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GOLD PLASMONIC ARRAY STRUCTURES FOR SENSING APPLICATIONS

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This article is devoted to the theoretical study of the plasmonic properties of periodically arranged arrays of gold nanoparticles. The Comsol Multiphysics software, which is based on the finite element method, was used to build 3D numerical models for the simulation and conduct research. In this work the electric field distribution and optical characteristics of the spherical gold nanoparticles array were studied. Individual localized surface plasmon resonance modes are influenced when metallic nanoparticles are in the close proximity and as a result the electric near- fields can couple, resulting in a new hybrid mode. We mainly focused here on the investigation of two crucial questions, particularly, influences of the gap between the nanoparticles and the refractive index of the surrounding medium on the resulting optical response of the gold nanoparticles arrays. The array of periodically arragement gold nanoparticles is characterized by an enhanced local electric field between the nanoparticles, which is inversely proportional to the gap between the particles. The field strength and optical properties (reflection, transmission, and absorption) can be conveniently manipulated by changing the gap between particles. In additional, their potential applications as sensetive plasmonic sensors element have been considered. The studied structure has a significant potential for practical applications due to its wide range of the operating wavelengths and ease of the high-throughput fabrication. In the course of the study, it was established that the change in the distance between the surface of nanoparticles by 1 nm leads to a significant shift in the spectral transmission and reflection curves on the spectral range. In addition, these studies showed that an increase in the distance between the surfaces of nanoparticles leads to the decrease in the near-field interaction between gold nanoparticles in the array. Therefore, the obtained results can be successfully used in the manufacture of highly sensitive plasmon sensors with the possibility of controlling the sensitivity and the working spectral range.

Keywords: *gold nanoparticles, array, localized surface plasmon resonance, sensing.*
UDC: 53.072:53:004

1. Introduction

Nowadays, noble nanoparticles demonstrate extraordinary size-dependent physical and chemical properties due to their localized surface plasmon nature and phenomenal light manipulating possibilities [1]. The conduction band electrons collective oscillations occur under light irradiation of the metallic nanoparticles and as a result the sufficiently enhancement of the nanoscale light-matter interactions and near-field optical intensities can be achieved [2]. Recently, studies of nanoparticles arrays with different

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geometries have exhibited that diffractive light coupling of particles plays a significant role in forming their near and far-field properties by enhancing the coupling efficiency to localized surface plasmon resonances [3]. The periodic arrangement of plasmonic nanoparticles influences their interaction with electromagnetic waves and is an effective approach to tune their optical properties and give rice new phenomena [4]. Array of metallic plasmonic nanoparticles is showed to be the most powerful platform to implement light–matter interactions through the control of the morphology and engineering parameter [5]. Conduction electrons in metal nanoparticles oscillate when localized surface plasmons are excited by illumination with electromagnetic radiation. The oscillation, known as surface plasmon resonance, results in extremely strong light scattering and absorption, accompanied by a significantly enhanced near field due to the high localization of light energy in nanoscale [6]. Localized surface plasmon resonance is significantly influenced by the size and composition of the nanoparticle, as well as the dielectric constant of the surrounding medium [7]. Individual localized surface plasmon resonance modes are influenced when metal nanoparticles are in close proximity and as result the electric near fields can couple, resulting in a new hybrid mode.

Plasmonic nanoparticle periodic or dimer structures leads to new surface plasmon resonances and creation of the strong electric field in the gap between them which called “hot-pots” [8]. The “hot-spot” in the gap of the plasmonic structures increase the coupled resonances and found wide usage in three application fields of plasmonic, namely, the sensing, solar energy conversion, and photodetection [9]. It should be noted that high sensitivity is realized only when specifies are located near the enhanced field, in another wors in the “hot-spot” region. This region can be principally defined by the nanostructure’s geometry and permittivity [10]. The highly localized and enhanced field caused by surface plasmon resonances is observable in many sensing applications [11, 12]. The spectral shift of the transmittance or reflectance spectrum of optical sensors increases significantly when the tested analytes are in an enhanced electromagnetic field [13].

Researchers have recently become interested in sensors based on gold nanoparticles since they can proffer magnificent features. Gold nanoparticles are the most stable metal nanoparticles characterized by unique basic physical properties [14]. Small size Au nanoparticles have a large extinction cross-section and as a result the capability to enhance the near electromagnetic field.

In this paper, the optical characteristics of the gold nanoparticles array were studied. We mainly focused on the investigation of two crucial questions, namely, influences of the gap between the nanoparticle surfaces and the refractive index of the surrounding medium on the resulting optical response of the gold nanoparticles arrays. In additional, their potential applications have been considered.

2. Results and Discussions

The unit cell of the studied array of periodically arrangement gold nanoparticles is shown in Fig. 1. Under initial conditions, normal incidence of the beam on the structure under study is assumed. The operating wavelength is 650 nm, the refractive index of the surrounding medium is 1.33, the radius of the nanoparticles is 10 nm, and the distance between nanoparticles in all directions is 1 nm. Refractive index of gold nanoparticles used from reference [15].

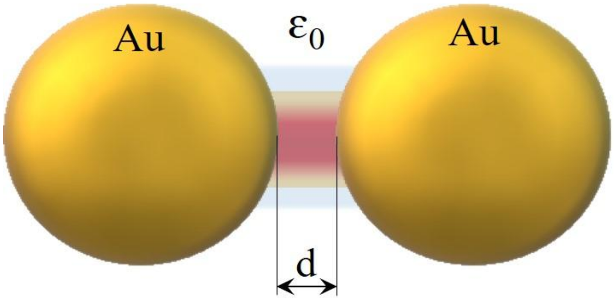


Fig.1. Schematic of a gold dimer consisting of two spherical particles separated by gap d between the surfaces in the surrounding medium ε_0.

The local electric field occurs in the gap between the particles under the influence of external excitation in an array of metal nanoparticles. The finite element method was used to calculate the electric field distribution, as well as the optical characteristics of the periodic structure under study. Nowadays, this method has become one of the most commonly used for solving issues that are described by partial differential equations or can be formulated as functional minimization. The region of interest is represented as a set of finite parts. Approximation functions in finite elements are determined through the nodal values of the desired physical field. The continuous physics problem is transformed into a discretized finite element problem with unknown nodal values. it is necessary to solve a system of linear algebraic equations for a linear problem. The values inside the leaf elements can be recovered using the node values [14].

Compared to an individual nanoparticle, the resonance wavelength of a nanoparticle in the gap mode exhibits a red shift because the presence of an adjacent metal nanoparticle weakens the restoring force acting on the electrons of the structure. In addition, the near field in the gap can be greatly enhanced due to the high localization of light energy in a small space. This is the basis for the high sensitivity of such elements. It should be noted that the force of interaction between metal nanoparticles increases with decreasing distance between them. Therefore, detailed control of the distance is crucial for manipulating the hybrid mode and therefore the sensitivity.

The electric field distribution depending on the thickness of the gap between the surfaces of nanoparticles is shown in Fig. 2. The distance between nanoparticles varied from 1 nm to 5 nm. As expected, the highest field enhancement between particles was observed at a distance of 1 nm, up to 1.0 10^6 V/m. As the gap increased, the field decreased and at a gap of 5 nm, almost separation of the near field of each particle can be observed. Therefore, conducting studies at large gaps between particles was impractical. It should be noted that the electric field of an individual particle is approximately 1.4 10^5 V/m.

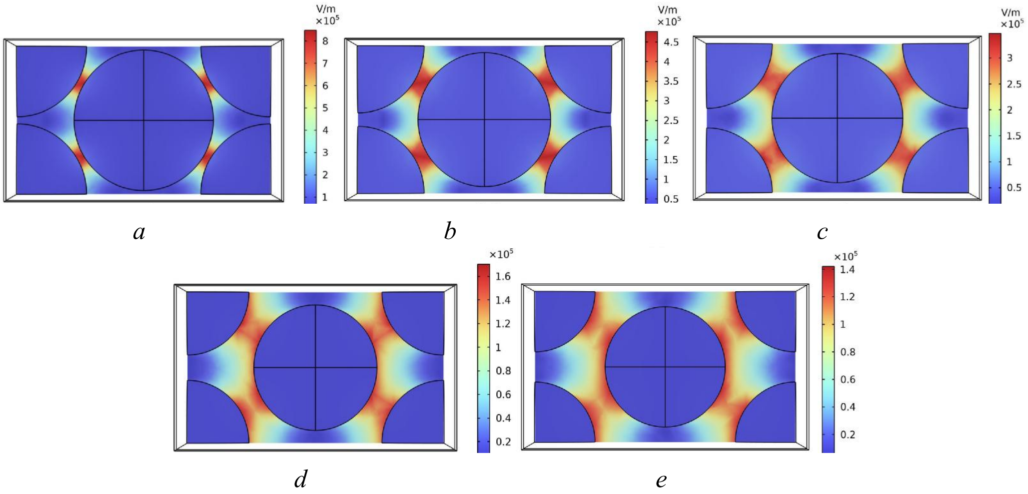


Fig.2. Distribution of the electric field of a normally incident electromagnetic wave with Au nanoparticles array with a radius of 10 nm and a gap between the nanoparticles surfaces of 1 nm (a), 2 nm (b), 3 nm (c), 4 nm (d), and 5 nm (e). The refractive index of the surrounding media is 1.33. The colour bar indicates the electric field intensity under the wavelength of 650 nm

The increase in the local electric field occurs in the gap between the particles under the influence of external excitation in an array of metal nanoparticles. It causes a modification of the optical properties associated with localized surface plasmon resonance. There is a shift in the plasmon peak in the ranges of reflection, transmission and absorption coefficients (Fig. 3). When the distance between nanoparticles increases from 1 to 5 nm, the plasmon peak shifts from 675 nm to 560 nm (Fig. 3a, c). As for the distribution of the electric field, it should be noted that an increase in the distance from the initial distance, even 1 nm, leads to a decrease in the intensity of the electric field by almost half from $1 \cdot 10^6$ V/m to $5.7 \cdot 10^5$ V/m. Although decreasing the gap between nanoparticles leads to an increase in the electromagnetic field (Fig. 3d). The absorption of an array of periodically placed nanoparticles decreases (Fig. 3b). It should be noted that at the gap of 1 nm there is practically no absorption peak observed for the structure under study.

Plasmonic nanostructures are widely used for detecting the refractive index due to their high sensitivity to changes in environmental parameters. Therefore, the distribution of the electric field at the operating wavelength (Fig. 4) and the dependence of the reflection, transmittance, absorption and normalized electric field on the wavelength were calculated for array gold nanoparticles for three different refractive indices of the environment (Fig. 5). The optimal gap between particles was 1 nm.

The electric field distribution at the operating wavelength for all three cases is in the vicinity of 10^6 V/m. Although the maximum electric field of about $2 \cdot 10^6$ V/m at the working length is characteristic only of the structure under study located in the air. The thicker the medium, the lower the normalized electric field will be depending on the wavelength (Fig. 5d). At the same time, the position of the plasmon peak, when the refractive index of the environment changes from 1.00 to 1.43, shifts to the longer wavelength region from 580 nm to 700 nm (Fig. 5a, c). In the absorption spectrum, a plasmon peak is clearly visible only for the structure located in the air.

Thus, the above structure of periodically arrangement gold nanoparticles can be a sensitive element of a plasmonic sensor, allowing one to detect the dependence of the wavelength of the resonance peak on the values of the refractive index of the surrounding medium when the change is large enough. However, such nanostructured metal plasmonic arrays can be used as ultra-highly sensitive sensors, since they provide the ability to excite ultranarrow plasmonic modes and, accordingly, detect extremely weak changes.

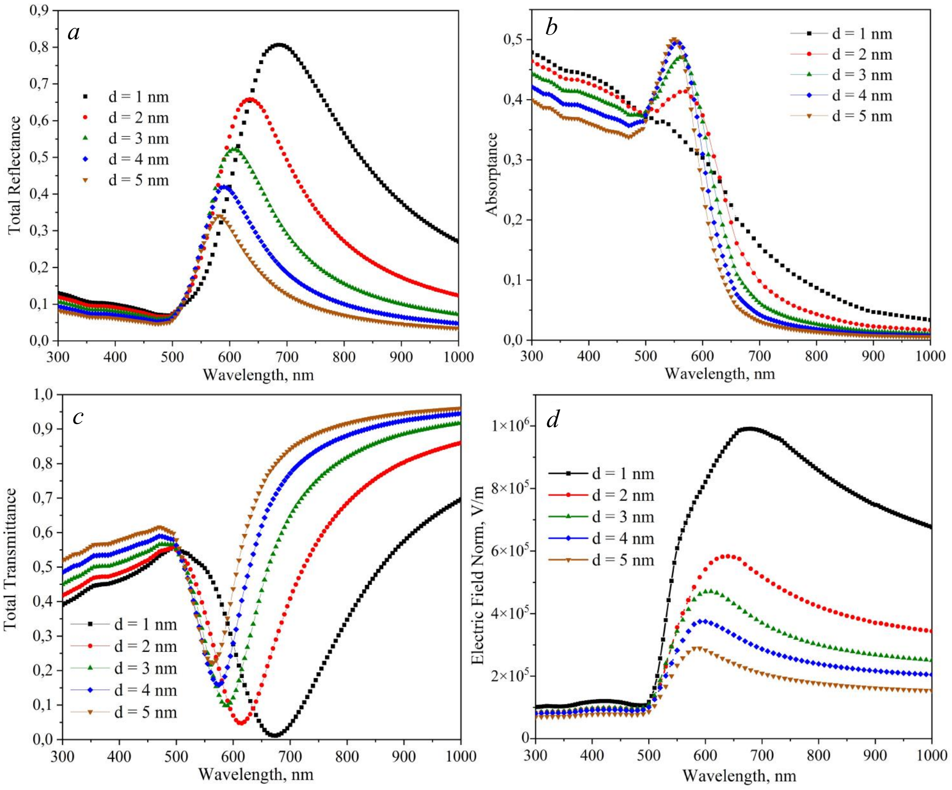
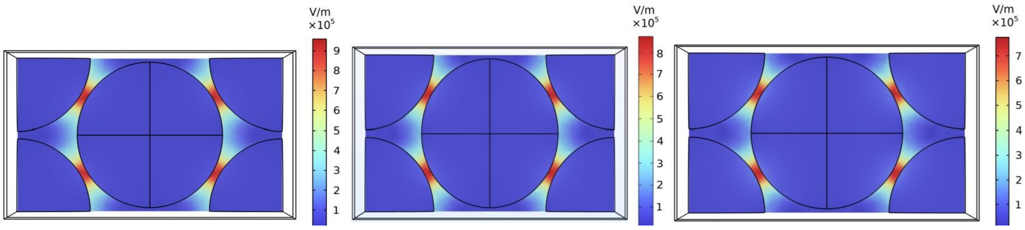


Fig.3. The total Reflectance (a), Absorptance (b), Transmittance (c) and Electric field distribution (d) spectra of Au nanoparticles array with a radius of 10 nm and a gap between the surface of the particles from 1 to 5 nm in a surrounding media with a refractive index of 1.33

Conclusion

In the summary, first of all we can state that numerical modeling is necessary within the limits of many specific assumptions in the process of designing and manufacturing sensor elements, which are complex and labor-intensive. The simulation results demonstrated that an array of periodically arrangement gold nanoparticles is characterized by an enhanced local electric field between the nanoparticles, which is inversely proportional to the gap between the particles. The field strength and optical properties (reflection, transmission, and absorption) can be conveniently manipulated by changing the gap between particles.

The work shows that an array of gold nanoparticles can be used as a sensitive element of a plasmonic sensor. The structure under study has great potential for practical applications due to its wide range of operating wavelengths and ease of high-throughput fabrication. Plasmonic nanosensing devices will be an important building block for both nanomaterials science and advanced industrial process monitoring in the future.



a *b* *c*

Fig.4. Distribution of the electric field of a normally incident electromagnetic wave with Au nanoparticles array with a radius of 10 nm and a gap between the nanoparticles surfaces of 1 nm in the surrounding media with refractive index of 1.00 (a), 1.33 (b) and 1.43 (c). The colour bar indicates the electric field intensity under the wavelength of 650 nm

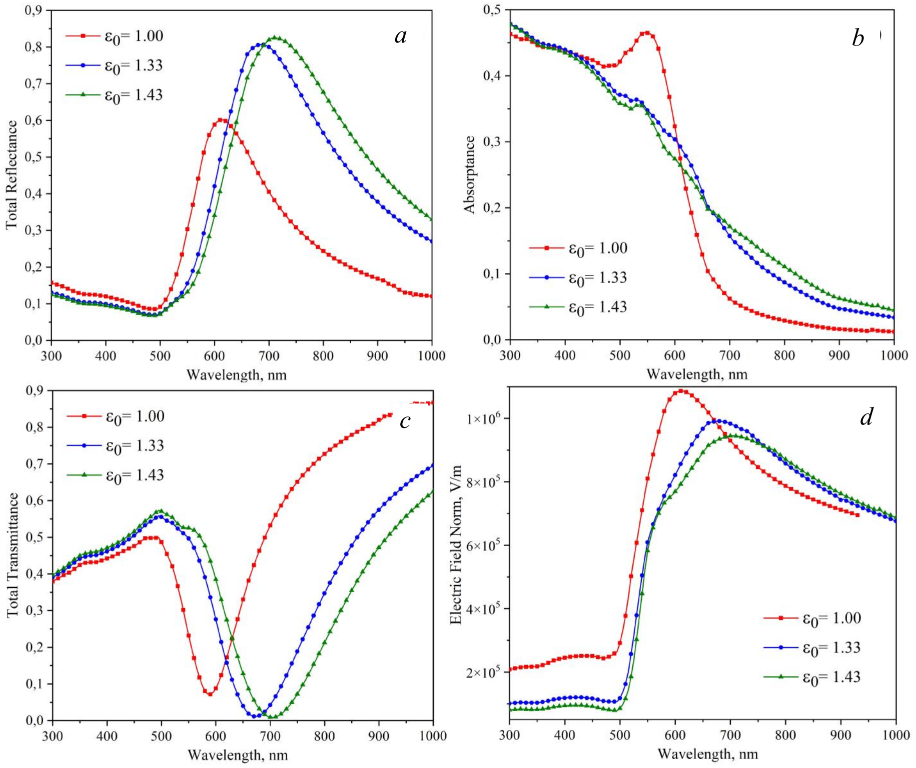


Fig. 5. The total Reflectance (a), Absorptance (b), Transmittance (c) and Electric field distribution (d) spectra of Au nanoparticles array with a radius of 10 nm and gap between the nanoparticles surfaces of 1 nm in the surrounding media with variable refractive index

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МАСИВ ПЛАЗМОННИХ ПЕРІОДИЧНО РОЗМІЩЕНИХ ЗОЛОТИХ НАНОЧАСТИНОК ДЛЯ СЕНСОРНОГО ЗАСТОСУВАННЯ

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Ця стаття присвячена теоретичному дослідженню плазмонних властивостей періодично розташованих масивів наночастинок золота. Програмне забезпечення Comsol Multiphysics, яке базується на методі скінченних елементів, було використано для побудови числових 3D моделей для моделювання та проведення досліджень. У роботі досліджено розподіл електричного поля та оптичні характеристики масиву сферичних наночастинок золота. Індивідуальні локалізовані моди поверхневого плазмонного резонансу зазнають впливу, коли металеві наночастинки знаходяться в безпосередній близькості, тож електричні ближні поля можуть з'єднуватися, створюючи новий гібридний режим. Ми зосередилися здебільшого на дослідженні двох ключових питань, а саме: впливу відстані між поверхнями наночастинок та впливу показника заломлення навколишнього середовища на кінцевий оптичний відгук масивів наночастинок золота. Масив періодично розташованих наночастинок золота характеризується підсиленим локальним електричним полем між наночастинками, яке обернено пропорційне відстані між поверхнями частинок. Напруженістю поля та оптичними властивостями (відбиванням, пропусканням і поглинанням) можна зручно керувати, змінюючи відстань між частинками. Крім того, розглянуто їхнє потенційне застосування у ролі чутливого сенсорного елемента. Досліджена структура має значний потенціал для практичного застосування завдяки широкому діапазону робочих довжин хвиль і простоті високопродуктивного виготовлення. Під час проведення дослідження встановлено, що зміна відстані між поверхнею наночастинок на 1 нм призводить до вагомого зміщення спектральних кривих пропускання та розсіяння на спектральній шкалі. Крім цього, результати дослідження показали, що збільшення відстані між поверхнями наночастинок призводить до значного зниження ближньопольової взаємодії між наночастинками золота в масиві. Отже, отримані результати можуть бути успішно використані при виготовленні вискочутливих плазмонних сенсорів із можливістю контролю чутливості та робочого спектрального діапазону.

Ключові слова: *наночастинки золота, масив, локалізований поверхневий плазмонний резонанс, детектування*