Improving The Sensitivity Of The Plasmon Based Sensor By Asymmetric Nanoarray

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Research Article

Abstract

In this work we investigate the effect of the symmetry in a 2-D arrays of gold nanoparticle on the sensitivity to the refractive index change. We demonstrate a generalized result that an asymmetric periodic arrangement of metallic nanoparticle leads to a higher sensitivity than a regular square of nanoparticle. Further decreasing the symmetry of the system by using asymmetric nanoparticle (nanorods, triangle) rather than symmetric nanoparticle (nanocylinder) will further improve this sensitivity. Finally, we suggest that such asymmetric nanostructure could operate as a SERS and LSPR plasmon based sensor by changing the polarization of the incident light.

Introduction

Metallic nanoparticles exhibit very interesting properties in the near field and the far field region that are used for sensing applications. When excited by light at proper frequency, a collective oscillation of the electron in the conduction band at a finite interface metal/dielectric arises leading to an electromagnetic mode (solution of Maxwell equations) called localized surface plasmon (LSP). LSP resonance frequency i.e. frequency at which maximum of electron are driven by the electric field, is extremely sensitive to the nanostructure size, shape and type, and vicinity [1]. Because of this sensitivity they are of great interest for the development of highly sensitive biosensors for detection of ultrasmall quantity of molecules. Two sensing approaches have emerged in the last two decades: SERS and LSP sensing. Surface- enhanced Raman spectroscopy (SERS) was discovered in the 1970 [2], it relies on the enhancement of the Raman signal of an active molecule in close vicinity of the nanoparticle by the LSP near field. The LSP sensing method employs the wavelength shift of the plasmon resonance to detect change in refractive index due to the deposition of the targeted molecule. Several groups have reported measurements of the sensitivity for isolated nanoparticle with different shapes and sizes [3–9]. In [10] it was demonstrated that for isolated nanoparticle the sensitivity depends only on the wavelength of the plasmon resonance and the dielectric properties of the metal. Gold nanoparticle arrays are another class of plasmon based sensor which have attracted the greatest interest in sensor applications. In fact, they are easily fabricated by a variety of techniques enabling mass pro- duction. Moreover, they are tunable versatile and simple. On a glass substrate, they can be easily functionalized enabling more efficient adsorption of the studied molecules. Gold nanograting are also interesting due to their biocompatibility and wide availability of linked molecules. They are not affected by oxidation, rather they are stable and can handle high temperatures. They could present a large surface area available for binding and detection. Finally, gold nanograting can sustain localized surface plasmon mode, as well as photonic mode or hybrid mode, leading to an improvement of the quality factor of the resonance peak. Sensitivity improvement of subwavelength nanograting based SPR sensor has then been studied in several articles [11–19]. It was demonstrated in [19] how the design of an ordered array of gold nanoparticle leads to a tunable plasmon-based sensor with resonance frequency that has any desired value within the visible and near-infrared spectrum. Also, in [20] it was demonstrated that coupling the localized surface plasmon resonance to the diffracted wave leads to an improvement of the sensitivity. It was even stated that the quality of the

sensor is governed by the frequency difference between the surface lattice resonance and the Rayleigh anomaly of the array. In [21] it was suggested that arrays with unit elements formed by two touching particles display a much higher sensitivity than single-particle arrays.

None of references cited above investigate the effect of symmetries broken on the sensitivity. In this letter, we comprehensively investigate the effect of the two-grating constant on the sensitivity to the refractive index change in an array of gold nanoparticle. We will demonstrate that by using gold asymmetric array, we could enhance the sensitivity of the plasmon based sensor, as well as the detected signal strength. We further demonstrate that by reducing the symmetry of the nanoparticle in the array we can further increase the sensitivity. The polarization of the incident light is an additional influent parameter in the asymmetric array that could tune the plasmon resonance wavelength enabling the proposed sensor to be used as SERS or LSP sensor simultaneously.

Description Of The Structure And Numerical Method

We use the FDTD (finite-difference time-domain) technique to solve Maxwell's curl equations in time domain [22]. A home-made code was developed where the computational volume is truncated in the x and y directions to simulate only a unit cell of the grating with the periodic boundaries' conditions. In the z direction, absorbing boundaries conditions are implemented to simulate the extension of the lattice to infinity using the CPML (Convolutional perfectly matched layer) technique. The CPML technique as compared to the UPML technique (uniaxial perfectly matched layer) has many advantages as it avoids specular reflection error from the front PML interface at low frequency (late-time). Moreover it allows for more efficient absorption at high angle of incidence and for evanescent waves [23].

The permittivity of gold is described using the Drude Lorentz model and implemented in the FDTD algorithm using the ADE (auxiliary differential equation) technique [24]. **Figure 1** shows the LSP-based sensor under interest consisting of a subwavelength grating structure sitting on a glass substrate. We define the distance to be the edge-to-edge distance between neighboring nanocylinders along the x direction, and to be similarly defined for nanoparticles along the y direction. The incident light is at normal incidence and is polarized parallel to the x axis. To calculate the shift of the plasmon resonance, and thus to evaluate the sensing ability of the system we assume that a thin dielectric film (12nm) with a refractive index n = 1.56 (corresponding to an average value for modeling a layer of biological molecules) is deposited on the glass substrate.

Sensitivity Of The Asymmetric Array As Compared To The Squarearray

A. Qualitative Analysis

In the following influences of the variation of the grating constant along the x and the y directions on the sensitivity will be presented qualitatively. For this goal, we calculate the plasmon resonance shift Δλ for a

nanocylinder with a diameter d = 150nm, and a height h = 60nm as well as for a nanocylinder with diameter d = 100nm and the same height. In **figure 2** we represent in color the shift $\Delta\lambda$ for different p_x and p_y. It shows that the variation of the distance p_y has greater impact on the sensitivity (S is proportional to $\Delta\lambda$) as compared to p_x. The highest sensitivity is observed for an asymmetric array with approximatively ($p_y = 2\ p_x$). We explain our result qualitatively by the 2D periodicity of the nanoparticle array. In fact, the geometrical arrangement may reduce for certain distance p_y the radiative losses as the energy scattered could be captured into plasmon, leading to a higher sensitivity to the refractive index change [25]. In the following, we will focus on the effect of the distance p_y on the sensitivity S as well as the effect of reducing the symmetry in each cell in the array.

B. Quantitative Analysis

In this section we investigate the effect of the variation of p_y (perpendicular to the incident light polarization) on the sensitivity for an array of nanocylinders with diameter d = 150nm.

Results are plotted in **figure 3a**, where we observe a non-monotonic variation with a little variation of the sensitivity for p_y < 350nm, then a strong increase for p_y >= 375nm. We attribute the enhancement of S to constructive interference between nanoparticles, especially the diffracted wave that ensure the coupling between proximal nano particle in the far field region. Note that S increases especially when the interparticle spacing multiplied roughly by the local refractive index (effective index of substrate, NP and polymer) approaches the wavelength of the isolated nanoparticle plasmon resonance (we reach 3 folds enhancement).

Similar results are observed for smaller nanoparticle (**figure 3b**).

Our numerical results show that the variation of the grating constant in the direction perpendicular to the polarization of the incident wave has significant influences on sensitivity. Unlike the isolated particle [10], the increase of the sensitivity here is not correlated to the red shift of the plasmon resonance wavelength (inset of **figure 3**). The asymmetric array with $p_y > 2\ p_x$ will exhibit the highest plasmon resonance shift. Our calculations are made for p_y > 200nm, for distance below 200nm we expect near field coupling to dominate, however such array will be more challenging for fabrication and are out of our interest.

Another interesting aspect of the asymmetric array is that the density of the metal in the nanoarray is greater than the symmetric array leading to a stronger signal detected in the sensor.

In the following, we further reduce the symmetry of the system, by investigating asymmetric nanoparticle in the asymmetric array. For this goal we investigate the plasmon resonance shift for three types of nanorods as well as for a nanotriangle. The major axis (parallel to the x direction) for each nanorods is fixed to 150nm. The aspect ratio will be varied from 1 to 3. In order to make a comparison between those nanorods, we normalize the shift $\Delta\lambda$ with the surface area of each nanorods. Results are depicted in **Fig. 4a** where we observe that the sensitive could be enhanced by 3 times if we increase the aspect ratio

of the nanorod. In **Fig. 4b**, we further con- firm our result by comparing the sensitivity of an array of nanotriangle and an array of nanocylinder. We choose the dimension of the nanotriangle such us it has approximatively the same surface area of the nanocylinder, i.e. same contact surface with the target molecule. We observe that with a nanotriangle we could reach the highest plasmon resonance shift. We attribute the increase of sensitivity, to the larger confinement of the electron cloud due to the geometry of the nanoparticle.

In conclusion we suggest that adding to the asymmetry of the array the asymmetry of each nanoparticle improve significantly the sensitivity of the nano system. The decrease of the symmetry in the nanograting could lead to higher near field confinement in each nanoparticle as well as efficient far field coupling between neighboring nanoparticles. The combination of these two factors leads then to the increase of the sensitivity (up to 6 times when comparing to a symmetric array).

Use Of The Developed Sensor As Sers Ans Lspr Sensor

In this section, we investigate the near field proper- ties and SERS enhancement when increasing the period along the y direction. For this goal we calculate the aver- age enhancement factor over a small surface area (12nm) surrounding a nanoparticle with d = 150nm (See the inset of **figure 5**). The excitation wavelength of the laser is assumed to be 785nm. The EM enhancement factor **G** resulting from electromagnetic mechanism of SERS is defined usually as:

$$G = \frac{|E(\omega).E(\omega + \delta\omega)|^2}{|E_0(\omega).E_0(\omega + \delta\omega)|^2}$$

where ω is the incident laser frequency, and $\delta\omega$ is the Stokes-shifted frequency, E is the total field at the molecule location and E_0 is the incident field. We demonstrate in **figure 5** that the SERS enhancement could be increased by modifying the period in one direction perpendicular to the polarization of the incident light. Our results seem to be coherent with the one found in [26] where authors demonstrate that higher enhancement factor were obtained for a rectangular array rather than square array of gold slit nanostructure.

One of the characteristics of an asymmetric array is that they are sensitive to the polarization of the incident light. Indeed, the polarization could be an additional degree of freedom that can change the properties and thus the application of the asymmetric nanostructure. To study this effect, we calculate for a grating with dimensions p_x = 200nm and p_y = 500nm the enhancement factor when the array is illuminated with a light polarized along the x axis (denoted p//) and when the incident light polarization is a long the y axis denoted p⊥. Those array dimensions were shown previously to be very suited for LSP sensing (**Figure 2 a**). We demonstrate in **figure 6** that the SERS enhancement factor for an ex- citation wavelength λ_{Laser} = 633nm could be enhanced by 4 order of magnitude by simply rotating the simple, i.e by changing the polarization of the incident light.

Consequently, an array with dimensions p_x = 200nm and p_y = 500nm is very suitable for LSPR sensing at near infrared wavelength as well as for SERS applications in the visible range.

Conclusion

We have demonstrated in this work that reducing the symmetry of an array of nanoparticle by variation of the period in the direction perpendicular to the incident light polarization, or by reducing the symmetry of the nanoparticle leads to a sensitivity of the resonance peak to the change in refractive index that is significantly higher than can be produced by a perfectly symmetric array. Moreover, such asymmetric nanostructure will be sensitive to the polarization of the incident light enabling them to be used as LSPR and SERS sensors. Our result has a general and predictive character that could help to develop simpler and cheaper surface plasmon based sensor for bio detection and environmental applications.

Declarations

*Conflicts of interest/Competing interest: No

 *Availability of data and material: All data are in the manuscript

*Code availability: Yes

*Authors' contributions:

- Aymen Bouali (email: aymen.bouali@ipest.u-carthage.tn Tel: +21652376349): Writing- Original draft preparation Reviewing and Editing, Investigation, Methodology, Software

- Montacer Dridi: Data curation, Writing- Visualization.

- Florent Colas: Conceptualization, Methodology, Software

- Chantal Compere: Supervision, Validation.

*Ethics approval: Yes

*Consent to participate: Yes

Consent for publication: Yes

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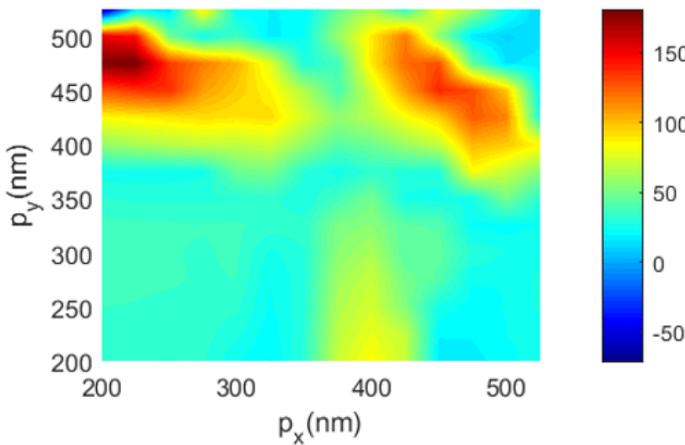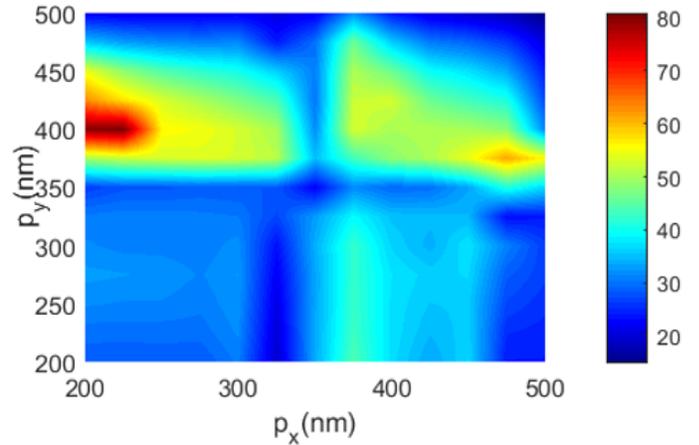
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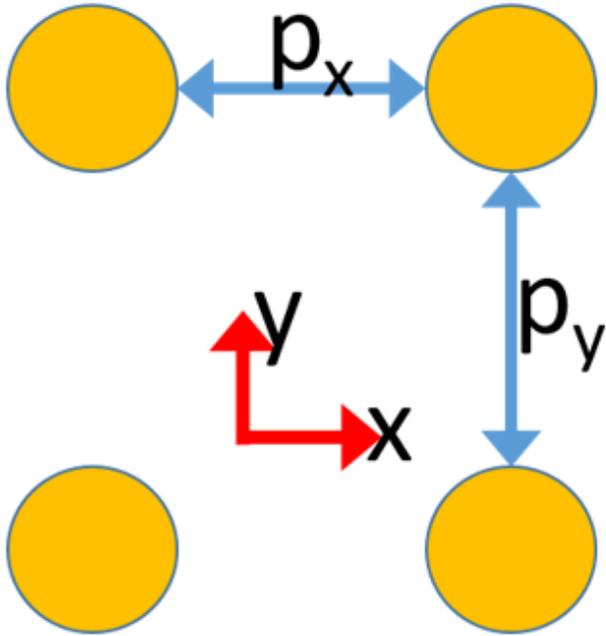
(a) In plane side view
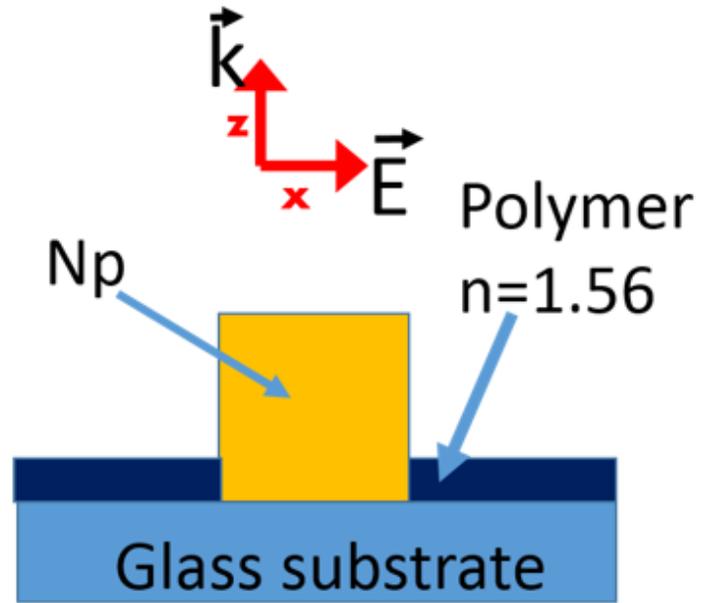
(b) Cross sectional side view
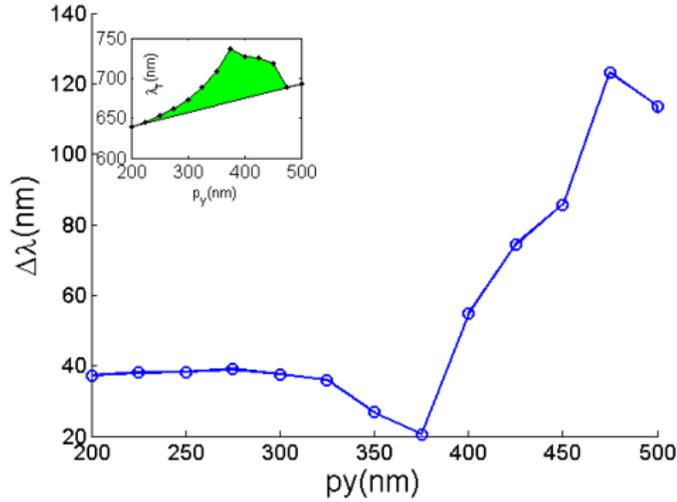
Figure 1

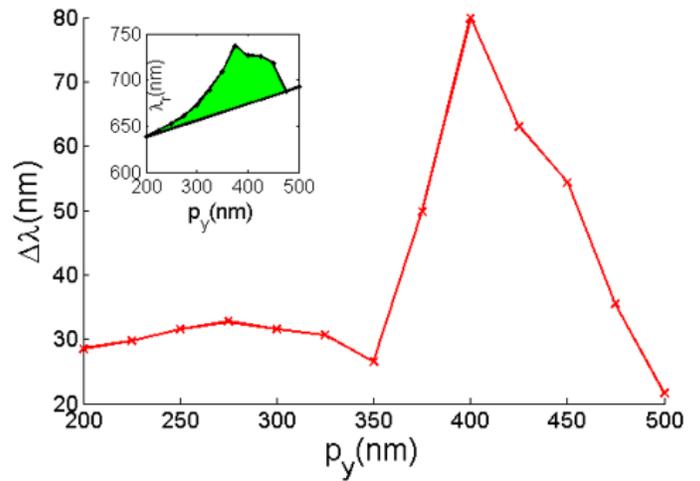Nanoparticles array for sensor applications

(a) d = 150nm

(b) d = 100nm

Figure 2

Effect of the periodicity along the y direction on the sensitivity: The highest shift is observed for the asymmetric array with py > px
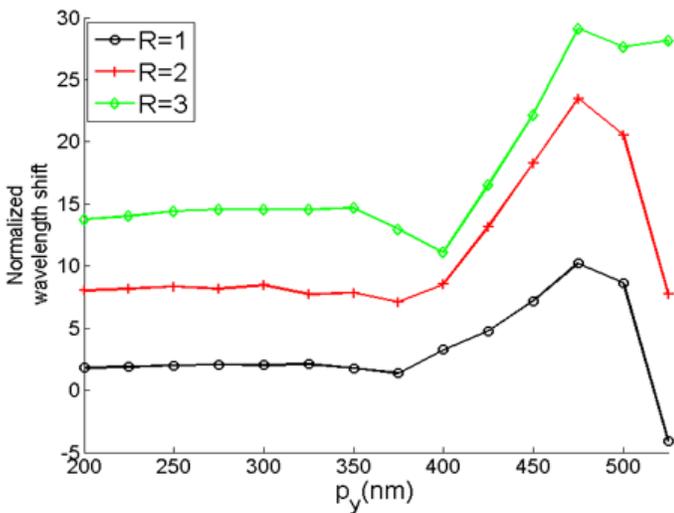

(a) d = 150nm

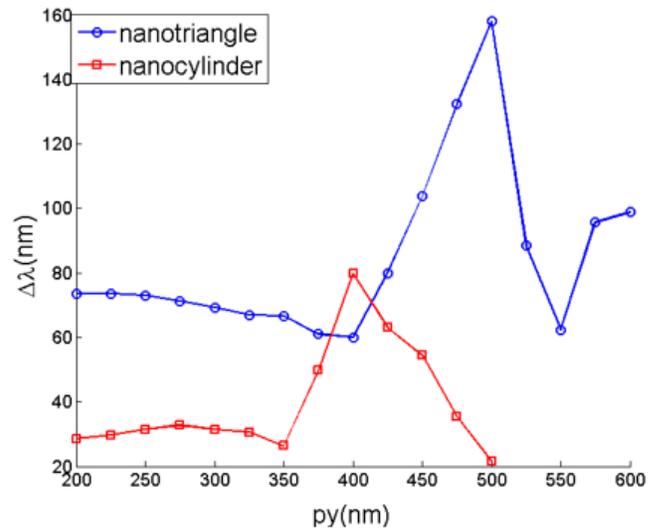(b) d = 100nm

Figure 3

Effect of the periodicity along the y direction on the sensitivity: Computations are made for a fixed px = 200nm. A significant increase of the sensitivity is observed with an optimal value of py = 475nm. The inset, red shift of the plasmon resonance wavelength while increasing py.

(a) a comparison between nanorods

with different aspect ratio

(b) a comparison between nanocylinder

and nanorods

Figure 4

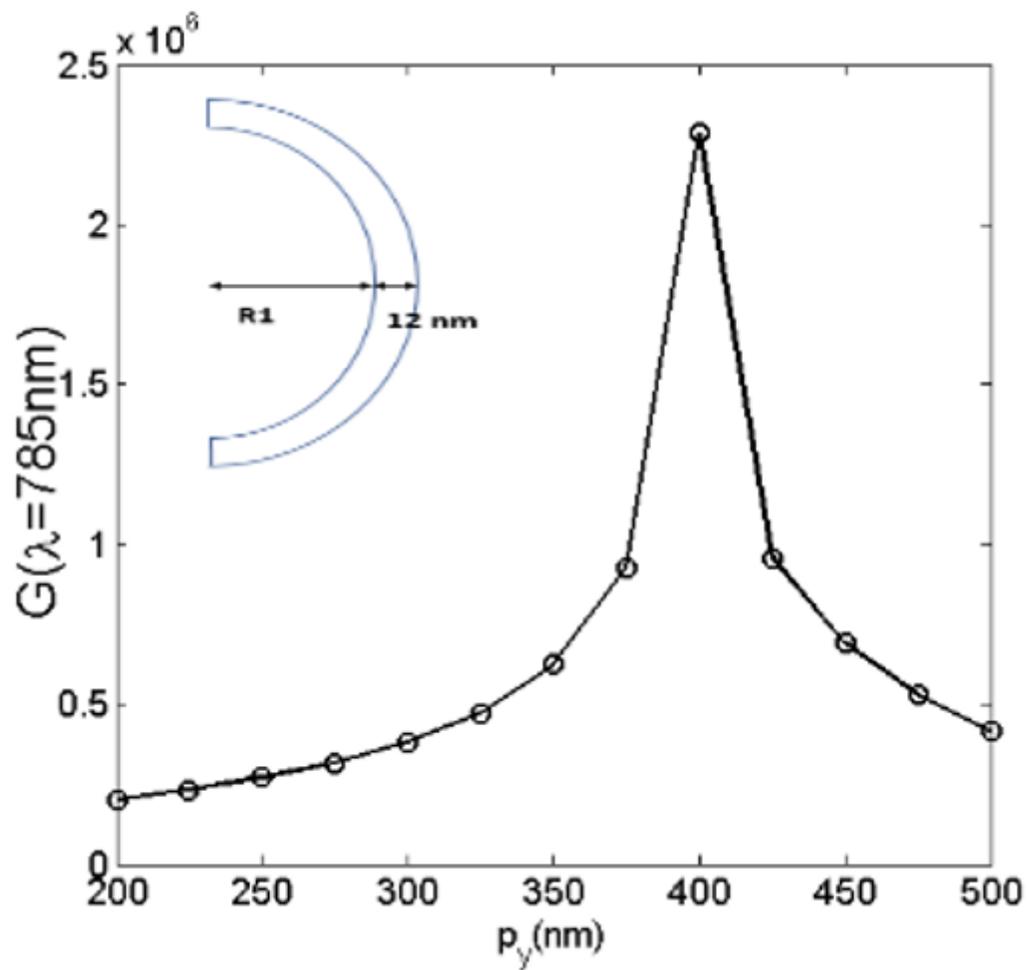Calculation of SERS enhancement for different polarizations

Figure 5

Effect of the symmetry along y direction on the SERS enhancement. The Inset, Region surrounding the NP where the enhancement was calculated
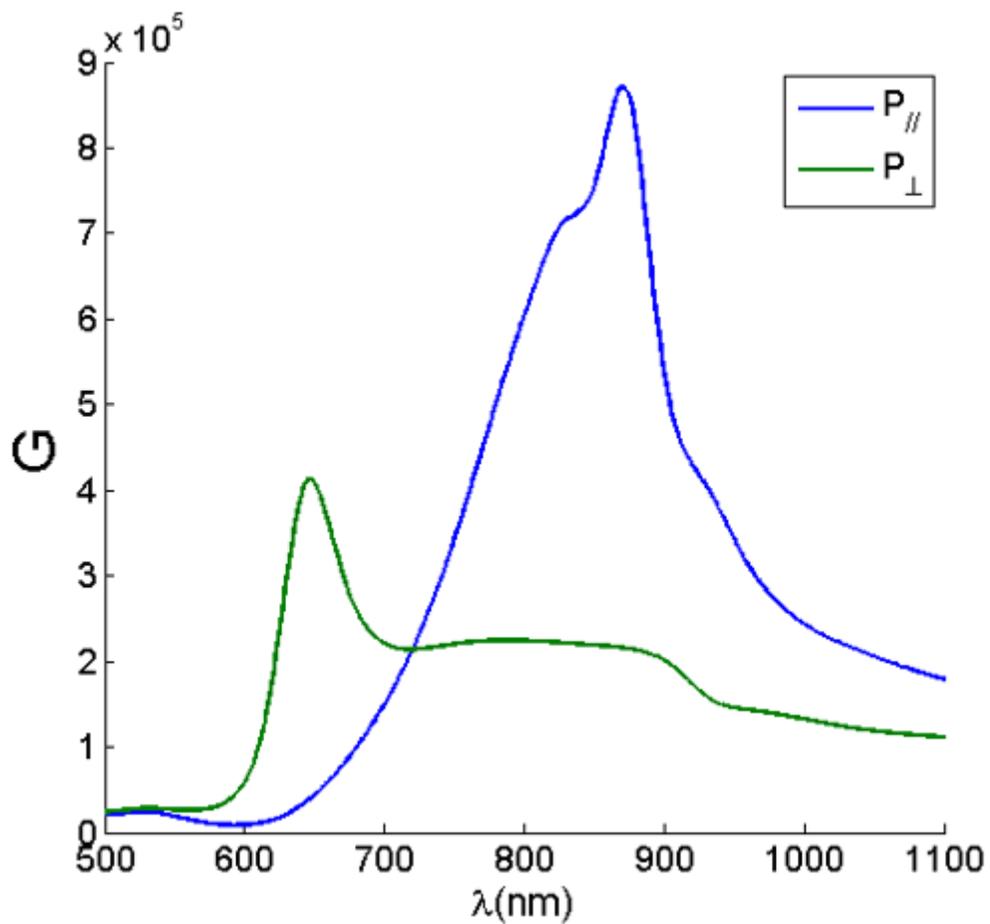
Figure 6

Effect of the periodicity polarization on the SERS enhancement