

Modeling of optical properties of hybrid metal-organic nanostructures

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INTRODUCTION

The development of modern nanotechnologies for the production of effective elements of nanophotonics, nanoplasmonics and nanoelectronics is largely aimed at the creation of hybrid nanostructures which include both plasmonic and organic components [1,2]. One of the types of such hybrid nanostructures are ultradisperse media consisting of plasmonic metal-containing nanoparticles embedded in a matrix of organic semiconductors. With dense packing of nanoparticles in such nanocomposites, interparticle electrodynamic interactions associated with near-field scattering and coherent reirradiation by particles of each other have the most important influence on their optical properties. By changing the material, size, shape or internal structure of plasmonic nanoparticles included in a hybrid metal-semiconductor nanocomposite, it is possible to adjust the degree of overlap of the spectral absorption bands of the nanocomposite components, which, in turn, affects the severity of near-field interparticle interactions. One of the ways to control the near-field scattering efficiency and absorption spectra characteristics of plasmon nanoparticles is to apply shells on their surfaces. This circumstance determines the importance of developing methods for modeling the optical properties of hybrid metal-organic nanostructures containing two-layer nanoparticles.

NUMERICAL SIMULATIONS AND RESULTS

Figures 1-3 show the spectral dependences of Q_{ext} and Q_{NF} factors for two-layer plasmon nanospheres consisting of a metallic core (Ag, Cu) coated with a dielectric shell, placed in the organic semiconductor matrix of copper phthalocyanine (CuPc). The near-field scattering efficiency factor was calculated for $R = R_2$, where R_2 is an external radius of a two-layer nanosphere. The Ag and Cu optical constants, used at the calculations, are given in [5].

As can be seen from **Figure 1**, the maximum of the SPRA band of a homogeneous silver nanosphere with a radius $R_1 = 10$ nm placed in the CuPc matrix is located near the wavelength of 450 nm. In this spectral region, copper phthalocyanine absorbs insignificantly, and its complex refractive index varies from $m_{CuPc} = 2 - i 0.12$ for $\lambda=400$ nm to $m_{CuPc} = 1.6 - i 0.02$ for $\lambda=500$ nm. The maxima of the CuPc absorption bands are located in the wavelength range of 370 nm, 624 nm and 690 nm; the value of $m_{CuPc} = 1.7 - i 0.06$ for $\lambda=450$ nm [3]. As is known, the presence of a shell on a small metal ball shifts the Frélich frequency, which determines the spectral position of the dipole maximum of the SPRA band [6]. It is important to note that the direction of the spectral shift of the maximum of the SPRA band depends on the ratio of the refractive indices of the shell and the matrix surrounding the two-layer nanoparticle. Therefore, when applying a shell with a refractive index $n < 1.7$, the maximum of the SPRA band shifts to the short-wavelength region of the spectrum regarding to the maximum of the SPRA band of a homogeneous silver nanosphere, and at values of the refractive index of the shell $n > 1.7$ – to the long-wavelength region of the spectrum. The data shown in **Figure 1** also demonstrate that the application of a dielectric non-absorbing shell to a silver nanoparticle placed in the CuPc matrix leads not only to a spectral shift of the maximum of the SPRA band, but also to a significant decrease in the maximum values of Q_{ext} and Q_{NF} . The attenuation is most significant at the short-wave shift of the SPRA. This fact is caused by an increase in the absorption of CuPc in this spectral region.

Figure 2 demonstrates the possibility of controlling the value of the spectral shift by changing the thickness of the shell on the metal core. First of all, we note that the maximum of the SPRA band for a homogeneous silver nanosphere $R_1 = 25$ nm is shifted by the wavelength $\lambda_{max} = 480$ nm due to the size effects. Herewith, $Q_{ext} = 12.5$, $Q_{NF} = 320$ at the maximum of the SPRA band. The application of quartz shells, for which the refractive index $n \approx 1.45$ in the spectral range 400 nm - 600 nm, leads to a short-wave shift λ_{max} , which increases with increasing thickness of the quartz shell. As can be seen from **Figure 2a**, the spectral position of the SPRA maximum varies from 470 nm for a shell with a thickness of 5 nm to 450 nm for a shell with a thickness of 25 nm. For a given $R_1 = 25$ nm of silver nanoparticles placed in CuPc, the available range of variation λ_{max} due to changes in the thickness of the quartz shell is 480 nm - 440 nm. The values of Q_{ext} , Q_{NF} in the maximum of the SPRA band decrease with the quartz shell thickness increase.

Comparison of the data shown in **Figures 1** and **2** allows us to evaluate the effect of the size of the metal core on the characteristics of the SPRA band and the amplification of the scattered field near the two-layer silver nanoparticle Ag@SiO₂ placed in the CuPc matrix. As already noted, an increase of the silver core radius from 10 nm to 25 nm leads to a long-wave shift of the SPRA band maximum of a homogeneous silver nanosphere from 450 nm to 480 nm, as well as to an increase in the Q_{ext} values in the maximum of the SPRA band (from $Q_{ext} = 9.3$ to $Q_{ext} = 12.5$). It is interesting to note that Q_{NF} decreases at the maximum of the SPRA band (from $Q_{NF}=800$ to $Q_{NF}=320$).

Figure 3 shows the results of calculations for Cu@SiO₂ two-layer nanoparticles placed in the CuPc matrix. Comparison of **figure 2** and **3** allows estimating the effect of plasmonic nanoparticle material on the ability to control the characteristics of their SPRA band by applying dielectric shells to the surface of metal nuclei. Unlike silver, copper has a strong interband absorption. Therefore, surface plasmon resonances in copper nanoparticles are less intense, and the SPRA bands are characterized by a large half-width. Besides, the peculiarities of the dispersion of the Cu and CuPc refractive indices lead to the possibility of the manifestation of two wide overlapping SPRA bands in the spectral range of 400-700 nm, with maxima $\lambda_{max} \approx 480$ nm and $\lambda_{max} \approx 580$ nm. As can be seen from **Figure 3**, when quartz shells are applied to a copper core with $R_1 = 25$ nm, the SPRA bands are even more blurred. At the same time, the maximum attenuation is realized in the region of 460-540 nm.

CONCLUSIONS

Results of numerical simulations show that attenuation spectra of hybrid metal-organic nanostructures, as well as the near field effects at the spectral range of absorption bands of organic component, can be regulated by changing plasmonic nanoparticle material, their size or shell refractive index and thickness. As one can see, dielectric shell allows shifting the surface plasmon resonance band of plasmonic nanoparticles absorption both to short- and long-wavelength spectral range depending on the relation between shell and matrix refractive indexes. However, for cases under consideration, the appearance of dielectric shells on the plasmonic core leads to strong decrease of the Q_{ext} and Q_{NF} values. Besides, the degree of near-field interactions with dense packaging can be regulated by the choice of the matrix in which the nanoparticles are placed.

ACKNOWLEDGMENTS

The work was partially supported by the Belarusian Republican Foundation for Basic Research (grant № 20E0A-006).

METHOD

To model the spectral characteristics of such nanostructures, the extended Mie theory was used, which makes it possible to calculate the extinction efficiency factor (Q_{ext}) and the scattering efficiency factor in the near zone (Q_{NF}) of two-layer spherical particles placed in an absorbing matrix [3,4]:

$$Q_{ext} = \frac{4m_i^2}{m_r [1 + e^n (\eta - 1)]} \text{Re} \left\{ \frac{1}{m_i - im_r} \sum_{n=1}^{\infty} [(2n+1)(\psi_n^* \psi_n' - \psi_n \psi_n'^* + b_n \psi_n'^* \xi_n + b_n^* \psi_n \xi_n' - a_n \psi_n^* \xi_n' - a_n^* \psi_n' \xi_n^*)] \right\}$$

$$Q_{NF} = \frac{(4\pi m_i R)^2}{\lambda_0^2 [1 + e^n (\eta - 1)]} \sum_{n=1}^{\infty} \left\{ |a_n|^2 [(n+1)|h_{n-1}|^2 + n|h_{n+1}|^2] + (2n+1)|b_n|^2 |h_n|^2 \right\}.$$

Here λ_0 is the wavelength of the incident radiation, $m = m_r - im_i$ – complex refractive index of the matrix, a_n, b_n – Mie coefficients, a – particle radius, $\eta = 2\pi am/\lambda_0$, Riccati-Bessel functions and their derivatives ($\psi_n, \xi_n, \psi_n', \xi_n'$), as the spherical Hankel function of the first kind of order h_n , depend on the diffraction parameter $\rho = 2\pi a/\lambda_0$. In the case of two-layer spherical particles, the Mie coefficients are functions of the complex refractive indices of the nucleus and shell, the diffraction parameters of the particle as a whole and its nucleus.

The Q_{ext} value determines the attenuation of the intensity of the incident light beam caused by absorption in the particle and scattering on it. The Q_{NF} factor characterizes an increase in the intensity of the field along the surface of a sphere of radius R when nanoparticles are introduced into the center of this sphere.

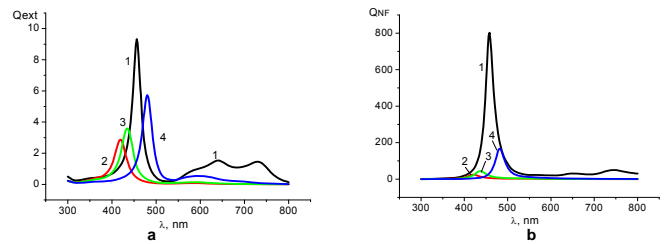


Figure 1. Spectral dependence of the extinction efficiency factor (a) and the near-field scattering efficiency factor (b) for silver nanoparticle (curve 1) and two-layer nanospheres with silver core and dielectric shell (curves 2-4) placed in the CuPc matrix. The radius of the silver core $R_1 = 10$ nm, the outer radius of the two-layer sphere $R_2 = 15$ nm. Refractive index of dielectric shell $n = 1.35, 1.5, 2.0$ (curves 2, 3, 4 correspondingly)

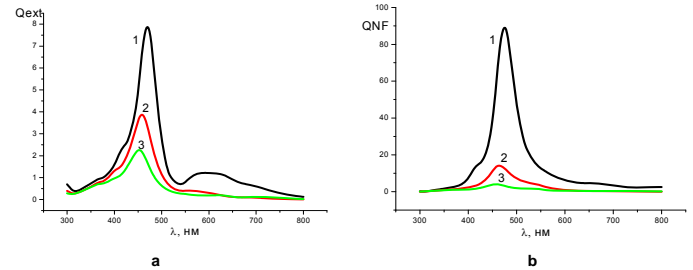


Figure 2. Spectral dependence of the extinction efficiency factor (a) and the near-field scattering efficiency factor (b) for two-layer Ag@SiO₂ nanospheres placed in the CuPc matrix. The radius core $R_1 = 25$ nm, the outer radius of the two-layer sphere $R_2 = 30$ nm (curve 1), 40 nm (curve 2), 50 nm (curve 3)

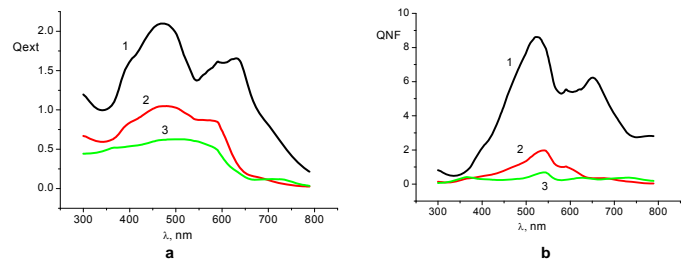


Figure 3. Spectral dependence of the extinction efficiency factor (a) and the near-field scattering efficiency factor (b) for two-layer Cu@SiO₂ nanospheres placed in the CuPc matrix. The radius of the copper core $R_1 = 25$ nm, the outer radius of the two-layer sphere $R_2 = 30$ nm (curve 1), 40 nm (curve 2), 50 nm (curve 3)

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