Original paper

UDC 535.343:541.1

MODELING OF OPTICAL PROPERTIES OF HYBRID METAL-ORGANIC NANOSTRUCTURES

ALINA N. PONYAVINA, KATSIARYNA A. BARBARCHYK, ANATOLY D. ZAMKOVETS,
SERGEY A. TIKHOMIROV

B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus (Minsk, Republic of Belarus)

Abstract. To model spectral characteristics of hybrid metal-organic 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. Two-layer plasmon nanospheres consisting of a metallic core (Ag, Cu) coated with dielectric shells and located into the copper phthalocyanine (CuPc) matrix were considered. The influence of dielectric shell thickness and refractive index on the characteristics of the surface plasmon resonance of absorption (SPRA) was studied. The possibility of the SPRA band tuning by changing the optical and geometrical parameters of dielectric shells was shown. It was established that dielectric shells allow to shift 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.

Keywords: surface plasmon resonance, hybrid nanostructures.

Conflict of interests. The authors declare no conflict of interests.

Introduction

Hybrid nanostructures which include both plasmonic and organic components are now under intensive investigation because of their great perspectives for the development and creation of effective modern nanophotonics, nanoplasmonics, and nanoelectronics devices [1, 2]. Among hybrid nanostructures there are ultradisperse plasmonic nanocomposites that consist of metal-containing nanoparticles embedded in a matrix of organic semiconductors. The unique properties of plasmonic nanoparticles are connected with the surface plasmon resonance of absorption (SPRA) and with a strong increase of electromagnetic fields near the plasmonic nanoparticle surface in this spectral region. Optical properties of densely packed arrays of plasmonic nanoparticles depend on interparticle electrodynamic coupling associated with near-field scattering and coherent reirradiation by particles of each other. The extent of the near-field interparticle coupling is connected with the spectral position of the SPRA maxima and may be regulated by a special choice of a metal

nanoparticle material and concentration as well as their morphological parameters such as nanoparticle size, shape, and its internal structure. The promising way to control the internal structure of plasmonic nanoparticles and in such way the SPRA spectra and the near-field scattering efficiency is an application of so-called two-layer nanoparticles with a metal core and a dielectric shell (M@D). Modeling and investigation of the optical properties of the M@D plasmonic nanoparticles was made based on the example of a spherical silver or copper core covered by a dielectric shell and embedded into a matrix of copper phthalocyanine.

Method

To model the spectral characteristics of such nanostructures, the extended Mie theory was used, which made 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]:

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

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

Here λ_0 is the wavelength of the incident radiation, $m = m_r - im_i$ is complex refractive index of the matrix, a_n, b_n – Mie coefficients, a – particle radius, $\eta = 4\pi a m_i/\lambda_0$. Riccati-Bessel functions and their derivatives (ψ_n, ξ_n, ψ_n', ξ_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 incident light beam intensity caused by the 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.

Results

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) are shown in Fig. 1–3. 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].
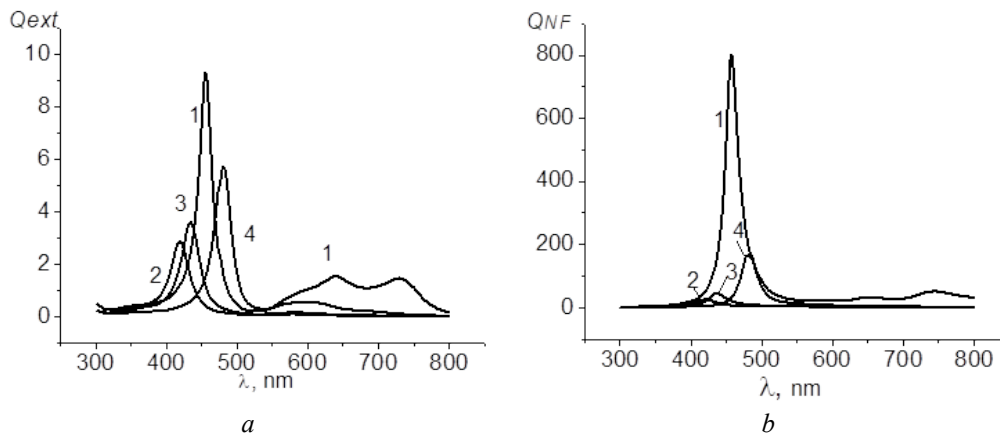

a

b

Fig. 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 a dielectric shell $n = 1.35, 1.5, 2.0$ (curves 2, 3, 4 correspondingly)

As can be seen from Fig. 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 CuPc absorption band maxima is located in the wavelength range of 370, 624, and 690 nm; the value of $m_{CuPc} = 1.7 - i\,0.06$ for $\lambda = 450$ nm [3]. As it is known, the presence of a shell on a small metal ball shifts the Frelich frequency, which determines the spectral position of the SPRA band dipole maximum [6].

The comparison of the curves 2–4 shows that at fixed core sizes and shell thicknesses the SPRA spectral shift may depend on the shell refractive index *n*. Using the Ag sphere nanoparticles in the CuPc matrix as an example, one can see that on covering the Ag core by a dielectric shell with $n < 1.7$ the SPRA band moves to a short-wavelength region relatively to the SPRA band of a homogeneous silver nanosphere (see curves 2, 3). On covering by the dielectric shell with $n > 1.7$, on the other hand, the SPRA band maximum moves to the long-wavelength region of the spectrum (see curve 4). This fact allows to conclude that both the value and the direction of the SPRA band spectral shift depend on the relative refractive index of the dielectric shell into the matrix surrounding the two-layer nanoparticle.

Fig. 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 is $n \approx 1.45$ in the spectral range 400 nm – 600 nm, leads to a short-wave shift λ_{max}, which increases with the quartz shell thickness increasing. As can be seen from Fig. 2, *a*, the spectral position of the SPRA maximum varies from 470 nm for a shell with a thickness of 5 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 the changes in the thickness of the quartz shell, is 480–440 nm. The values of Q_{ext} and Q_{NF} in the maximum of the SPRA band decrease with the quartz shell thickness increase.
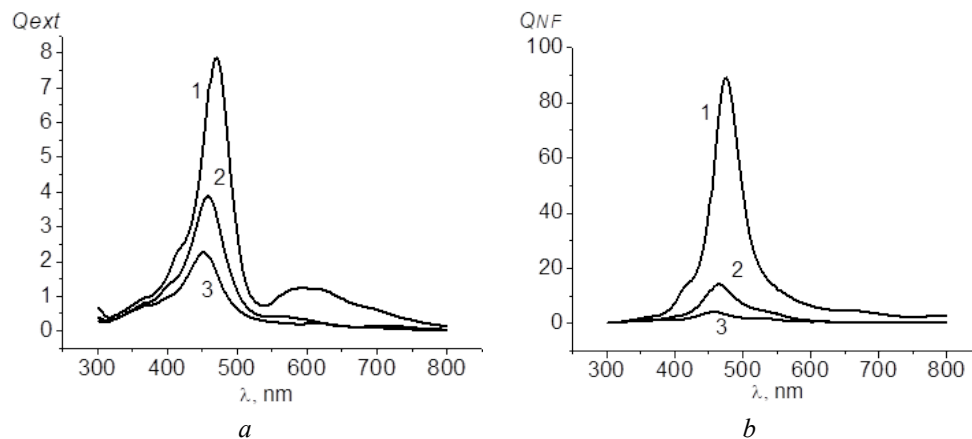

Fig. 2. Spectral dependence of the extinction efficiency factor (*a*) and the near-field scattering efficiency factor (*b*) for two-layer Ag @SiO$_2$ nanospheres placed in the CuPc matrix. The radius core $R_1 = 25$ nm, the outer radius of the two-layer sphere $R_2 = 30$ nm (curve 1), 40 nm (curve 2), 50 nm (curve 3)

Comparison of the data shown in Fig. 1 and 2 allows us to evaluate the effect of the metal core size on the SPRA band characteristics and the amplification of the scattered field near the two-layer plasmon nanoparticle Ag@SiO$_2$ placed in the CuPc matrix. As it was already noted, the growth of the silver core radius from 10 to 25 nm leads to a long-wave shift of the SPRA band of the homogeneous silver nanosphere from 450 to 480 nm, as well as to the 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 $Q_{NF} = 320$).

Fig. 3 shows the results of calculations for Cu@SiO$_2$ two-layer nanoparticles placed in the CuPc matrix. Comparison of Fig. 2 and 3 allows to estimate the effect of a 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 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 it can be seen from Fig. 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.
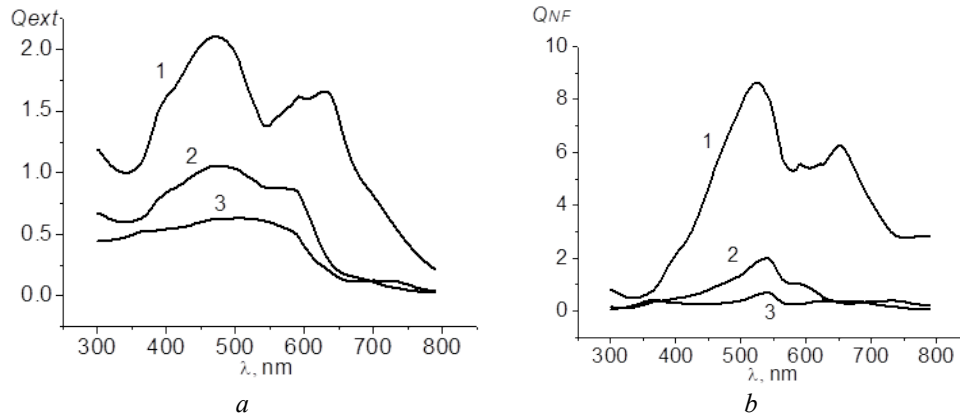

Fig. 3. Spectral dependence of the extinction efficiency factor (*a*) and the near-field scattering efficiency factor (*b*) for two-layer Cu@SiO$_2$ nanospheres placed in the CuPc matrix. The radius of the copper core $R_1 = 25$ nm, the outer radius of the two-layer sphere $R_2 = 30$ nm (curve 1), 40 nm (curve 2), 50 nm (curve 3)

Conclusion

The results of numerical simulations show that the 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 the plasmonic nanoparticle material, their size or shell refractive index and thickness. As one can see, a dielectric shell allows to shift 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.

References

1. Lepeshov S., Krasnok A., Belov P., Miroshnichenko A. Hybrid Nanophotonics. *Physics Uspekhi*. 2018;188(11):1137-1154.
2. Zamkovets A.D., Aksiment'eva E.I., Ponyavina A.N. Spectral manifestation of surface plasmon resonance in polyparaphenylene–silver nanostructures. *J. of Optical Technology*. 2011;78(2):84-87.
3. Sudiarta I.W., Chylek P. Mie scattering formalism for spherical particles embedded in an absorbing medium. *J. Opt. Soc. Am. A*. 2001;18:1275-1278.
4. Dunich R.A., Ponyavina A.N., Filippov V.V. Local field enhancement near spherical nanoparticles in absorbing media. *J. Appl. Spectr.* 2009;76:705-710.
5. Palik E.D. *Handbook of Optical Constants of Solids*. Orlando: Academic Press Inc.; 1985.
6. Kreibig U., Volmer M. *Optical Properties of Metal Clusters. Springer-Verlag*. Berlin; 1995.

Authors' contribution

Ponyavina A.N. proposed the method for modeling, made numerical simulation.
Barbarchyk K.A. made numerical simulation, prepared the manuscript.
Zamkovets A.D. chose the objects for the investigation.
Tikhomirov S.A. performed the task for the study.

Information about the authors

Ponyavina A.N., D.Sc., Principal Researcher at the Center of Photonics of Atoms and Molecules Structures of B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus.

Barbarchyk K.A., Researcher at the Center of Photonics of Atoms and Molecules Structures of B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus.

Zamkovets A.D., PhD., Leading Researcher at the Center of Photonics of Atoms and Molecules Structures of B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus.

Tikhomirov S.A., D.Sc., Corresponding Member, Scientific Head of the Center of Photonics of Atoms and Molecules Structures of B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus.

Address for correspondence

220072, Republic of Belarus,
Minsk, Nezavisimosti Ave., 68-2,
B.I. Stepanov Institute of Physics
of the National Academy of Sciences of Belarus;
tel. +375-17-270-87-53;
e-mail: kananovich.ek@gmail.com
Barbarchyk Katsiaryna Alexandrovna