansion in a series of vector spherical harmonics of an analytical solution of Maxwell's equations and the determination of the expansion coefficients by numerical methods. The Mie theory provides a reliable field distribution and allows quantitative description of the SPR spectrum dependence on the single nanoparticle size and is a particular case of the T-matrix method that allows obtaining information on the particles aggregate and also determining the agglomeration degree of the nanoparticles.

The high computational efficiency of the T-matrix method opens up broad prospects. For example, in Figure 2, the extinction spectra of periodically ordered arrays of gold nanoparticles located at the apex of a cubic lattice with the parameter 21 nm are given. The particle size was 16 nm, so that the gap between them is 5 nm. The need to consider such structures is due to the fact that they can be used as detectors, optical antennas [11] and metamaterials. Figure 2 shows that the characteristics of the surface plasmon resonance (the position of the maximum, the width of the resonance curve) of a three-dimensional periodic array of nanoparticles depend on the number of particles in the array.

In this paper, the T-matrix method is applied to disordered agglomerates of gold nanoparticles. In a number of experimental studies it was shown that SPR spectrum depends on the nanoparticles packing, and this effect is often called '*plasmon coupling*'. This coupling is short-ranged and decays as the gap between the particles increases to values on the order of particle size. For example, for the chains of gold nanoparticles, the experimental [12, 13] and theoretical [14, 15] studies demonstrate the saturation behavior at about ten particles. Thus, only a finite group of particles effectively interacts, and the interaction between more distant randomly located groups can be neglected. The saturation effect of SPR with respect to the nanoparticles number in the agglomerate allows one to expect that the SPR spectrum can be described theoretically using only the finite group of nanoparticles.

4. Results

To describe the experimental SPR spectra, an external Python script, wrapped over MSTM executable, was developed [16], in which the nanoparticles coordinates and their radii were varied to achieve the best agreement of the experimental UV/vis and theoretical spectrum.

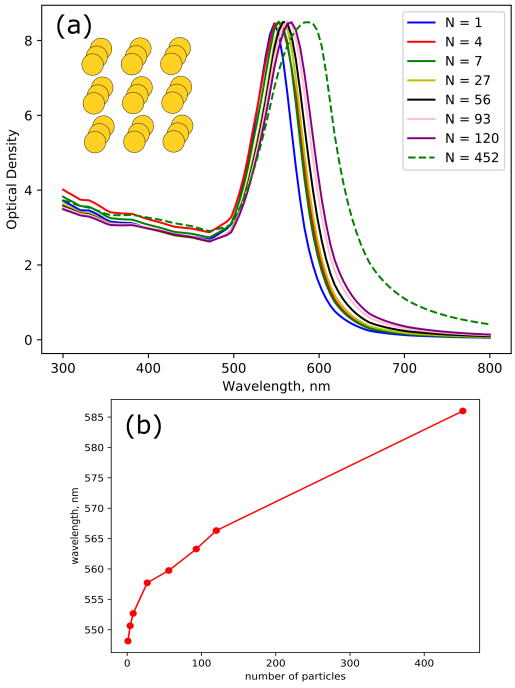

Figure 2. a) Extinction spectra of ordered three-dimensional mesh of gold nanoparticles with 16 nm diameters and interparticle spacing of 8 nm corresponding to different number of particles in the array; b) Dependence of the SPR maximum wavelength on the number of particles in the array.

Two more parameters, varied in the fitting, are the constant background contribution, which should be considered to account for the modification of the matrix during the nanoparticles formation by laser irradiation; and the scaling factor, which depends on the depth of the nanoparticles and their density. The cases of overlapping spheres are detected prior the MSTM run and are discarded, since for this case the MSTM approach is not applicable. The dependence of the gold dielectric constant from the wavelength is taken from the experimental data of Johnson and Christie [17].

Figure 3 shows the results of fitting of the experimental SPR spectrum of gold nanoparticles in the silicate glass near-surface layer obtained by irradiation of gold film by 50 laser pulses. For the obtained set of spheres, simulating the aggregate of nanoparticles, the geometric characteristics of gold nanoparticles averaged over all particles in the agglomerate are established: the mean diameter is 15 ± 3 nm, the average interparticle distance is 30 ± 8 nm. The obtained results are consistent with observations by X-ray diffraction, EXAFS and transmission electron microscopy [5].

It is known that inverse problem in scattering theory is ill-defined and there could be multiple solutions corresponding to the same observed spectrum, so that additional stability study is required. To perform such a study of the stability of obtained result, the series of fittings of the same experimental extinction spectrum was performed using different initial configurations and different number of particles ($N = 4, 8, 11$).

Figure 4 illustrates the structure of obtained aggregates (middle section) and the

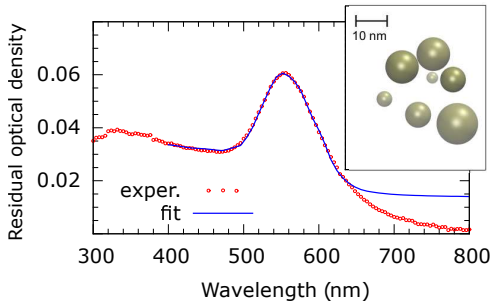

Figure 3. Comparison of the experimental and fitted theoretical SPR spectra of gold nanoparticles. The inset illustrates the structure of aggregate obtained as a result of fitting.

corresponding particle size distribution functions (the left-hand side) and the interparticle distance distribution function (right-hand side). The shown smooth distribution curves were calculated from discrete data using the nonparametric kernel density estimation (KDE) [18] method with the dynamic core width [19] as it implemented in R statistical system [20].

The results shown on Figure 4 demonstrate that the distribution functions become smoother with increasing of number of particles, and slowly converge to an average curve. The visual consideration of aggregates containing 8 and 11 particles can show weak effect of sub-aggregation of nanoparticles in groups within consideration aggregate, which is, probably, one of the consequence of saturation behavior of plasmon coupling.

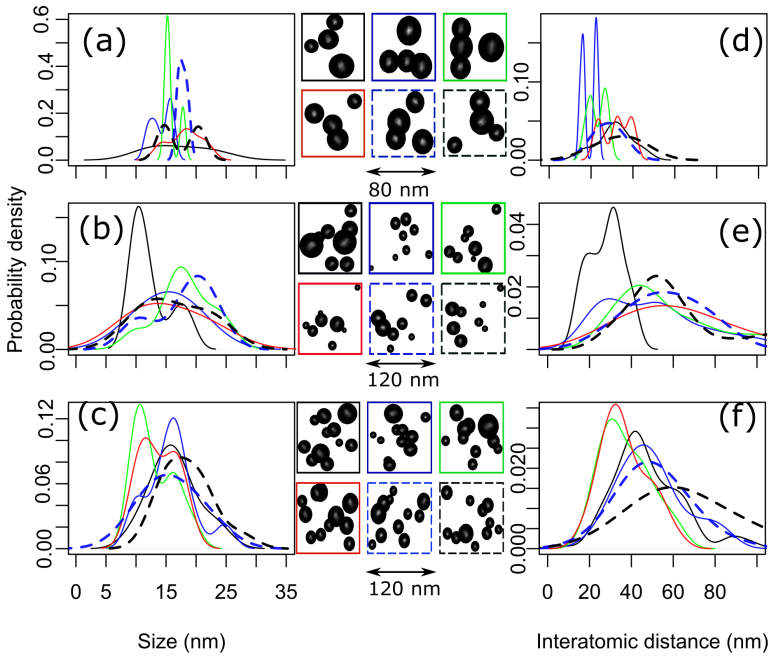

Figure 4. The resulting agglomerates (middle part) and corresponding particle size distribution functions (a, b, c) and the interparticle distance distribution function (d, e, f).

5. Conclusions

Application of the method of calculation of optical SPR spectra of agglomerates of gold nanoparticles by the multi-spheres T-matrices method, implemented in MSTM program and wrapped by a Python script, which allows to perform the variation of aggregate structure to fit experiment, allows to build model of aggregations of nanoparticles and determine their average statistical characteristics. For the considered gold nanoparticles in a glass formed under 50 laser pulses of intensity 140 mJ/cm^2, it is sufficient to consider aggregate of 8 particles, which allows us to estimate the average nanoparticle size and the average distance between them with an accuracy of ~ 5 nm.

6. Acknowledgements

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7. References

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