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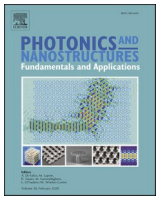

A comprehensive study on the Rod-based plasmonic structures sensing using the modified discrete dipole approximation method

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ABSTRACT

Using the previously introduced modified discrete dipole approximation (DDA) method by applying the full details of the nanoparticle and its surrounding environment, the detection sensitivity of molecules by plasmonic Rod-based nanosensors, including U-shaped and Rod-shaped structures, was investigated. In the calculations, the two factors of the magnitude of the wavelength shift and the ability to distinguish molecules with similar properties were of significant interest. The results indicated that the sensitivity of Rod-based nanostructures is significantly higher than that of spherical nanoparticles. Among the plasmonic Rod-based nanosensors, the silver U-shaped structure performs better than others. The wavelength shift of the absorption spectrum of different nanosensors for a given molecule was very different, making it possible to detect very similar molecules from each other by testing different sensors.

1. Introduction

The use of the optical properties of noble metals for sensing has been of great interest to researchers [1–3]. Since the number of natural plasmonic materials is limited and their optical properties are completely defined, there is a significant need for nanoengineering of the properties of these structures in order to perform better and create more diverse properties. Geometrical investigation of nanostructures is one of the essential tools in the nanoengineering of optical and plasmonic properties [4–15]. Spherical nanoparticles have symmetrical structures, and their limited optical and plasmonic properties have been investigated repeatedly [1, 12, and 13]. It was observed that the slightest geometrical asymmetry has led to the creation of various absorption peaks with various plasmonic oscillation properties (dipolar, quadrupolar, and octapolar) [8, 10, and 11].

Rod-based nanostructures, including rod-shaped and U-shaped, are of great interest, and the effects of their dimensions on the shift of absorption spectrum peaks have already been considered [4–10]. Since the construction and characterization of Rod-based structures are more accessible than other structures [8,9,14,15], it seems necessary to investigate the sensing properties of these structures in more detail.

In the previous research [1], by modifying the usual discrete dipole approximation (DDA) method [16–18], the sensing properties of spherical silver nanoparticles were investigated theoretically and experimentally in order to identify gastric cancer microRNA-21. The usual DDA method is a very powerful method to calculate the scattering cross section of nanoparticles. But to investigate the effect of molecules in the vicinity of nanoparticles this method needs a slight modification by applying molecular polarizability [19,20]. Such a modification in the previous work [1] led to entering the exact details of the space around the nanoparticle and the exact atomic details of the guest molecules. It caused much better results to be obtained compared to the methods that deal with the surroundings of the nanoparticle as an effective medium [14,15,21–24].

Our aim in the current research was to investigate the sensitivity of Rod-based structures for detecting the different types of gas molecules that may have similar physical properties. Therefore, a diverse set of different gases were selected as guest molecules for nanoparticles with Rod-based structures of noble metals gold, silver, and copper. The most critical factor in the current method is the polarizability of the guest molecule, which is strongly affected by the type of constituent atoms and the geometry of the molecule. The effect of different molecules on the wavelength shift of the absorption peak of U-shaped and Rod-shaped plasmonic nanoparticles is investigated using the modified DDA method [1]. The calculations showed that Rod-based plasmonic nanostructures have far better sensitivity than spherical nanostructures, and among Rod-based plasmonic structures, U-shaped silver structure performs better. The diversity of the calculations made it possible to distinguish molecules with similar properties.

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2. Theory and model

2.1. Modified discrete dipole approximation method

In the previous research [1], the modified DDA method was introduced to investigate the effect of the molecules around the plasmonic nanoparticle on the wavelength shift of the nanoparticle's absorption peak. In this method, the existing dipoles divide into two parts: plasmonic nanoparticle dipoles and molecular dipoles. The polarizability of nanoparticle dipoles is calculated from the Clausius Mossotti relation [16–18] using the complex refractive index of plasmonic material (n_r+ik_r) and the polarizability tensor of molecular dipoles is calculated from the method presented in references [19,20]. The three eigenvalues of the calculated polarizability tensor are placed in the main diagonal of the matrix of the coefficients of the usual DDA method [1,19,20], and for N dipoles (including the nanoparticle dipoles and the molecular dipoles) a system of $3\,N$ equation with $3\,N$ unknowns is solved, where the unknowns are the components of the polarization vector of the dipoles. After calculating the polarization vectors, the absorption cross section of the desired nanoparticle is obtained using the optical theorem [16–18]:

$$C_{abs} = \frac{4\pi k}{|E_0|^2}\sum_{j=1}^{N}\left\{\mathrm{Im}\left[P_j\cdot\left(\alpha_j^{-1}\right)^{*}P_j^{*}\right]-\frac{2}{3}k^3|P_j|^2\right\} \quad (1)$$

where k is the wavenumber of the incident light, E_0 is the amplitude of the incident light electric field, P_j is the polarization vector of j^{th} dipole. For a nanoparticle with an arbitrary spatial shape, an equivalent spherical nanoparticle can be considered, whose radius is obtained from the following equation:

$$Nd^3 = \frac{4\pi}{3}R_{eff}^3, \quad (2)$$

where d is the average distance between dipoles (lattice distance), and R_{eff} is the effective radius of the equivalent spherical nanoparticle. There is a validity criterion of $mkd < 1$ for the method where m is the amplitude of the complex refractive index.

Full details of the DDA method and the modified DDA method are available in references [1,14–16], and here, only a brief discussion was given to relate to the concepts of the current work.

2.2. Materials and nanostructure details

Fig. 1 is a schematic representation of the structures investigated in the current work.

In the calculations, it was assumed that the plasmonic nanoparticle and its surrounding molecules are enclosed in a spherical region with a radius of approximately *10 nm* (dashed circles inside the figure). Two main structures, U-shaped and Rod-shaped, were considered for the nanoparticle, and the equivalent spherical structure was also examined for comparison. Therefore, when comparing the results of different structures, the common parameters between the structures will be the spherical area with a radius of *10 nm* (this value is optional), the effective radius of the plasmonic nanoparticle, and the number of molecules around the nanoparticle. A random distribution in a spherical space with a radius of 10 nm was considered for the surrounding molecules. Structural parameters in different calculations are specified in the figure. Three plasmonic materials, silver (*Ag*), gold (*Au*), and copper (*Cu*) were used for nanoparticles. For the surrounding environment, several molecules, including CO_2, NO_2, SO_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, H_2O and NH_3 were used in various calculations. The values of optical constants of plasmonic nanoparticles were extracted from reference [25]. Using interpolation, the values of optical constants were obtained with a wavelength step of 0.01 nm. To calculate the polarizability of molecules, the polarizability of single atoms was extracted from reference [19,20], and using the molecular polarizability method of reference [19,20], the polarizability tensor eigenvalues were calculated as$[\alpha_x, \alpha_y, \alpha_z]$. Reference [26] was used for bond length and angle values. In all calculations, the value of d was 1 nm, and the validity criterion mkd [14–16] was between 0.0163 and 0.06.

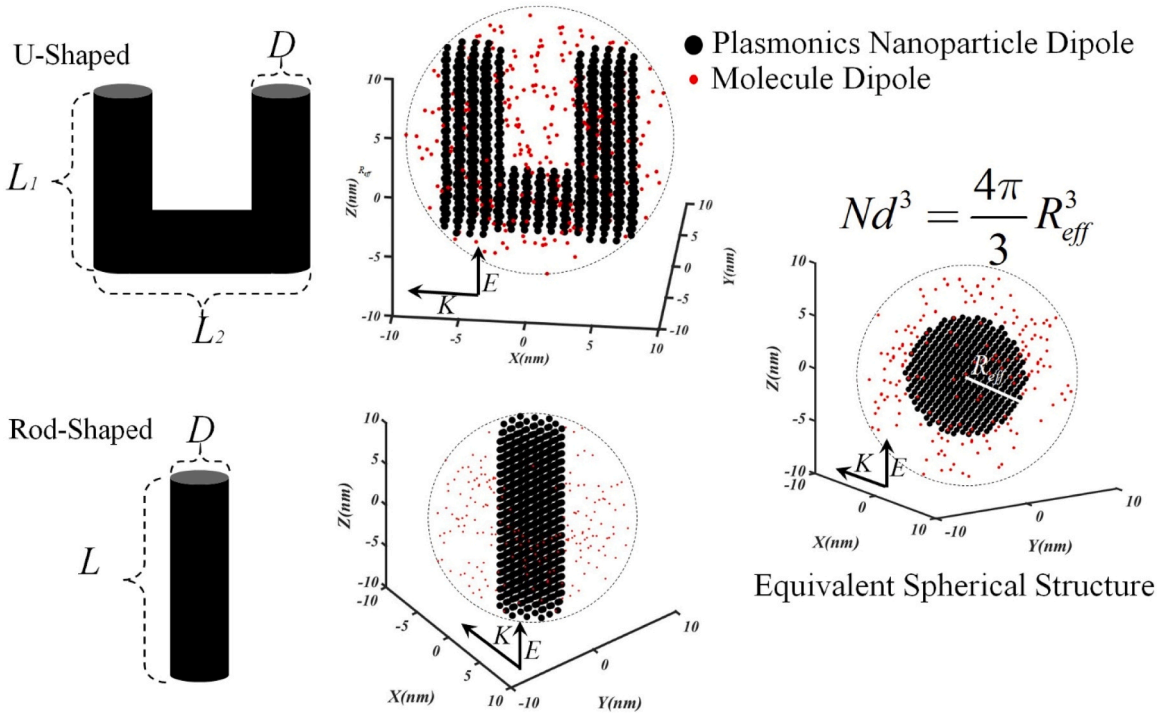

Fig. 1. Schematic representation of the investigated structures and incident light orientations.

3. Results and discussions

3.1. Preliminary calculations and discussions related to Rod-based structures

In previous studies [1,12,13], it was found that in nanoparticles with spherical structures, the wavelength of the absorption peak will be longer with the increase in the radius of the nanoparticle, and for Rod-shaped structures, increasing the ratio of L to D (see Fig. 1) leads to a longer absorption wavelength [8,9]. In order to complete the previous results, calculations were made for plasmonic nanoparticles with a U-shaped structure, the results of which are shown in Fig. 2.

The results of Fig. 2 indicate that with L_1 and D parameters remaining constant, increasing L_2 leads to a longer wavelength of the absorption peak. Another significant point that can be obtained from previous research [1, 8, 9, 12, and 13] and Fig. 2 is that the wavelength of the absorption peak of Rod-based structures is significantly higher than the wavelength of the equivalent spherical structure. This point will be visible in the future calculation results. So, in calculations, the largest Rod-based structure, which can be surrounded by a spherical region with a radius of *10 nm*, is used, and the variables of the problem will be the type of plasmonic material and the type and concentration of surrounding molecules. The values used in the future calculations for the U-shaped nanoparticle are L_1= *15 nm*, D= *5 nm,* and L_2= *15 nm*, and for the Rod-shaped nanoparticle are L= *19* and D= *7.1342 nm*. Two structures will be compared with the equivalent spherical nanoparticle with an effective radius of R_{eff}= 5.66 nm. In future calculations, the number of molecules around the nanoparticle will be 228, and the effect of higher concentrations will be investigated separately at the end of the work. Placing 228 molecules inside a spherical shell between two radii of 5.66 nm and 10 nm means the number of molecules per unit volume is 0.0665 particles per cubic nanometer. To have a standard for comparison, in an ideal gas at a pressure of 1 atmosphere, considering 6.02×10^{23} molecules in 22.4 liters, the number of particles per unit volume is 0.0269 particles per cubic nanometer.

3.2. The results related to the U-shaped structure

First, we want to perform calculations with CO_2 and NO_2 molecules and compare the results. The reason for this comparison is to check the sensitivity of nanosensors because the mentioned two molecules have molecular masses of 44.01 (g/mol) and 46.0055 (g/mol), and the magnitude of the calculated polarizability for them is 4.3965($\mathring{A}^3$) and 4.2061($\mathring{A}^3$), respectively. These two molecules have very close properties, so distinguishing them using a plasmonic sensor can be particularly important.

Fig. 3 shows the results related to U-shaped silver nanoparticles surrounded by CO_2 molecules and the results related to the equivalent spherical structure. In the performed calculations, to achieve very accurate and precise results, first, the range of the peaks of the spectra was determined, then the calculations were performed with an accuracy of 0.01 nm to determine the minor displacements of the peaks. According to the results of reference [8], in the case that the electric field of incident light is parallel to the direction of the rod structure, the absorption spectrum will be the most intense. For this reason, in all calculations, the electric field of incident light was in the same direction as the *z*-axis (see Fig. 1). In Fig. 3a, it is clear that for the spherical nanoparticle, the presence of CO_2 molecules around the nanoparticle has led to the shift of the peak wavelength by 0.06 nm compared to the single spherical nanoparticle. Meanwhile, the results of Fig. 3b show that the calculations related to the U-shaped structure have led to a peak displacement of 0.2 nm, which is more than three times the shift of the spherical nanoparticle. The results of the electric near-field contour distributions in Fig. 3c and d show that in the absence of molecules (Fig. 3c), a region of very low field intensity is formed between the two tips of the U-shaped structure and leads to a dipolar oscillation [8–11]. However, the presence of molecules (Fig. 3d) causes confusion of the field gradient in space, which weakens the oscillation and reduces the energy and increases the wavelength of the absorption peak.

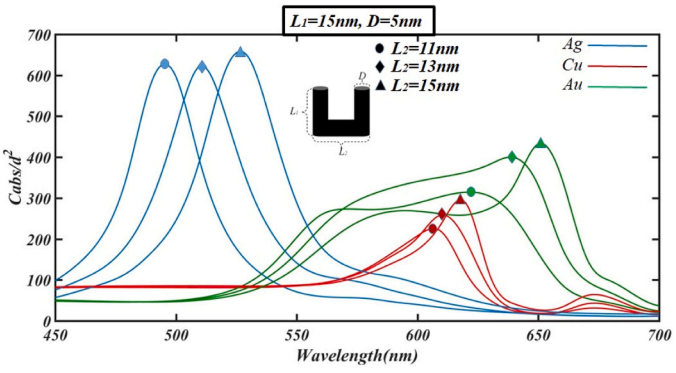

Fig. 2. The results of calculations related to plasmonic nanoparticles with a U-shaped structure with the same D and L_1 and different L_2.

Calculations similar to those shown in Fig. 3 were performed for U-shaped nanoparticles of Cu and Au. The results are shown in Fig. 4. Fig. 4a shows the results of spherical Cu nanoparticles. The changes in the spectra related to the presence and absence of CO_2 molecules have become so close to each other that no difference is observed within a hundredth of a nanometer. At the same time, the U-shaped Cu structure (Fig. 4b) shows a difference of about 0.04 nm in the structure's peak with the presence of CO_2 molecules compared to the single nanoparticle. Similar calculations for Au show much more significant differences in absorption peak shifts (Fig. 4c and Fig. 4d). Results of Figs. 3 and 4 clearly show that the U-shaped structure is much more sensitive than the equivalent spherical structure. Considering that the sensitivity of structures with *Au* and *Ag* is significantly higher than the structure of *Cu*, calculations and comparisons will be made only for *Au* and *Ag* from here on.

According to what has been discussed so far, calculations with a U-shaped structure with NO_2 molecules were performed for Au and Ag, the results of which are shown in Fig. 5. The value of the wavelength shift compared to the case of the plasmonic nanoparticle alone (without the presence of molecules) is included in the graphs of Fig. 5. The most obvious result of these calculations, when compared with the previous figures, is that the spherical Au nanoparticle is not able to distinguish between CO_2 and NO_2, and the Ag nanoparticle can hardly distinguish the two (compare Fig. 5a with 3a and also Fig. 5c by 4c). In contrast, the U-shaped nanoparticle can detect a more obvious difference between CO_2 and NO_2 for both Au and Ag (compare Figs. 5b and 3b and also Figs. 5d and 4d).

3.3. The results related to the Rod-shaped structure

Calculations results similar to those of the U-shaped structure performed for the rod structure are shown in Fig. 6. The results of Fig. 6 show that the silver rod structure has more wavelength shift than the U-shaped structure for CO_2 and NO_2 molecules, but the detection sensitivity of the mentioned two molecules by the rod structure is weaker than that of the U-shaped structure. In the case of Rod-shaped Au nanoparticles, both factors are weaker than U-shaped nanoparticles. However, it is still observed that the rod structure works better than the spherical structure. Similar results of the near-field distribution contours of the U-shaped structure can be seen in Fig. 6c and d for the Rod-shaped structure. If there is no molecule around the nanoparticle, two regions with a strong field are created at both ends of the rod structure, which leads to dipolar oscillations in the middle space of the rod structure. However, the presence of surrounding molecules causes the oscillations

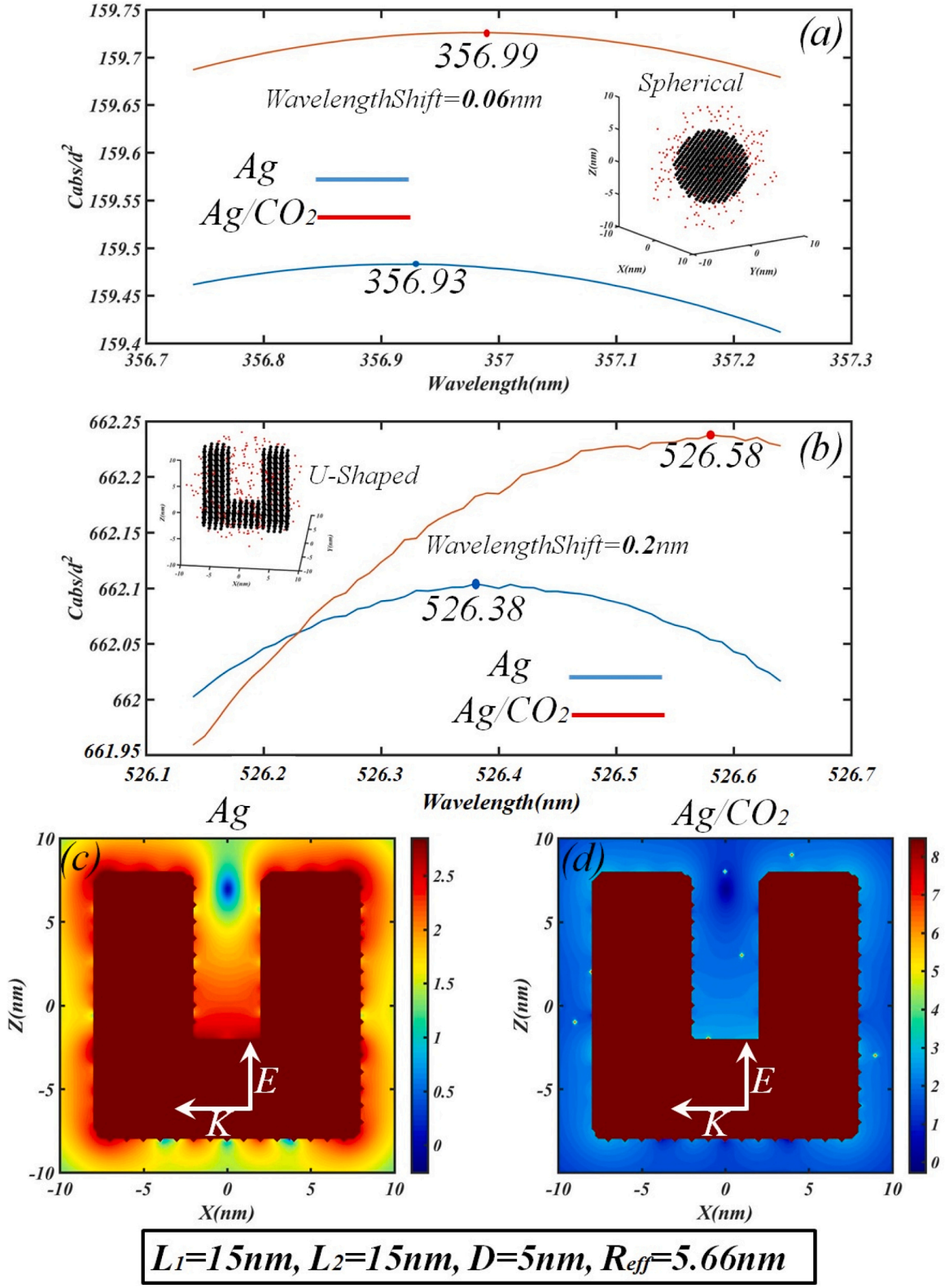

Fig. 3. The results of calculations related to U-shaped silver nanoparticles in the vicinity of CO_2 molecules and comparison with the results of the equivalent spherical structure.

to be weakened, and a redshift is observed.

3.4. Comparison of sensing properties of U-shaped and Rod-shaped structures

The calculation results for several different molecules for U-shaped and Rod-shaped structures of Ag and Au are given in Table 1. In Table 1,

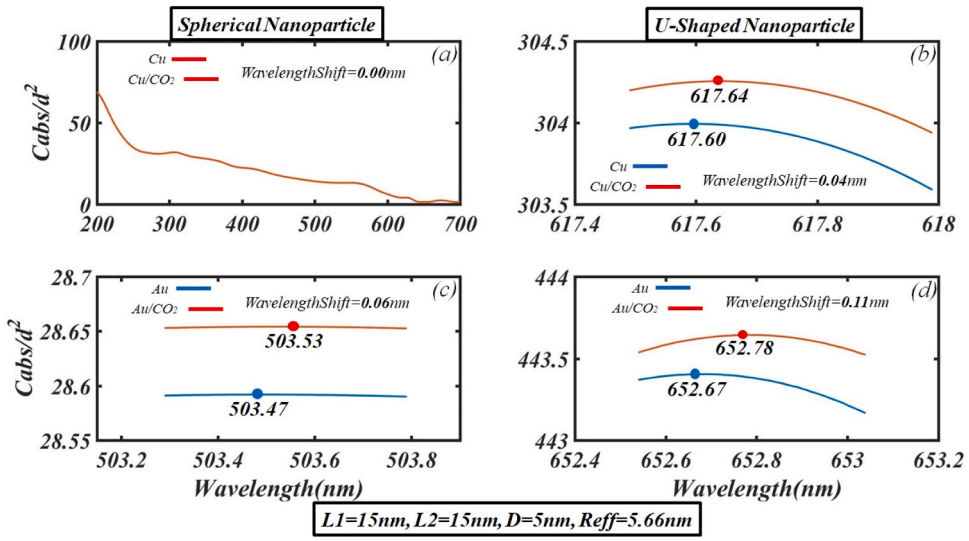

Fig. 4. The results related to U-shaped nanoparticles of Cu and Au in the vicinity of CO_2 molecules and comparison with the results of the equivalent spherical structure.

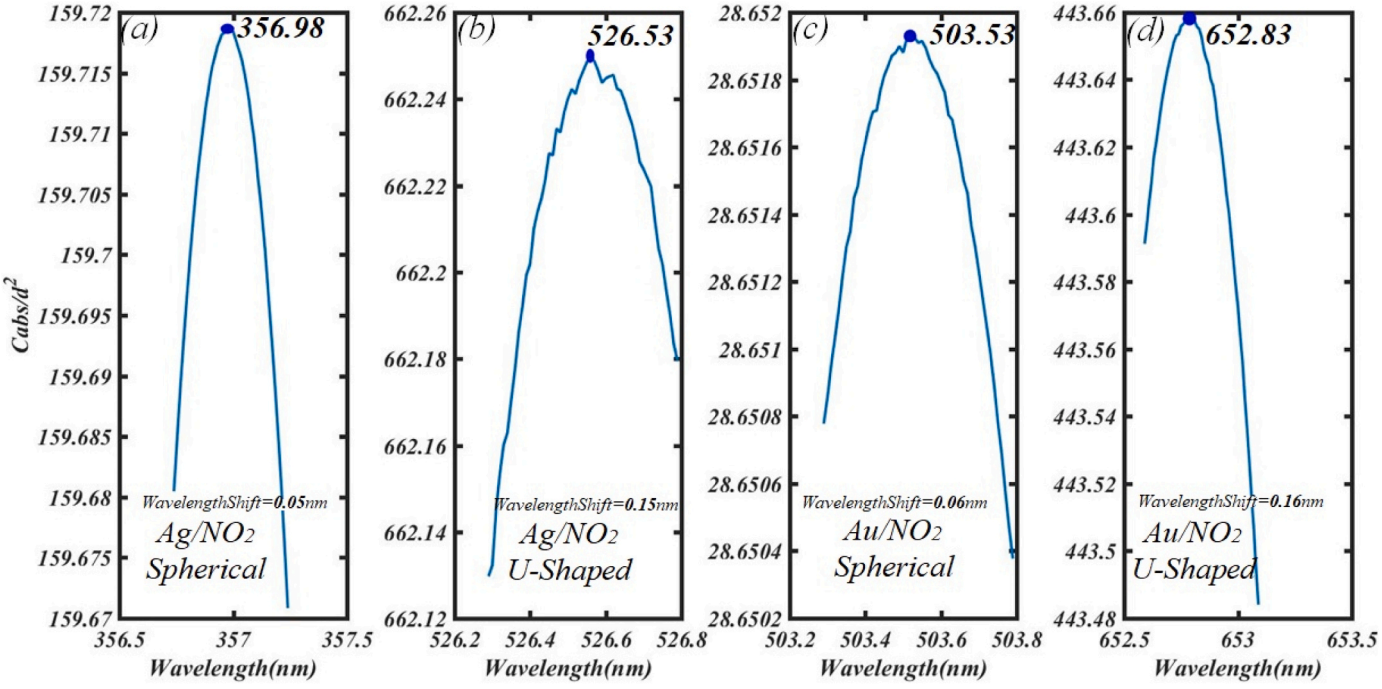

Fig. 5. The results of the calculations performed for the U-Shaped structure and NO_2 molecule for Au and Ag.

in the second and third columns, the values of the molecular mass and the magnitude of the polarizability vector are given, respectively. In columns 4 to 9, in addition to the wavelength of the absorption peak, the values of the wavelength shift compared to the single nanoparticle (second row of Table 1) are reported in parentheses. Comparing the results of different molecules shows that the most critical factor in the amount of wavelength shift is the magnitude of the polarizability vector, not the molecular mass. The accuracy of the presented method and the diversity of plasmonic structures and materials have made them detectable even in cases where two molecules have close polarizabilities. In general, it can be seen that the U-shaped structure of Ag (see the sixth column of the Table) performs better among the rest of the structures, both in terms of the amount of wavelength shift and in terms of the ability to distinguish between molecules with close polarizability values. Indeed, the variety of calculation results for a particular molecule using different structures of Ag and Au makes it possible to make a more accurate interpretation by designing different sensors and performing different measurements.

Finally, to show the linear behavior of plasmonic sensors, calculations were done with 488, 682, 853, and 1137 molecules, and the wavelength shift was obtained with changes in the number of molecules per unit volume and the best fit with the linear function was obtained. Some of the results of these calculations are shown in Fig. 7. In the diagrams, NR stands for Norm of Residuals. The results show that the discussed nanosensors show good linear behavior. Increasing the concentration leads to better detection, even in cases with a weaker sensor performance. Pay attention to Fig. 7c, which is related to NO_2 and CO_2 with a gold Rod-shaped sensor.

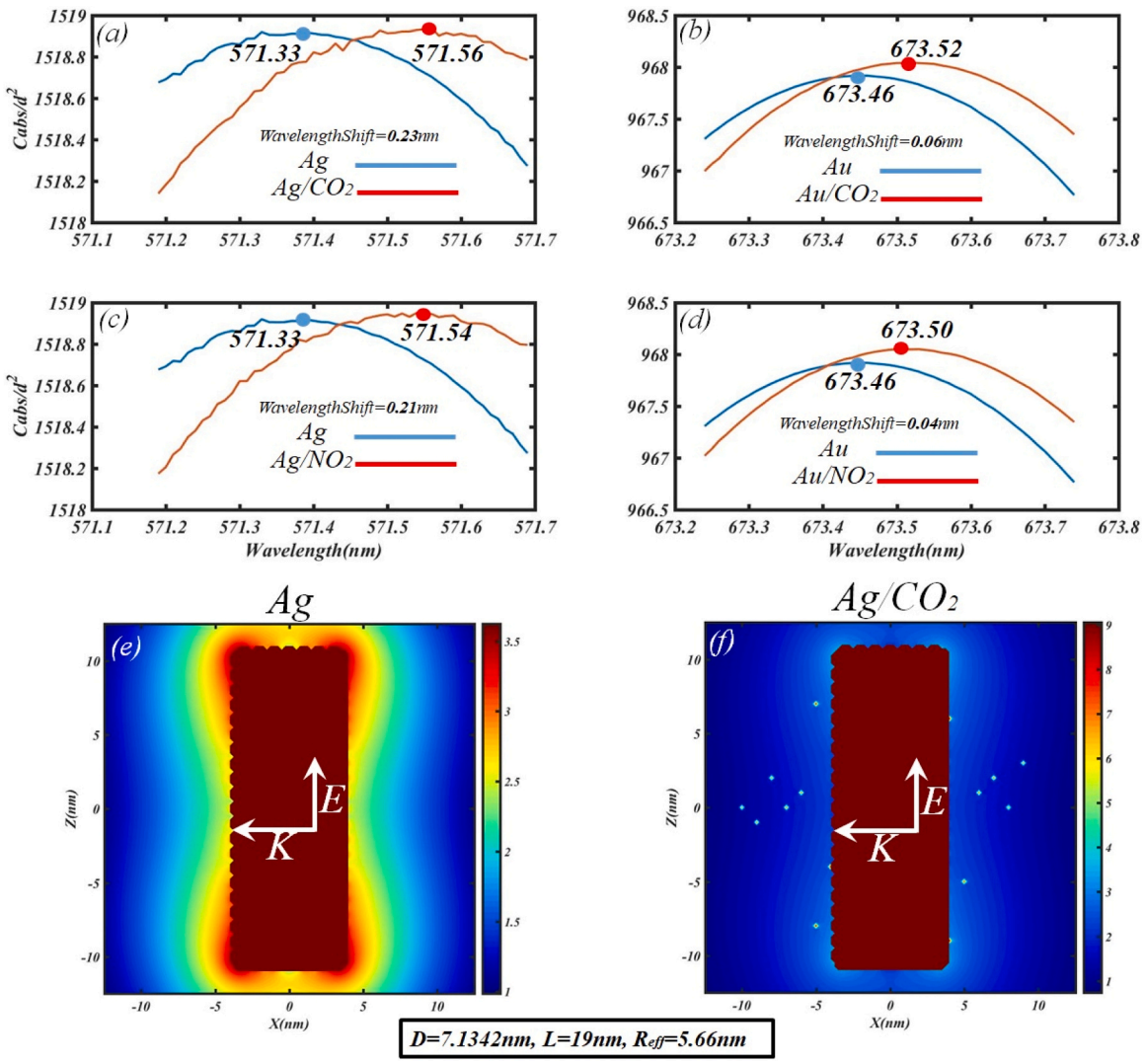

Fig. 6. The results related to calculations of Ag and Au Rod-shaped structure for CO_2 and NO_2 molecules.

Table 1
Calculation results for absorption peaks related to three spherical, U-shaped, and Rod-shaped structures of silver and gold for several different molecules.

Chemical Formula of Molecule	*Molecular Mass (gr/mol)*	*Magnitude of Polarizability vector (A^3)*	*Ag Spherical Wavelength ($\Delta\lambda$)*	*Au Spherical Wavelength ($\Delta\lambda$)*	*Ag U-Shaped Wavelength ($\Delta\lambda$)*	*Au U-Shaped Wavelength ($\Delta\lambda$)*	*Ag Rod Wavelength ($\Delta\lambda$)*	*Au Rod Wavelength ($\Delta\lambda$)*
Single nanoparticle	———————	———————	***356.93 (0.00)***	***503.47 (0.00)***	***526.38 (0.00)***	***652.67 (0.00)***	***571.33 (0.00)***	***673.46 (0.00)***
SO_2	***64.07***	***6.8299***	***357.01 (0.08)***	***503.53 (0.06)***	***526.72 (0.34)***	***652.86 (0.19)***	***571.63 (0.30)***	***673.57 (0.11)***
C_4H_{10}	***58.12***	***14.4268***	***357.13 (0.20)***	***503.61 (0.14)***	***527.05 (0.67)***	***653.07 (0.40)***	***571.96 (0.63)***	***673.68 (0.22)***
C_3H_8	***44.10***	***10.9539***	***357.08 (0.15)***	***503.57 (0.10)***	***526.90 (0.52)***	***652.98 (0.31)***	***571.76 (0.43)***	***673.63 (0.17)***
C_2H_6	***30.07***	***7.6771***	***357.04 (0.11)***	***503.55 (0.08)***	***526.75 (0.37)***	***652.89 (0.22)***	***571.71 (0.38)***	***673.57 (0.11)***
H_2O	***18.02***	***2.5842***	***356.95 (0.02)***	***503.51 (0.04)***	***526.51 (0.13)***	***652.74 (0.07)***	***571.48 (0.15)***	***673.49 (0.03)***
NH_3	***17.03***	***3.4096***	***356.97 (0.04)***	***503.51 (0.04)***	***526.57 (0.19)***	***652.77 (0.10)***	***571.50 (0.17)***	***673.51 (0.05)***
CH_4	***16.04***	***4.4038***	***356.99 (0.06)***	***503.54 (0.07)***	***526.59 (0.21)***	***652.81 (0.14)***	***571.55 (0.22)***	***673.53 (0.07)***

4. Conclusion

The modified DDA method was used to investigate the U-shaped and Rod-shaped structures of plasmonic nanoparticles for molecular sensing. The results indicated that the U-shaped and Rod-shaped structures performed much better than the spherical nanostructure, and also,

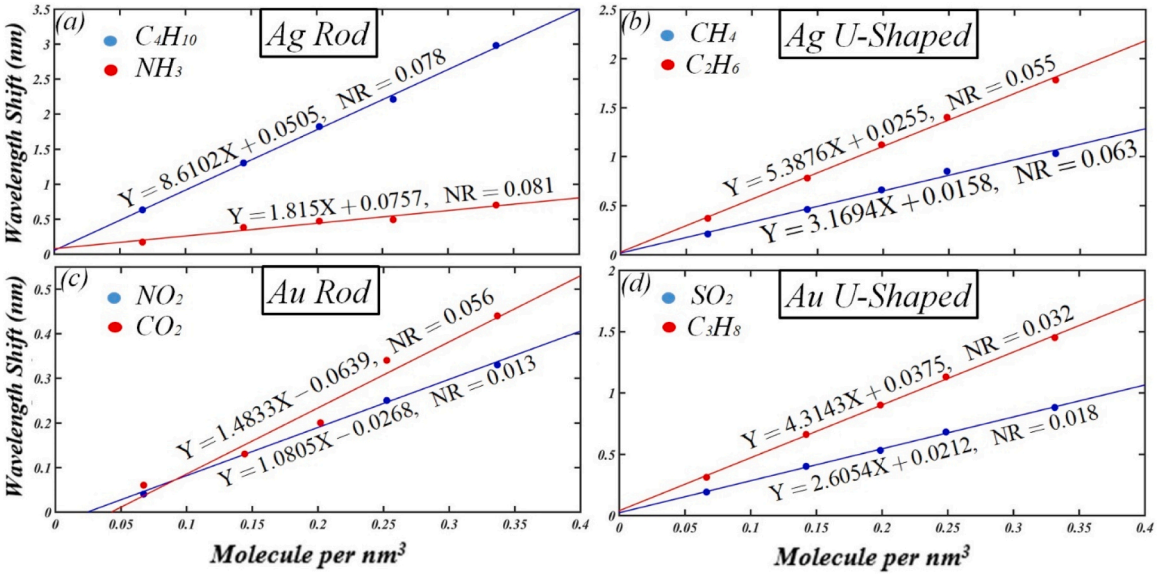

Fig. 7. Calculations related to the investigation of linear changes of the wavelength shift in terms of the number of molecules per unit volume.

among the investigated structures, the U-shaped silver structure performed better than other structures in identifying the surrounding molecule. The applied method can be used to investigate any sensor structure to detect any desired molecule. The great variety of results with different structures for a particular molecule significantly increases the possibility of identifying the molecule.

CRediT authorship contribution statement

Siabi-Garjan Araz: Conceptualization, Investigation, Methodology, Software, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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