Tailoring plasmonic nanoparticles and fractal patterns

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ABSTRACT

We studied new three-dimensional tailoring of nano-particles by ion-beam and electron-beam lithographies, aiming for features and nano-gaps down to 10 nm size. Electron-beam patterning is demonstrated for 2D fabrication in combination with plasmonic metal deposition and lift-off, with full control of spectral features of plasmonic nano-particles and patterns on dielectric substrates. We present wide-angle bow-tie rounded nano-antennas whose plasmonic resonances achieve strong field enhancement at engineered wavelength range, and show how the addition of fractal patterns defined by standard electron beam lithography achieve light field enhancement from visible to far-IR spectral range and scalable up towards THz band. Field enhancement is evaluated by FDTD modeling on full-3D simulation domains using complex material models, showing the modeling method capabilities and the effect of staircase approximations on field enhancement and resonance conditions, especially at metal corners, where a minimum rounding radius of 2 nm is resolved and a five-fold reduction of spurious ringing at sharp corners is obtained by the use of conformal meshing.

Keywords: Plasmonics, field enhancement, FDTD, bow-tie nano-antennas, fractal nano-antennas, visible-to-THz

1. INTRODUCTION

Plasmonics is an emerging field with the ability to transform engineering and science in many ways, growing fast with substantial prospects to provide miniaturization of opto-electronic chips and the highest field enhancement1, with emphasis on the capability to localize light within ~10 nm gaps and slots. Nano-gaps can be used for various trapping applications2-12 as already demonstrated with cells13 and conducting molecules14 efficiently and without damage to biological material, due to their ability to produce strong light intensity gradients with low power.15 Nano-gaps in metal nano-particles on dielectric substrates are promising for nano-focusing and nonlinear plasmonics16-19 as the localized surface plasmon resonance (LSPR) of particles is used to achieve a boost of sensitivity by field enhancement enabling single-molecule detection20, tweezing21,22, and can find applications in controlled polymerization on nano-scale23-26 and micro-electrochemistry.27

We developed bow-tie nano-antennas defined by electron-beam lithography (EBL) both with rounded shapes and fractal patterns designed to achieve broadband field enhancement from visible wavelength pushing to THz. Patterning processes of gold cylinders on dielectric substrate permit to obtain highly localized field enhancement in hot-spots for surface-enhanced Raman scattering (SERS) sensing applications. As we have the capability of performing fine and repeatable sample processing on large areas, novel plasmonic structures are realizable. We proved fabrication capabilities by gold patterning, and we used 3D finite-differences time domain (FDTD) numerical simulations (Lumerical) to systematically investigate spectral properties of the light field enhancement for the different shapes of EBL-tailored nano-structures. We calculated the optical response taking into account the actual material properties by using experimentally defined dielectric functions available in the Lumerical database, interpolated by a polynomial time-domain function.

A thorough examination of the capabilities offered by the modeling method is given by considering the plasmonic resonances elicited in rounded wide-angle bow-tie nano-antennas: we consider the effect on wide-angle metal corners of the staircase approximation implicit in the FDTD structured mesh and we show its impact on the simulated field enhancement values. We show that a realistic rounding approximation of straight corners holds above a minimum radius dependent on mesh size, and we consider the spurious resonances which result from abrupt mesh size changes in the vicinity of metal corners.

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Figure 1. 3D-FDTD model of the bow-tie gold nano-antenna on silica. The gold layer is 40 nm thick, and the antenna radius is 100 nm, while the gap is set to a length of 10 nm. The flare angle of the bow-ties is $\alpha$, and the effective widths due to the staircase approximation are $g$ for the nano-gap, $a$ for the bow-tie tip, and $b$ for the bow-tie corner. The red dotted lines depict the cross-section planes for the field enhancement plots.

2. FABRICATION

The bow-tie structures we introduce are prepared by standard EBL, sputtering of a 40-nm gold layer over a 2-nm thick Cr adhesion layer, and lift-off. In the case of fractal patterning, it is engraved in order to increase short-wavelength performance. The equipment used also permits a processing sequence consisting of consecutive EBL and ion-beam lithography (IBL) steps due to a shared sample handler delivering high repeatability in sample positioning and processing. It is possible to pattern a large 1 cm$^2$ area of a sensor or solar cell by $\sim$100 nm nano-particles by slicing and creating large volumes with high SERS enhancement.

We use EBL for the pattern definition of nano-particles of circular circumference, followed by development for removal of exposed regions in a positive type of resist (polymethyl methacrylate), then electron-beam evaporation of gold and the final lift-off. It is important to tailor the exposure (current and time) of resist in such a way that the deposited dose would result in undercut grooves (pits or holes) after development. This settle tuning is essential for a good lift off, which is also critically dependent on the normal incidence direction during metal deposition. In order to avoid resist adhesion to the nano-particles, the resist film should be a few times thicker than the height of the metal film, which is about 40 nm. For a better substrate to plasmonic metal adhesion, a few nanometers of Cr or Ti are typically deposited first. For the EBL, we use a sub-10 nm resolution Raith 150TWO equipped with a 30 keV electron gun. To the best of our knowledge, other plasmonic structures can deliver the same or better field enhancement performance only at the expense of a much more complicated and difficult to control fabrication process.

For the effective modeling of the nanostructures, it’s important to note that fabrication of plasmonic nanoholes/gaps/grooves already reached limits where surface tension effects determine structural sharpness and edges at few nanometers in curvature. This saturates the achievable light enhancement at the level where practical devices for biosensing and optical circuitry of all-optical control of plasmon propagation are still not feasible.

3. 3D-FDTD MODELING

The field enhancement of the nano-antennas is simulated with a finite differences time domain (FDTD) numerical solver (Lumerical), applied to the model depicted in Fig. 1, having a bow-tie radius of 100 nm, a bow-tie flare angle $\alpha$, and a gold thickness of 40 nm, sitting on a silica substrate. The nano-gap width is fixed at 10 nm, however to take into account...
the staircase effect we define effective widths \( g \) for the nano-gap, \( a \) for the bow-tie tip, and \( b \) for the bow-tie corner. We notice significant trends depending from the mesh size: for 1 nm size, we have consistent values of \( a = 1 \) nm, \( g = 9 \) nm, and \( b = 2 \) to 3 nm, up to 160°, beyond which the flare angle becomes large enough to make the staircase approximation unavoidable. For 2 nm size, the value of \( a \) varies between 2 and 12 and \( b \) between 2 and 6 for angle less than 160°. The gap width \( g \) results 12 nm up to 140° and 8 nm above.

Reticule gradation is employed to increase mesh accuracy in the areas of greatest field enhancement, especially in the central nano-gap, however in this case we fix the cubic mesh size to specific values in a box enclosing the bow-tie and part of the substrate, to study the impact of the staircase effect; in particular, we simulate meshes with precisions of 2 nm and 1 nm. The nano-antenna is simulated in the band from 400 to 1500 nm, for a memory occupancy of around 24 GB and a variable simulation time which can range from 4 to 10 hours. This is due to the impact of the plasmonic resonances, which slow down the field decay around the particle and can require up to 1.0 ps propagation of the time-domain broadband pulse. Materials are modeled by their complex permittivity values according to the Lumerical database.

Numerical error is made consistent by keeping the alignment of the bow-tie axis along the \( x \)-axis of the 3D domain. In order to estimate the impairment due to abrupt mesh size changes, we use a cylindrical particle of 500 nm diameter and we search for modes having hot spots along the upper nano-particle interface far from the substrate, when the free outer corners are rounded due to surface tension effects. As we will show, the field divergence effect as rounding radius is reduced to zero (sharp corners) has been correctly modeled for radii equal to or greater than 2 nm.

To estimate the performance of the bow-tie, we explored the intensity maps for varying wavelength to identify the resonance modes having hot-spots at the metal corners and separate them from the many spurious modes having hot-spots along the small corners created by the staircase effect. The search is simplified to a 2D problem by the fact that the maximum field enhancement is found at the interface between metal and substrate. The change in mesh size affects these modes differently: in particular we identify two distinct modes, a lower-wavelength one whose main hot-spots exist at the outer corner of the bow-ties (corner mode) and a higher wavelength one with hot-spots in the nano-gap (center mode).

### 4. RESULTS AND DISCUSSION

#### 4.1 Rounded and fractal bow-tie nano-antennas

![Figure 2](http://spiedl.org/terms/figure2.png)

Figure 2. (a) Resonant wavelength and (b) E-field intensity \( |E|^2 \) enhancement for the center and corner modes of the rounded bow-tie nano-antennas as a function of the flare angle \( \alpha \).

In Fig. 2 we show the evolution of the resonant wavelength and field enhancement of the two modes for varying flare angle and mesh size. For the corner mode, we notice that the resonant wavelength tends to increase as the flare angle does, as the hot-spots are pushed further apart, while the field enhancement is well correlated with the corner size \( b \).
seen in Fig. 2(a), the larger mesh size gives a wavelength trend that has a peak for 130°, while for 1 nm size the trend is increasing more smoothly. The field enhancement in Fig. 2(b) shows values 2 to 5 times higher for the narrower mesh and trends closely matching the evolution of \( b \), the maximum for 2 nm mesh being 1380 at 130° where \( b = 6 \text{ nm} \); the overall maximum for 1 nm mesh is 4449 at 150°. For the center mode, the resonant wavelength tends to peak in mid-range and drop for high angle because of the predominance of the staircase error on \( a \), to rise again for 180° where the edge becomes flat. Although this is generally true of the enhancement as well, it impacts differently as for the narrower mesh there is a primary maximum of 67636 at 130° and a secondary one of 20000 at 170°, while for the wider one the maximum is 16258 at 140°.

![Figure 3](image-url)

**Figure 3.** E-field intensity \( |E|^2 \) enhancement spectra at the interface between gold and silica for \( \alpha = 120° \) and mesh size of (a) 2 nm and (b) 1 nm. The inset shows the bow-tie shape.

![Figure 4](image-url)

**Figure 4.** E-field intensity \( |E|^2 \) enhancement of the **corner** mode for \( \alpha = 120° \) along (a,b) z-x-plane in middle of the nano-gap and (c,d) x-y-plane at the interface. The mesh size is (a,c) 2 nm (560 nm resonant wavelength) and (b,d) 1 nm (570 nm wavelength). The maximum enhancement values reported in linear scale are 1000, 4300, 1000, and 4300, respectively.

![Figure 5](image-url)

**Figure 5.** E-field intensity \( |E|^2 \) enhancement of the **center** mode for \( \alpha = 120° \) along (a,b) z-x-plane in middle of the nano-gap and (c,d) x-y-plane at the interface. The mesh size is (a,c) 2 nm (650 nm resonant wavelength) and (b,d) 1 nm (690 nm wavelength). The maximum enhancement values reported in linear scale are 1300, 4300, 13000, and 65000, respectively.
Figs. 3, 4, and 5 depict the enhancement spectra and field distributions for $\alpha = 120^\circ$, where the impact of the staircase effect on the slanted section of the bow-tie is minimal. It can be seen how the enhancement spectrum features very few spurious modes and is dominated by the center mode peak; the effect of reducing mesh size in Fig. 4(b) with respect to 4(a) brings a five-fold increase in enhancement, a sharper peak and a reduction of spurious modes. For the corner mode, we see the field energy for finer mesh more tightly focused to the interface (Figs. 4(a) and 4(b)) and more tightly bound to the corners (Figs. 4(c) and 4(d)). For the center mode, in addition to sharper nano-gap focusing we see the suppression of a spurious oscillation in the nano-gap length (Figs. 5(a) and 5(b)), and the tighter focusing to the nano-gap on the interface (Figs. 5(c) and 5(d)).

Figure 6. E-field intensity $|E|^2$ enhancement spectra at the interface between gold and silica for $\alpha = 180^\circ$ and mesh size of (a) 2 nm and (b) 1 nm. The inset shows the bow-tie shape.

Figure 7. E-field intensity $|E|^2$ enhancement of the corner mode for $\alpha = 180^\circ$ along (a,b) $xz$-plane in middle of the nano-gap and (c,d) $xy$-plane at the interface. The mesh size is (a,c) 2 nm (620 nm resonant wavelength) and (b,d) 1 nm (600 nm wavelength). The maximum enhancement values reported in linear scale are 150, 300, 800, and 3500, respectively.

Figure 8. E-field intensity $|E|^2$ enhancement of the center mode for $\alpha = 180^\circ$ along (a,b) $xz$-plane in middle of the nano-gap and (c,d) $xy$-plane at the interface. The mesh size is (a,c) 2 nm (680 nm resonant wavelength) and (b,d) 1 nm (710 nm wavelength). The maximum enhancement values reported in linear scale are 300, 1000, 2600, and 7900, respectively.

Figs. 6, 7, and 8 depict the enhancement spectra and field distributions for $\alpha = 180^\circ$, where the nano-gap becomes a 10-nm slot in the cylinder, giving rise to a large number of resonating modes along the slot breadth; the effect of reducing mesh size in Fig. 6(b) with respect to 6(a) changes the energy distribution of the modes, in general increasing

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enhancement but shifting it to other wavelengths. For the corner mode, as before we see it for finer mesh more tightly focused to the interface (Figs. 7(a) and 7(b)) and more tightly bound to the corners (Figs. 7(c) and 7(d)). For the center mode, we see more energy moving into the nano-gap, but more evenly distributed in height (Figs. 8(a) and 8(b)), and the tighter focusing to the nano-gap tends to be at the corners rather than the center (Figs. 8(c) and 8(d)).

Figure 9. (a) Ringing effect on the upper corner of a cylindrical gold particle due to abrupt transition along the z-direction of the mesh size as indicated, producing spurious resonances evident in the enhancement spectrum (b). By the use of conformal meshing (c), the intensity of spurious resonances is greatly reduced.

4.2 Effect of the actual shape of corners/ridges

To gain more insight on the phenomena related to the discretization error, we examined the modeling performance of perfect corners in the presence of abrupt mesh transitions, taking a cylindrical nano-particle of 500 nm diameter to emphasize the short wavelength resonances. As shown in Fig. 9(a), we create a 1-nm mesh area around the top 10 nm of the particle, while the mesh of the bottom part changes to around 5 nm size at the boundary, with the effect of creating a Fabry-Perot-like discontinuity in the domain that is enough to arise significant spurious resonances as shown in the intensity enhancement spectrum in Fig. 9(b). Besides avoiding such a large discontinuity, we tackled the problem by introducing conformal meshing which, while requiring more computational effort, helps reduce the spurious considerably: as shown in Fig. 9(c), the main resonance peak is reduced at least five-fold by the switch.

Figure 10. (inset) Model of cylindrical gold nano-particle on silica, when the corners far from the interface are rounded to a radius \( R \). (a) Resonant wavelength and (b) field intensity enhancement of transverse plasmonic mode for varying \( R \). (c) E-field intensity enhancement spectra for slotted case of sharp-corner particle, for silica and varying substrate refractive index.
We can show the physical soundness of our model by taking into account what happens in a more realistic situation when the upper corners of the round 500-nm nano-particle are rounded while the interface corners remain sharp, which correctly models the real situation, for example after methanol washing. As we show in Fig. 10(a), we model a rounding of the corners of radius equal to 1, 2, 5, and 10 nm and compare with the sharp corners case. We inspected the E intensity values on the corners on the plane parallel to the excitation polarization and we found discrete enhancement peaks corresponding to transverse resonant modes. We followed the evolution of the mode that had the highest impairment due to model approximations (Fig. 10(a) and 10(b)) and we found that its wavelength and field enhancement values tend to increase from the sharp case for radius values up to 2 nm, after which they decrease with the radius. This last behavior is in accord with what has been experimentally observed in the case of silver nano-cubes, making us agree that for rounding radius below 2 nm the study is qualitative, but above that value it confirms our ability to fully control and account for the approximations inherent in the numerical model.

The results for \( \alpha = 180^\circ \) reconnect to the case of a slotted nano-particle sitting on a substrate (see inset of Fig. 10(c)). Slotted nano-particles of the same size and shape sitting on substrates of different refractive indices can deliver very different values of field enhancement. Regarding the origin for this difference, we argue that, since the slotted particle is sitting on dielectric substrates with different refractive indices, the original plasmon resonance that the particle would support inside a homogeneous medium is instead split into two different resonances due to the mismatched refractive index at the two interfaces, as has been shown experimentally for silver nano-cubes. The same reasoning applies to flat cylindrical nano-particles like the ones considered, which have been theoretically shown to have a qualitatively similar behavior. For a constant geometrical nano-particle structure, the field enhancement value is maximum at certain wavelengths corresponding to resonant modes. By changing the substrate refractive index, the resonant wavelengths of the modes, at which the maximum enhancement is seen, can be tuned or detuned with respect to the intrinsic maximum, as we show in Fig. 10(c), where the enhancement shows a maximum value for a certain refractive index. As the particle diameter is kept constant, the same results cannot be reached with other materials due to the different refractive index, but the difference can be mitigated by adjusting the other structural parameters. Moreover, if we consider materials such as silicon, whose refractive index varies strongly within the operation bandwidth, we can tailor its strong interaction with gold to contribute complex wide-band resonances around 1 micron wavelength, interesting for energy harvesting purposes.

### 4.3 Broadband enhancement and long wavelengths

![Figure 11. (a) Scanning electron microscopy (SEM) photo of a third-order Sierpinski nano-antenna. (b) 3D-FDTD model of fourth-order nano-antenna used for the simulations.](image)

We also explored the performance of Sierpinski fractals in connection with bow-ties for a broadening of spectral features, interesting in the THz band and for optical trapping. EBL methods allow to increase resolution and define nanometric-size details, as shown in Fig. 11(a) where a 12-nm wide nano-gap is obtained in a third-order fractal nano-antenna. The smallest-triangle side length of this first-trial structure is of 200 nm, which can be reduced to 100 nm or less. Overlap between the triangles is around 80 nm. The gap width is finely controlled and can be replaced by a bridge to reduce the resonating frequency, as the plasmonic resonances associated can be tuned and broadened by introducing a
The nano-antenna is simulated in the band from 400 nm to 7500 nm (40 THz to 750 THz, see model in Fig. 11(b)), showing that the fractal structure has several plasmon resonances, and consistent extinction below 1500 nm, outperforming similarly-sized traditional bow-ties. A plasmonic mode at 6420 nm has 20,000 times enhancement in the nano-gap, and the one at 2540 nm having a 28,000 times enhancement. Even more importantly, we notice that an optical field of 10 μm wavelength can be focused in a 10-nm nano-gap, suggesting that a proper structure scaling can focus a 100 μm field (3 THz) in a 100 nm gap with comparable enhancement.

5. CONCLUSIONS

We studied the performance of plasmonic bow-tie nano-antennas with rounded shape and fractal structure engravings machined with state-of-the-art EBL tools. Their spectral and light field enhancement dependencies on the mesh size and discretization parameters provide insight on the modeling capability of 3D-FDTD and permit to estimate the maximum field enhancement and optimum flare angle for best nano-focusing with application potential in sensing and SERS. Significant light enhancement over 67000 is predicted at the interface for a flare angle of 130°. Insight in the method performance is gained by studying the modeling of sharp and rounded corners in a structured mesh environment. Also, EBL patterning of gold on silica with Sierpinski fractal shapes achieves a strong broadband field enhancement from 40 THz to visible, with a simple and cost-effective fabrication process. We show the ability to resolve a minimum corner rounding radius of 2 nm and by conformal meshing we reduce five-fold the spurious ringing at sharp corners.

REFERENCES


