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Authors

Xia, M
Zhang, P
Qiao, K
[et al.](#)

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Coupling SPP with LSPR for Enhanced Field Confinement: A Simulation Study

Ming Xia,[†] Pei Zhang,[†] Kuan Qiao,[‡] Yu Bai,[§] and Ya-Hong Xie^{*,†,⊥}

[†]Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States

[‡]School of Physics, Peking University, Beijing 100871, P. R. China

[§]School of Nano-Science and Nano-Engineering, Suzhou & Collaborative Innovation Center of Suzhou Nano Science and Technology, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[⊥]Jonsson Comprehensive Cancer Center, University of California, Los Angeles, Los Angeles, California 90095, United States

S Supporting Information

ABSTRACT: By using finite-difference time-domain simulation, we investigate the enhancement of local electrical field by combining localized surface plasmon (LSP) of Au nanopyramid array and surface plasmon polaritons (SPPs) focused by Au nanorings. We report on the systematic investigation of structural variables that could affect the coupling efficiency between SPPs and LSP to obtain optimal design. The study aims at finding the quasi-quantitative relation between several key-variables of the pyramid-ring combination and the overall surface enhanced Raman spectroscopy (SERS) enhancement at the center of the structure. We consider the following factors that could affect the interaction between SPPs and LSP: ring radius, number of rings, pyramid spacing, number of pyramids, and the relative position of ring center and pyramid array center. By adjusting these structural variables, high electric field enhancement of up to 140× and large volume of hot spots can be achieved. We also investigate the incorporation of the LSP–SPP hybrid structure onto the facet of optical fiber for SERS-based detection.

1. INTRODUCTION

Surface enhanced Raman spectroscopy (SERS) is an important analytical technique that is able to provide single molecule detection and high-resolution spectral information.^{1–4} Two mechanisms are known to contribute to the enhanced Raman signal in SERS, electromagnetic (EM) enhanced mechanism, and chemical enhanced mechanism.⁵ In most cases, the electromagnetic enhancement is the major mechanism, in which local EM field is enhanced due to the excitation of localized surface plasmon (LSP) of metal nanostructures. This enhancement of EM field accounts for the increase of the Raman signal intensity of adsorbates on (typically) metallic surfaces. In addition to LSP, surface plasmon polaritons (SPPs) are another potential source of EM enhancement. It has been shown that metallic ring structure can focus the SPP into its geometric center and create an intense spot of near field optical intensity on a flat metal surface.^{6–10} However, Raman enhancement factor (EF) due to the focused SPPs by ring structure is low compared with LSP.¹¹ Coupling between SPP and LSPR on nanohole/nanocone arrays has also been explored to enhance the local electrical field recently and shown improved Raman detection performance.¹²

To achieve strong Raman signal, high local EM field is required in SERS metallic nanostructures. Tremendous efforts have been spent on engineering the structure of metal nanostructures to obtain high local EM field.^{13–17} Among these nanostructures, nanogap formed between metal nanoparticles (NPs) is a highly effective SERS nanostructure, which can boost the Raman signal up to $\sim 10^9$ times.¹⁶ The deficiency of this kind of structure is the small detection volume, typically below 10 nm. With such small size of detection volume, it is difficult for large molecules like proteins to fit in the gap where the hot spots are located. Compared with nanogap between adjacent NPs, nanopyramid array is an open structure, in which hot spots locate between neighboring pyramids.^{18,19} As such, large molecules can easily move into these regions, and their Raman signals can be enhanced. The shortcoming of nanopyramid arrays is that the magnitude of EM field at the hot spots is not as high as that in NPs. Here we report the use of SPP induced by circular ring structure combined with the LSP generated near nanopyramids to enhance local EM field.

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Figure 1. (a) Two-dimensional electric field distribution of 4-pyramids array along x - y , x - z , and y - z plane (excitation wavelength = 633 nm). (b) Schematic diagram of the 4-pyramids array used for simulation.

We report on our systematic investigation of structural variables that could affect the coupling efficiency between SPP and LSP to obtain optimal design using finite-difference time domain (FDTD) simulation. This study aims at finding the quasi-quantitative relation between several key-variables as detailed below of the pyramid-ring combination and the overall SERS enhancement at the center of the structure. Such highly localized (within ~ 10 nm range) and extremely intense (as high as 10^4 times the intensity of a tightly focused laser beam) nonpropagating electric field has many potential applications including biosensing, surgery, and biomedical research. The structural variables affecting the focus of SPPs are adjusted systematically to optimize performance. We consider the following factors that could affect the interaction between SPP and LSP, ring radius, number of rings, pyramid spacing, number of pyramids, and the relative position of ring center and pyramid array center. The SERS performance of different structures is evaluated based on integral of $|E|^4$ value over space. We also carry out the study of the LSP–SPP hybrid structure on the tip of optical fiber probes with the intended application for *in vivo* biosensing (Section 3.4).

2. THEORETICAL METHODS

Concentric rings of Au are employed for launching SPPs. An Au pyramid array is placed at the center of the rings to generate LSP. The magnitude of electric field of Au pyramid array is calculated using FDTD method (Lumerical FDTD Solutions). The calculations are set up as a three-dimensional system with a 4 nm resolution cubic grid, including the appropriate boundary conditions. The excitation light is modeled as a normal incident plane wave of 633 nm wavelength, considering that 633 nm laser is one of the most commonly achievable lasers. The polarization of light is along x -axis. The direction of the incident light is set to illuminate the pyramid array from the top side onto the apex of the pyramids (along $-z$ -axis) for simulation in sections 3.1 to 3.3, and from the bottom side onto the bases of the pyramids (along $+z$ direction) for section 3.4.

The amplitude of electric field of incident light ($|E_0|$) is set to be 1. The calculated amplitude of electric field ($|E|$) appears as the ratio of $|E|/|E_0|$. The local electric field enhancements depend strongly on the exact position of the SERS substrate surface. Thus, the SERS EFs on the surface of a typical SERS

substrate are highly nonuniform, even at a molecular scale of nanometers. For detection of trace amount of molecules, both hot spots and their size need to be considered for the evaluation of the overall enhancement of SERS substrates. The metrics we use to quantify SERS performance consist of a combination of high electric field and large volume with sufficiently high electric field. We choose 10 as a threshold value of $|E|$ for SERS hot spots. In other words, when the value of $|E|$ within one mesh box is larger than 10, we consider that mesh box as a SERS hot spot. To quantitatively characterize the overall SERS enhancement of each pyramid-ring combination, we apply an integral of $|E|^4$ value over space based on the common $|E|^4$ -approximation.²⁰ More specifically, we calculate the sum of $|E|^4$ value of every hot spot ($\sum_{|E| \geq 10} |E|^4$) within a fixed space ($640 \times 640 \times 160$ nm). So, obtained is the overall enhancement value used to evaluate the performance of various Au nanostructures in the following discussion.

3. RESULTS AND DISCUSSION

3.1. Electric Field Distribution of a 4-Pyramids Array.

A 4-pyramids array pattern is chosen as the basic structure. Figure 1b shows the schematic diagram of the pyramid model. Each pyramid has a 200 nm base length and 140 nm height. The continuous Au film beneath the pyramids is 20 nm thick. Figure 1a shows the two-dimensional (2D) electric field distribution of the 4-pyramids array along x - y , x - z , and y - z plane. Hot spots are mainly located on the ridge and the apex region of the pyramids, and the volume of hot spots is small compared to the Au pyramid structure. The total volume of hot spots only accounts for less than 0.5% of the volume of one Au pyramid, and the maximum $|E|/|E_0|$ value at hot spots is 12. The simulation results indicate that Au pyramid array alone cannot render high electric field together with large detection volume. Therefore, improvement of both hot spot number and electric field at hot spots around the pyramid array are needed for highly sensitive detection of trace amount molecules.

3.2. Enhancement of Electric Field by Focusing SPPs to a 4-Pyramids Array. Circular metallic rings are known to possess the ability of launching and focusing SPPs into its center.^{9,10} By placing the pyramid array in the center of the metallic circular ring, it is possible to enhance the electric field of Au pyramids further. In this section, we will discuss the

Figure 2. (a) Schematic diagram of Au pyramid array located at the center of the ring and its cross-section view. (b) Two-dimensional electric field distribution at the center of single Au ring ($R = 22\lambda_{\text{spp}}$). (c) Two-dimensional electric field distribution of 4-pyramids array after adding one Au ring ($R = 22\lambda_{\text{spp}}$). (d) Overall SERS enhancement with increasing radius of the ring (excitation wavelength = 633 nm).

structural variables directly influencing the electric field of Au pyramids. These variables include the radius of the rings and the number of rings.

3.2.1. Effect of Ring Radius on Electric Field. A circular ring is designed to excite SPPs and focus them into the center. Figure 2a shows the schematic diagram of Au ring and its cross-section view. The height of the ring is 60 nm and the width of the ring is 200 nm. For 633 nm light excitation, SPP wavelength (λ_{spp})²¹ on Au is 598.2 nm and propagation length (δ_{spp})²¹ of the SPP is 8 μm , which is about 13 times of the SPP wavelength. Plasmon focusing with linearly polarized light usually results in an inhomogeneous plasmon focal spot owing to the symmetry mismatch between incident polarization and plasmonic structures.¹⁰ Figure 2b shows the 2D electric field distribution at the center of bare Au ring structure with radius of $22\lambda_{\text{spp}}$. A minimum electric field is created at the geometric focus, which is due to the destructive interference between counter-propagating surface plasmon waves. This inhomogeneous plasmon focal spot can be viewed as two SPP focal spots, at which $|E|/|E_0|$ value is about 3, apparently lower than the $|E|/|E_0|$ value of hot spots of the 4-Au pyramids array (Figure 1a).

By placing the 4-pyramids array at the center of the ring, focused SPPs are able to couple with the LSP generated by pyramid structure, leading to stronger electric field around pyramids. We then consider the effect of ring radius (R) on the overall SERS enhancement. The radii of the rings range from $2\lambda_{\text{spp}}$ to $35\lambda_{\text{spp}}$. Figure 2c shows the 2D electric field distribution of Au pyramid array after adding one Au ring ($R = 22\lambda_{\text{spp}}$). Figure 2d shows the dependence of the overall SERS enhancement of Au pyramids-ring structures on the ring radius. As the ring radius increases from 2 to $35\lambda_{\text{spp}}$, the overall enhancement of Au pyramids-ring first increases and then decreases with maximum value at the radius of about $22\lambda_{\text{spp}}$. Compared with bare Au pyramids array, Au pyramids array with ring structure enhances both the number of hot spots and the maximum $|E|/|E_0|$ value at hot spots (Figure S1).

For bare metallic ring, the intensity of electric field at the center first increases and then decreases as the radius of the ring is increased.¹⁰ This trend of the intensity is determined by two competing processes, increased source of SPPs and enhanced intensity loss due to SPP damping. Assuming each small segment of the ring as an SPP generator, total electric field generated by the whole ring should be in proportion to its radius R . Meanwhile, the field intensity also decays as $\exp(-R/$

δ_{spp}). Thus, the SPP intensity in the center of the ring should be proportional to $R \exp(-R/\delta_{\text{spp}})$. We can easily obtain a “first increasing then decreasing” trend with a critical point at $R = \delta_{\text{spp}}$. After combining Au pyramids array with Au ring, a similar trend is observed on our structure, but the focused SPPs start to couple with LSP generated by Au pyramid structure, which should make the dependence relation more complicated. That is probably why our maximum overall enhancement is found at about $22\lambda_{\text{spp}} \approx 1.6\delta_{\text{spp}}$ rather than δ_{spp} . Table 1 shows the

Table 1. Contribution of the Various Site Enhancements to the Total SERS Enhancement ($R = 22\lambda_{\text{spp}}$)

$ E / E_0 $	percentage of mesh boxes	percentage of contribution to the total enhancement
1–5	99.76%	43%
5–10	0.21%	22%
10–16	0.03%	35%

contribution of the various site enhancements to the total SERS enhancement (here defined as $\sum_{|E| \geq 1} |E|^4$) for Au pyramid array with one ring ($R = 22\lambda_{\text{spp}}$). The hottest sites ($|E|/|E_0| > 10$) contain just 0.03% of all the mesh boxes (within $640 \times 640 \times 160$ nm region) but contribute 35% of the total SERS enhancement, illustrating the reason why we define 10 as a threshold value of $|E|/|E_0|$ for SERS hot spots.

3.2.2. Effect of the Number of Rings on Electric Field. In this section, we increase the number of rings to enhance the excitation of SPPs. For multiple concentric ring structures, if the locations of the additional rings satisfy the circular Bragg condition for plasmonic wavelength, the electric intensity of the plasmonic focus will get stronger, while the focal spot remains approximately the same size as more rings are added. In the following simulation, the number of rings is increased from 1 to 18. We start from the largest ring with a radius of $20\lambda_{\text{spp}}$ and each new ring is added with one λ_{spp} smaller radius. For the 18th ring, radius is $3\lambda_{\text{spp}}$. Figure 3a shows the 2D electric field distribution along x – y planes for Au pyramids with 15 rings added. The electric field between pyramids and the hot spot volume are strongly enhanced compared with the situation without rings (Figure 1a). The increased rings contribute to the dramatically enhanced excitation of SPPs, which mainly account for the enhancement of electric field near pyramids. Figure 3b shows the overall SERS enhancement with increasing number

Figure 3. (a) Two-dimensional electric field distribution of 4-pyramids array (with 15 rings) along x – y plane. (b) Overall enhancement with increasing number of the rings (excitation wavelength = 633 nm). (c) Extinction absorption and scattering curve of Au pyramid array with 15 rings, and the overall enhancement change with excitation wavelength.

Figure 4. Two-dimensional electric distribution of pyramids array with different spacing between pyramids: (a) 250 nm and (b) 500 nm. Mappings in (a) and (b) have the same scale bar for $|E|/|E_0|$. (c) Overall enhancement with increasing spacing between pyramids (excitation wavelength = 633 nm).

of the rings. The overall enhancement of substrate first gradually improves as more rings are added, but starts to decrease as ring number further increases to 18. As the ring number increases, SPP sources increase, but scattering due to the presence of inner ring will also increase. These two competing mechanisms determine the amount of SPPs that could be coupled into the central pyramid array. As the number of rings increases to a certain amount, scattering starts to dominate, and we see that the overall enhancement decrease as the number of rings is increased.

Figure 3c shows the calculated extinction, absorption, and scattering curve of the 4-pyramids array with 15 rings, and the wavelength dependence of its overall SERS enhancement. The extinction curve does not show an apparent resonance peak, but the overall enhancement shows a clear maximum value near 610 nm. At the wavelength smaller than 575 nm, the enhancement of electric field near Au pyramid is very small with no electric field amplitude ($|E|/|E_0|$) being larger than 10. The discrepancy between extinction curve and overall enhancement dependence on wavelength can be understood from the following two aspects. First, the distance between neighboring Au rings is set as one plasmonic wavelength based on the 633 nm excitation. When excitation wavelength is far away from 633 nm, the plasmonic wavelength will change correspondingly, and thus the neighboring rings will no longer satisfy the circular Bragg condition for the plasmonic wavelength. As such, SPP wave is not constructively interfered, and the amount of SPPs focused to the center of the ring will decrease

dramatically, leading to the low enhancement of electric field. Second, scattering starts to dominate the extinction for longer wavelength despite the reduction in plasmon resonance related absorption, as seen in Figure 3c. In addition, the enhancement of local electrical field around pyramids are mainly due to the coupling between SPP and LSP. Extinction curve can reflect the LSPR frequency but probably are not appropriate to characterize the optimum frequency for the coupling between SPP and LSP. In the following simulation, we will continue to use 633 nm wavelength for excitation of SPP and LSP.

3.3. Coupling Efficiency of SPPs and 4-Pyramids Array. In this section, the coupling efficiency of the focused SPPs and pyramid array is discussed. The structural variables that could affect the coupling efficiency are investigated, including the pyramid spacing, the distance of pyramid array center to the ring center, and the number of pyramids. We assume that the structural variables affecting the LSP and SPP interaction do not have an obviously convoluted effect with one another. In other words, the change of one structural variable will not influence the way that another variable affects the LSP and SPP coupling. Based on the assumption, the number of rings is fixed to be 6 with smallest ring size of $15\lambda_{\text{spp}}$ and the largest ring size of $20\lambda_{\text{spp}}$ for simulation in sections 3.3 and 3.4 in order to save the computational resource.

3.3.1. Simulation of Varying Spacing between the Pyramids. In this section, the spacing (S) between neighboring pyramids varies from 200 to 600 nm to couple with SPPs. Figure 4 shows the 2D electric field distribution and overall

Figure 5. x - y plane 2D electric field distribution of increasing distance between pyramids center to the ring center: (a) 200 nm and (b) 400 nm. Mappings in (a) and (b) have the same scale bar for $|E|/|E_0|$. (c) Overall enhancement with increasing distance between pyramid center to ring center (excitation wavelength = 633 nm).

Figure 6. x - y plane 2D electric field distribution for different number of pyramids: (a) two pyramids and (b) three pyramids. Mappings in (a) and (b) have the same scale bar for $|E|/|E_0|$. (c) Overall enhancement with increasing number of pyramids (excitation wavelength = 633 nm).

SERS enhancement for varying spacing between pyramids. The pyramids with 250 nm spacing generate larger hot spot volume than pyramids with 500 nm spacing (Figure 4a,b). When the spacing is increased from 200 to 600 nm, the general trend of overall enhancement is first increasing and then decreasing. This can be understood from the relative position between Au pyramids and SPP focal spots. The Au rings focus SPPs into its center to form two SPP focal spots (Figure 2b). The more the Au pyramids overlap with SPP focal spots, the stronger the coupling between SPP and LSP. Therefore, pyramids that overlap with the SPP focal spots the most will lead to the highest overall SERS enhancement.

3.3.2. Simulation of Varying Distance of Pyramid Array Center to the Ring Center. In this section, the position of 4-pyramids array is shifted from the ring center to study the coupling efficiency of LSP and SPPs. The distance (D) of the pyramid array center to the ring center varies from 0 to 600 nm along the x -axis. Figure 5 shows the 2D electric field distribution and overall SERS enhancement with various distances. SPPs are focused into the center of the ring pattern, and thus, the general trend is that the further the pyramid array is from the ring center, the less efficient they are coupled and thus have weaker enhancement. However, when the pyramids are moved away from the ring center, it will encounter the peaks and troughs of SPPs along the way, which will lead to fluctuation of coupling efficiency and thus the fluctuation of overall enhancement, as seen in Figure 5c.

3.3.3. Simulation of Varying Number of Pyramids. In this section, one, two, and three pyramids are taken away from the 4-pyramids pattern. The positions of the left three, two, and

one pyramid are chosen to overlap most parts of the hot spot region generated by SPPs. Figure 6 shows the 2D electric field distribution of different pyramid pattern and the overall enhancement with increasing number of pyramids. When the number of pyramids becomes smaller than 4, the enhancement can actually be stronger. The underlying mechanism is that a pyramid right on the SPP focal spot can provide the strongest enhancement, as is mentioned in section 3.3.1. For the 4-pyramids array, SPP focal spots only appear in the gaps between pyramids (Figure 3a), while the one, two, and three pyramid arrays all have at least one pyramid standing right on the SPP focal spot. Not only would the results give us a hint of how to couple LSP and SPP efficiently, it also suggests that by reducing pyramid number, the electric field can be further confined spatially without sacrifice of the electric field intensity.

3.4. Fiber-Based Probe with Back Illumination and Signal Extraction. One objective of this simulation is to guide the fabrication of SERS optical fiber probe for remote sensing. The fabrication process requires transferring the 4-pyramids pattern onto the optical fiber end, where the incident light is illuminating from the backside (bottom) of the pyramids. In this case, signal extraction could be difficult for certain reasons. One of the main issues is that Au film substrate will absorb the signal, while it travels through. Two approaches can be employed to address this issue, one is to reduce the thickness of continuous film, the other is to open a window in the continuous film to let light pass through. The following simulations are to determine the signal extraction efficiency in the case of fiber-based probe with back illumination

Figure 7. Two-dimensional electric field distribution for different thickness of Au films: (a) 0 nm and (b) 20 nm with opening window between pyramids. (c) Overall enhancement with increasing substrate thickness from back illumination (excitation wavelength = 633 nm). Inset shows the schematic diagram of noncontinuous Au film substrate.

In this simulation, the thickness of Au continuous film beneath rings is adjusted from 20 to 0 nm. When the thickness of the film changes from 20 to 0 nm, the enhancement of electric field increases dramatically. Figure 7a shows the 2D electric field distribution of 0 nm Au film. Because substrate without a continuous film will reduce the chance that the incident light and Raman signal are absorbed by Au film, thus it has a higher signal extraction efficiency. For comparison, pyramids without ring structure are also simulated, whose performance is shown in Figure 7c. Again, it can be seen that by adding ring structure the enhancement increases significantly, indicating effective coupling between SPP and LSP. Another way of increasing the signal extraction efficiency is to remove part of the continuous Au film substrate, as shown in the inset of Figure 7c. The 2D electric field distribution of the broken film is shown in Figure 7b. Compared with 20 nm continuous film, broken film generates higher enhancement, which is yet lower than that with 0 nm film thickness.

The common single-ended SERS fiber probe is prepared by coating metallic NPs or transferring nanopatterns on the facet of one optical fiber.^{22–24} Because the Raman signal came back to spectrometer through the same fiber core, SERS fiber probes prepared using this method detects signal from across the entire fiber facet (usually larger than 10 μm) rendering the SERS spatial resolution on the same order of magnitude. With the pyramid-ring structure, however, the excitation EM field energy is concentrated to the array of pyramids, which could cover orders of magnitude smaller area compared to the area of the fiber facet. Because SERS yield is proportional to the fourth power of the amplitude of the EM field, this concentration of the EM field leads to drastically improved spatial resolution. Our simulation results indicate that the Au pyramid-ring can confine the electric field within a 700×700 nm region. The pyramid-ring structure could provide higher spatial resolution for SERS optical fiber probe than those of the previously reported SERS fiber probes if the pyramid–ring SERS platform was transferred onto the optical fiber facet.

4. CONCLUSIONS

This research demonstrates a novel open-structured Au pyramid SERS platform with enhancement of the spatial confinement of the electric field. Excitation of SPPs by circular Au rings and coupling of SPPs with Au pyramids are studied to improve the electric field and the overall SERS enhancement of the platform. By combination of Au pyramids with Au rings, the hot spot volume as well as electric field intensity at hot spots

around Au pyramid are increased significantly compared with bare Au pyramids array. We also find out that the more pyramid overlaps with the SPP focal centers, the higher coupling efficiency can be achieved, therefore leading to more hot spots and higher electric field enhancement. By changing the number of pyramids and their positions, the electric field enhancement up to 140 $\times$ can be achieved and the anticipated SERS signal enhancement of up to 8 orders of magnitude. The results of simulation with back light illumination demonstrate that the thickness of Au film substrates plays a significant role for the signal extracting from backside when the SERS platform is transferred onto a fiber facet. Highest electric field enhancement can be achieved without the Au film for fiber application. Au pyramids combined with rings could achieve the confinement of the electric field within a 700×700 nm region, which could provide higher spatial resolution for SERS fiber probe.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b08847.

Statistical distribution of electric field around bare pyramid array and the pyramid array with one Au ring (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yhx@ucla.edu. Tel: +1-310-825-2971.

Notes

The authors declare no competing financial interest.

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