ІНФОКОМУНІКАЦІЙНІ ТЕХНОЛОГІЇ ТА ЕЛЕКТРОННА ІНЖЕНЕРІЯ
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SIZE EFFECT IN PLASMON RESONANCE OF GOLD-COPPER SULFIDE CORE-SHELL NANOPARTICLES

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This paper studies the nature of changes in extinction spectra when changing the core/shell size ratio in spherical and ellipsoidal (prolate and oblate) gold-copper sulfide (Au-CuS) core-shell nanoparticles. The obtained results are analyzed to establish the regularity of changes in the nanoshells extinction spectra, which can be used to develop devices based on them for different applications. The plasmon properties of spherical and ellipsoidal Au -CuS nanoparticles with different sizes were determined. It is established that the intensity of the extinction cross-section of spherical nanoshells strongly depends on the ratio between the thickness of the core and the shell. It is possible to configure the plasmon properties of oblate and prolate ellipsoidal core-shell nanoparticles by changing the core and shell thickness in both directions. Thus, the results of the study suggest that Au-CuS nanoparticles can be used as potential elements of various sensitive sensors.

Keywords: *nanoshells, localized surface plasmon resonance, copper monosulfide.*
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1. Introduction

Modern trends in the development of materials and technologies demonstrate the relevance of creating objects whose dimensions are commensurate with the length of the electron's free path. Plasmonic nanoobjects are crucial for determining the properties and functionality of materials and devices based on them. Research of these nanostructures makes it possible to study and adjust the properties of materials and interfaces at various scales, covering the scientific fields of physics, chemistry, and nanotechnology [1, 2]. The study and synthesis of plasmonic nanostructures not only satisfies the need to create materials with unique linear and nonlinear optical properties, but also helps to find the answer to how the properties of matter change when passing from individual atoms and molecules to organized nanostructures, and then to the solid state.

Recently, core-shell nanoparticles exhibit new and improved electronic, optical, catalytic, or photocatalytic properties that are significantly different from those of monometallic nanoparticles. This is due to the synergistic effect of the combination of properties corresponding to two separate materials. That is why, such nanoparticles are used in various technological fields, from energy production and storage to sensor applications. In addition, they are widely used in plasmonic solar cells or SERS applications. The main influence here is the specific interactions between nanoshells, nanoparticles, and electromagnetic radiation. There are a lot of examples of successful use of metal-semiconductor structures and bimetallic

nanoparticles [3]. However, recently there have been works related to enhanced properties of nanoparticles containing metals and colloidal nanocrystals of chalcogenides and metal oxides [4]. This is because such materials are characterized by both semiconductor and plasmonic nature. As a result, they demonstrate a synergistic combination of the nanoscale semiconductors characteristic optoelectronic properties and the optical response of localized surface plasmon resonance. Importantly, such nanoparticles are characterized by enhanced plasmonic properties in the near-infrared wavelength range, making them suitable for wide applications [5]. The properties of both localized surface plasmon resonances and extinction (absorption and scattering) efficiency are determined by the structure and shape of the core-shell nanoparticles.

2. Theoretical Background

The principle of dipole equivalence [6] was used in the modeling of spherical nanoparticles optical parameters since the small size of nanoparticles (relative to the visible range wavelengths) allows one to be limited to the dipole approximation. For example, the nanoparticle extinction cross-section depends on the electrostatic polarizability α_0 and is determined by the formula:

$$C_{ext} = \frac{12\pi k}{(V/4\pi)^3}\frac{\varepsilon_m \operatorname{Im}(\varepsilon)}{|\varepsilon-\varepsilon_m|^2}|\alpha|^2 + \frac{8\pi}{3}k^4|\alpha|^2, \quad (1)$$

where for nanoparticles the polarization is equal:

$$\alpha_0 = \frac{3V}{4\pi}\frac{\varepsilon_m-\varepsilon_h}{\varepsilon_m+2\varepsilon_h} = R^3\frac{\varepsilon_m-\varepsilon_h}{\varepsilon_m+2\varepsilon_h}, \quad (2)$$

where V – nanoparticle volume; R – nanoparticle radius; ε and ε_h - dielectric functions of the nanoparticle material and surrounding medium, respectively; k - the wave number of the surrounding medium.

In the case of spherical nanoshells, the polarizability can be written taking into account the equivalent average permittivity of a certain equivalent homogeneous sphere as follows [7]:

$$\delta = \frac{\varepsilon_{1,2}-\varepsilon_m}{\varepsilon_{1,2}+2\varepsilon_m}, \quad (3)$$

where

$$\varepsilon_{1,2} = \varepsilon_m\frac{1+2f_{12}\delta_{12}}{1-2f_{12}\delta_{12}}, f_{12} = \frac{R_1^3}{R_2^3}, \delta_{12} = \frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}.$$

One of the simple, but widely used models is the model of the shell-covered ellipsoid. Combining the shell structure with the rod shape provides additional opportunities for controlling the plasmonic properties of such nanoparticles. This model includes ellipsoidal and spherical nanoshells as limiting cases. Thus, the polarizability of the ellipsoidal nanoshells is determined by the following formulas:

$$\alpha_{av}^{(2)} = \frac{V_2}{4\pi L_2}\frac{\varepsilon_{av}-\varepsilon_m}{\varepsilon_{av}+\varphi_2\varepsilon_m}, \quad (4)$$

where

$$\varepsilon_{av} = \varepsilon_2\frac{1+\varphi_2 f_{12}\alpha_{12}}{1-f_{12}\alpha_{12}}, \alpha_{12} = \frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varphi_1\varepsilon_2}, f_{12} = \frac{V_1L_2}{V_2L_1}.$$

The dielectric constant of Au was calculated according to the analytical equations presented in [8]. The dielectric constant of copper monosulfide was calculated within the Drude theory. Detailed data for ellipsoid calculations are given in [6]. The theoretical methods of studying the optical parameters of copper monosulfide nanoparticles make it possible to assess the influence of geometrical parameters on their optical response and effectively tune the resonance of surface plasmons, shifting it to the working range of the spectrum.

3. Results and Discussions

Changing the spatial configuration, namely the size, shape, and core-to-shell ratio of bilayer nanoparticles, has a strong effect on the nanoshells plasmonic properties.

Modeling of the spherical Au and CuS nanoparticles extinction spectra of varied sizes was carried out. It allows further comparison of the plasmon response behavior of nanoparticles with nanoshells of varied sizes and shapes. The calculated extinction spectra of spherical gold nanoparticles with variable diameters from 10 to 100 nm are presented in Fig. 1. As can be seen from the figure, as the diameter of the nanoparticle increases, the amplitude of the plasmon peak increases. In addition, an increase in the gold nanoparticle diameter leads to a slight shift of the extinction peak to the region of longer wavelengths from 506 to 530 nm.

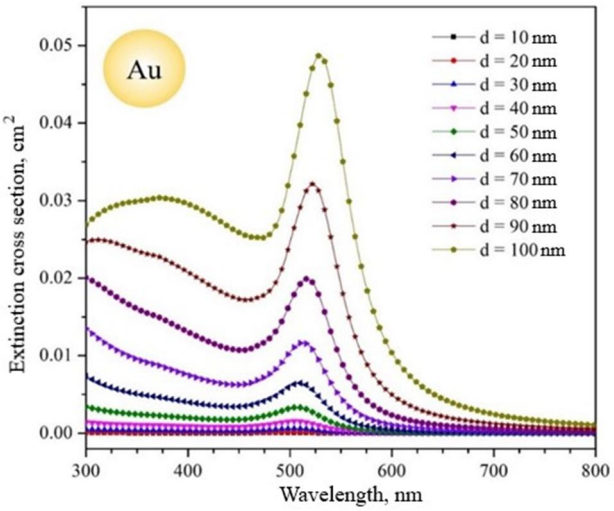

Fig. 1. Extinction spectra of spherical Au nanoparticles with diameters from 10 to 100 nm located in the surrounding medium with a refractive index of 1.0

The extinction spectra of spherical copper monosulfide nanoparticles with variable diameters from 10 to 100 nm, similar to gold nanoparticles are presented in Fig. 2. Extinction peak increases in amplitude and shifts to the region of the longer wavelengths with an increase in the CuS nanoparticles diameter, as for Au nanoparticles. In this case, the peak of interest to us in the near-IR region shifts from 930 to 950 nm when the diameter of CuS nanoparticles increases.

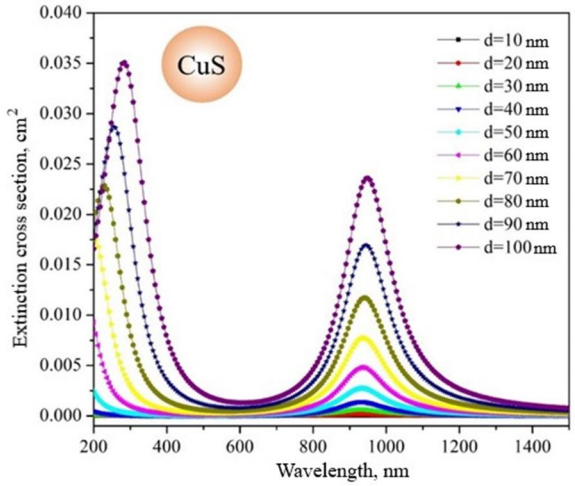

Fig. 2. Extinction spectra of copper monosulfide spherical nanoparticles with variable diameters from 10 to 100 nm located in a medium with a refractive index of 1.0

It is known that gold nanoparticles are widely used in various fields of science and industry due to their unique optical, biological, electrical, and thermal properties and high electrical conductivity. In recent years, many applications of copper monosulfide nanoparticles in photocatalysis, optoelectronics, sensors, and biomedicine have been demonstrated. The combination of the plasmonic metal core (gold nanoparticles) and semiconductor shell (copper monosulfide) can provide a significant enhancement of the optical characteristics of such nanostructures. Therefore, the next step in the work the extinction of Au/CuS spherical nanoshells at different core and shell sizes was calculated, and the obtained results were analyzed.

The extinction cross sections of Au/CuS spherical nanoshells were calculated at the constant nanoshell size of 100 nm (Fig. 3). The core diameter varied from 1 to 99 nm in steps of 10 nm. Au/CuS nanoshells have characteristics similar to copper monosulfide nanospheres at the constant diameter of the shell of 100 nm and small values of the core diameter up to 40 nm. This is manifested in the position of the extinction peak (at 930 nm) and the shape of the spectrum curve.

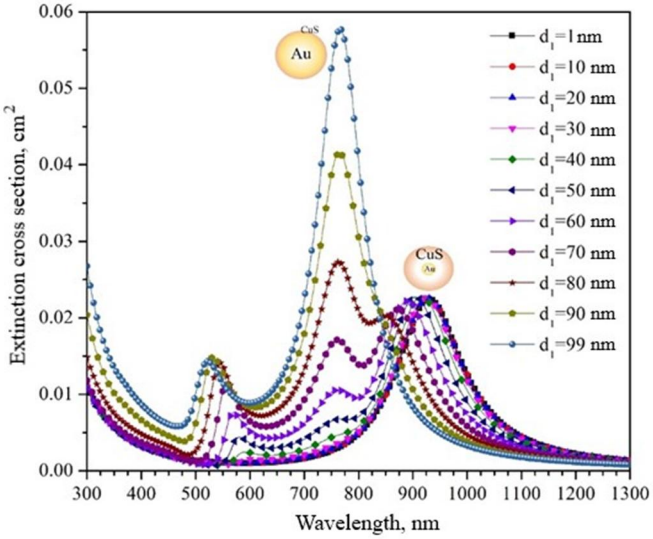

Fig. 3. Extinction spectra of spherical Au/CuS nanoshells with a constant diameter d2 = 100 nm located in a medium with a refractive index of 1.0. The core diameter d1 varies from 1 to 99 nm

The extinction peak shifts to the short-wavelength region and increases in amplitude when the diameter of the core increases and, accordingly, the thickness of the shell decreases. Moreover, peak splitting is observed. The additional extinction shoulder appears at the wavelength of 525 nm, which is characteristic of core/shell nanoparticles. The plasmon peak at the wavelength of 750 nm appeared when the core diameter is 99 nm and the CuS shell thickness is 1 nm. The extinction peak at the wavelength of 530 nm which is characteristic of gold nanoparticles (see Fig. 1) is weak.

The spherical Au/CuS nanoshell extinction spectra at the constant core diameter d_1 = 10 nm and the different shell diameters are presented in Fig. 4.

There is a significant shift of the extinction peak from a wavelength of 760 nm (1 nm shell thickness) to 905 nm (10 nm shell thickness) at the small shell thicknesses. The amplitude of the extinction peaks increases when the shell thickness increases up to 100 nm at the constant core diameter. There is a shift on the spectral scale to the wavelength of 930 nm. At the same time, the properties of the core material (Au) cease to manifest, and the optical response of the Au/CuS nanoshell behaves like a spherical CuS nanoparticle with a large thickness of the CuS shell.

Shape control in the manufacture of nanostructures is an extremely important task. The nanoshell shape is a parameter that critically affects the optical response. It allows tuning characteristics of nanostructures by adjusting the plasmon peak in the given spectrum region. It is difficult to produce perfectly spherical nanostructures. Therefore, understanding how the nanosphere spatial deformations affect

its optical response will help analyze the obtained experimental results and optimize the technological processes of synthesis. Therefore, the next step of the work is the modeling of the extinction spectra of Au/CuS nanoshells deformed along the vertical and horizontal axes. In this case, we operate not only with diameter values (as in spherical nanoparticles) but with the lengths of the vertical and horizontal axes of the nanoellipsoid. In addition, the change of a larger number of spatial parameters provides a wider space for tuning the extinction peaks position and amplitude of the nanoparticles. The extinction spectra of vertically placed ellipsoidal Au/CuS nanoshells with fixed lengths of major axes a_2 = 50 nm; b_2 = 100 nm are presented in Fig. 5. The lengths of the minor axes a_1 and b_1 vary in the range from 1 to 49 nm and from 2 to 99 nm, respectively.

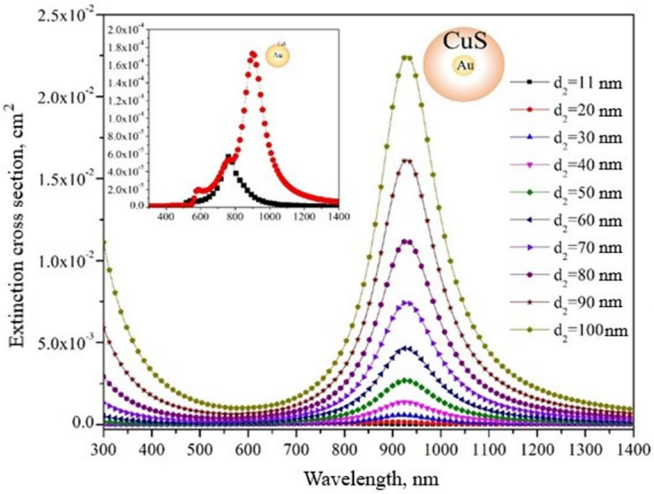

Fig. 4. Extinction spectra of spherical Au/CuS nanoshells with the constant core diameter d1 = 10 nm located in a medium with a refractive index of 1.0. The shell diameter d2 varies from 11 to 100 nm

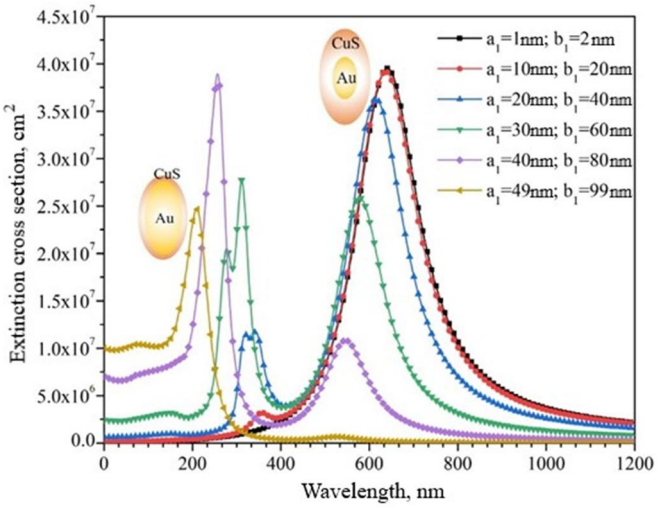

Fig. 5. Extinction spectra of vertically placed ellipsoidal Au/CuS nanoshells with fixed axis lengths a_2 = 50 nm; b_2 = 100 nm located in a medium with a refractive index of 1.0. The lengths of the a_1 and b_1 axes vary from 1 to 49 nm and from 2 to 99 nm respectively

The extinction spectra of Au/CuS ellipsoidal nanoparticles take on the shape of the curve characteristic of CuS nanospheres at large shell thicknesses as in the case of spherical nanoshells. The extinction peaks near 600 nm decrease when the length of the core axes increases. The amplitude of the peaks in the near-UV range increases. The results of modeling with the increase in the shell thickness, namely, the in-

creased lengths of the axes a_2 and b_2 from 6 to 50 nm and from 12 to 100 nm, respectively at the constant core size (a_1 = 5 nm; b_1 = 10 nm) are presented in Fig. 6. Decreasing the shell thickness to a minimum value (a_2 = 6 nm; b_2 = 12 nm) at the constant core size (a_1 =5 nm; b_1 = 10 nm) results in a significant enhancement of the extinction peak at the wavelength of 230 nm. The extinction peaks shift to the long-wavelength region when the shell thickness of the vertically placed Au/CuS nanoellipsoid increases. Therefore, the extinction peaks in the near-UV range disappear when the shell thickness increases since the key role in the nanostructure begin to be played by the CuS material.

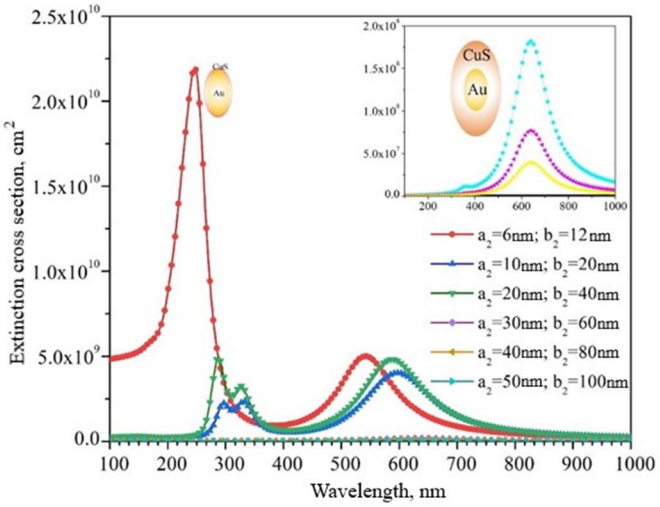

Fig. 6. Extinction spectra of vertically placed ellipsoidal Au/CuS nanoshells with fixed axis lengths a_1 = 5 nm; b_1 = 10 nm located in a medium with a refractive index of 1.0. The lengths of the a_2 and b_2 axes vary from 6 to 50 nm and from 12 to 100 nm respectively

Similar calculations were performed for Au/CuS nanoshells deformed along the horizontal axis (Fig. 7). The lengths of the axes a_1 and b_1 (core size) vary from 2 to 99 nm and from 1 to 49 nm, respectively. The total size of the horizontal nanoellipsoid remains constant with the lengths of the axes a_2 = 100 nm, and b_2 = 50 nm.

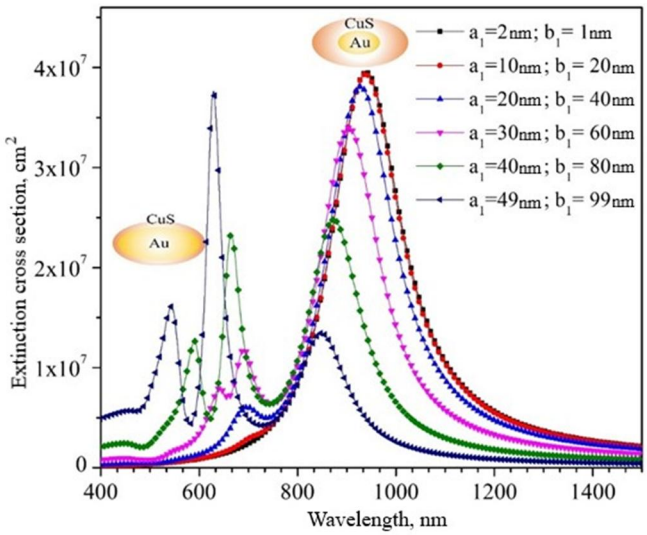

Fig. 7. Extinction spectra of horizontally placed ellipsoidal Au/CuS nanoshells with constant axis lengths a_2 = 100 nm; b_2 = 50 nm located in a medium with a refractive index of 1.0. The lengths of the a_1 and b_1 axes vary from 2 to 99 nm and from 1 to 49 nm respectively

The calculated extinction spectra of horizontal Au/CuS nanoellipsoids (Fig. 7) demonstrate behavior similar to vertical nanoellipsoids (Fig. 6). There the increase in the length of the core axes leads to the decrease in the extinction peaks in the green region of the spectrum and the increase in their amplitude in the near UV range. However, in the case of horizontal Au/CuS nanoellipsoids, the extinction peaks are placed in the near-IR region. It opens the possibility of their biomedical application.

The extinction spectra of horizontal Au/CuS nanoellipsoids with the constant core size (a_1 = 10 nm; b_1 = 5 nm) and a variable shell thickness, where the lengths of the a_2 and b_2 axes vary from 12 to 100 nm and from 6 to 50 nm, respectively, are shown in Fig. 8.

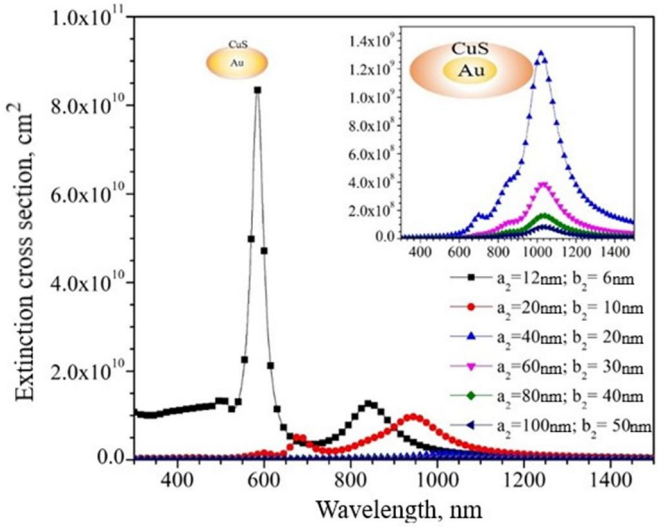

Fig. 8. Extinction spectra of horizontally placed ellipsoidal Au/CuS nanoshells with constant axis lengths a_1 = 10 nm; b_1 = 5 nm located in a medium with a refractive index of 1.0. The lengths of the a_2 and b_2 axes vary from 12 to 100 nm and from 6 to 50 nm respectively

Decrease of the horizontal nanoellipsoids shell thickness to the minimum value (a_2 = 12 nm; b_2 = 6 nm) at the constant core size (a_1 = 5 nm; b_1 = 10 nm) leads to the significant enhancement of the extinction peak at the wavelength 590 nm. It corresponds to the extinction peak of gold nanoparticles. Extinction peaks in the near-IR region of the spectrum shift to the long-wavelength region when the shell thickness increases and their amplitude decreases.

Conclusions

Therefore, significant enhancement of plasmon peaks in the NIR region of the spectrum can be obtained using horizontal Au/CuS nanoellipsoids characterized by a large thickness of the CuS shell.

Thus, spherical Au/CuS nanoshells with a core diameter of 10 nm and a shell diameter of 100 nm are characterized by an extinction peak at a wavelength of 930 nm, and the value of the extinction cross-section is equal to $2.25 \cdot 10^{-2}$ cm^2. Horizontal Au/CuS nanoellipsoid with axis lengths a_2 = 100 nm; b_2 = 50 nm and a_1 = 10 nm; b_1 = 20 nm are characterized by an extinction peak at a wavelength of 950 nm, and the value of the extinction cross-section significantly exceeds previous results and is $4 \cdot 10^7$ cm^2.

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РОЗМІРНИЙ ЕФЕКТ У ПЛАЗМОНОМУ РЕЗОНАНСІ НАНОЧАСТИНОК СУЛЬФІД МІДІ-ЗОЛОТО ТИПУ ЯДРО–ОБОЛОНКА

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У цій роботі представлено дослідження природи змін у спектрах екстинкції сферичних та еліпсоїдних (витягнутих і сплюснутих) нанооболонок Au-CuS за зміни співвідношення їхніх розмірів ядро–оболонка. Проведено аналіз отриманих результатів моделювання з метою встановлення закономірностей зміни спектрів екстинкції нанооболонок, що може бути використано для розробки пристроїв різного призначення на їхній основі. Визначено плазмонні властивості сферичних та еліпсоїдних наночастинок Au-CuS різного розміру. Встановлено, що амплідупа піків перерізу екстинкції сферичних нанооболонок сильно залежить від співвідношення товщини ядра та оболонки. Це дає можливість налаштувати плазмонні властивості еліпсоїдних наночастинок ядро–оболонка, змінюючи товщину ядра та оболонки в обох напрямках. Отже, результати дослідження свідчать про можливість використання наночастинок Au-CuS як потенційних елементів різноманітних чутливих сенсорів.

Ключові слова: *нанооболонки, локалізований поверхневий плазмонний резонанс, моносульфід міді.*