

CONCENTRATION-RELATED ENHANCEMENT OF THE SENSITIVITY OF SURFACE PLASMON RESONANCE OF METALLIC NANOPARTICLES TO THE CHARACTERISTICS OF A DIELECTRIC ENVIRONMENT

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We present the results of theoretical and experimental studies of the optical attenuation spectra of planar nanocomposites consisting of close-packed monolayers of metallic nanoparticles placed in different dielectric matrices. We have analyzed the dependence of the spectral position of the collective surface plasmon resonance (collective SPR) on the refractive index of the dielectric environment. The experimental samples were created by successive thermal vaporization under vacuum of a metal and a dielectric. The theoretical calculations were performed using the quasicrystal approximation of multiple wave scattering theory. We have shown that an increase in the concentration of nanoparticles of noble metals shifts the maximum of the collective SPR band toward longer wavelengths, and significantly increases the sensitivity of its spectral position to the refractive index of the dielectric environment.

Key words: metal-dielectric nanocomposites, surface plasmon absorption resonance, optical spectra.

Introduction. The recent increasing interest in metal-dielectric nanostructures including metallic nanoparticles with sizes on the order of 1–100 nm is connected with their unique optical properties, which are determined by the appearance of a surface plasmon absorption resonance on metallic nanoparticles in the visible and near IR regions of the spectrum [1]. Studies of such systems are important for creating new types of detectors, absorbent coatings, planar optoelectronic elements. All active plasmon nanostructures are used in diagnostics of the state of the surrounding medium, in chemical and biological sensors [2]. The spectral shift of the localized surface plasmon absorption resonance, which is typical for colloids of small metallic nanoparticles and is sensitive to local changes in the refractive index n of the surrounding medium, is used most often for these purposes. The values of the sensitivity factor $S = \Delta\lambda_{\max}/\Delta n$ achieved in such an approach depend on the nanoparticle material, the shape and internal structure of the nanoparticles. For example, according to theoretical estimates made for isolated nanoparticles with equivolume diameter $d_{\text{eq}} = 15\text{--}60$ nm [3], the sensitivity factor increases in the order of materials copper–gold–silver, and also in the following order of change in the particle shape: sphere (for $d_{\text{eq}} = 60$ nm, $S = 200$) — spheroid (for $d_{\text{eq}} = 60$ nm, $S = 337$) — cylinder — spherical nanoshell (for $d_{\text{eq}} = 60$ nm, $S = 350$) — bisphere — hollow spheroid (for $d_{\text{eq}} = 60$ nm, $S = 500$). With an increase in the thickness of a metallic nanoshell up to 20 nm, its sensor ability is reduced down to the sensor ability of a sphere. With a decrease in d_{eq} , the sensitivity factor S also decreases. However, it is important for the nanoparticles available today for broad application to have a shape close to spherical or cylindrical. It is difficult at this time to make nanoparticles with a more complicated structure. Therefore the problem arises of searching for other ways to improve the sensitivity factor for metal-dielectric nanostructure that are not connected with a change in the shape of the individual nanoparticles. A separate important problem is expanding the spectral range available for analysis, in particular moving into the range of the biological transparency window (700–1100 nm).

In this respect, for purposes of optical detection there is significant interest in planar self-organizing systems of metallic nanoparticles. In such close-packed ensembles of plasmon nanoparticles, due to strong interparticle electrodynamic interactions, a new localization scale for surface plasmons arises, determined by the scale of their short-range order. The electrodynamic interaction is connected with coherent scattering and multiple scattering of light in a par-

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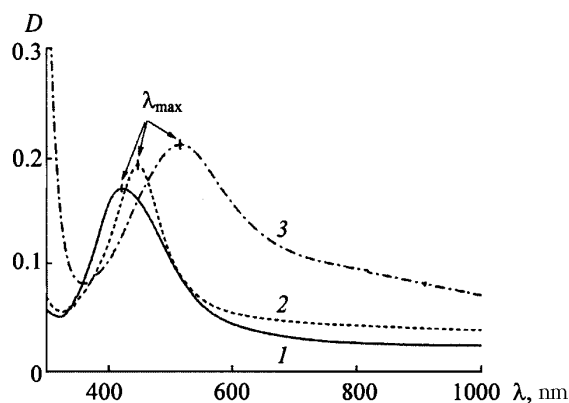


Fig. 1. Experimental optical density spectra of monolayers of silver nanoparticles ($d = 5$ nm, $\eta = 0.45$) in matrices of Na_3AlF_6 (1), KCl (2), and SiO (3) on quartz (for monolayers in Na_3AlF_6 , KCl) and glass (for the monolayer in SiO) substrates.

tially ordered ensemble of nanoparticles, and leads to the appearance of a collective surface plasmon resonance (collective SPR), the characteristics of which (in particular, the spectral position of λ_{max}) depend substantially on the microstructural parameters and topology of the ultradisperse medium [4, 5]. Collective interactions in close-packed systems of metallic nanoparticles shift the collective SPR toward longer wavelengths and create the weight prerequisites for enhancement of the sensitivity of its characteristics to the dielectric properties of the environment [6].

However, despite the relative availability and diversity of methods for making close-packed metal-dielectric nanocomposites, to date there have been no systematic studies of their sensor ability. The aim of this work was to determine the effect of the optical properties of the dielectric environment on the characteristics of collective SPR of close-packed planar systems of metallic nanoparticles. The object of the experimental studies was monolayers of silver nanoparticles. The theoretical calculations were carried out for silver, gold, and copper nanoparticles.

The Experiment. The samples were prepared in a VU-1A vacuum apparatus by successive thermal vaporization of the matrix materials and silver onto glass and quartz substrates [5, 6]. The residual gas pressure was $(2-5) \cdot 10^{-5}$ torr. The thickness of the deposited layers was monitored with a quartz sensor. The optical spectra were recorded on a Cary 500 spectrophotometer.

The silver monolayers were deposited in all cases under identical conditions on unheated substrates, where migration of atoms along the surface of the substrate or matrix layer is slow. This allows us to assume that differences in the distribution of the surface potential when different materials are deposited does not lead to significant difference in the topology of the monolayers.

Figure 1 gives the experimental optical density spectra of monolayers of silver nanoparticles in different matrices, formed on glass and quartz substrates. The thicknesses of the matrix layers were ≈ 40 nm. The micrographs obtained using an Hitachi 800 transmission electron microscope suggest that the mean size of the Ag particles is 5 nm, while the monolayer coverage parameter η , describing the fraction of the layer surface occupied by the nanoparticles, is close to 0.45. As we see, for a monolayer of Ag nanoparticles located between Na_3AlF_6 layers (refractive index $n = 1.35$), the maximum of the collective SPR band is located in the 425 nm region. For monolayers obtained under identical conditions with the same weight of deposited silver and placed between two layers of KCl ($n = 1.5$) or SiO ($n \sim 1.9$), the maximum of the collective SPR band is shifted to longer wavelengths and is detected at $\lambda \sim 450$ and 520 nm.

The long-wavelength shift of the collective SPR is especially pronounced for a monolayer of Ag nanoparticles in a ZnS matrix ($n \sim 2.3$). In this case, the broad attenuation band is located in the $\sim 600-900$ nm region. We should note that for such high values of the refractive index, in the visible region of the spectrum, multiple-beam interference effects in thin films framed by a monolayer become important. Furthermore, some effect on the characteristics of collective SPR can come from little studied effects of charge transfer between metallic nanoparticles and the semiconductor matrix.

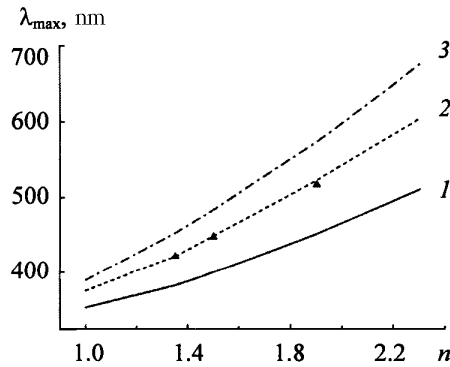


Fig. 2. Wavelength (λ_{\max}) of the plasmon resonance for individual silver nanoparticles ($d = 5$ nm) and close-packed monolayers with different surface concentrations of such nanoparticles vs. the refractive index of the matrix; 1) sphere, 2) and 3) monolayer (collective surface plasmon) $\eta = 0.45$ and 0.60 ; the points indicate the experiment, monolayer $\eta = 0.45$.

Thus the experimental results suggest that, by varying the refractive index from 1.35 to 2.3 for the matrix on which the close-packed monolayer of silver particles is placed, the plasmon resonant absorption band can be shifted over a broad range, spanning the entire visible range of the spectrum. At the same time, numerical estimates show that a change in the Frolich frequency, determining the position of the plasmon resonance for an individual nanoparticle, occurs in a significantly narrower spectral range (about 70–80 nm). Therefore the fundamentally important condition for the results given above is to ensure close packing of the nanoparticles in the monolayer.

Discussion of Results. In order to identify the features of the interaction of optical radiation with metallic nanoparticle systems when the nanoparticles are close-packed, we carried out a theoretical modeling of the processes of multiple scattering and absorption of light in such nanostructures and analyzed their effect on transformation of the spectral characteristics. We modeled the spectral characteristics of planar close-packed systems of metallic nanoparticles using the quasicrystal approximation in the theory of multiple wave scattering [4, 5], an important feature of which is taking into account electrodynamic coupling between the nanoparticles under both near-field and far-field interaction conditions. The main steps in the approach used include: description of the characteristics of single scattering using Mie theory; taking into account the size dependence of the optical constants for the metallic nanoparticles within the model of limitation of the electron free path [7]; use of the Percus–Yevick approximation to calculate the radial distribution function $g(r)$ characterizing the relative arrangement of the particles.

Numerical analysis of the light attenuation spectra in the collective SPR region was carried out for an ensemble of silver, copper, and gold nanospheres for different sizes d of the nanoparticles and the monolayer coverage parameters η , and also for different values of the refractive index n of the dielectric medium surrounding the monolayer.

Figure 2 shows the dependences of the resonant wavelength λ_{\max} on n , calculated for monolayers of silver nanospheres of different packing densities. We considered packing with $\eta = 0.45$ and 0.6 , and also the limiting case of sparse packing, for which interaction between particles becomes negligibly small and the characteristics of collective SPR coincide with the characteristics of localized surface plasmon resonance. As we see, for an increase in the concentration of nanoparticles, we observe a long-wavelength shift in λ_{\max} . For example, for $n = 1.5$, we have $\lambda_{\max} = 410$ nm for a sparse system of non-interacting particles, and $\lambda_{\max} = 465$ nm for a close-packed monolayer with $\eta = 0.6$. Furthermore, the considered $\lambda_{\max}(n)$ dependences are monotonic and practically linear, and are substantially determined by the value of η : the higher the surface concentration of nanoparticles in the monolayer, the greater the spectral shift of the maximum for the collective SPR band $\Delta\lambda_{\max}$ for a specified increment Δn , i.e., the higher the sensitivity factor $S = \Delta\lambda_{\max}/\Delta n$. We also note that the calculations performed are in good quantitative agreement with experimental data for the case with packing density $\eta = 0.45$.

We should emphasize that the concentration-related increase in the sensitivity of the collective SPR of the monolayer to a change in the refractive index of the surrounding medium (like the concentration-related long-wave-

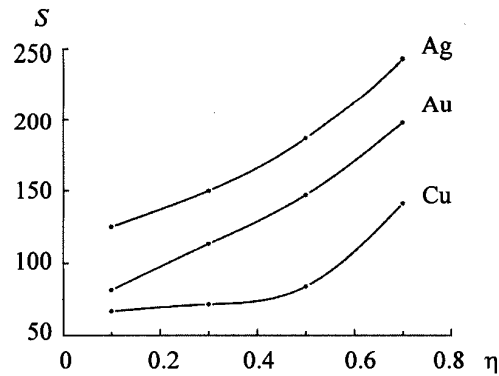


Fig. 3. Sensitivity factor S of monolayers of noble metal nanoparticles vs. their packing density ($d = 10$ nm).

length shift) is observed for small nanoparticles of size within the limits of the range for Rayleigh scatterers (for silver, this range is $d < 20$ nm).

In our opinion, the physical reason for the observed concentration-related increase in the sensitivity of collective SPR of a monolayer is similar to the reason discussed earlier in [4] for the concentration-related long-wavelength shift of the maximum in the collective SPR. It involves the fact that as the packing density of the nanoparticles increases in the monolayer, short-range order in the arrangement of nanoparticles appears and the correlated particles, located within a few nearest-neighbor coordination spheres, form aggregates such that coherent interparticle interactions effectively occur inside the aggregates. Such collective effects are connected first of all with the change in the effective field as a result of multiple scattering and near-field interactions in the plane of the monolayer. The increase in the region of localization of the plasmon excitation in close-packed monolayers, with individual particle size up to the size of the correlated aggregate, is analogous to the increase in the equivolume diameter of an individual plasmon nano object and also leads to an increase in the sensitivity factor of the nanostructure. Thus assessment of the theoretical and experimental data obtained for monolayers of silver nanoparticles with packing density $\eta = 0.45$ shows an increase in the sensitivity by a factor of ≈ 1.4 (see Fig. 2). For monolayers of silver nanoparticles with maximum packing density ($\eta = 0.7$), the calculated value of the sensitivity factor (estimated as close to $n = 1.5$) is twice the value calculated for a sparse colloid of the same nanoparticles as a result of the appearance of strong lateral electrodynamic interactions.

Figure 3 shows the results of calculation of the sensitivity factor S for monolayers of nanoparticles (estimated as close to $n = 1.5$) of different noble metals (silver, gold, and copper), as a function of their packing density. As we see, for these metals, with an increase in the concentration of the nanoparticles we observe an increase in the sensitivity of the collective SPR to the dielectric properties of the environment. For a fixed surface concentration, the highest sensitivity is characteristic for silver monolayers and the lowest sensitivity is characteristic for copper monolayers. This is probably connected with the fact that for silver nanoparticles, in contrast to gold and copper nanoparticles, the plasmon resonance absorption band does not spectrally overlap the interband absorption edge.

We note that in the low-frequency region, to which the collective SPR is shifted as a result of lateral interparticle interactions in the monolayer, interband absorption of the metals decreases. Due to the decrease in the non-radiative decay of surface plasmon oscillations in individual nanoparticles, the contribution from the radiative component increases, and the efficiency of electrodynamic interparticle interactions increases. This mechanism, as we see from the example of copper, leads to an additional concentration-related increase in the sensor ability of the monolayer.

Conclusion. Based on our investigations, we can conclude that an increase in the surface concentration of metallic nanoparticles and the associated enhancement of interparticle electrodynamic interactions lead to a shift of the surface plasmon absorption resonance of close-packed planar nanostructures to the spectral range of biological transparency, and substantially increase its sensitivity to a dielectric environment.

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