Numerical investigation of plasmonic bowtie nanorings with embedded nanoantennas for achieving high SEIRA enhancement factors

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Abstract
This paper presents the numerical investigation of several complex plasmonic nanostructures — bowtie nanoring and crossed-bowtie nanoring nanoantennas with embedded bowtie nanoantennas and crossed-bowtie nanoantennas — for surface enhanced infrared absorption (SEIRA) spectroscopy-based substrates. The proposed nanostructures exhibit substantially large SEIRA enhancement factor (∼8.1 × 10^5) compared to previously reported enhancement factor values for bowtie nanoantennas or nanoring antennas. The plasmonic properties of the proposed nanostructures have been studied by the numerical evaluation of the near-field electromagnetic enhancement at resonant plasmon mode excitation wavelengths in the mid-IR spectral regime. The highest SEIRA enhancement of ∼8.1 × 10^5 occurs at a wavelength of ∼6800 nm (6.8 μm). A substantial electric field enhancement as large as ∼375, corresponding to SEIRA EF of ∼1.4 × 10^5 is noted even when the minimum gaps between the plasmonic nanostructures is as large as 10 nm, which can easily be fabricated using the conventional nanolithography techniques. The occurrence of several electric field hotspots due to the presence of plasmonic nanoantennas embedded inside the nanorings was observed, as the electric fields are enhanced in the vicinity of the plasmonic nanostructures being proposed. The multiple electric field hotspots in the proposed nanostructures can lead to larger average electric field enhancement as well as the average SEIRA enhancement for these substrates. Moreover, by embedding plasmonic nanoantenna structures inside the bowtie nanorings and crossed-bowtie nanorings, large spectral tunability of plasmon resonance wavelengths is achieved in the spectral regime from 4 μm to 8 μm. This is done by varying a larger number of spectral parameters that are present in these complex nanostructures. This paper also reports a novel configuration of crossed-bowtie nanoring plasmonic structure exhibiting less polarization dependence of the SEIRA enhancement factor. This structure also exhibits tunability of hotspot positions when the direction of the polarization of the incident light is rotated. The proposed structures in this paper can be fabricated by the state-of-the-art nanofabrication technologies. The proposed structures could find potential applications in chemical and biological sensing and biochemical detection of analyte molecules.

Introduction

Plasmonics is an intriguing field of research in photonics which involves manipulation of light at the nano-scale as well as enhanced light–matter interactions, with multitude of applications in plasmonic semiconductors [1–4], nonlinear plasmonics [5, 6], near-field optical imaging [7–9], chiral plasmonics [10–14], plasmonic solar cells [15–17], topological insulator based optoelectronic devices [18, 19], metamaterial absorbers [20–22],
surface enhanced spectroscopies (SES) [23–26], Fano-resonant metamaterials [27–29], and graphene plasmonics [30, 31].

Light is manipulated through the phenomena of surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR) in engineered plasmonic nanostructures. This results in strong confinement of light beyond the diffraction limit into subwavelength dimensions and strong local field enhancements. SPR and LSPR are optical phenomena based on resonant oscillations of conduction electrons at the interface of metals and dielectrics that are induced by incident optical radiation. These phenomena have been extensively applied for the detection of molecular binding interactions. These electron oscillations could be propagating in nature on a planar interface, also known as surface plasmon polaritons (SPPs), or confined to subwavelength dimensions of the engineered plasmonic nanostructures, known as localized surface plasmons (LSPs).

Excitation of plasmon resonances in plasmonic nanostructures has been employed for applications pertaining to surface enhanced spectroscopies (SES) and predominantly for surface enhanced Raman scattering (SERS). The demand of the existing biomedical research relies on substantially improving analytical sensitivity of detecting single molecules under native physiological conditions. SERS is an efficient technique for the detection of pathogens and other molecules present at extremely low concentrations. Such sensitive detections can help in early-stage detection of cancers and other diseases. A complementary spectroscopic technique to SERS is surface enhanced infrared absorption (SEIRA), which was first observed by Hartstein et al [32]. Over the past few years, SEIRA has been applied for observing the dipole-active vibrational modes of organic chemical or biological molecules that characteristically absorb in the mid-infrared spectral regime. Hence, it has found immense applicability in sensing of chemical and biological molecules of interest.

Detailed investigations of the technique by Osaka et al [33] revealed that the enhancement mechanism in SEIRA is similar to that in SERS and that the SEIRA enhancement arises mainly due to electromagnetic enhancement. In SEIRA, the molecular vibrational modes with dipole moments perpendicular to the substrate surface are preferentially enhanced [34]. While the electromagnetic enhancement factor (EF) in SERS is approximately proportional to the fourth power of the electric field enhancement (which is the ratio of the magnitude of the optical electric field in the vicinity of the analyte molecules to the magnitude of the electric field of the incident radiation), the SEIRA enhancement factor is proportional to the electric field intensity enhancement, i.e. the square of the electric field enhancement [35]. However, while the typical Raman scattering cross-section is within the range $\sim 10^{-27}$–$10^{-30}$ cm$^2$ [36], the infrared absorption cross-section is many orders higher, typically $\sim 10^{-20}$ cm$^2$ [37] suggesting robust efficacy of the technique even for subtle SEIRA enhancements. The latest advances and principle mechanisms of SERS and SEIRA have been enumerated in the latest report by Wang et al [24].

The intrinsic property of substantially enhanced electromagnetic field intensity in plasmonic active metal-based nanostructures due to the resonant plasmon mode excitation has immensely been exploited for enhanced light–matter interactions. Bowtie nanoantennas (BNAs) have been employed for several plasmonic applications due to the characteristic electric field confining geometry which is known to provide higher intensities of localized electromagnetic field and better spatial confinement compared with other nanoantenna designs, and thus is promising for high performance photonic devices and applications such as optical tweezers [38], single molecule fluorescence enhancement [39], bowtie driven Yagi–uda nanoantenna [40] and graphene photonic devices [41].

The past decade has seen several reports based on experimental and theoretical investigations of BNA-based surface enhanced spectroscopies such as SERS [42–46], which is widely studied and is comparatively a more mature spectroscopic technique than SEIRA. Further, nanoring or nanocavity based plasmonic nanostructures have also been extensively studied and employed for relevant photonic applications other than SES [47–50]. The transmittance properties of contour BNAs in mid-infrared have been studied by Yang et al [51]. Plasmonic nanoantennas are highly desirable in many biomedical optics and biophotonic applications. More specifically, they have been applied for enhanced absorption spectroscopy in the near-infrared (NIR) and mid-infrared (MIR) spectral regimes for detection of biomolecules of interest. As the resonant wavelengths of nanoantennas are directly proportional to antenna lengths, nanoantennas operating in the NIR or MIR spectral regimes can have dimensions in the micrometer scale, which makes it difficult to incorporate these nanoantennas into nanoscale devices [52]. Hence, several research groups have strived to red-shift plasmon resonances of the plasmonic nanoantennas to the NIR or MIR spectral regimes to ensure their application to enhanced NIR and MIR absorption spectroscopy while keeping the dimensions of the nanoantennas in the nanometer scale.

Although the resonance wavelengths of the nanoantennas can be slightly shifted by changing the dielectric constant of the material around the nanoantennas [52], engineering the geometry of the plasmonic nanoantennas has been found to be effective means of tuning the plasmon resonance wavelengths of the nanoantennas over a wide range of wavelengths. Contour BNAs with tunable optical response with variable contour thickness was proposed by Sederberg and Elezzabi [3]. Further, a novel Sierpinski fractalization concept in plasmonic BNAs for optimizing the nanoantenna optical response in NIR or MIR spectral regimes was...
proposed in [52, 53], S Cakmakyapan et al [54] have demonstrated localized near-infrared electromagnetic field enhancement by incorporating the same concept of Sierpinski fractalization in a conventional BNA. These works were intended to optimize the plasmonic response of nanoantennas for operation over a wide spectral range including the NIR and MIR spectral regimes. Hui-Hsin Hsiao et al [55] have modified the contour bowtie antenna geometry to further red-shift the nanoantenna optical response. The resonant mode excitation and plasmon hybridization of plasmonic gold contour BNAs were investigated by Nien et al [56]. Hu et al in their work [57] have shown by FEM calculations, that plasmonic BNAs support both bonding and anti-bonding modes and exhibit enhanced electric field intensities in the bowtie gaps. Hollow cavity contour plasmonic BNAs can align electric dipoles on both outer and inner surfaces of the nanoring, thereby effectively funneling the incident electric field inside the nanoscale gap regions.

There have been several interesting reports on metallic nanostructures and nanoantennas based SEIRA substrates for mid-infrared to far-infrared sensing. For instance, aluminium cross-antennas have been employed for detection of vibrational resonances in mid-infrared region of the electromagnetic spectrum [58]. Yin et al [59] have employed high aspect ratio gold nanonails for investigating the SEIRA enhancement mechanism in these nanostructures. They have reported a high enhancement factor of 108000 in the far infrared spectral range. Neubrech et al [60] have enhanced molecular infrared vibrations using periodic array of gold nanoantennas. Enhanced SEIRA enhancement factor of the order of \( \sim 10^5 \) using nanoantenna dimers with nanoscale gaps of \( \sim 3 \) nm has been reported by Huck et al [61]. Aouani et al [62] have also reported broadband detection of molecular vibrational modes in the mid-infrared spectrum using log-periodic antennas with large SEIRA enhancement. Further, Wu et al [63] have demonstrated distinct absorption of infrared vibrational modes in Fano-resonant metamaterial in the wavelength range \( \sim 4.7–7.5 \) \( \mu \)m. There are several other reports for SEIRA sensing in mid-infrared spectral regime using distinct shapes of nanostructures such as fan-shaped gold nanoantennas [64], linear rod nanoantennas [65], and gold cross nanoantennas [66].

In general, there has always been an immense interest in infrared absorption spectroscopy and detection and quite recently, several intriguing reports on infrared detection have also surfaced. Fathi et al [67] in their work have developed CuS nanocrystals as infrared photovoltaic material which exhibits enhanced detectivity and responsivity by manipulating optical and electrical properties of the developed nanocrystals. In another report by Huang et al [68], the authors have demonstrated that the quantum mechanical effects due to subnanometer nanocavity gaps in nanoantennas elevates infrared absorption detection of molecular moieties by blue-shifted plasmonic resonances due to the inherent quantum tunnelling effects in such subnanometer gap nanoantennas. Further, Gao et al [69] have developed a generalized classical model of SEIRA spectroscopy that shows that mid-IR surface plasmon resonances can be used for detection of vibrational bands. SEIRA spectroscopy has also been incorporated to monitor protein denaturation in the infrared regime using engineered plasmonic metasurfaces [70]. In a latest report by Najem et al [71] enhanced infrared sensing is demonstrated using aluminium nanostructured bowties on a metal-insulator-metal (MIM) platform.

In this work, we have demonstrated by numerical calculations several configurations of novel geometries of bowtie nanorings and crossed-bowtie nanorings with embedded bowtie nanoantennas and crossed-bowtie nanoantennas based SEIRA substrates that exhibit substantially large SEIRA electromagnetic EF (\( \sim 8.1 \times 10^5 \)) compared to previously reported conventional bowtie nanoring (\( \sim 2025 \)) [72]. This value of SEIRA electromagnetic EF is larger than what has been in previous reports of theoretical calculations of the SEIRA enhancement factor. By employing numerical Finite Difference Time Domain (FDTD) simulations, we have investigated the near field electric field enhancement and electric field distribution patterns at resonant plasmon mode excitation wavelengths and have found that the electric fields are significantly enhanced in the vicinity of the plasmonic nanostructures being proposed in this paper. The electric field intensity enhancement values were obtained in the vicinity of the bowtie nanoring and crossed-bowtie nanoring nanoantennas with embedded bowtie nanoantennas and crossed-bowtie nanoantennas for near-IR and mid-IR spectral regimes (2000 nm to 8000 nm) for detection of chemical and biological molecules of interest. Further, we demonstrate the occurrence of several electric field hotspots present in the proposed plasmonic nanostructures compared to the conventional bowtie nanoring nanoantenna [72] in which the electric field hotspot is only confined between the central gap of the nanoantenna. The proposed structures demonstrate multiple spatial regions of enhanced electric field hotspots owing to the presence of embedded plasmonic nanostructures in the nanoring cavity. The multiple spatial regions of enhanced electric field hotspots in the proposed nanostructures with embedded plasmonic nanoantennas can lead to larger average electric field enhancement as well as the average SEIRA enhancement for these substrates. Embedding plasmonic nanoantennas inside the nanoring bowtie nanoantennas, leads to a change in the polarizing ability of the nanoantennas, which allows tunability of the plasmon resonances of the consolidated structures. Moreover, by embedding plasmonic nanoantenna structures inside the bowtie nanorings, we can achieve large spectral tunability of plasmon resonance wavelengths by varying a larger number of spectral parameters that are present in these complex nanostructures. We also report crossed-bowtie nanoring plasmonic structures that have significantly less polarization.
dependence compared to bowtie nanoring structures. Moreover, the crossed-bowtie nanoring plasmonic structures allow the tunability of the hotspot positions when the direction of the polarization of the incident light is rotated. The proposed bowtie nanoring and crossed-bowtie nanoring plasmonic nanoantennas with embedded nanostructures can be fabricated by employing electron beam lithography [73] followed by electron beam deposition of gold and subsequent lift-off. These nanostructures can also be fabricated by first employing DC sputter deposition to deposit thin gold films on silica substrates, followed by focused ion beam milling [74] or transmission electron beam ablation lithography [75] for milling out these complex plasmonic nanostructures. A possible fabrication process flow is shown in Fig. S1 (available online at stacks.iop.org/MRX/9/096201/mmedia) in the supplementary section.

**Numerical finite difference time domain simulations**

The numerical analysis of the proposed bowtie nanoring and crossed-bowtie nanoring structures with embedded complex nanostructures has been performed using Finite Difference Time Domain (FDTD) simulations. FDTD [76] is a numerical analysis technique based on Yee’s algorithm and is employed in computational electromagnetics for solving differential forms of discretized coupled Maxwell’s equations by updating electric and magnetic field vectors to obtain stabilized electromagnetic field behaviour [61]. The details of the equations employed for FDTD modeling of the plasmonic nanostructures proposed in this work are given in the Note S1 of the supplementary section.

The numerical simulations were performed using a commercial FDTD software known as FDTD Solutions from Lumerical Solutions. The software incorporates several dispersion models such as Drude, Lorentz-Drude and Debye models. The simulations are performed with periodic boundary conditions in x and y directions and PML boundary condition along the z-direction. In order to estimate the SEIRA enhancement due to the bowtie nanoring and crossed-bowtie nanoring structures, the electric field intensity enhancement values were obtained in the vicinity of these nanostructures for near-IR and mid-IR spectral regimes (2000 nm to 8000 nm) for detection of chemical and biological molecules of interest. The incident plane wave was polarized in the direction of the axis of the plasmonic nanoring bowtie nanostructures.

FDTD simulations were performed after convergence of mesh size was achieved. After carrying out convergence testing, a mesh size of 1 nm was used in x and y directions, while a mesh size of 4 nm was used in the z-direction. The material constants for gold and SiO₂ were obtained by the dispersion relations provided by Palik [77]. For simulations carried out for larger structures in higher wavelength range, the optical properties of gold were taken from Olmon et al [78]. The FDTD simulations of the proposed structures were carried out by considering a curvature at the bowtie tip [79] as fabrication of extremely sharp bowtie tips is limited by the capabilities of present nanofabrication techniques. The time step in FDTD simulations was selected such that the Courant stability condition [80] was satisfied. The time step stability factor was set to 0.99 corresponding to a time step of 0.00229134 fs. Further, the autoshtoff threshold was set to the Lumerical default value of 10⁻⁵ for ensuring negligible residual energy in the simulation domain. The autoshtoff threshold estimates the energy contained in the simulation domain as a fraction of input power and the autoshtoff criteria was satisfied for all simulations. Once the energy in the simulation region falls below the threshold, it is ensured that the fields completely decay and thus reliable solutions are obtained.

**Results and discussion**

In this section, we analyze the results obtained by the numerical simulations of the proposed bowtie nanoring and crossed-bowtie nanoring geometries to be employed as efficient SEIRA substrates for applications pertaining to identification of molecular signatures and biochemical detection. The near-field electric field enhancement and electric field distributions in the proposed structures at several resonance wavelengths were numerically investigated. We mainly investigate four nanoring geometries, namely, bowtie nanostructures embedded bowtie nanoring antenna (B-B NA), crossed-bowtie nanostructures embedded bowtie nanoring antenna (CB-B NA), bowtie nanostructures embedded crossed-bowtie nanoring antenna (B-CB NA) and crossed-bowtie nanostructures embedded crossed-bowtie nanoring antenna (CB-CB NA). Figure 1 shows FDTD simulation results obtained for B-B NA. The schematic of the structure is shown in figures 1(A) and (B). From figure 1(C), we note distinct dipolar and quadrupolar resonances occurring at wavelengths 3640 nm and 6810 nm respectively. The enhanced light–matter interactions due to the proposed plasmonic nanoantennas result in amplification of SEIRA signals as the supported plasmon resonances in the nanoantennas lead to enhanced EM fields in the vicinity of the nanoantennas where the molecules are present. Further, the optimal SEIRA sensing occurs when the resonance band matches with the absorption band of the specific molecular substances of interest, and this can be achieved with precise engineering of the geometrical parameters of the
nanoantennas. The electric field distributions in the nanoantenna structure at the two distinct resonances (see figures 1(D) and (E)) show the dipolar and quadrupolar field distribution patterns, respectively, which originate from the resonances of the bowtie nanoring. Further, the far-field spectral characteristics of B-B NA are distinctly shown in Fig. S2 of the supplementary section. We note transmission dips around the peak electric field enhancement wavelength, which do not necessarily coincide with the peak electric field enhancement resonances. This is possible since the far-field spectral characteristics determine the consolidated behavior of the periodic array. Thus the far-field resonances may deviate from the near-field resonances due to the additional pronounced effect of the periodic coupling in the nanoantenna array.

The specific spectral regime of interest for SEIRA sensing lies in the wavelengths of infrared absorption typically larger than 2.5 μm (specifically between 4 μm and 8 μm). Thus, we investigate spectral tunability for SEIRA sensing applications with variation of \( L \) and \( t \), the results of which are shown in figure 2. We note that, as the length of the antenna \( L \) is increased (see figure 2(A)), the plasmon modes redshift, which is understandable because there is an increase in the distance between the charges at the opposite interfaces with increase in \( L \), leading to a lower restoring force. From the electric field enhancement spectra at point \( O \) for variation of \( L \), we also note the occurrence of fundamental dipolar resonances at 4900 nm, 5740 nm, 6810 nm and 7930 nm for \( L \) values 700 nm, 850 nm, 1000 nm and 1150 nm respectively. This shows a large tunable SEIRA spectrum, with broad resonance peaks of great interest for SEIRA detection. Additionally, from the electric field enhancement spectra at point \( M \) for variation of \( L \) (see figure 2(B)), we note a distinct asymmetric lineshape at the quadrupolar resonance wavelength. As \( L \) increases, this mode is distinctively broadened which could intuitively be explained by the plasmon hybridization. For instance, for \( L = 1150 \text{ nm} \), although we note that the peak electric field enhancement is less compared to that noted at point \( O \), a distinctively broad resonance peak having a spectral width of \( \sim 2.7 \text{ μm} \) is noted with an electric field enhancement of \( \sim 50 \).

![Figure 1](image_url)

Figure 1. (A) Schematic representation of bowtie nanostructures embedded bowtie nanoring antenna (B-B NA) in periodic array. (B) Single unit cell showing key dimensions of the structure: Hollow bowtie nanoring x-span, \( L \); bowtie nanoring thickness, \( t \); bowtie nanoring gap, \( G \); embedded bowtie nanoantenna gap, \( g \); embedded bowtie triangles side length, \( l \); structure height, \( H \); bowtie nanoring central flare angle is kept constant at 60°. \( O \) and \( M \) are at the middle of the gaps between the tips of bowtie nanoring and embedded bowtie nanostructures. (C) Electric field enhancement spectra at points \( O \) and \( M \) correlated with far-field reflection and transmission spectral profiles. Spatial distribution of the electric field enhancement at the two resonance wavelengths M1 and M2 noted from electric field enhancement spectra (D) \( \lambda = 3640 \text{ nm} \) and (E) \( \lambda = 6810 \text{ nm} \). The dimensions of the structure are \( L = 1000 \text{ nm} \), \( t = 20 \text{ nm} \), \( l = 300 \text{ nm} \), \( G = 10 \text{ nm} \), \( g = 10 \text{ nm} \), and \( H = 40 \text{ nm} \).
We next study the effect of varying bowtie nanoring thickness \( t \) in B-B NA. The electric field enhancement spectra for variation of \( t \) at locations \( O \) and \( M \) are shown in figures 3(A) and (B). From these spectra we note that the variation of \( t \) can also profusely alter the spectral properties and is therefore an important geometric parameter for SEIRA spectral tuning. It can be observed from figures 3(A) and (B) that the plasmonic modes undergo a red-shift as \( t \) (the thickness of the nanoring) decreases, which could be explained based on plasmon hybridization [81].

The primary focus of this work is to demonstrate the applicability of the proposed nanostructures for applications pertaining to surface enhanced infrared sensing. We have accordingly designed our structures to work in the desired infrared spectral regime with fundamental resonant mode between \( \sim 5000 \) to \( \sim 8000 \) nm, at which peak electric field enhancement is noted in figures 2 and 3. However, besides the fundamental mode, we also note the occurrence of several higher order modes at lower wavelengths. Harnessing multi-wavelength response on a single plasmonic substrate could find interesting applications in surface enhanced infrared spectroscopy based biosensing. The far-field reflection and transmission spectra of the structure are shown in Fig. S2 of the supplementary section.

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We next study the effect of varying gaps between the bowtie nanorings \( G \) on the electric field enhancement spectra at the center of the bowtie nanorings (point \( O \)) and at the center of the embedded nanoantennas (point \( M \)). The parameters kept constant are \( l = 60 \) nm, \( H = 40 \) nm, \( L = 350 \) nm, and \( t = 20 \) nm. The electric field enhancement spectra for variation of \( G \) at location \( O \) and location \( M \) are shown in figures 4(A) and (B), respectively. We note that as the gap decreases, the peak electric field intensity increases. With a decrease in the gap \( G \) between the arms of the nanoring bowtie nanoantennas, the near-field coupling
between the tips of the bowtie nanorings increases. This increases the E-field enhancement in the gap region of the nanoring bowtie nanoantennas. The resonant wavelength at which the peak electric field intensity is noted exhibits a very subtle red-shift with decrease in $G$ (see figure 4(A)).

This red-shift could again be attributed to the fact that when the spacing between the nanostructures reduces, there is a reduction in the restoring force of the conduction electrons. This results in a decrease in the resonance frequency, which implies a spectral red-shift. We can observe from figure 4(A) that as the gap between the bowtie nanorings $G$ decreases from 16 nm to 3 nm, there is a substantial increase in the peak E-field enhancement ($\sim 6800$ nm) from $\sim 175$ (for $G = 16$ nm) to $\sim 900$ (for $G = 3$ nm). This implies that the SEIRA enhancement factor increases from 30635 to 810000 as the gap between the bowtie nanorings $G$ decreases from 16 nm to 3 nm. We observe from figure 4(B) that the E-field enhancement at point M is almost independent of the variation of the gap between the bowtie nanorings $G$. We also observe that even for a small change in the gap between the bowtie nanorings $G$ from 6 nm to 5 nm, there is a substantial increase in the peak E-field enhancement ($\sim 6500$ nm) from $\sim 480$ to $\sim 650$, which implies a substantial increase in the SEIRA enhancement factor from 230400 to 422500.

From figures 1(D) and (E), we note that there are multiple hotspots present in a plasmonic bowtie nanoring antenna containing embedded nanoantennas (due to redistribution of energy to the gaps in the embedded bowtie nanoantennas). Hence, the proposed structure (plasmonic bowtie nanoring antenna containing embedded nanoantennas) could be preferred for SEIRA detection applications as it produces multiple electromagnetic hotspots in the desired spectral regime and this property is useful not only due to a larger average SEIRA enhancement for the SEIRA substrate but also because it could find useful applications in detection of biomolecules since the target molecules would have more locations of enhanced electric field hotspots. It should be mentioned that a substantial electric field enhancement at the fundamental mode $M_1$ (peak electric field enhancement as large as $\sim 375$, corresponding to SEIRA EF $\sim 140625$) is noted (see figure 2(A)), while a comparatively less electric field enhancement is noted between the gaps in the embedded bowtie nanostructures (peak electric field enhancement $\sim 70$, corresponding to SEIRA EF $\sim 4900$). It has to be noted that the gap between the bowtie nanorings $G$ in these nanostructures is 10 nm. It should be noted that when the gap between the bowtie nanorings $G$ decreases to 3 nm, there is a substantial increase in the SEIRA enhancement factor (EF) to 810000 (E-field enhancement being $\sim 900$) for the fundamental mode (see figure 4(A)). It has to be noted that while 10 nm gaps between nanostructures can be fabricated easily using the conventional nanolithography techniques (such as E-Beam lithography as shown in Fig. S1), sub-5 nm gaps can also be fabricated using certain fabrication techniques such as extreme UV lithography and TEBAL (transmission electron beam ablation lithography). The effects of varying all other structural parameters — such as the embedded bowtie nanoantenna gap $g$, embedded bowtie triangle side length $l$, and the structure height $H$ — are given in the supplementary section (see Figs. S3–S6 of the supplementary section).

Further, to understand the noted behavior of spectral E-field enhancement, we compare our results with the case of solid bowtie geometry case. We note from the enhancement spectra for the solid bowtie geometry (See Fig. S7 of the supplementary section) that there is only one plasmonic mode. This mode is substantially blue-shifted compared with that of the fundamental modes of B-B NA. Several modes in B-B NA could occur due to the plasmon hybridization in the bowtie nanoring [82, 83] resulting in higher order multipolar response. Although the solid bowtie structure seems to confine higher electric field in the nanogap region of the antenna compared with the proposed B-B NA, we must note that the structure is rather a conventional nanoantenna with

![Figure 4. Demonstration of spectral tunability for applications related to SEIRA sensing with variation of gaps between the bowtie nanorings $G$ in B-B NA. (A) Electric field enhancement at point O with variation of $G$. (B) Electric field enhancement at point M with variation of $G$. Other constant parameters are $L = 1000$ nm, $l = 300$ nm, $t = 20$ nm, $g = 10$ nm, and $H = 40$ nm.](image-url)
only a single electric field hotspot. The proposed structure B-B NA has multiple hotspots of enhanced electric field which can be employed for detection of chemical and biological sensing of target analytes as these molecules have a larger probability for accessing multiple regions of enhanced electric field hotspots and thus enhanced detection and SEIRA sensing. Additionally, with the proposed bowtie nanoring structures, we obtain an extra degree of spectral tunability by varying the contour bowtie nanoring thickness and thus suitable resonances can be utilized in the spectral regime of interest for SEIRA detection. We evaluated the electric field enhancement spectra for bowtie nanoantennas with larger length spans (lying between 800 nm and 1100 nm) for a constant periodicity of 2500 nm and found that the peak electric field enhancement reduces as \( L \) is increased (see Fig. S7 of the supplementary section). Although the peak electric-field enhancement obtained for these lengths is larger for the case of solid bowtie nanoantennas as compared to ring bowtie nanoantennas (B-B NAs), the peak resonance occurs around 3500 nm in the case of solid bowtie nanoantennas (see Fig. S7 of the supplementary section). Moreover, the E-field enhancement drops below 200 between 5000 and 7500 nm in the case of solid bowtie nanoantennas. As the spectral region of interest for the detection of certain molecules using SIERA lies in the spectral region between 5000 to 7500 nm, the ring bowtie nanoantennas (B-B NAs) are more suitable as they have their peak E-field enhancements (>300) in this spectral region (see figure 2(A)). Moreover, we can observe from figure 2(A) that the peak resonance wavelength in B-B NAs can be tuned from 5000 nm to 8000 nm by varying the value of \( L \).

We next investigate the spectral properties of crossed-bowtie nanostructures embedded bowtie nanoring antenna (CB-B NA) shown in figure 5. The schematic perspective representation of the structure in periodic array arrangement and a single unit cell with labelled key dimensions are shown in figure 5(A) and 5(B) respectively. The electric field enhancement spectra at locations \( O \) and \( M \) are shown in figures 5(C) and (D). We observe from figure 5(E) that there are several spatially distributed electric field hotspots at the fundamental resonance mode of the structure. This could be due to the several sub-20 nm nanogaps that are present inside the nanoring bowtie nanoantennas besides the nanogap ‘G’ between the tips of the nanorings of the nanoring bowtie nanoantennas — i.e. nanogaps between the arms of the crossed bowtie nanoantennas as well as those between the crossed bowtie nanoantennas and the inner walls of the nanorings of the nanoring bowtie nanoantenna. However, we note that the peak electric field intensity is reduced in a CB-B NA compared with that of a B-B NA (see figure 5(D)). This could be explained on the basis that energy is redistributed and funneled into the several nanogaps present in the CB-B NA structure. The maximum value of electric field enhancement noted in the CB-B NA structure is \( \sim 370 \), corresponding to a SEIRA EF \( \sim 136900 \).

The spectral properties of bowtie nanostructures embedded crossed-bowtie nanoring antenna (B-CB NA) are shown in figure 6. Figures 6(A) and (B) represent the schematic of the structure in perspective periodic array and unit cell representation respectively. The electric field enhancement spectra at locations \( O \), \( M \), and \( M' \) for the structure with embedded nanostructures are shown in figures 6(C) and (D). Further, from the electric field enhancement spectra, we note the existence of several higher order multipolar modes at lower wavelengths which could be ascribed to the plasmon hybridization in the structure due to the bowtie nanorings and the additional crosswise bowtie nanorings with embedded complexes. The peak electric field intensity noted at the fundamental resonance mode at 6400 nm for B-CB NA is \( \sim 140 \) corresponding to a SEIRA EF \( \sim 19600 \) (see figure 6(E)). We note that the electric field is distinctively less in the nano-gaps of the embedded small bowtie antenna structure inside the orthogonal crossed bowtie arms. This is because the structure is simulated for incident light which is horizontally polarized and thus only the horizontal bowtie arms and their embedded antennas confine stronger electric field compared to the crossed-bowtie arms and their embedded antennas. To further demonstrate the effect of polarization of the incident light with color maps of electric field distributions, we have also evaluated a less polarization dependent structure containing crossed-bowtie nanostructures embedded crossed-bowtie nanoring antenna (CB-CB NA) in periodic array which is discussed next. We note from figure 6(E) that there are multiple hotspots present in a plasmonic crossed-bowtie nanoring antenna containing embedded bowtie nanoantennas — these hotspots are present not just between the tips of the plasmonic crossed-bowtie nanoring antennas but also in the gaps at the center of the bowtie nanoantennas.

Next, we study the spectral properties of crossed-bowtie nanostructures embedded crossed-bowtie nanoring antenna (CB-CB NA), which is a less-polarization sensitive structure and can be employed for the relevant applications. The schematic of the structure in perspective periodic array and unit cell representation are shown in figures 7(A) and (B). The spectral lineshapes of the electric field enhancements show the existence of several higher order multipolar resonances again attributed to the plasmon hybridization in the structure (see figures 7(C) and (D)). The electric field distributions of the nanostructure at the resonance wavelength of 6400 nm — for x- and y-polarizations of the incident radiation — are shown in figures 7(E) and (F), respectively. The peak electric field intensity enhancement (noted at the fundamental resonance mode at 6400 nm) for CB-CB NA is \( \sim 140 \) corresponding to a SEIRA EF \( \sim 19600 \) for both the x-polarization and the y-polarization of the incident radiation, showing the less polarization dependence of these nanostructures. We note from figures 7(E) and (F) that there are multiple hotspots present in a plasmonic crossed-bowtie nanoring
antenna containing embedded crossed-bowtie nanoantennas—these hotspots are present not just between the tips of the plasmonic crossed-bowtie nanoring antennas but also in the gaps at the center of the crossed-bowtie nanoantennas. Moreover, we can observe from figures 7(E) and (F) that the positions of the hotspots inside the crossed-bowtie nanoring plasmonic structures can be tuned by rotation of the direction of the polarization of the incident radiation.

The variations of the structural parameters of the different designs of the plasmonic nanostructures—bowtie nanoring antennas and cross-bowtie ring nanoantennas with embedded bowtie nanostructures—were carried out to obtain the maximum possible SEIRA enhancement factor, to obtain tunability of the plasmon resonance wavelengths from 2 μm to 8 μm spectral regime, to obtain a large number of hotspots for SEIRA based sensing, and to obtain less polarization dependence of the structures. A comparison of SEIRA EF evaluated for the proposed structures in this work with that published in literature is shown in table 1.

**Conclusions**

In this paper, we have numerically evaluated several novel plasmonic nanostructures of bowtie nanorings and crossed-bowtie nanorings with embedded complex nanostructures which could be employed as SEIRA substrates demonstrating a large SEIRA enhancement factor (≈8.1 × 10^5) compared to previously reported nanostructures including conventional bowtie nanorings without embedded complexes. By the numerical FDTD simulations carried out in the spectral regime from 2 μm to 8 μm, we have investigated the plasmonic properties of the proposed structures such as near-field electric field enhancement and electric field distribution patterns at resonant plasmon mode excitation wavelengths. The highest SEIRA enhancement of ≈8.1 × 10^5
occurs at a wavelength of \( \sim 6800 \text{ nm} \) (6.8 \( \mu \text{m} \)). A substantial electric field enhancement as large as \( \sim 375 \), corresponding to SEIRA EF of \( \sim 1.4 \times 10^5 \) is noted even when the minimum gaps between the plasmonic nanostructures is as large as 10 nm, which can easily be fabricated using the conventional nanolithography techniques. From the numerical calculations, we also noted the occurrence of several higher order modes at lower wavelengths. Further, we have found that the proposed plasmonic structures exhibit the occurrence of several electric field hotspots. This is due to the presence of embedded complexes in the nanoring cavities and substantially enhanced electric fields noted in the vicinity of the plasmonic nanostructures being proposed. The spectral tunability of the plasmon resonance (in the spectral regime from 4 \( \mu \text{m} \) to 8 \( \mu \text{m} \)) is noted upon variation of structural dimensions of both the nanorings and the embedded complexes in the nanoring cavities. Embedding plasmonic nanoantennas inside the nanoring bowtie nanoantennas also leads to a change in the polarizing ability of the nanoantennas. This allows tunability of the plasmon resonances of the consolidated structures. We also report a novel configuration of crossed-bowtie nanoring plasmonic structure exhibiting less polarization dependence less polarization dependence of the SEIRA enhancement factor as well as tunability of hotspot positions when the direction of the polarization of the incident light is rotated. The proposed structures in this paper can be fabricated by the state-of-the-art nanofabrication technologies. The proposed multiple hotspots based novel configurations of plasmonic bowtie and crossed-bowtie nanorings could be useful for chemical and biological sensing and in the detection of molecular fingerprints.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Conflicts of interest

There are no conflicts to declare.
Table 1. Comparison of the SEIRA EFs of the proposed structures in this work with published literature.

| Reference | Nanostructure                                      | SEIRA EF  | Resonant wavelength |
|-----------|---------------------------------------------------|-----------|---------------------|
| [72]      | Contour nanoring bowtie nanoantenna               | 2025<sup>a</sup> | ~2.25 μm             |
| [66]      | Gold cross antennas                               | 13500     | ~10 μm              |
| [65]      | Au rod-shaped nanostructures                      | 13800     | ~5.8 μm             |
| [64]      | Fan-shaped antenna                                | 10<sup>3</sup> | ~3.57 μm           |
| [63]      | Asymmetric metamaterial                           | ~13255<sup>a</sup> | ~6.9 μm           |
| [62]      | Log periodic nanoantenna                          | ~1.9 × 10<sup>5</sup> | ~7.1 μm          |
| [61]      | NANOANTENNA dimer                                 | ~2 × 10<sup>3</sup> | ~6.9 μm           |
| [60]      | Periodic antenna array                            | 25000     | ~6.1 μm             |
| [58]      | Asymmetric crossed-antennas                       | ~9025     | ~3.4 μm             |
| [59]      | Gold nanonails                                     | 108000    | ~5.8 μm             |
| This work | Bowtie and crossed-bowtie nanorings with embedded nanostructures | ~8.1 × 10<sup>3</sup> | ~6.8 μm          |

<sup>a</sup> Calculated from printed enhancement spectra

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