Intra-particle plasmonic coupling of tip and cavity resonance modes in metallic apertured nanocavities

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Abstract: Based on numerical studies of apertured metallic nanocavity structures, we describe a new intra-particle plasmonic interaction pathway that couples the plasmon resonance modes of the aperture edge and the cavity. In contrast to the inter-particle coupling schemes that require precisely arrayed nanoparticles, this intra-particle coupling scheme achieves the tunability in plasmonic resonance wavelength using a single standalone nanostructure. In addition, when the aperture edge is made sharp, it functions dually as a tip that amplifies its near-field producing the local field enhancement effect. We investigate the details of the coupling mechanism and identify the dominant role of the tip mode in determining the coupling efficiency numerically. The numerical model results in good agreement with recent experimental results. This intra-particle coupling mechanism will help the monolithic integration of plasmonic functionalities and its application for the nanoscale spectroscopy of biological structures in vivo.

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Reference and Links
1. Introduction

The local field enhancement (LFE) associated with the plasmon resonance in metallic nanostructures has attracted intense research interest for its role in a number of useful nanophotonic phenomena such as surface-enhanced Raman scattering (SERS). The improvement of the LFE factor has been the focus of research. Especially for biological SERS applications, the ability to tune the plasmon resonance wavelength toward the “biological window” (700~1100 nm) in near-infrared (NIR) regime has been emphasized due to the low optical absorption and scattering within the spectral regime. The intrinsic resonance wavelengths of plasmonically active noble metals, however, mostly fall in UV-visible regimes. The inter-particle plasmonic coupling scheme, while being successful in lowering the resonance energy precisely as designed [1], requires the structure to be fixed on a substrate. For many in vivo and in vitro applications, mobile, standalone structures are needed.

In order to modify the resonance characteristics of standalone nanostructures, the intra-particle plasmonic coupling scheme has often been adopted. In the scheme, multiple plasmon resonance modes hosted within a single nanostructure are coupled to generate a new mode. The nanostructure must be configured to host multiple, localized surface plasmon-polariton resonances (SPPR) modes within interaction range. The resonance modes residing on the vertices of polygonal metallic nanostructures are good examples [2]. In curved nanostructures such as nanoshells [3] or nanorings [4], the coupling between the spherical or cylindrical SPPRs is utilized.

In this Letter, we investigate the intra-particle plasmonic coupling phenomenon of metallic aperture nanocavities (ANCs) with an emphasis on LFE and resonance wavelength tuning. The ANC structure is schematically shown in Fig. 1(a). Such a geometry is already demonstrated based on masked deposition technique [5]. 3-D ANC exhibiting geometries of the 2-D ANC axiomsymmetrically are also demonstrated [6-9]. Owing to its complex geometry, the ANC hosts a wider variety of SPPR resonance modes than its concentric counterpart and hence induces different intra-particle plasmonic coupling effects. While a number of ANC have been experimented [5-9] and studied theoretically [9] and numerically [7,8,10], an analysis in terms of plasmonic coupling has rarely been reported. Our numerical studies focus on sharp-edged nanocavities with radii ranging from 1/4~1/3 of the excitation wavelength which facilitates intra-particle coupling. The sharp edge shown in Fig. 1(a) is naturally formed in deposition-based fabrication processes. We reveal that in such ANCs, the intra-particle coupling between the edge and nanocavity SPPR modes takes place and a hybrid mode with modified resonance characteristics is formed. Due to the sharpness, the edge plays a dominant role in the coupling process and causes high LFE. The edge modes are also sensitive to the shape and environment of the edge and the wavelength and polarization of the excitation. From an electromagnetic point of view, the ANC is an amplifying antenna feeding into a resonator.

2. Simulation Model

To investigate the LFE in ANCs, we compute their local fields by solving the Maxwell’s equations. We adopt the finite element method (FEM) mainly for its compatibility with curved geometry and adaptive meshing capability. The latter becomes critical when dealing with a structure consisting of features differing by several orders in dimensions, i.e., the apex radius of the tip (0.5–4 nm) and the whole ANC (~400 nm). We use the complex permittivity of bulk gold [11]. All simulations are transverse magnetic and the retardation is fully considered. The ambience is set as vacuum in accordance with the experimental setup.

3. Supported 2-D Plasmonic Modes

In 2-D, the localized SPPR modes supported by the ANC structure becomes more identifiable, as illustrated in Fig. 1(a). They reside at the tips, on the inner surface of the cavity, and the outer-surface. In addition, the surfaces [3,4,12] and the paired tips [13] are known to form coupled modes. Brief surveys of individual modes will be informative for the discussion of their interactions. Figure 1(b) shows the relation between the cylindrical cavity radius $R$ and the excitation wavelength obtained from the characteristic equation

$$k_x J_x(k_x R)H_y(k_y R) = k_y J_y(k_x R)H_x(k_y R)$$

where $J_x$ and $H_x$ are Bessel and Hankel functions, $k_{x,y} = \sqrt{\varepsilon_{x,y} \omega / c_0}$, and the prime denotes the differentiation with respect to its argument. $\varepsilon_{x,y}$ are the dielectric constants of the cavity and its surroundings [14]. All parameters are consistent with the simulation. It is clear that with $R = 150$ nm, the nanocavity supports only the lowest TM ($l=1$) mode within the bandwidth of interest. As indicated in Fig. 1(b), the TM ($l=1$) mode attracts and repels charges to and from the cavity diametric points and its vicinities. Since there is no closed form description for the tip near-fields, we characterize those using numerically obtained field patterns shown in Fig.
1(c). Beginning from the apex, the near-field repeatedly converges and diverges vertically along the tip and exhibits multiple nodes $N_n$. As the excitation wavelength increases, the nodes move away from the tip apex and the convergence angle varies. Note that the amplification of the local fields also occurs near the tip apex due to the lightning rod effect (LRE). The interaction between two nanoscale tips becomes stronger at shorter gap width and/or longer excitation wavelength and is able to generate huge LFE [13]. The near-field of the tip-to-tip interaction mode resembles the field pattern of an electric dipole [15]. Considering the dimensions of the present ANC, we exclude the outer-surface SPPR and its interaction with the cavity mode from further considerations.

4. Plasmonic Coupling Analysis

Based on the survey, we hypothesize that a strong intra-particle plasmonic between the tip and the cavity SPPR modes takes place within the ANC structures and that a strong LFE at a modified wavelength originates from it. The proximity of the tip and the cavity warrants the existence of such coupling effects. The phase retardation-induced SPPR coupling between two closely positioned nanostructures and the resultant LFE have already been predicted numerically [16]. Such LFE can be attributed to the near-field interaction that increases the surface charge, and consequently the field density, of the SPPR. In the case of sharp-edged ANCs, an additional improvement in LFE occurs owing to the LRE-induced amplifier action of the tip.

Rigorous analysis of the coupling between the two SPPR modes is not straightforward. Due to the dissimilar and asymmetric geometries of tip-cavity, the elegant analytical approaches of Ref. 3 are not applicable. The tip-cavity coupling also depends on the phase retardation, which makes analytical approaches more complicated. Since the coupling occurs through the overlapping of the mode near-fields, we investigate the coupling mechanism and its optimum condition by closely examining the electric field patterns at wavelengths of LFE maxima and minima.

Fig. 2. (a)-(c) LFE spectra at incidence angles at 0°, 25°, and 90°. (d) LFE spectra of a spoiled cavity with sharp tips and a dull-tip ANC (inner cavity radius: 150 nm).
The FEM simulation results for identifying the LFE maxima and minima are shown in Figs. 2(a)-(c). The LFE factor is defined as the amplitude ratio between the excitation wave and the maximum value of the ANC near-field which occurs at the tip apex for all cases in our study. To emphasize the role of the sharp tip and its SPPR mode, the tip apex radius is set to 0.5 nm. The ANCs with tips of practical thickness will be discussed in the following section. The computation domain has dimensions of 1.6×3 µm and employs low-reflection boundary conditions. The width is made longer along the direction of wave propagation to ensure the generation of quasi-plane waves. The mesh consists of 46,588 adaptive triangular elements. Near the tip apices, the size of elements is kept under 0.1 nm. The sensitivity of the LFE spectra on the incidence angle of the excitation wave is evident from Fig. 2(b) and (c). This incidence angle dependence, however, is far lower than the extreme polarization sensitivity of LRE from an isolated tip. Figure 2(d) shows simulation results of two additional structures; a spoiled cavity with sharp tips that emphasizes mainly the tip-induced effects and a dull-tip ANC that mainly emphasizes the cavity-based effects. The fact that the computed LFE factor of a full ANC, ~10^3 at maximum, far exceeds those of the partial structures corroborates that the LFE in an ANC depends on the plasmonic coupling mechanism.

Figures 3(a)-(c) show the field patterns within the ANC of Fig. 2(a) at wavelengths of the LFE peaks and valley. By examining the superimposed surface plots of LFE factors, we can examine the plasmonic coupling conditions for higher LFE. At LFE peaks, the TM (l=1) mode supported by the cavity is at least partially excited along with the tip mode. At the LFE valley, however, the field pattern within the cavity takes similarity to TM (l=2) mode which is

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Fig. 3. (a)-(c) Simulation results at P1, V, and P3 of Fig. 2(a). The electric field patterns are superimposed over surface plots of the LFE factors in log scale. The dotted boxes indicate the location of modal overlap. (d)-(f) Schematic representations of tip-cavity plasmonic coupling corresponding to (a)-(c), respectively.
not supported by the cavity. The inefficient excitation of a cavity mode leads to a weakened coupling between tip-cavity and lower LFE. Among the LFE peaks, the P₃ that exhibits minimally perturbed cavity mode results in higher LFE. The field patterns in the dotted boxes also indicate that it is the near-field of the tip mode at the nodes Nₙ that determines the excitation efficiency of a certain cavity mode. This selective excitation is illustrated in Figs. 3(d)-(f). At P₁, the field pattern at N₁ matches that of the TM (l=1) cavity mode at the position approximately and the mode is partially excited. The robustness of the cavity SPPR against the perturbation due to an aperture makes this partial excitation possible. Coyle et al reported that cavity SPPR modes persist until a spherical cavity becomes a hemispherical shell [9]. At P₃, the field lines are matched at N₁ which is closer to the tip apex than N₂. This results in an almost full excitation of a TM (l=1), as evidenced by ~10 dB LFE over the whole cavity. In contrast, the field pattern of the tip mode at V does not match the TM (l=1) field pattern at any node and consequently a cavity mode is not excited. This dominance of the tip mode can be attributed to its intensity much higher than that of cavity modes. The role of the tip SPPR makes the aperture width the most important geometric parameter in tuning the LFE peak wavelength. According to our model, a blue-shift of the LFE peak is expected with increasing aperture width since the shortened tip length enables the field patterns match near N₁ at shorter wavelengths. The LFE spectra as a function of the aperture width are plotted in Fig. 4 and show a good agreement with the prediction. The increase in LFE with increasing aperture width (shorter resonance wavelength) can be attributed to the influence of the intrinsic plasmon resonance which occurs near 500 nm.

![Fig. 4. Computed LFE factors at the tip as a function of the aperture width w (cavity radius: 150 nm, TM input at 0° incidence angle).](image)

### 5. Discussion

This model successfully explains the LFE characteristic between 600 and 900 nm. The increase in excitation wavelength required to match the tip and cavity field patterns is the origin of the LFE red-shifted into the NIR regime in ANCs. For < 600 nm, multipolar SPPR becomes dominant and the role of the tip mode diminishes. For > 900 nm, the tip-to-tip interaction mode becomes dominant and the cavity mode cease to be excited. The study of P₂ and P₄ due to 90° incidence angle is under way. We are aware that LFE from similar nanoscale apertured cavities have been reported, either directly or indirectly. Lopez-Rios et al reported strong field intensity near the upper corners of deep grooves of metallic gratings [17]. It is also numerically demonstrated that 2-D ANCs with multi-valued cross-section exhibit LFE near the aperture [10]. While the LFE effects are well described, neither their intra-particle origin nor the role of the geometry has been investigated explicitly.

We set the tip thickness to a practical value of 4 nm in accordance with the TEM image in the inset. We notice that as the sharpness of the tip is decreased, the tip-to-tip interaction...
mode begins overshadow the SPPR of the isolated tips at wavelengths shorter than the sharp-tip ANC case. The LFE peak near 700 nm is caused by the coupling between the tip-to-tip and nanocavity modes. The fact that the dipole-like near-field of the tip-to-tip mode does not overlap well with the cavity mode, in addition to the diminished LRE, explains the LFE factor lower than that of the sharp-edged ANCs. The simulated LFE is \( \sim 17 \) dB near 700 nm which is lower than experimental observation by \( \sim 7.7 \) dB [6]. This discrepancy indicates the possible existence of a sharper edge and/or the involvement of additional Raman enhancement mechanisms such as the chemisorption effect. The \( \sim 600 \) nm peak is still from the tip-nanocavity coupling.

6. Conclusion

In conclusion, we have investigated a novel intra-particle plasmonic coupling mechanism in metallic nanocavities with sharp-edged apertures. In such structures, our numerical simulations reveal that the sharp edge functions as an antenna that feeds the excitation wave into the nanocavity and also as an amplifier that enhances the local field utilizing its large curvature. The preliminary 3-D simulation results indicate that it is possible to adopt the 2-D approximation in which the aperture edge-nanocavity interaction is transformed into the coupling between two well-known SPPR modes: the tip mode and the cylindrical cavity mode. The interaction takes place through their near-fields and the requirement for matching the near-field patterns at the modal interface governs the wavelength and efficiency of the coupled mode. By examining the simulated electric field patterns, we show that the intense tip near-field plays a dominant role in this matching process. Accordingly, our simulations with varying geometric parameters reveal that changing the proximity of the tip to the cavity strongly affects the resonance wavelength of the coupled mode. It is important to note that the tip near-field under the tip-cavity coupled resonance exhibits higher LFE than the maximum achievable with paired tips without cavity support. This additional enhancement may be attributed to the synchronized transport of the free electrons due to the retarded modal interactions [16] but needs to be studied in more detail as a future work. This intra-particle coupling study provides criteria useful for the analysis and synthesis of monolithically integrated plasmonic functionalities.

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