ІНФОКОМУНІКАЦІЙНІ ТЕХНОЛОГІЇ ТА ЕЛЕКТРОННА ІНЖЕНЕРІЯ
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PLASMON RESONANCE OF SILVER AND GOLD NANOPARTICLES IN ORGANIC MEDIA: PHYSICAL MECHANISMS AND SPECTRAL MANIFESTATIONS

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The paper studies the mechanism of localised surface plasmon resonance in metal nanoparticles incorporated into organic matrices. The physical nature of plasmon excitations as coherent oscillations of the conduction band electron gas arising from interaction with electromagnetic radiation is analysed. Unlike surface plasmon polaritons, which propagate along an extended metal-dielectric interface, localised plasmons are confined to the volume of nanoparticles and exhibit radiative properties. Research into the dispersion characteristics of surface plasmon polaritons in silver-organic and gold-organic material systems shows significant deviations from the linear dependence characteristic of free electromagnetic radiation. It is shown that plasmon modes are characterised by an increased wave vector value compared to photons of similar energy, which causes the surface excitation effect and intense spatial localisation of the optical field. The dimensional correlations of the frequency and spectral width characteristics of localised surface plasmon resonance have been analysed. Two main physical mechanisms that control the dimensional correlations of plasmon characteristics have been identified. Increase in geometric dimensions results in a shift in long-wave resonance due to the retardation effect associated with the finite speed of electromagnetic excitation for large nanoparticles with a diameter greater than 20 nm. For ultrasmall nanoparticles with a diameter of less than 20 nm, quantum size effects dominate when the linear dimensions become comparable to the free path length of electrons. This leads to an increase in the intensity of surface scattering of charge carriers and a broadening of the spectral half-width. The results obtained demonstrate that the size correlations of the resonance frequencies of surface plasmons in metal nanoparticles are controlled by a variety of competing physical processes. The contribution of these processes varies depending on the size range and specifics of the material system. Obtained results allows to enhance fundamental understanding of the mechanisms by which plasmons and photons interact in nanocomposite systems, providing a theoretical basis for the targeted design of plasmonic nanostructures with specific functional properties.

Keywords: *nanoparticles; localized surface plasmon resonance; scattering cross-section.*
UDC: 53.072:53:004

Introduction

The development of modern nanotechnologies is closely linked to the study of the optical properties of metal nanostructures and surface plasmon resonance phenomena. Metal nanoparticles form a distinct class of materials with unique properties. Studying these materials is of considerable scientific and practical value, as they can be used in many areas of science and technology. Examples include their use as active elements in sensors [1], photoelectric devices [2], waveguides [3], filters [4] and optoelectronic elements [5].

A key feature of metal nanoparticles is their ability to sustain localized surface plasmon resonances (LSPRs), which are coherent oscillations of the conduction band electron gas that occur when it interacts with electromagnetic radiation [6]. Unlike surface plasmon polaritons, which propagate along an extended metal-dielectric interface, localised plasmons are confined to the volume of nanoparticles. They manifest as the first Frolik mode, which consists of dipole and multipole oscillations of the electron gas near the surface [7]. The resonance characteristics of LSPR significantly depend on the geometric parameters of nanoparticles (size, shape) and the dielectric permeability of the surrounding medium [8]. The high sensitivity of plasmonic nanostructures to local changes in the dielectric properties of the matrix makes them extremely promising for creating highly sensitive sensors and devices for amplifying spectroscopic signals, as well as for efficient energy harvesting and conversion [9–11].

Organic matrices are of particular interest as a medium for plasmonic nanoparticles thanks to their unique optical and dielectric properties, the potential for controlled structural modification and the relatively straightforward process of manufacturing composite materials. The interaction between the plasmon modes of metal nanoparticles and the electronic states of the organic matrix can result in the development of hybrid optical properties, offering new opportunities for creating functional photonic materials [12]. The basis for the development and manufacture of modern photonic and electronic components is mathematical modelling of such phenomena to find the parameters of real structures with maximum electromagnetic field resonance, followed by experimental confirmation.

This work is devoted to the study of the plasmon resonance mechanism of nanoparticles embedded in an organic matrix. Particular attention is paid to establishing correlations between the morphology of the composite and its optical characteristics, with the aim of achieving a comprehensive understanding of the relationship between these two elements. Understanding the fundamental mechanisms of interaction between plasmonic nanoparticles and the organic environment is essential for developing new types of optoelectronic devices, photocatalytic systems and sensors that offer enhanced functionality.

2. Theoretical background

It is important to emphasize that the correlation between the resonance frequency of surface plasmons and the dielectric properties of their surroundings is fundamental to the application of plasmonic metal nanostructures in optoelectronics. At the same time, the key parameters of surface plasmon resonance, such as the resonance frequency and the half-width of the resonance line (i.e. the attenuation parameters), demonstrate a pronounced dependence on the geometric dimensions of metal nanoparticles [13]. Within the framework of the weak attenuation approximation, the following condition is valid [13] as follows:

$$\varepsilon_2(\omega) \ll |\varepsilon_1(\omega) + 2\varepsilon_m|, \tag{1}$$

where $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ is the real and imaginary parts of the dielectric permeability of a metal nanoparticle, ε_m is the dielectric permeability of the matrix (surrounding environment).

The optical absorption and scattering spectra of nanocomposite systems containing finely dispersed nanoparticles are characterized by the presence of an intense maximum. This maximum is positioned according to the relationship:

$$\varepsilon_1(\omega) = -2\varepsilon_m. \tag{2}$$

This effect is caused by optical excitation of localised polarization oscillations in nanoparticles, in particular surface plasmon and phonon modes. These oscillatory states are characterized by their localised nature. This distinguishes them fundamentally from surface plasmon polaritons and phonon polaritons, which propagate along the interface in a wave-like manner. Surface plasmon and phonon excitations are confined to the spatial boundaries of the nanoparticle. They represent localised oscillations of the electronic conduction subsystem or vibrations of the crystal's ionic sublattice. The surface nature of such oscillatory states in nanoparticles is confirmed by a number of characteristic experimental features of optical spectra.

Resonance frequencies for bulk samples and nanoparticles of identical material show differences in spectral position. Spectral maxima of optical absorption and scattering by nanoparticles exhibit size dependence and are critically sensitive to morphological characteristics. Particle geometry can radically change the spectral picture. This includes the appearance of additional bands. These bands appear for non-spherical objects. The position of the resonance peaks in the absorption and scattering spectra correlates strongly with the dielectric parameters of the matrix medium.

These observations clearly demonstrate that surface elementary excitations participate in the formation of the optical response. The registration of corresponding bands in the absorption spectra deserves special attention. This indicates the possibility of direct photon excitation of surface plasmons, i.e. direct photon-plasmon conversion, and the reverse process. Thus, surface plasmon excitations in nanoparticles exhibit radiative properties.

In order to obtain the spectrum of electromagnetic modes of an isolated particle, it is necessary to solve the wave equations for vectors $\vec{E}$ and $\vec{H}$ [13]:

$$\left(\Delta + \varepsilon^{i}(\omega)\frac{\omega^2}{c^2}\right)\vec{E} = 0, \tag{3}$$

$$\left(\Delta + \varepsilon^{i}(\omega)\frac{\omega^2}{c^2}\right)\vec{H} = 0, \tag{4}$$

provided there is no external exciting electromagnetic wave.

The dispersion law for the intrinsic electric modes of a spherical particle, small compared to the wavelength of light, is determined from the equation

$$Re\big(\varepsilon(\omega)\big) = \varepsilon_1(\omega) = -\varepsilon_m\frac{n+1}{n}, \tag{5}$$

where $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is dielectric permeability of a particle, $n = 1, 2, 3, \ldots$ is a fashion number.

Dipole polarization of a particle corresponds to n=1, quadrupole polarization corresponds to n=2, etc. The electric field outside a particle, created by surface plasmons excited in it, depends on the distance to its centre r_1 as:

$$E(r_1) \sim \left(\frac{r}{r_1}\right)^{2n+1}, \tag{6}$$

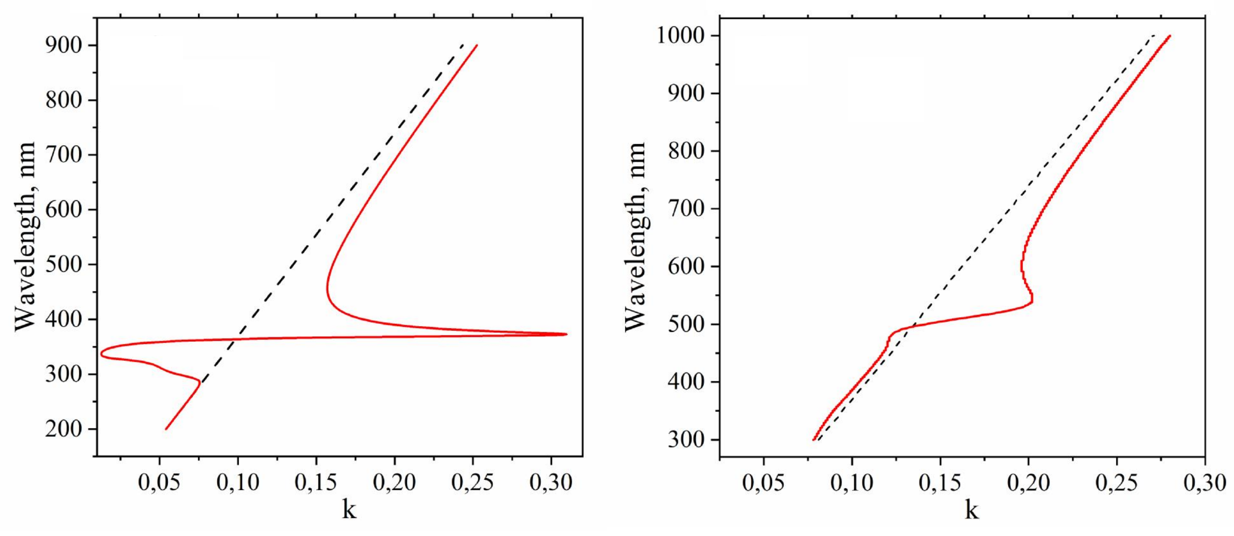
which shows that as the distance from the particle increases, the plasmon modes with higher n decay faster than those with lower n. Therefore, the dipole mode (n=1) has the longest range. Thus, strong resonant absorption and scattering of light by small particles is caused precisely by the resonant excitation of dipole surface plasmons. Therefore, we will consider only them further in this work.

3. Results and discussion

Silver (Ag) and gold (Au) are two of the most effective plasmonic materials, thanks to their low optical losses in the visible spectrum and their high concentration of free electrons. These properties give rise to pronounced plasmonic resonances, which are put to active use in nanophotonics, biosensors and surface-enhanced Raman scattering spectroscopy [14]. The optical properties of these nanoparticles were studied using the dipole approximation method. The values of dielectric permittivities were determined for calculations using the analytical expressions given in [15]. The refractive index of the organic matrix in which the nanoparticles are located was taken to be 1.7. The diameter of the nanoparticles varied from 10 to 100 nm.

It should be noted that the dispersion relation characterizes how the frequency parameters of surface plasmon polaritons depend on their momentum as they propagate at the metal-dielectric interface. Firstly, the values of the wave vector of plasmon-polaritonic excitations were calculated as a function of wavelength for silver- and gold-organic matrix systems (see Fig. 1).

The dispersion characteristics of surface plasmon excitations at the metal-dielectric interface differ significantly from the linear dependence typical of electromagnetic radiation in a medium. This indicates that plasmon modes are characterized by a higher wave vector value than photons of a similar energy. This difference causes the surface excitation effect and the intense spatial localization of the optical field. Analyzing dispersion relations is a fundamental approach to developing and optimizing plasmonic functional elements.

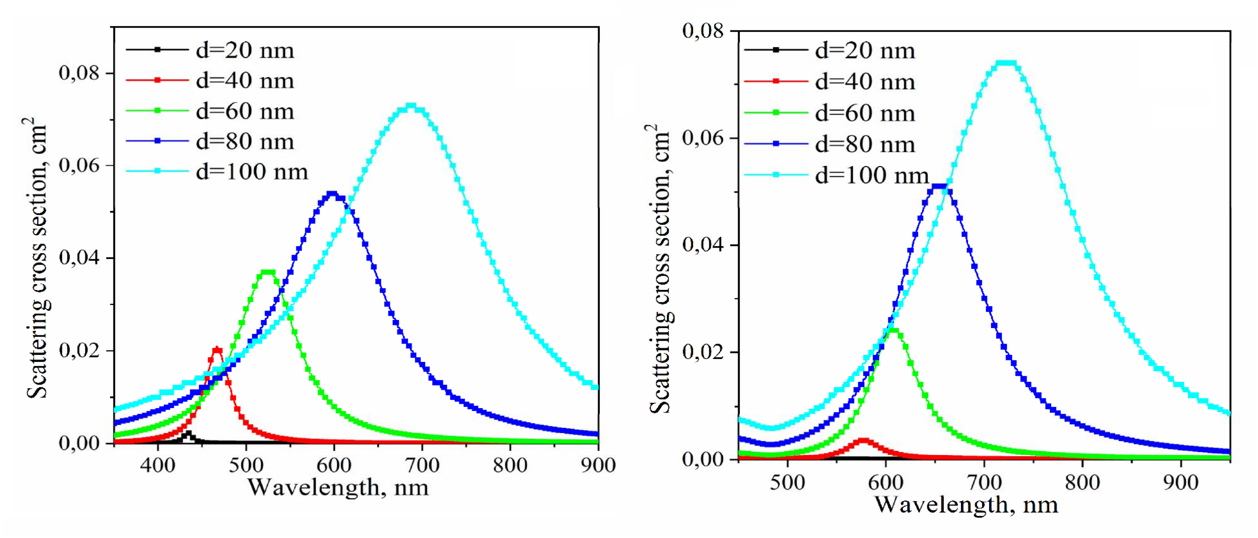


a *b*

Fig. 1. Dependence of wavelength on the wave vector of the plasmon-polaritons for the silver-organic material (a) and gold–organic material (b) interfaces

Let’s consider how the spectral shift of plasmon resonances changes when the dimensional parameters of spherical silver (Ag) and gold (Au) nanoparticles incorporated into an organic medium are varied. It is important to emphasize the fundamental difference between surface plasmons in nanoparticles, which exhibit radiative properties, and surface plasmon polaritons on flat interfaces, which are characterized by their non-radiative nature.

The dimensional evolution of the dielectric function of metal nanoparticles, and consequently the modification of the frequency and spectral width characteristics of surface plasmon resonance, is determined by a complex of physical processes. According to Fig. 2, an increase in geometric dimensions for relatively large nanoparticles (diameter >20 nm) is accompanied by a red shift of the resonance wavelength (i. e. a decrease in resonance energy) and an increase in the spectral half-width of the resonance band. In the case of silver nanoparticles, a shift to the long-wave region of the spectrum is observed when the diameter of the nanoparticle changes from 20 to 100 nm, moving from 430 nm to 690 nm (almost 300 nm). A red shift is also observed for gold nanoparticles placed in an organic matrix, although it is not as large as for silver nanoparticles: from 575 nm to 750 nm. Additionally, the scattering cross-section spectra of both types of nanoparticles are characterized by an increase in the half-width of the spectrum as the size of the nanoparticles increases. The amplitude of the spectra also increases with an increase in the size of the nanoparticles.



a *b*

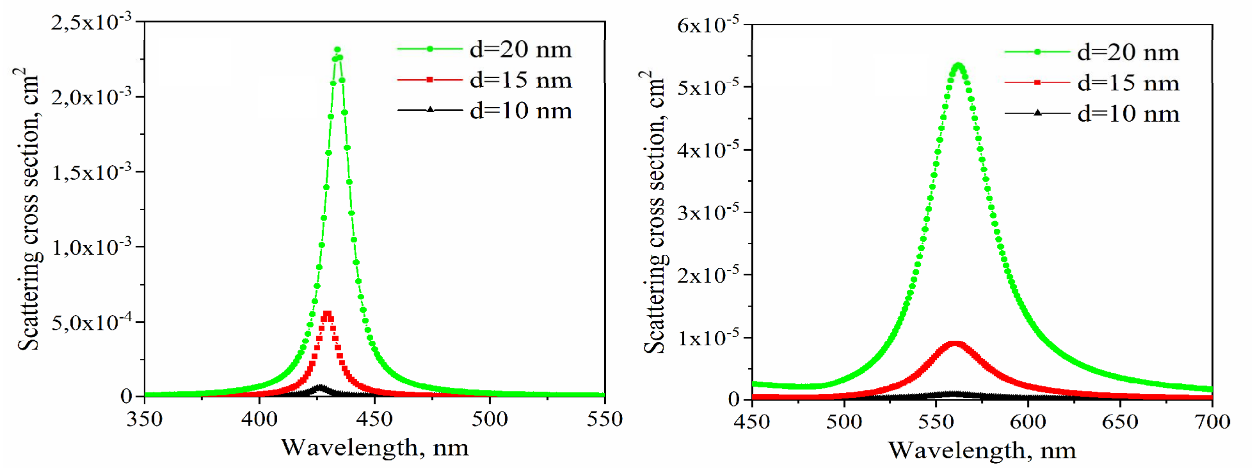
Fig. 2. Dependence of the scattering cross section on the wavelength of large silver (a) and gold (b) nanoparticles placed in an organic matrix

The shift in plasmon resonance towards longer wavelengths as the particle size increases is associated with the need to consider higher-order multipole contributions alongside the main dipole moment in the expansions for extinction and scattering cross sections. This is because an increase in the dimensional parameter leads to an increase in the real part of the dielectric permittivity of the metal. Since this has a negative value and decreases in absolute value, it causes a bathochromic shift of the dipole resonance to the region of longer wavelengths. This phenomenon is associated with the retardation effect, which occurs because electromagnetic excitations travel at a finite speed inside the particle. This effect becomes more significant for larger particles and intensifies as they grow in size.

In plasmon oscillations of the electronic conduction subsystem, the electromagnetic field's limited propagation speed prevents polarization from being established instantly throughout the entire volume of the particle. An increase in particle size leads to an increase in the time taken for characteristic polarization to establish. Since the natural frequency of electron oscillations is inversely correlated with this time, this explains why the resonance frequency decreases with increasing size. At the same time, the spectral broadening of plasmon resonance in large particles is caused by the loss of radiation by surface plasmons.

Now, let us turn to analyzing the dimensional correlations between the frequency and spectral width characteristics of surface plasmon excitations in nanoscale particles with small diameters. According to Fig. 3, a decrease in geometric parameters for ultrafine nanoparticles with a diameter of less than 20 nm is accompanied by an expansion of the spectral half-width of the plasmon resonance. This phenomenon occurs when the linear dimensions of the particle become comparable to the mean free path of conduction electrons, resulting in a limitation of the transport properties of charge carriers due to quantum size effects. This intensifies electron scattering processes at the nanoparticle’s boundaries, resulting in an increased relaxation rate of plasmon excitations.

However, it is clear that the position of the plasmon resonance peak does not change when the size of the nanoparticle changes. For silver nanoparticles, this is 450 nm, and for gold nanoparticles, it is 530 nm. Additionally, unlike in previous studies, we observe a difference in the half-width of the scattering cross-section spectra for silver and gold nanoparticles. Compared to gold nanoparticles, silver nanoparticles are characterized by narrower half-widths of the scattering cross-section spectra and much higher scattering intensities (10^{-3} compared to 10^{-5}).



a *b*

Fig. 3. Dependence of the scattering cross section on the wavelength of small silver (a) and gold (b) nanoparticles placed in an organic matrix

Therefore, we can conclude that the quantitative analysis of the dimensional evolution of the plasmon band's spectral half-width in the scattering or absorption cross section has significantly greater diagnostic value. The systematic increase in this parameter alongside a decrease in the size of small nanoparticles clearly indicates particle miniaturization, making it a reliable method of dimensional characterization.

It should be noted that a wide range of spectral transformations has been experimentally observed for nanoparticles of various metals dispersed in different matrix environments, including bathochromic and hypochromic shifts of resonance peaks and cases where no noticeable shift is observed. This variability means that plasmon band size shift cannot be used as a reliable diagnostic tool to determine the geometric parameters of nanoparticles.

Conclusion

The physical nature of localised surface plasmon resonances in metal nanoparticles has been established as coherent oscillations of the conduction band electron gas. These differ fundamentally from surface plasmon polaritons due to their localised structure and radiation properties. It has been demonstrated that plasmonic excitations in nanoparticles are confined to the particle's spatial boundaries and behave as dipolar and multipolar oscillations of the electronic conduction subsystem.

The dispersion characteristics of surface plasmon polaritons in silver- and gold-organic material systems, which demonstrate significant nonlinear deviations from the dispersion of free electromagnetic radiation, have been analysed. Two main physical mechanisms that control the dimensional correlations of plasmon characteristics have been identified. For large nanoparticles, the delay effect predominates, resulting in a red shift of the resonance and an increase in the spectral half-width due to radiation losses. For ultra-small nanoparticles, quantum size effects become decisive when the geometric parameters are comparable to the free path length of conduction electrons. The obtained regularities demonstrate that the dimensional correlations of surface plasmon resonance frequencies in metal nanoparticles are controlled by a variety of competing physical processes. The contribution of these processes varies depending on the dimensional range and the specifics of the material system. Additionally, they enhance our fundamental understanding of the mechanisms by which plasmons and photons interact in nanocomposite systems, providing a theoretical basis for the targeted design of plasmonic nanostructures with specific functional properties.

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ПЛАЗМОННИЙ РЕЗОНАНС НАНОЧАСТИНОК СРІБЛА ТА ЗОЛОТА В ОРГАНІЧНИХ СЕРЕДОВИЩАХ: ФІЗИЧНІ МЕХАНІЗМИ ТА СПЕКТРАЛЬНІ ПРОЯВИ

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У роботі досліджено механізм локалізованого поверхневого плазмонного резонансу в металевих наночастинках, інкорпорованих в органічні матриці. Проаналізовано фізичну природу плазмонних збуджень як когерентних коливань електронного газу зони провідності, що виникають під час взаємодії з електромагнітним випромінюванням. Вказано, що, на відміну від поверхневих плазмон-поляритонів, які поширюються вздовж протяжної межі поділу метал-діелектрик, локалізовані плазмони обмежені об'ємом наночастинок і проявляють радіаційні властивості. Досліджено дисперсійні характеристики поверхневих плазмон-поляритонів для систем срібло – органічний матеріал та золото – органічний матеріал, які демонструють істотні відхилення від лінійної залежності, притаманної вільному електромагнітному випромінюванню. Показано, що плазмонні моди характеризуються підвищеним значенням хвильового вектора порівняно з фотонами аналогічної енергії, що зумовлює ефект поверхневого збудження та інтенсивну просторову локалізацію оптичного поля. Виявлено два основні фізичні механізми, що контролюють розмірні кореляції характеристик плазмонів. Проаналізовано розмірні кореляції частотних та спектрально-ширинних характеристик локалізованого поверхневого плазмонного резонансу. Для великих наночастинок з діаметром понад 20 нм збільшення геометричних розмірів супроводжується довгохвильовим зміщенням резонансу внаслідок ефекту запізнювання, пов'язаного зі скінченністю швидкості електромагнітних збуджень. Для ультрамалих наночастинок з діаметром менше ніж 20 нм домінують квантоворозмірні ефекти, коли лінійні розміри стають співмірними з довжиною вільного пробігу електронів, що призводить до розширення спектральної напівширини через інтенсифікацію поверхневого розсіювання носіїв заряду. Отримані результати підтверджують, що розмірні кореляції резонансних частот поверхневих плазмонів у металевих наночастинках контролюються комплексом конкурентних фізичних процесів, внесок яких варіюється залежно від розмірного діапазону та специфіки матеріальної системи. Отримані результати допоможуть поглибити фундаментальне розуміння механізмів взаємодії плазмонів і фотонів у нанокомпозитних системах, створивши теоретичну основу для цілеспрямованого проєктування плазмонних наноструктур із конкретними функціональними властивостями.

Ключові слова: *наночастинки; локалізований поверхневий плазмонний резонанс; поперечний переріз розсіювання.*