Size and shape effects on the field enhancement induced at a silver triangular tip

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Abstract. A computational study is conducted on the near field enhancement induced by localized surface plasmon resonance (LSPR) around a silver nanotape of various sizes and shapes. The results show the consistent dominance of the dipole field generated at the rectangular Ag nanotape surfaces of various lengths by a normal incident electromagnetic plane wave of polarization along the long edge. The dipole field is further shown to exhibit monotonous spectral redshifts and increased magnitudes with increased length ($\ell$) of the rectangular nanotape. In contrary, the spectral peak and the field magnitude do not show the simple consistent variations with varied apex angle ($\theta$) of the triangular nanotape. The calculated result for the triangular tape does exhibit the largely concentrated near field magnitude at the tip. It is found that a remarkable enhancement factor of $10^7$ is attained at $\theta = 45^\circ$ and $\ell = 50$ nm.

1. Introduction

The surface plasmon generated by an incident light at a metal surface is known to produce a highly concentrated field which is largely confined near the metal surface. This near field effect has long been studied and explored for spectroscopic and optical imaging [1-2]. One of the earliest and well known applications is the dramatic enhancement of Raman spectroscopic signal, as reported by Richard P. Van Duyne in 1977 with the use of Ag electrode for the deposition (adsorption) of the analytes [3]. Interestingly it was found that $10^5$-$10^6$ fold increase of the Raman signal was achieved upon roughening of the Ag surface compared to the signal detected by using a smooth Ag surface. This modified Raman spectroscopy and its continuously improved version has come to be known as the surface-enhanced Raman spectroscopy (SERS) [4]. Meanwhile, further studies on the large enhancement produced by a roughened adsorption surface and colloidal systems [5-7] have led to the idea concerning the role of local hotspots that are mainly responsible for the generation of very strong local near-field and a huge enhancement factor for the Raman signal [8]. This idea was first implemented as tip-enhanced Raman spectroscopy (TERS) using the metal tips of AFM or STM [9-12]. TERS has the advantage of overcoming of the drawbacks of SERS which was shown to have its enhancement depending on the specific nature of the adsorbed analytes. It also has the additional advantage of offering Raman spectroscopy with extremely high spatial resolution [13]. The possibilities of nanoscaled chemical imaging [14-15] and single molecule TERS [16-17] have been reported.

While the estimated enhancement factor of TERS has been formulated in terms of the far-field and near-field intensities of the Raman signals using metallic tips [18-19], little has been reported in the literature about the effects of the size and shape of the tip itself on the spectral and spatial distributions of the near-field enhancement factor around the metal tip. Reported in this paper is the result of a
computational study on the detailed variations of the spectral profiles and spatial distributions of the near-field enhancement factor around a simple rectangular Ag tips of various sizes and shapes generated by a normal incident electromagnetic wave of certain polarization. For this purpose, the computation of the electric field is performed employing the surface integral equation (SIE) method [20]. Finally, the optimal geometrical parameters yielding the most favorable field enhancement is presented.

2. Computational method
There are many kinds of computational methods for calculating the electric fields scattered from a scatterer. One of these is the integral equations (IE) method which solves electromagnetic scattering problem by representing the scattered field in terms of its associated Green’s function [21]. Generally, the integral equations methods are divided into two types, one employs the volume integral equation (VIE) based on the discrete dipole approximation (DDA) and the other one uses surface integral equation (SIE) involving the equivalent electric and magnetic surface current densities. This second method is the one adopted in this study.

The IE method is known to yield reasonably small errors with the requirement of considerably smaller computational memory compared to FDTD and FEM methods which require a large memory for background space discretization. This requirement is avoided in the calculation by means of integral methods, in particularly the surface integral equation method. In addition to that, SIE method can be applied to scatterer of arbitrary shapes and the calculation can be performed on the mathematical surface surrounding the scatterer instead of carrying out the calculations over the entire volume. This method therefore works best for piecewise homogeneous media [22].

Basically, the total electric field in a light scattering problem can be obtained by solving the Helmholtz equation:

\[
\nabla \times \nabla \times E_\gamma(r) - k_\gamma^2 E_\gamma(r) = i\omega \mu_\gamma j(r),
\]

\( \gamma = 1, 2 \) correspond to the regions outside and inside the scatterer indicated in figure 1 and \( j(r) \) is the volume current density representing the effect of the scatterer.

![Figure 1. Geometry of the electromagnetic scattering problem [20]](image)

The complete solution of this differential equation consists of the incident electric field, given by:

\[
E_{\gamma}^{inc}(r') = i\omega \mu_\gamma G_\gamma(r, r') \cdot j(r') \, dV,
\]

and the scattered field which is included in the total electric field as presented by the following equation [20]:

\[
E_\gamma(r) = \left\{ \begin{array}{ll}
\int_{\partial V_\gamma} \left[ \frac{\omega \mu_\gamma}{i} \vec{G}_\gamma(r, r') \cdot \vec{j}(r') \right] \times \vec{M}_s(r') \, dA' + \left( E_{\gamma}^{inc}(r), \gamma = 1; r \in V_1 \right), \\
0, \quad \gamma = 2; r \in V_2.
\end{array} \right.
\]
In this equation, the dyadic Green's tensor $\mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}')$ is the solution of the corresponding Helmholtz equation with a single point source at $\mathbf{r} = \mathbf{r}'$ as written below.

$$\nabla \times \nabla \times \mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') - k_{\gamma}^2 \mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') = \mathbf{I}\delta(\mathbf{r} - \mathbf{r}').$$  \hspace{1cm} (5)

Equation (3) shows that the total electric field can be obtained in either region for the source in the associated region, provided the dyadic Green's tensor $\mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}')$ and the equivalent electric and magnetic surface current densities $\mathbf{I}_s(\mathbf{r}')$ and $\mathbf{M}_s(\mathbf{r}')$ are known. The dyadic Green's tensor $\mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}')$ can be related with the homogeneous scalar Green's function according to the following expression [23].

$$\mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') = \left[ \mathbf{I} + \frac{\nabla \nabla}{k_{\gamma}^2} \right] \mathbf{g}_{\gamma}(\mathbf{r}, \mathbf{r}') = \left[ \mathbf{I} + \frac{\nabla \nabla}{k_{\gamma}^2} \right] \frac{e^{ik_{\gamma}|\mathbf{r} - \mathbf{r}'|}}{4\pi|\mathbf{r} - \mathbf{r}'|}.$$  \hspace{1cm} (5)

Meanwhile the equivalent current densities are written as linear combinations of $N$ linearly independent basis functions [24] as

$$\mathbf{I}_s(\mathbf{r}') = \sum_{n=1}^{N} \alpha_n \mathbf{f}_n(\mathbf{r}'),$$  \hspace{1cm} (6)

and

$$\mathbf{M}_s(\mathbf{r}') = \sum_{n=1}^{N} \beta_n \mathbf{f}_n(\mathbf{r}').$$  \hspace{1cm} (7)

where the basis functions $\mathbf{f}_n(\mathbf{r}')$ are generally taken to be the Rao-Wilton-Glisson (RWG) basis functions [25] using triangular meshes. The $n$-th basis function is then defined as:

$$\mathbf{f}_n(\mathbf{r}') = \begin{cases} \frac{L_n}{24 \alpha_n} (\mathbf{r} - \mathbf{p}_n^+), & \mathbf{r} \in T_n^+ \\ 0, & \mathbf{r} \not\in T_n^\pm \end{cases} \hspace{1cm} (8)$$

In equation (8), $L_n$ is a $n$-th common edge length that separates a pair of adjacent triangular meshes ($T_n^+$ and $T_n^-$). The “+” and “-” notations denote respectively the divergent and convergent surface current directions on the scatterer surface, while $A_n^\pm$ is the area of mesh, $\mathbf{r}$ denotes the observation point, and $\mathbf{p}_n^\pm$ are the $A_n^\pm$ free vertices of the meshes.

![Figure 2](image_url) Illustration of the RWG basis functions [25]

Next, the expansion coefficients of the equivalent current densities $\{\alpha_n\}$ and $\{\beta_n\}$ are determined by substituting Equation (6)-(7) into the electric field and magnetic field integral equations given below.

$$\left( \omega \mu_r \frac{\partial}{\partial t} \mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{I}_s(\mathbf{r}') \right) dA' - \frac{\partial}{\partial t} \left[ \nabla \mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') \right] \times \mathbf{M}_s(\mathbf{r}') dA' \bigg|_{\tan} = \begin{cases} (\mathbf{E}^inc(\mathbf{r}))_{\tan}, & \gamma = 1; \mathbf{r} \in S \\ 0, & \gamma = 2; \mathbf{r} \in S \end{cases} \hspace{1cm} (9)$$

$$\left( \omega \varepsilon_r \frac{\partial}{\partial t} \mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{M}_s(\mathbf{r}') \right) dA' - \frac{\partial}{\partial t} \left[ \nabla \mathbf{G}_{\gamma}(\mathbf{r}, \mathbf{r}') \right] \times \mathbf{I}_s(\mathbf{r}') dA' \bigg|_{\tan} = \begin{cases} (\mathbf{H}^inc(\mathbf{r}))_{\tan}, & \gamma = 1; \mathbf{r} \in S \\ 0, & \gamma = 2; \mathbf{r} \in S \end{cases} \hspace{1cm} (10)$$
These equations are solved for $\{\alpha_n\}$ and $\{\beta_n\}$ using the so-called Method of Moments (MoM) [24], where a set of expansion functions and a testing procedure are developed and used to derive the elements of the moment matrices. The resulted $\mathbf{J}_s(r')$ and $\mathbf{M}_s(r')$ together with $\mathbf{G}_y(r,r')$ from equation (5) are then substituted into equation (3) to give the total electric field determined by equation [26]. The resulted field $\mathbf{E}_y(r')$ is further normalized by the incident field $\mathbf{E}^{inc}_y(r')$ to give the associated enhancement factor.

The geometry of the meshes used in this study are created with the total number ranging within 800-1500 for optimizing the computation time and memory. There is no significant changes of the result for finer meshes. The frequency-dependent permittivity of the silver scatterer is taken from the experimental data of Babar and Weaver [27].

3. Size effect
For the study of size effect on the near field spectra and its spatial distributions, we consider the simple case of a rectangular silver (Ag) nanotape of 5 nm thickness and 5 nm width as shown in figure 3. In the following computation, we restrict ourselves to the case of transversal electromagnetic plane waves incident on the nanotape surface with its electric field polarized along the x-axis direction. The size effect is first investigated by computing the near-field spectra at one end of the tape located at $x = (\ell/2 + 0.1)$ nm, $y = z = 0$ nm, where $\ell$ is the tape length, as well as the spectral variations for various tape lengths.

![Figure 3. Geometry of the tape. The coordinate origin is located at the center of the tape.](image)

The spectrum computed for the nanotape with $\ell = 45$ nm is presented in figure 4 which shows that the multimode resonance peaks at: $\lambda = 905.2$ nm, $\lambda = 459.3$ nm, and $\lambda = 403.9$ nm corresponding to the dipole, and the successively higher field modes, respectively. It is seen that the higher modes are increasingly blueshifted with rapidly diminishing field enhancement factor as shown in the inset, which is separately presented from the dipole spectral profiles due to the largely different peak values. The highest spectral peak which is designated as belonging to the dipole mode of the electric field is found to be the lowest mode found for the tape. The basically similar patterns of the spectra are also found in the cases of different tape lengths. However, the field enhancement factor of the resonance modes are generally found to decrease with shorter tape length. This will be further elaborated figure below.
Figure 4. Near field spectrum generated at the end of an Ag nanotape of $\ell = 45$ nm. The inset shows the much lower spectral peaks at $\lambda < 750$ nm

In view of the much more dominant appearance of the dipole mode spectral profile, the following analysis will be focused on the electric dipole spectra calculated for various tape lengths. The result is presented in Fig. 5 for a number of tape lengths. Two features stand out in this figure. Firstly, there is a consistent redshift of the spectral profiles with increasing tape length, which is related with the larger oscillation path length of the electron. Secondly, one also observes a monotonous growth of the spectral peak with increasing $\ell$ without much changes of the shape of the profiles. Again, this may be due to the larger numbers of electrons contributing to the associated resonant oscillations. This clearly suggests that higher near field intensity is generally supported by longer $\ell$.

We turn next to the spatial distributions of the dipole fields at the corresponding peak wavelengths and the variations with respect to changes in $\ell$. The computed results are described in figure 6 for several tape lengths indicated in the figure. One sees that the induced electric fields are generally concentrated near the end surfaces of the tape, which decays very fast away from the surface, which is
indicative of the typical feature well known for induced surface plasmon field. The frequency redshift is likely related with the longer oscillation path length of the surface electrons. We note further that one barely observes the near field at the tape surface for $\ell = 10$ nm, while a clearly visible larger enhancement with more spread out spatial distribution of the field is seen for $\ell = 80$ nm, suggesting the benefit of longer tape length.

4. Shape effect
For the investigation of the shape effect, we consider the equilateral triangular Ag tape shown in figure 7. The effects are represented by the variations of spectral profile and spatial distribution of optical near field induced at the tape surface for varied apex angle $\theta$ as indicated in the figure.

The effects of the tape geometry on the near-field at the tip are studied by comparing the dipole field spectral profiles and its spatial distributions computed for various values of the tape parameters ($\ell$, $\theta$). To begin with, a comparison is made between the field enhancement generated at the tip of the triangular tape and at the end point of the rectangular, both computed at their corresponding peak wavelengths. The result given in figure 8 for certain $\ell$ and $\theta$ clearly exhibits a larger (more than 4 fold) enhancement effect obtained by the tip geometry.
In order to explore the optimal geometry of the triangular nanotape for the largest field enhancement at the tip, further variations of $\ell$ and $\theta$ are separately studied. Presented in figure 6 is the result showing the effect of computed for various $\theta$. It is seen that the field enhancement factor varies respectively on $\theta$, with the obviously dominant maximum value attained at $\theta = 45^\circ$ recurring at $\lambda = 688.9$ nm. Further exploration of the optimal geometry is performed by varying the tape length ($\ell$) with $\theta = 45^\circ$. The result of the computed $|E|^2$ is depicted in figure 10. It is clear that both the peak wavelength of the dipole field as well as the field enhancement factor do not show the monotonous changes with respect to both $\ell$ and $\theta$. Nevertheless, the field enhancement factor is found to exhibit its largest value $10^7$ for $\theta = 45^\circ$ and $\ell = 50$ nm at $\lambda = 688.9$ nm.
5. Conclusions
The results of this study have shown the geometrical effects on the near-field enhancement and its spectral shift generated at the tip of a silver nanotriangular tape illuminated by a normal incident plane wave polarized along the long axis of the tape. It is shown that the dipole field generally dominates the spectra generated on the silver nanotape surfaces. Further, consistent monotonous spectral frequency shift and field enhancement factor variations are found in the case of rectangular tape of various tape length. On the other, both the spectral shift and field enhancement factor variations are shown to exhibit complicated non-monotous variation with the tip angle $\theta$ and the length of the triangular Ag nanotape $\ell$. It is shown that the maximum enhancement factor of $10^7$ is attained for $\ell = 50$ nm, $\theta = 45^\circ$ at resonance wavelength of $\lambda = 688.9$ nm.

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