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ELECTRIC FIELD ENHANCEMENT BY GOLD NANO-SPHERE AND ITS CLUSTERS

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The confinement of electrons in gold nanoparticles results in Surface Plasmon Resonance (SPR), which is characterized by electric field enhancement in the vicinity of these nanoparticles. This property has been extensively studied and applied in various fields. In our research, we conduct a detailed investigation of plasmonic coupling in spherical gold nanoparticles. Specifically, we use the Discrete Dipole Approximation (DDA) method implemented in DDSCAT to simulate the coupling of electric fields in a doublet of nanoparticles as a function of the distance between them. Our simulations show that the coupling of SPR between two nanoparticles occurs up to a separation of 12 nm. Moreover, we extend our simulations to study the coupling of nanoparticles in linear chains consisting of up to five nanoparticles and in clustered forms. Our results indicate that the SPR coupling in a linear chain occurs, and as the number of nanoparticles increases, the field enhancement also increases. However, we observe that this effect saturates after four nanoparticles in a line. Our study provides insights into the plasmonic coupling in gold nanoparticles, which can aid in the design and optimization of plasmonic devices for various applications.
Keywords: *Surface Plasmon resonance (SPR); Gold Nano particles; Discrete Dipole Approximation (DDA); DDSCAT; Field Enhancement*
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INTRODUCTION

Noble metal particles exhibit exceptional optical properties owing to plasmonic resonances at metal-dielectric interfaces [1]. These resonances are a collective oscillation of free electrons on the surface of the nanoparticle triggered by incident electromagnetic waves. As a result, there is a strong confinement of the electromagnetic field along the surface normal of the nanoparticle, leading to a significant enhancement of the electromagnetic field. This enhancement causes strong absorption and scattering near the plasmon resonance frequency. Raman Spectroscopy has gained considerable attention due to its ability to provide molecular information with high sensitivity by analyzing molecules absorbed on metallic surfaces or metal nanostructures [2].

To fully utilize the potential of these enhanced electric fields, it is necessary to understand the various phenomena resulting from the highly intense and confined field. These fields generate strong electric field gradients, which alter selection rules, and mode intensities and have profound effects on Raman Spectra [3-9]. Knowledge of field distribution and polarization is critical to arrive at approximate enhancement factors. In light of this, we conducted a study of the electric field distribution around gold nanoparticle clusters. Several methods have been presented in the literature for simulating the electric field distribution around a particle. The most commonly used among these are Mie-Scattering, T-matrix method, Finite Element Method (FEM), Finite Difference Time Domain (FDTD), and Discrete Dipole Approximation (DDA) based methods. Each of these methods has its advantages and disadvantages. Mie Scattering and T-matrix methods are fast but are limited to structures with certain symmetry in the geometry. FEM and FDTD methods can determine the scattered electric field distribution of arbitrarily shaped particles, but the computation time for these methods is very large [10]. We opted to use the DDA method because it is fast and can compute field distribution for arbitrarily shaped particles [11-14].

DISCRETE DIPOLE APPROXIMATION (DDA) METHOD

The Discrete Dipole Approximation (DDA) is an effective method to model particles as a group of finite cubic elements [11]. By considering only dipole interactions with the incident electric field and induced-fields from neighboring elements, the solution of the Maxwell equations can be simplified into an algebraic problem of many coupled dipoles. Each dipole in the assembly responds to both the external electric field and the electric fields from its neighboring dipoles by acquiring a dipole moment. To solve the electromagnetic scattering problem of a continuous assembly, the induced dipole moment of each dipole is given by $\mathbf{P}_i = \alpha_i \mathbf{E}_{local}$, where α_i denotes the polarizability of the material associated with the dipole element. The polarizability, which can be expressed as Clausius-Mossotti polarizability, plays a crucial role in determining the behavior of the electromagnetic scattering problem and can be used to predict the electromagnetic responses of the assembly.

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$$\alpha_i^{CM} = \frac{3d^3}{4\pi}\frac{\varepsilon_i - 1}{\varepsilon_i + 2}. \tag{1}$$

The Clausius-Mossotti polarizability is a concept used to describe the interactions between electric fields and matter. However, it is only accurate in the limit of a DC (direct current) field, which means when the wave vector is very small. This model does not take into account the size-dependent effects that are observed in nanoparticles. To address this discrepancy, Draine and Goodman [11] conducted a study on wave propagation on an infinite lattice with discrete spacing between lattice points. They were able to derive a dispersion relation in the long wavelength limit, which led to a more accurate description of polarizability in nanoparticles.

$$\alpha^{LDR} = \frac{\alpha^{CM}}{1+\left(\alpha^{CM}/d^3\right)\left[\left(b_1 + m^2 b_2 + m^2 b_3 S\right)(kd)^2 - (2/3)i(kd)^3\right]}, \tag{2}$$

b1= -1.891531; b2=0.1648469; b3 = -1.7700004; $S = \sum_{i=1}^{3}\left(\hat{a}_i\hat{e}_i\right)^2$.

Where *a* and *e* are unit vectors defining the incident direction and polarization state, "m" are complex refractive index of the material in the medium and "d" is lattice spacing and ε is the complex dielectric constant of the material in medium. Equation (2) holds good in the long wavelength limits and is also accurate to O $(kd)^3$.

The electric field at any point in the space due to the incident plane wave is given by the

$$\vec{E}_{local} = \vec{E}_{inc,i} + \sum_{j=1, j\neq i} \vec{E}_j , \tag{3}$$

$$\vec{E}_{local} = \vec{E}_{inc,i} - \sum_{j=1, j\neq i} A_{ij}\vec{P}_j . \tag{4}$$

Where $\mathbf{E}_{local}$ is the electric field at $\boldsymbol{r}_i$ due to the incident wave ($\mathbf{E}_{inc,i}$), plus a contribution $\mathbf{E}_j$= - $\mathbf{A}_{ij}\mathbf{P}_j$, the radiated electric field of an individual dipole at $\boldsymbol{r}_j$. The interaction matrix ($\mathbf{A}_{ij}$) is given by

$$A_{ij} = \frac{\exp(ikr_{ij})}{r_{ij}}\left[k^2\left(\hat{r}_{ij}\hat{r}_{ij} - 1_3\right) + \frac{ikr_{ij} - 1}{r_{ij}^2}\left(3\hat{r}_{ij}\hat{r}_{ij} - 1_3\right)\right].\ i \neq j , \tag{5}$$

Where $k=\omega/c$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, 1_3 is a 3x3 unit matrix.

Defining $\mathbf{A_{ii}} = \alpha_i^{-1}$ reduces the scattering problem to finding the polarizations $\mathbf{P_i}$ that satisfy a system of 3N complex linear equations

$$\sum_{j=1}^{N} A_{ij}\vec{P}_i = \vec{E}_{inc,i} . \tag{6}$$

Once the equation (6) is solved for unknown polarization $\mathbf{P_i}$, the extinction and absorption cross-section C_{ext} and C_{abs} may be evaluated as

$$C_{ext} = \frac{4\pi k}{\left|E_0\right|^2}\sum_{i=1}^{N}\mathrm{Im}\left(E_{inc,i}^{*}\cdot P_i\right), \tag{7}$$

$$C_{abs} = \frac{4\pi k}{\left|E_0\right|^2}\sum_{i=1}^{N}\left\{\mathrm{Im}\left(P_i.(\alpha_i^{-1})^{*}\cdot P_i^{*}\right) - \frac{2}{3}k^3\left|P_i\right|^2\right\}. \tag{8}$$

The scattering cross-section $C_{sca} = C_{ext} - C_{abs}$. In the far field, the scattered electric field is given by

$$E_{sca} = \frac{k^2\exp(ikr)}{r}\left[\sum_{i=1}^{N}\exp\left(-ik\hat{r}\cdot\vec{r}_j\right)\left(\hat{r}\hat{r} - 1_3\right)\vec{P}_j\right]. \tag{9}$$

The DDA computations have specific criteria that must be met to be applicable [12]. These criteria are as follows:

1) The distance between the dipoles, also known as the inter-dipole separation 'd', must be smaller than the wavelength in the medium, such that $|m|kd \leq 1$.
2) The inter-dipole separation 'd' should be small enough or the number of dipoles 'N' should be large enough to accurately represent the target shape.

SIMULATION RESULTS

Simulation of Surface Plasmon Resonance (SPR) of Spherical Nanospheres

The present study concerns the wavelength dependence of the extinction cross-section of an isolated spherical gold nanoparticle with a diameter of 40 nm. The calculations were performed within the wavelength range of 450-700 nm,

which corresponds to the surface plasmon resonance (SPR) band. To investigate the influence of the number of dipoles on the results, the calculations were repeated several times with varying numbers of dipoles, ranging from approximately 500 to 22500, as shown in Table 1.

In this study, we compared the results obtained through experimental analysis with the analytical calculations for a sphere, using the well-known Bohren and Huffman code based on the Mie scattering theory [14]. Our research focuses on the extinction spectra of a 20 nm radius Au sphere in an aqueous medium (water n = 1.33), with the refractive index of the gold nanoparticles taken from Johnson and Christy [15]. Figure 1 displays the obtained extinction spectra, which demonstrate that the accuracy of the computed extinction coefficients improves with an increasing number of dipoles used in the computation. This observation is consistent with the existing literature, which highlights that the inter dipole spacing of 1-2 nm range is required to obtain the optical properties of the metallic nanoparticles with great accuracy.

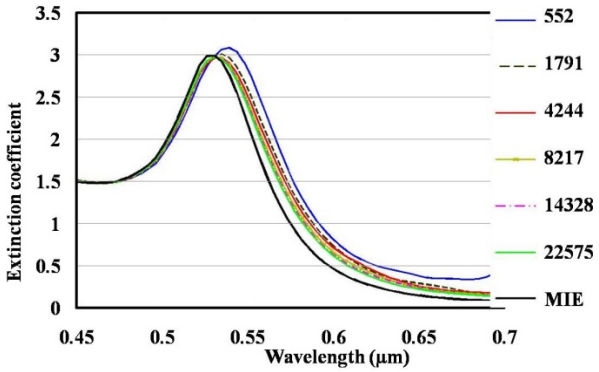


Figure 1. Convergence of extinction spectra obtained by DDA to Mie - Scattering with the increase in the number of the dipoles

Table 1. The lattice spacing corresponding to the number of dipoles

Number of Dipoles	Lattice Spacing (nm)
552	3.930
1791	2.665
4224	1.994
8217	1.598
14328	1.327
22575	1.141

We conducted a study to examine the impact of the size of a sphere on the spectral position of resonance. To do this, we analyzed three spheres with varying radii of 10, 20, and 30 nm, while keeping the lattice spacing at approximately 1.5 nm. We then calculated their surface plasmon resonance (SPR), and the results are presented in Figure 2. We also included a table (Table 2) that lists the SPR for each nanoparticle.

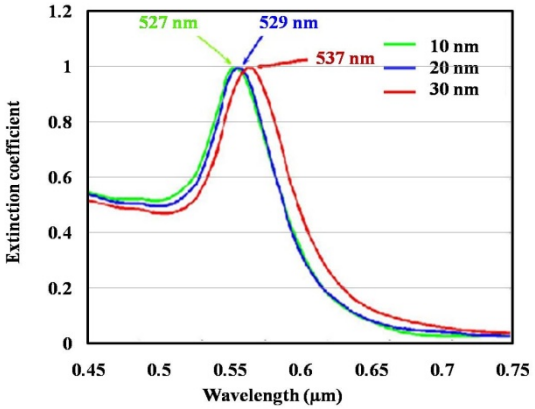


Figure 2. Extinction spectra of 10, 20, and 30 nm radius sphere in water

Table 2. Surface Plasmon Resonance vs. Radius

Radius (nm)	Resonance Peak (nm)
10	527
20	529
30	537

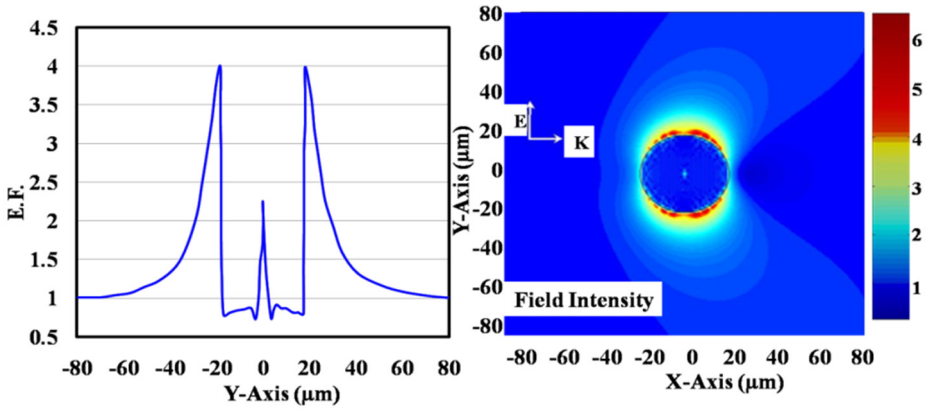


Figure 3. Electric field pattern of a 20 nm radius sphere (K||X, E||Y) on the right, and on the left field enhancement around a nano-sphere along the Y-axis

As expected, we observed a red shift in the SPR peak with an increase in the sphere's diameter (size). Moreover, we studied the scattered electric field distribution around 20 nm radius gold (Au) sphere in water (Figure 3).

We analyzed the variation of the electric field enhancement (FE) across the nanoparticle and found that within the range of a few tens of nanometers, the field value drops to the magnitude of the incident electric field. This information can be used to compute the electric field gradient near the nanoparticles.

AGGREATES OF NANO SPHERES

Self-assembled clusters of nanospheres have garnered significant interest due to their low-cost approach for a wide range of plasmonic applications. Compared to other nanofabrication techniques, such as electron beam lithography and focused ion beam, these clusters offer an affordable alternative. By varying the composition, number, and position of the nanoparticles in these clusters, the plasmonic properties can be controlled and exhibit sharp resonances and steep enhancements, also known as hot spots. We have conducted simulations of the electric field of simple clusters consisting of up to five spherical particles of nano size.

DOUBLETS OF NANOSPHERES

The plasmonic properties and electric field distribution around doublets of nano-sphere were simulated for various separations between spheres. It was observed that there are two SPR peaks in the case of doublets; one identical to that obtained in an isolated sphere (transverse mode) and a red-shifted mode attributed to the longitudinal SPR mode. The longitudinal mode is due to plasmon oscillation along the line joining the two spheres. The longitudinal mode is very sensitive to the separation between the two spheres and shifts towards the transverse mode as the spacing is increased. It merges with the transverse mode when the separation becomes too large for any significant interaction between the plasmonic oscillations in the two spheres. Figure 4 shows the extinction spectra of the doublet structure for various separations, and the spectral position of the longitudinal mode is listed in Table 3. The field enhancement increases as the separation between two spheres decreases.

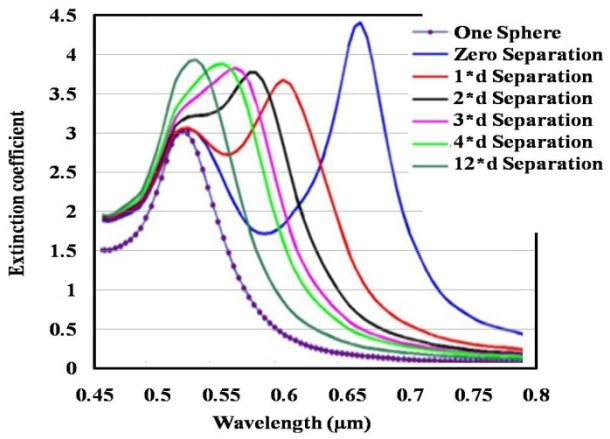
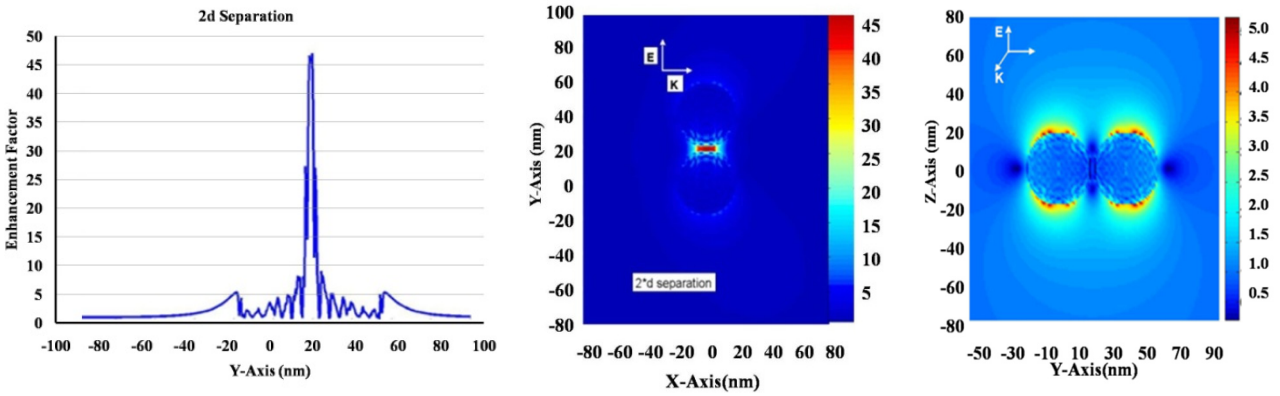


Figure 4. Extinction spectra of doublet structure with the separation.

Table 3. Longitudinal modes with separation

Separation Between two spheres in terms of d (d = 1.1nm)	Longitudinal mode (nm)
Zero	665
1*d	605
2*d	584
3*d	570
4*d	560
12*d	540



a) **b)** **c)**

Figure 5. Electric field patterns (5b & 5c) and its magnitude (5a) along Y-axis of a doublet of 20 nm radius sphere separated about 2 nm (2*d, d = 1.1 nm)

Figure 5 depicts the electric field distribution around a doublet structure consisting of two nano-spheres with a 2 nm separation. In figure 5a, the field enhancement factor along the Y-axis for the orientation of the particle shown in

Figure 5b is demonstrated. It indicates that the gradient field is significantly high in the region between the two spheres. The coupling between the two spheres is only feasible for a specific polarization of the incident light, i.e., coupling occurs only when the polarization is along the longer axis of the doublet, as shown in Figure 5c.

CLUSTERS FORMED BY THREE OR MORE NUMBER OF NANO SPHERES

A comprehensive electric field simulation was conducted to analyze the clusters formed by up to five nanospheres. To create these nanoscale structures, three nanospheres were arranged either in a linear chain or at the vertices of an equilateral triangle, as illustrated in Figure 6.

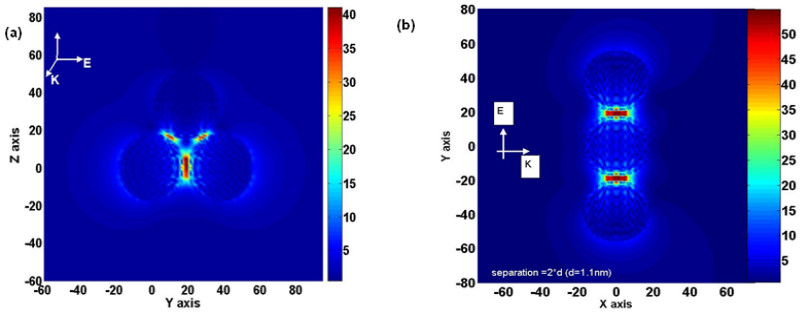


Figure 6. Electric field patterns when 3-spheres are in triangular (a) and linear (b) configurations

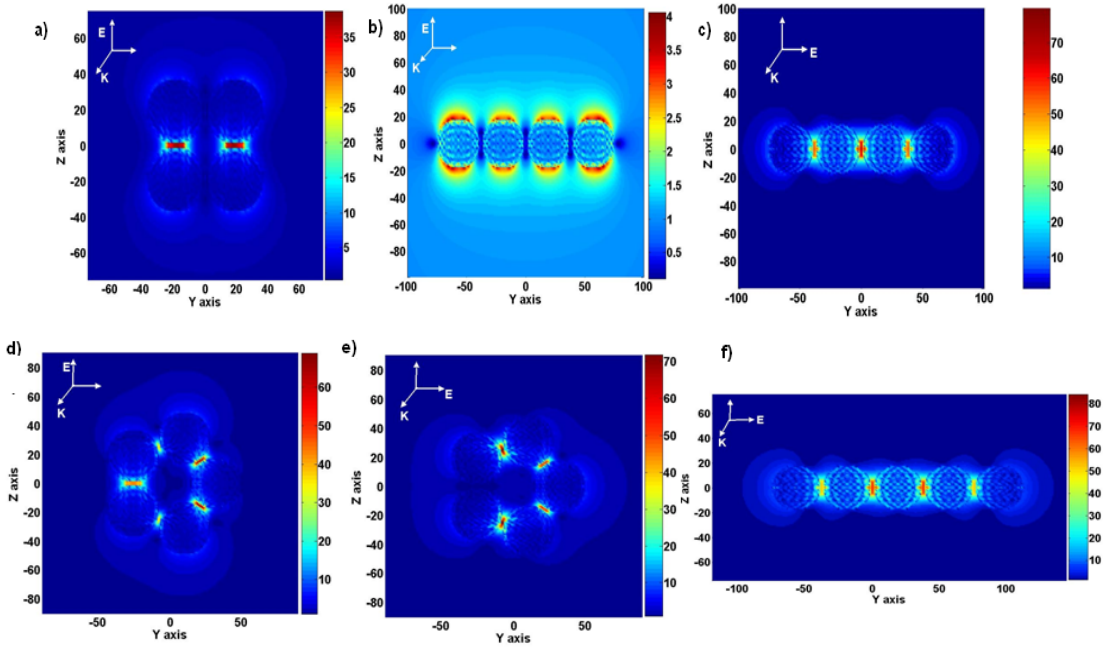


Figure 7. Electric field patterns for 4 & 5 spheres in different configurations

To ensure symmetry, a pair of nanospheres spaced 2 nm apart was chosen as it demonstrated the maximum field enhancement. A third nanosphere was then added to create a symmetrical object either in a linear chain or a triangle. A detailed analysis of the electric field distributions within the resulting object was carried out and is also depicted in Figure 6. The results demonstrate that the field enhancement is more prominent in linear chains of nanospheres as compared to that of triangles. This study provides valuable insight into the behavior of nanoscale structures under an electric field and can aid in the development of novel nanoscale devices with enhanced performance.

Figure 7 shows the electric field pattern of clusters containing four and five spheres. The enhancement is higher in a linear pattern for all cases. However, it is important to note that the enhancement factor does not increase linearly with the number of spheres. It tends to saturate. The enhancement factor of the incident field is polarization-dependent, as mentioned above. The saturation in the field enhancement occurs due to the resistive losses taking place during the oscillations of electrons.

CONCLUSIONS

This study conducted extensive simulations to investigate the characteristics of field enhancement in gold nanospheres. Through our analysis, we found that the number of spheres present has a direct influence on the degree of field enhancement, with greater numbers leading to more significant enhancements. Moreover, we found that the linear arrangement of these spheres produces a higher degree of enhancement compared to other arrangements. Our research

also revealed that the enhancement factor exhibits a saturation effect beyond a certain threshold of spheres, implying that the maximum level of enhancement can be reached. Overall, our investigations provide valuable insights into the field enhancement properties of gold nanospheres, which can be useful in a variety of scientific and technological fields.

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ПІДСИЛЕННЯ ЕЛЕКТРИЧНОГО ПОЛЯ НАНОСФЕРОЮ ЗОЛОТА ТА ЇЇ КЛАСТЕРАМИ

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Утримання електронів у наночастинках золота призводить до поверхневого плазмонного резонансу (SPR), який характеризується посиленням електричного поля поблизу цих наночастинок. Ця властивість була широко вивчена і застосована в різних областях. У нашому дослідженні ми проводимо детальне дослідження плазмонного зв'язку в сферичних наночастинках золота. Зокрема, ми використовуємо метод дискретної дипольної апроксимації (DDA), реалізований у DDSCAT, щоб симулювати зв'язок електричних полів у дублеті наночастинок як функцію відстані між ними. Наше моделювання показує, що зв'язок SPR між двома наночастинками відбувається на відстані до 12 нм. Крім того, ми розширюємо наше моделювання, щоб вивчити зв'язок наночастинок у лінійних ланцюгах, що складаються з п'яти наночастинок, і в кластерних формах. Наші результати показують, що відбувається зв'язок SPR у лінійному ланцюзі, і зі збільшенням кількості наночастинок посилення поля також збільшується. Однак ми спостерігаємо, що цей ефект насичується після чотирьох наночастинок у рядку. Наше дослідження дає уявлення про плазмонний зв'язок у наночастинках золота, що може допомогти в розробці та оптимізації плазмонних пристроїв для різних застосувань.

Ключові слова: *поверхневий плазмонний резонанс (ППР); наночастинки золота; дискретне дипольне наближення (DDA); DDSCAT; покращення поля*