

Localized Raman Enhancement from a Double-Hole Nanostructure in a Metal Film

Qiao Min,[†] Marcos Jose Leite Santos,^{‡,§} Emerson M. Girotto,[§] Alexandre G. Brolo,[‡] and Reuven Gordon^{*,†}

Department of Electrical and Computer Engineering, University of Victoria, Victoria, B.C. V8W 3Z8, Department of Chemistry, University of Victoria, Victoria, B.C., Canada V8W 3V6, and Departamento de Química, Universidade Estadual de Maringá, Av: Colombo 5790, 87020900 Maringá, Parana, Brazil

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An isolated double-hole indentation, with concentric rings, in a metal film was used to obtain highly localized surface-enhanced Raman scattering (SERS) from regions much smaller than the optical wavelength. The structure was created by a focused ion beam (FIB) milling partially through the 100 nm thick gold film to a depth of 50 nm. Significant SERS enhancement was observed for both oxazine 720 and rhodamine 6G. The SERS was polarization-dependent because of the biaxial symmetry of the double-hole at the apexes where the indentations overlap; these apexes were responsible for the strong subwavelength focusing. The finite-difference time-domain method was used to calculate the electromagnetic field of the nanostructure, and it showed strong polarization-dependent focusing, in agreement with the experimentally observed SERS enhancement. On the basis of these calculations, it is estimated that the 60% polarization-dependent SERS enhancement is the result of only ~ 1300 molecules in the region of the apexes, and it is estimated that the limit of detection is 20 molecules for the best-case configuration. This work is an important step toward single-molecule SERS from tailored nanostructures designed for predictable field enhancement.

Surface plasmons in nanostructured metals generate highly concentrated electromagnetic fields which are responsible for the surface-enhanced Raman scattering (SERS) phenomenon.¹ SERS allows the magnification of the normal Raman signal by many orders of magnitude, making it comparable to single-molecule fluorescence.² As a result of this extreme sensitivity in conjunction with vibrational spectroscopic information, SERS has attracted interest for use in chemistry, physics, and biology.^{3–6} The original demonstrations of single-molecule SERS used random metal nanostructures which give unpredictable field enhancement, both in terms of location and magnitude. Following that, several research groups avoided the stochastic nature of the SERS from random substrates by fabricating specifically designed metallic nanostructures that enhanced the Raman signal in a predictable way.^{7–12} For instance, reproducible SERS from individual bowtie nanoantennae have been reported from just 10^4 molecules adsorbed at the hot spot.¹³ SERS enhancement factors as high as 6×10^{10} have also been claimed for species adsorbed at nanoplasmonic resonators.¹⁴

In this paper, we propose and demonstrate the use of an isolated double-hole indentation with concentric rings as a highly efficient SERS substrate. The concentric rings couple the incident light into surface plasmons and then focus the electromagnetic field to the location of the double-hole.^{15–17} The double-hole indentation has a set of apexes (sharp tips) where the holes overlap, which serve to further concentrate the

electromagnetic field to length scales of <30 nm.¹¹ As a result, significant Raman enhancement was measured at the apex tips both from oxazine 720 (oxa) and from rhodamine 6G (R6G), which could be controlled by the excitation light polarization since the apex focusing is polarization-dependent.^{18,19} Finite-difference time-domain (FDTD) calculations were used to estimate the electric field enhancement and compare it with the SERS observations.²⁰ From these calculations, it is estimated that the polarization-dependent SERS enhancement of 60% is from only ~ 1300 molecules at the metal surface in the vicinity of the apex tips.

Figure 1 shows the scanning electron microscope image of a double-hole indentation structure with apexes surrounded by concentric rings. The structure was created by a focused ion beam (FIB) milling partially through the 100 nm thick gold film to a depth of 50 nm; therefore, the double-hole is not an aperture, but rather, it is an indentation. Several structures with different periodicities and inner ring radii for the concentric rings were fabricated. Each structure had five rings to scatter normally incident light into surface plasmons. This concentric ring structure has been considered previously for single holes.¹⁵ All of the patterns had a milling depth of only 50 nm into the gold film, so that only the reflection (backscattering) geometry was used. A gallium beam current of 50 pA at 30 kV was used for milling. The gallium beam spot size was 10 nm. A milling time of 300 ns was applied for all of the patterns with a milling rate of 150 nm/ms, which was calibrated using energy-dispersive X-ray analysis. For the double-hole indentation, each hole had a diameter of 220 nm, and the center-to-center spacing was 210 nm. The double-hole structure is useful because it provides two

* To whom correspondence should be addressed.

[†] Department of Electrical and Computer Engineering, University of Victoria.

[‡] Department of Chemistry, University of Victoria.

[§] Universidade Estadual de Maringá.

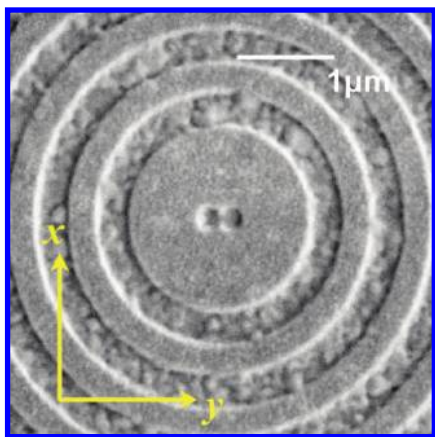


Figure 1. Scanning electron microscope image of a double-hole structure with concentric rings milled 50 nm into a 100 nm thick gold film. The inner ring has a radius of 900 nm, and the ring periodicity is 600 nm.

sharp apexes with a radius of curvature of ~ 20 nm at the tip that can be readily fabricated from two larger holes.

SERS properties were investigated by modifying the surface of the nanostructure with organic dyes commonly used as SERS probes. Oxa (Lambdachrome) and R6G (Lambdachrome) were drop-casted on the metallic nanostructure. A $10 \mu\text{M}$ solution of oxa (in methanol) was deposited on the sample, the solvent was allowed to evaporate, and then, the surface was rinsed with a copious amount of ultrapure water ($18.2 \text{ M}\Omega\text{cm}$ from a Barnstead NANOpure Diamond water purification system). To measure the SERS from a different dye, R6G was deposited by following the same procedure; however, $20 \mu\text{M}$ of the dye was drop-casted three times onto the nanostructure.

Figure 2a shows the SERS spectra of oxa dye adsorbed on an array with 600 nm periodicity patterns and an inner radius of 900 nm (as shown in Figure 1) with different incident light polarizations. A polarized 35 mW He–Ne laser was used as the excitation source (wavelength of 632.8 nm). The laser was focused at the sample using a $50\times$ ultralong working distance objective, leading to a $5 \mu\text{m}$ spot size that illuminated the nanostructure completely. Additional details about our Raman setup have been published elsewhere.¹¹ The measurement was repeated to verify that the dependence on the Raman intensities was not due to the photodecomposition of the dye. During the FIB milling, the long axis of the nanostructure was aligned parallel to the edges of the square gold-on-glass slide. Therefore, different polarizations were accessed by manually rotating the sample, and this was sufficient to observe strong variations in the SERS intensities. The experiments were repeated several times (and with different dyes) to ensure that the polarization dependence was reproducible. Moreover, experiments with arrays of circular holes were also performed using the same procedure, and no significant polarization dependence was observed. The rotation of the sample was preferred over using a half-wave plate to avoid any polarization effect introduced by the reflections in the microscope.

There is a strong Raman scattering peak at 598 cm^{-1} for both polarizations in Figure 2, which corresponds to the main vibrational modes of the phenoxazine ring of the dye. The peak Raman scattering intensity for the x -polarization of the laser was 60% higher than that for the y -polarization. Since the only part of the structure without rotation symmetry is the double-hole apex at the center, this is expected to be the source of the polarization dependence of the Raman enhancement (as will

be explored in further detail below using comprehensive electromagnetic calculations). It should be noted that the y -polarization still provides significant signal enhancement due to the presence of the concentric ring nanostructure; for the conditions of this experiment, the signal from the bare gold was not detectable above the noise.

Figure 2b shows the dependence of the SERS intensity peak at 598 cm^{-1} with the inner radius of the nanostructure. The maximum signal occurs for inner radius values of 600 and 900 nm, which corresponds to the standing wave maxima of the surface plasmons that are scattered by the 600 nm concentric rings of the structure. The experiments were repeated with 500 and 700 nm periodicity rings, which showed similar polarization dependence, but overall, SERS intensities were an order of magnitude lower than those for the 600 nm concentric rings.

Oxa has an internal electronic transition at 620 nm (in ethanol), which is resonant with the laser excitation source at 632.8 nm (He–Ne). Hence, the results presented so far contains additional contributions to the enhancement from a resonance Raman mechanism, surface-enhanced resonance Raman scattering (SERRS). In order to isolate the effect of the nanostructure from the resonance Raman contribution to the overall enhancement, we have performed further experiments with R6G. R6G absorbs at 530 nm in ethanol; therefore, its internal electronic transition is nonresonant at the excitation wavelength. The results confirmed the efficiency of the substrate by generating intense SERS from R6G. The polarization-dependent enhancement observed for oxa was seen for the rhodamine 6G as well, with good quantitative agreement.

FDTD calculations were carried out to reveal the electromagnetic field-enhancement mechanism of the polarization dependence.¹⁸ A small mesh size of 5 nm was chosen to accurately capture SP effects, as was verified by finite-difference mode calculations and repeating the calculations with varying grid sizes (both smaller and larger). To reproduce the conditions of the experiment, a 632.8 nm Gaussian wave source was normally incident on the top surface of the double-hole structure. A near-field monitor was used to obtain the electric field distribution at the surface. Perfectly matched layer boundary conditions were used on all sides except for below the gold surface, which was set to be a perfect electric conductor (since the electromagnetic field does not penetrate that far into the gold). The ring structure acts as a focusing grating to couple the incident light into the surface plasmons toward the center of the rings.²¹ To quantify the focusing ability of the ring structure, additional FDTD simulations were performed without the rings, and the peak electric field intensity was reduced by two orders of magnitude. Clearly, the ring structure is important to obtain the SERS enhancement seen in this work.

Figure 3a and b shows the FDTD-calculated z -component of electrical field at the surface of the concentric apex structure surface for the x and y incident polarization source at the 632.8 nm wavelength. (The z -component was chosen for visualization because it is characteristic of the surface plasmon excitation and it is not present in the excitation source.) The periodicity was 600 nm, and the inner ring radius was 900 nm, to match the experimental configuration with the greatest SERS signal. The FDTD calculations showed that the 600 nm ring structure had a field intensity maximum at 620 nm with a FWHM of 32 nm. This peak is wide enough to encompass both the source and Raman scattered photons. It is clear that the surface plasmon waves are concentrated at the sharp apex region for the x -polarization, which leads to strong electrical field enhancement in that region. For y -polarization, the local electric field intensity

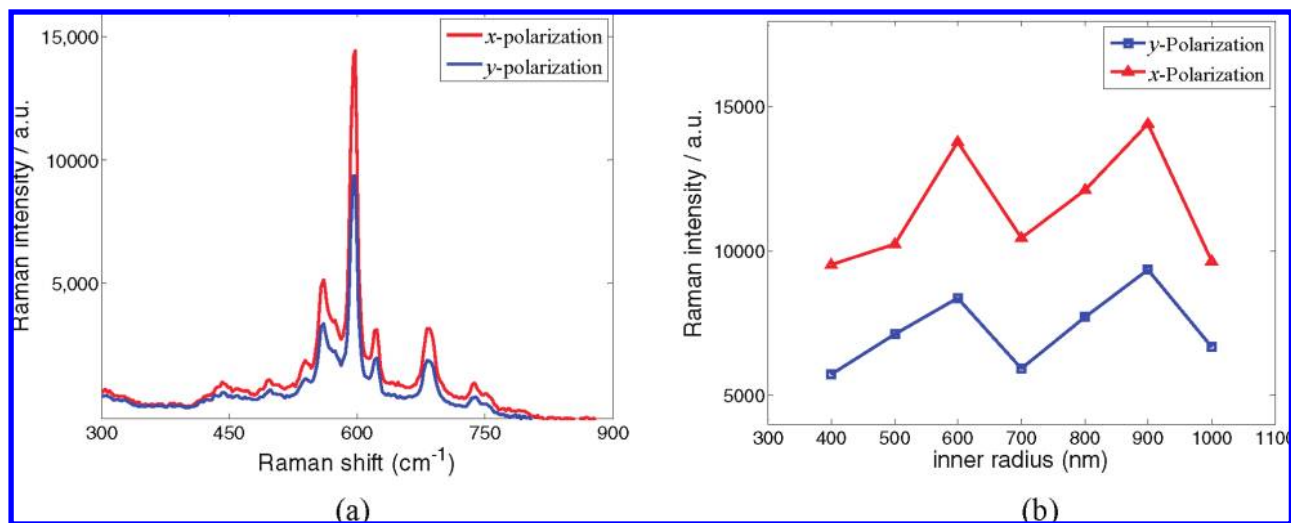


Figure 2. (a) SERS of oxazine 720 adsorbed on the concentric apex structure (900 nm inner radius and 600 nm periodicity) at two polarizations of the incident laser (defined in Figure 1). (b) Dependence of the SERS intensity of the 598 cm⁻¹ oxazine 720 band with the inner radii of the concentric apex structure.

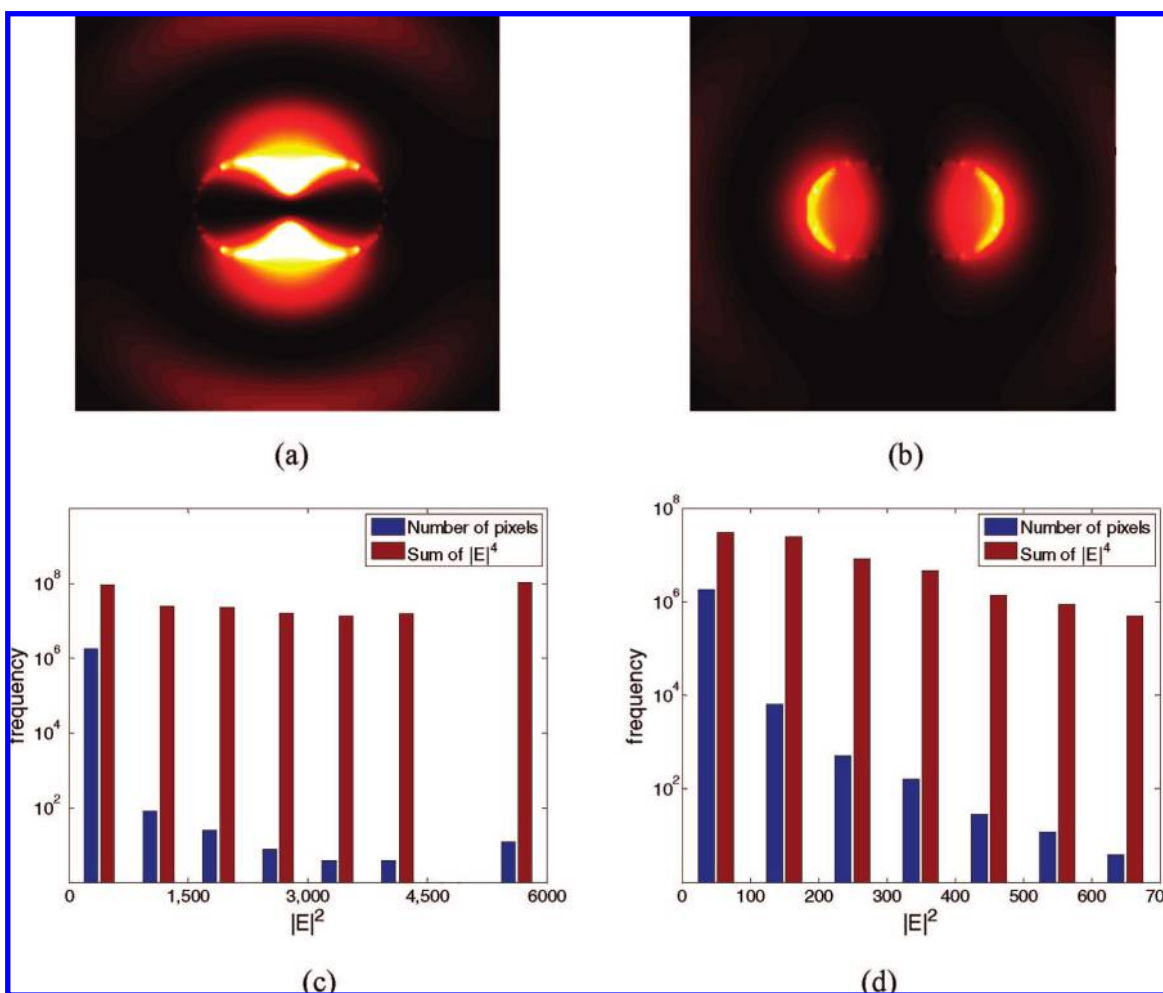


Figure 3. FDTD-calculated electrical field intensity at the surface of a double-hole apex structure with a concentric rings concentric apex structure surface at 632.8 nm. Profile of the z-component of the electrical field intensity (for the center region only) for (a) x-polarized incident light and (b) y-polarized incident light. Also shown are histograms, binned by field intensity, of the number of pixels over the whole surface area (blue bar) and the sum weighted by |E|⁴ at each pixel (red bar) for (c) x-polarized incident light and (d) y-polarized incident light. All of the electrical field intensities were normalized by the source.

enhancement was seven times lower, and the most intense electrical fields were distributed in the lateral sides. Considering these comprehensive numerical calculations, it appears that the double-hole apex structure provides strong subwavelength

focusing that is responsible for the observed Raman enhancement observed in the experiments above.

To further quantify this enhancement in terms of the number of molecules contributing to the SERS, we consider histograms

taken over the simulation area. Figure 3c and d shows with blue the binning of the numerical calculation pixels (mesh-points) as a function $|E|^2$ for the x and y source polarizations. Shown in red is the binning for the number of pixels multiplied by $|E|^4$ as a weighting factor. The different $|E|^2$ scaling for Figure 3c and d should be noted. One feature that stands out from this figure is that only 32 pixels (around the apexes of the double-hole) provide more than a third of the $|E|^4$ weighted contribution for the x -polarization. We have considered the effect of the bin width on the histograms presented in Figure 3. The effect of the hot spots on Figure 3c will be smeared out for high values of bin size. We then decided to use a bin size (750 for Figure 3c and 100 for Figure 3d) that emphasizes the role of the hot spots for the x -polarization.

Using these results, we can estimate the number of molecules contributing to the 60% increase in SERS with changes in polarization, that is, from focusing by the double-hole nanostructure. The electromagnetic contribution to the total SERS enhancement is commonly considered to be proportional to the fourth power of the field enhancement factor^{22,23}

$$R = \frac{|E_{\text{loc}}|^4}{|E_0|^4}$$

Using this equation, from the red bars of Figure 3, it shows that an enhancement of 113% can be expected from the x -polarization excitation compared to that from the y -polarization. This is larger than the 60% enhancement measured in the experiments, and the discrepancy is likely due to imperfections (including duller apexes) in the fabricated nanostructure sample. Furthermore, more than 1/3 of the x -polarization signal comes from only 32 of the pixels with an intensity between 4500 and 6000 (normalized to incident field). There are 32 pixels in hot spots (in which $|E|^2 > 4500$), and each pixel represents a 25 nm² area.

The number of molecules that contribute to the polarization effect observed can be estimated by considering a monolayer of oxa, the molecular dimensions of the dye as 1.2 nm (long axis) and 0.9 nm (short axis), and adsorption onto the gold along the long axis (where the nitrogen atoms are located). Each molecule occupies an area of around 0.6 nm² in this adsorption mode, which leads to the highest packing. The number of adsorbed molecules would be even smaller if a flat orientation was considered. The number of molecules in the hot spots is then 1300 within these assumptions. It is these molecules alone that lead to the 60% Raman enhancement under different incident light polarization. Considering that the standard deviation of the noise in Figure 2a is 50, the estimated limit of detection (defined as three times the standard deviation of the noise) for oxa from the best-case configuration is about 20 molecules.

In summary, we demonstrated the use of an isolated double-hole indentation in a metal film with concentric rings for surface plasmon focusing for SERS. Due to the symmetry of the double-hole, which has strong subwavelength focusing at the apexes

where the indentations overlap, the SERS enhancement factor was found to be strongly polarization-dependent. Using FDTD calculations of the fabricated nanostructure, an intense field was observed at the sharp apex region under the appropriate incident mode polarization, which is responsible for the polarization-dependent SERS enhancement. On the basis of these calculations, it was estimated that only 1300 molecules provide a 60% increase in the SERS when the incident polarization of the laser source coincides with the apexes and that the limit of detection is about 20 molecules. These results show that the isolated double-hole indentation is a promising nanostructure for SERS that, with suitable optimization, may approach the ultimate goal of reliable and predictable single-molecule SERS.

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