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Plasmonic “Nanowave” Substrates for SERS: Fabrication and Numerical Analysis

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Abstract

The “Nanowave” substrate, comprising a close-packed array of nanospheres onto which a thin metal shell of silver or gold is deposited, was first fabricated in our laboratory in 1984 and used as a surface-enhanced Raman scattering (SERS)-active substrate for the sensitive and reproducible detection of analytes. More than twenty-five years after the first experimental demonstration of the effectiveness of this substrate, numerical simulations are sufficiently powerful and versatile to mimic this geometry in three dimensional space and confirm the experimentally measured plasmonic behavior at the substrate’s surface. The study confirms that an in-plane polarized incident plane wave generates strong enhancements in the interstitial spaces between individual metal-coated nanospheres, thus producing closely packed arrays of hot spots underlining the strong SERS effect of the Nanowave substrate structures. The surface-averaged SERS enhancement exhibited by the Nanowaves was evaluated and compared for different metal thicknesses. The effect of structural confinement on the plasmonic behavior of the Nanowave structure was investigated by varying the structural confinement of the substrate in the plane parallel to the incident excitation. The Nanowave is an inexpensive, reproducible and effective plasmonics-active substrate that has the potential to be used for SERS studies requiring high detection sensitivity.

Keywords

Surface Enhanced Raman Scattering (SERS); Plasmonics; Nanowave; Finite Element Method; Gold; Silver; Nanoshells; Nanoparticles

Following the discovery of the surface-enhanced Raman scattering (SERS) effect^{1,2}, our laboratory has first demonstrated the general applicability of the SERS effect for trace analysis using solid substrates having silver-coated nanospheres.³ In 1984 Vo-Dinh et al. exploited the spin-coating and electron beam evaporation techniques to fabricate close-packed arrays of nanospheres, onto which a thin silver shell was deposited, effectively forming a controlled, reproducible substrate of ‘hotspots’,³ here referred to as the Nanowave due to its analogy to a periodic waveform. Although this type of substrate produced large SERS effects and has been used in a wide variety of chemical and biological sensing

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applications,⁴ the origin of this plasmonic behavior as a result of this topography has only been induced.

During the last two decades, there has been an explosive interest in both practical applications of SERS as sensing techniques as well as fundamental studies of the plasmonic theory of the electromagnetic (EM) enhancement of SERS. In 1996, Garcia-Vidal et al.⁵ developed an implementation of Maxwell's equation for modeling a rough silver surface as an array of half-cylinders of silver enclosed in a silver substrate. The authors demonstrated that the strongest E-field enhancement, up to 10^7 , occurred in the crevices or pores of the rough surface; the structure they analyzed was infinite in extent along the cylinder's length, lacking confinement along that direction, thus effectively being analogous to the evaluation of a 2-D geometry. Moreover, the crevices were not 'smoothened' by rounding, which, although generating the extremely large enhancement factors reported, are unrealistic from an experimental perspective. Finally, the analyzed structure comprised only a single material, silver, such that the underlying structure of the substrate was intrinsically different to the Nanowave substrate synthesized by the Vo-Dinh group, and thus no analysis of the effect of varying metal thickness on the substrates' plasmon band could be undertaken. Three-dimensional studies of nanoparticle structures have also been investigated in 2008 and 2009,⁶⁻⁸ but focus on nanocylinders or chains of nanoshells, which have significantly simpler geometries than that of the Nanowave substrate, which translates to a much reduced computational complexity.

Recently, various simulation programs developed for computational electromagnetics have become available; these simulation programs facilitate the characterization of the EM field behavior in the vicinity of arbitrarily-shaped nanostructures that lack axial symmetry and can therefore not be analyzed via the Mie-theory. For irregular shapes, two widely acknowledged computational techniques are the Finite Difference Time Domain (FDTD) and the Finite Element Method (FEM). Although the FDTD method has its own merits for various applications,^{9,10} its intrinsic cubic discretization algorithm makes it impractical to accurately solve the near-field electromagnetics around curved boundaries and structures. The FEM's meshing algorithm employs tetrahedra to efficiently follow curved contours, thereby providing higher spatial resolution and quantitative accuracy. We have recently shown that FEM is able to accurately solve near-field electromagnetics in the vicinity of 3-D nanoshell dimers to a good spectral and spatial accuracy and resolution when compared to the multipole expansion theory.¹¹ We have also further confirmed excellent agreement of the FEM algorithm compared to the Mie theory when excited by an oscillating electric dipole, again, for a 3-D nanoshell geometry.¹²

In this study, we experimentally demonstrate the fabrication of the Nanowave substrate using 100nm silica spheres, and then use FEM to perform numerical simulations of the spatial and spectra behavior of such a model as a function of metal thickness. Both gold and silver metals are used as model metals in the simulation and analysis. The model is constructed with periodic boundary conditions to take into account the infinite nature of the substrate relative to a single particle, and 3-D smoothing of the sharp crevices is enforced to ensure both reliable results and a more realistic model.

Experimental Procedure

The substrate fabrication involved two separate steps. The first step involved washing glass cover slips by incubating them in nitric acid, followed by a careful rinsing process with ultrapure DI water. This ensured removal of organic residue on the glass surface and populated the surface with hydroxyl groups. The cover slips were dried in a stream of nitrogen and placed on a spin coater. Silica nanospheres (100nm diameter, Polysciences), dispersed in a ethanol:ethylene glycol solvent (85%: 15% v:v), were dropcast on the cover slip and spun at 6000 rpm for 5 seconds. The nanospheres adhered to the coverslip, producing a close-packed array of silica nanospheres. The second step entailed coating the sphere-covered slides with a metal (gold or silver), achieved by transfer to an E-beam evaporator. To ensure uniform metal coating the substrates were rotated above the silver source during deposition, which was conducted at a vacuum pressure below 5×10^{-6} Torr. The desired thickness of metal was evaporated onto the array of nanospheres, producing an array of silica@metal half-nanoshells, referred to as the Nanowave. Characterization was done under the scanning electron microscope (SEM) at inclination angles ranging between 0 and 45 degrees. It is noteworthy that although ethylene glycol was found to help spread the beads (most probably by reducing the rate of solvent evaporation and increasing solvent viscosity), similar close-packed substrates could be obtained without ethylene glycol by tweaking the volume and speed of the spin-coating process.

Theoretical Simulation

The theoretical simulation was performed using the RF module of COMSOL Multiphysics v3.4, and the substrate was analyzed in 3-D by modeling a generic subset of particles as observed under the SEM and delimited by a contour in Figure 1; the detailed schematic for this model is illustrated in Figure 2.

A unit cell model of the Nanowave substrate was built in four distinct steps: first, a model for the single metal-capped silica particle was designed. Seven of these were then positioned such as to form a hexagonally close-packed array. The sharp crevices formed by this assembly were then smoothed, in three dimensions, by the manual fusion of unique structures whose geometry and dimensions are detailed in Figure 2 and Table 1, respectively. Finally, the hexagonal structure was sliced through the 6-outer particles to form a cuboidal computational domain, such that the unit cell possessed symmetry in the x-y plane, Figure 2. Periodicity in the x-y plane was ensured by setting the boundaries along the x- and y-directions to Perfect Electric Conductors (PECs) and Perfect Magnetic Conductors (PMCs), respectively, and the PML boundaries along the z-direction prevented unwanted reflections onto the substrate.

The meshing of structures in FEM is particularly important to guarantee solution convergence as well as solution accuracy. The maximum mesh size in the metal shell was set to 5nm to ensure fine special meshing, to typically yield 1 to 2 million degrees of freedom (DOF), which corresponds to 7 – 20 GB of RAM when solving using the direct PARDISO solver. Fine spectral sampling was ensured by solving the fields at wavelength

intervals $\lambda = 10$ nm to capture the rapid spectral changes or fluctuations that typically occur around peaks.

The unit cell substrate was placed in a surrounding medium of air. The silica is described by a wavelength-independent refractive index of 1.45^{11–14} and the metal coating was modeled by the Lorentz-Drude dispersion models for gold and silver:

$$\varepsilon(\omega) = 1 + \sum_{k=1}^6 \frac{\Delta\varepsilon_k}{-a_k \omega^2 - i b_k \omega + c_k}, \quad (1)$$

where λ_k , a_k , b_k and c_k are constants that provide the best fit for either metal.¹⁵

The substrate was excited by an incident plane wave at 633 nm, propagating perpendicular to the substrate along the negative z-direction (from above), and containing only x-polarized components; as such, the E-field has the form $\mathbf{E}(\mathbf{r}, t) = E_x e^{j(\omega t + k^z z)}$ and is schematically shown in Figure 2. The model was solved for the scattered fields for wavelengths ranging the 300–1200 nm region. For each of the five metallic shell thicknesses (10, 20, 30, 40 and 50 nm) investigated in this study, a new unique model had to be constructed, meshed and simulated.

This model does not take into account geometrical imperfections and further losses that dampen and broaden the surface plasmon of the close-packed NP network; these mainly include small size-effects, which are significant when the metal thickness is smaller or on the order of the electron mean free path.

Results and Discussion

The spin coating method is a rapid, inexpensive substrate fabrication technique that yields a reproducible, homogeneous thickness of polymer films or distribution of nanoparticles on substrate. The monolayer, close-packing of 100 nm silica nanospheres was achieved by optimizing the solvent composition and concentration, particle concentration, spin speed and solution volume drop cast on the glass slide. The spin duration did not affect the final distribution of nanospheres on the substrate; beyond the spin time at which the solvent evaporated, the particles remained immobile and adhered to the glass surface even with continued spinning.

Following evaporation of 50 nm of gold or silver onto the silica nanospheres, each individual NP could still be perceived, suggesting deposition of a uniform coating of metal on top of the underlying structure (Figure 1). Although a few cracks and irregularities are observed in the NP close-packing pattern, the overall distribution is ordered, predictable and therefore reproducible, which is of utmost importance when attempting to quantify SERS measurements.

The inset of (Figure 1) is an enlarged view of a portion of the substrate, and depicts the repetitive unit of interest, consisting of seven particles arranged as a “ring”, and denoted by a white rectangle. This characteristic pattern is repeated throughout the entire substrate and

is a practical model to investigate the plasmonic behavior of the Nanowave substrate when excited by a plane wave incident beam.

A typical SERS measurement on such a substrate is achieved, in our laboratory, by delivering a $5\mu\text{L}$ sample of the analyte of interest onto the substrate surface allowing it to dry in air, and then placing it on an inverted Raman microscope, equipped with a linear polarizer (field polarized in the plane of the substrate), and excited by a 633nm He-Ne laser source oriented perpendicular to the substrate. To investigate the substrate's plasmonic behavior, these experimental conditions were mimicked by designing a 3-D numerical structure that was modeled on the rectangular unit cell in (Figure 1), a schematic of which is presented in (Figure 2).

The geometry and orientation of this unit cell was purposefully chosen to ensure two lines of symmetry, one along the x-axis and the other along the y-axis. This enabled x-y plane periodicity to be enforced with PEC and PMC boundaries normal to those axes, rather than Comsol's in-built Periodic Boundary Condition, which we found was unable to solve this particular geometry given the normal propagation vector of the incident excitation. With regards to unit cell size, it is noteworthy that the unit cell effectively comprises four nanoparticles (1 whole and 6 halves), and that the same result could be achieved at a lower computational cost by a four-time reduction of the unit cell in the x-y plane to one quarter of its current size, such that it effectively comprises only a single nanoparticle. However, for visualization purposes, due to the availability of RAM and to test the computational limits of the software, this cell size was employed as the generic Nanowave solution in Figure 4, but the subsequent analyses were performed with a two-particle unit cell (half the size along the x-axis) for solution conciseness while maintaining solution clarity.

As indicated, the incident plane wave $\mathbf{E}(\mathbf{r}, t) = E_x e^{j(\omega t + k_z z)}$ was defined to have amplitude of 1, a wavelength $\lambda = 633\text{ nm}$, propagate in the negative z-direction and contain only x-polarized E-field components. The latter condition was imposed to probe the surface plasmon formed in the two inter-particle crevices that are parallel to the x-axis. The values corresponding to the parameters in Figure 2 and presented in Table 1, for each shell thickness z . The smoothing thickness, δ , was limited to a minimum of 2nm for the 10nm metal coating, since this value was assumed to be the smallest experimentally-achievable rounding in the crevices which, given the deposition rate of 0.5nm/sec , is reasonable. Similarly to the experimental metal-deposition process, it is important for modeling purposes to ensure that, as the metal deposition thickness increases, the metal layer is indeed uniformly "deposited" over the silica nanoparticles. This means that although the thickest part of the shell will be directly above the center of the silica sphere (when looking top-down on the substrate), the inter-particle crevices should also have a significant layer of metal above it, albeit slightly thinner due to the larger effective area over which the metal is deposited. This concept is illustrated in Figure 3 with snippets of the actual geometrical structures solved in FEM: as the metal thickness increases, the triangular opening between any three adjacent nanoparticles gradually closes (top-view), and the height of the metal shell rises (side-view), both trends that are experimentally consistent and thus expected. It is critical to appreciate that this geometrical trend is only possible if the rounding thickness δ is also increased as the metal-shell is increased; if δ is maintained

equal to $2nm$ for all metal thicknesses, the metal-layer over the crevice would not thicken much, and the triangular opening would remain unchanged for all metal thicknesses. Although this latter geometry would constitute a fairer theoretical comparison of the effect of metal thickness on the plasmonic behavior of Nanowave substrates, it would be experimentally inconsistent and was purposely avoided. Instead, the rounding thickness δ was increased by $0.5nm$ for every additional $10nm$ metal thickness, reaching a smoothing of $4nm$ for the $50nm$ shell. The five other parameters (rounding heights and widths) were adjusted such that the same δ was maintained three-dimensionally around the entire rounding junction.

A typical simulation result is presented in Figure 4 and Figure 5, where isosurfaces of $|E_x|$ are plotted to illustrate the behavior of the electric field in the vicinity of a $50nm$ gold Nanowave substrate. The motivation behind fabricating such substrates over 25 years ago³ was based on the idea that the E-field would be particularly strong in the interstitial space between the metal covered nanospheres. Indeed, Figure 4(b) emphasizes that the strongest E-field enhancement occurs at each x-oriented interstitial space between adjacent nanoparticles; more specifically, these fields are most intense at the gold surface on either side of the inter-particle junction, clearly seen in Figure 5(a,b), which is intuitively expected since the local geometry is similar to that of a dimer nanoshell, which also generates the strongest field at these locations.⁵⁻⁹ Figure 4 and Figure 5 also confirms that the periodicity in the $x-y$ plane is successfully enforced by the PEC-PMC boundaries, since the E-field in the six interstitial spaces that are cut by these boundaries (four junctions in the PMC/PEC corners and two junctions on the PMC boundaries) are identical to that in the two middle junctions, which suggests that any long-range plasmonic behavior that may be induced over the infinite extent of the substrate would be accounted for.

Experimentally, chemical detection on such substrates requires the molecules of interest to physisorb or chemisorb onto the metal surface, which is where these regions of intense plasmonic activity reside. This effectively demonstrates that the Nanowave substrate exhibits a “closely-packed array of hot spots”, thus making it an effective SERS substrate for sensitive, reproducible measurements. In this study, the EM enhancement is defined as $EME_x = |E_x|/|E_0| = |E_x|$ since the incident amplitude $|E_0| = 1$; for the $50nm$ Nanowave, a maximum enhancement of 15 was achieved at $\lambda = 580nm$. Since the SERS signal enhancement factor $SERSEF$ is approximately proportional to the fourth power of the EM enhancement, $SERS_{EF} = |E_x|^{4.16}$ the $50nm$ Nanowave produces $SERS_{EF} = 5 \times 10^4$. Evidently, maximizing the $SERS_{EF}$ provided by a SERS-active substrate is important for obtaining the lowest detection limit, which is the key towards achieving ultra-sensitive detection.

Rather than map the three-dimensional E-field behavior at a single wavelength, which is useful for understanding the spatial distribution of the field, spectral information can be gleaned by calculating the absorption spectra of the Nanowaves as the metal thickness is varied, Figure 6.

It is noteworthy that the thin-shelled Nanowaves exhibit two sharp absorption bands, a short-wavelength band and a longer-wavelength band, whereas the thicker-shelled

Nanowaves have a single, short-wavelength absorption band and a hint of a longer-wavelength shoulder. As shell thickness increases, both absorption bands undergo a blue-shifting. Specifically, the short-wavelength bands blue-shift toward the typical absorption band positions of large 100nm spherical nanoparticles: 550nm for gold and 450nm for silver. The longer wavelength bands also blue-shift, but disappear with increasing shell thickness at 650nm for gold and 600nm for silver. The nature of these peaks is addressed later on in the manuscript. It is noteworthy that the absorption peaks are of the same order of magnitude (1×10^{-14}) across all thicknesses for both metals.

To understand the SERS potential of Nanowave substrates as a function of metal thickness, the E-field $|E|$ in the inter-particle space was probed at the positions reported in the last column of Table 1. Again, the dual-peak nature of the thin-shelled Nanowave spectra is apparent, and the plasmon band blue-shift with increasing shell thickness, for both metals, points toward the possibility of plasmon tuning for optimizing the SERS detection sensitivity of adhered analyte molecules. Interestingly, the maximal E-fields achievable for both silver and gold Nanowaves are quantitatively similar, which is unexpected because silver is renowned to be a stronger SERS material than gold. At the current probed position in 3-D space, gold Nanowaves exhibit a maximum $SERS_{EF} = 28^4 = 6 \times 10^5$ at $\lambda = 980nm$ and silver's $SERS_{EF} = 31^4 = 9 \times 10^5$ at $\lambda = 640nm$. It is noteworthy that the measurement point is located in the air medium in the inter-particle junction, exactly at equidistance from both particles, and is therefore not the location of the strongest E-field that would be experienced by surface-bound molecules.

The plasmonic behavior of both gold and silver Nanowaves is summarized in Figure 8. With increasing thickness, both gold and silver Nanowaves experience a decreasing peak until a plateau is reached at 50nm for both metals. For a given thickness, the peak of gold is red-shifted relative to that of silver, as expected given the permittivities of each metal. As the metal thickness increases for both gold and silver, the E-field enhancements at the peak wavelength also decreases, which suggests that thinner shells have the potential to provide the best SERS sensitivity, if excited at the appropriate wavelength.

Localization of the E-field hotspots

Understanding where the strongest fields occur on the Nanowave is critical in determining whether they would be efficient SERS substrates. Given the complex 3-D geometry of the structure, this is only achievable to analyzing the E-field isosurface plots, which capture the complexity of the E-field behavior in three-dimensions; the conventional slice plots are insufficient for this purpose and are therefore avoided. The spatial distribution of the $|E|$, probed at the low-wavelength peak for each metal-shell thickness, is presented in Figure 9. For conciseness, only gold Nanowaves are depicted since the silver Nanowaves exhibit similar characteristics in terms of their E-field distribution in 3-D space. The first row is the top view of the substrate and the bottom row represents the side view, to clearly depict the 100nm Silica nanoparticles and the overlaying metal shell. To simplify the discussion, the encircled letters A and B are used to denote two distinct locations of the E-field enhancement: A refers to the top of the interparticle junction and B refers to the bottom of the metal shell, on either side of the junction.

As a first observation, the E-field at A defocuses from a tightly confined focal spot for the 10nm shell to cover a wider area for the 50nm shell, most likely due to the smaller x- and y-dimensions of the junction for thinner shells relative to thicker ones, as depicted in Figure 3.

Secondly, it is noteworthy that over the entire 3-D Nanowave geometry and for all metal thicknesses, the E-field is strongest at locations A and B, but the relative extent to which the E-fields at A and B are enhanced by the local geometry is dependent on the metal thickness. The E-field $|E|$ is equally strong at A and B for a 10nm gold shell, but $|E|_B$ decreases with increasing shell thickness, such that the relative intensity $|E|_A/|E|_B$ also increases. For a gold thickness of 50nm, $|E|_B$ is no stronger than the background E-field. This is interesting because it can be geometrically inferred and measured that the shell thickness at B does not increase much as overall shell thickness increases, yet $|E|_B$ decreases, which suggests that the high $|E|_B$ for thin shells reflects the underlying 3-D geometry of the Nanowave.

Therefore, the short-wavelength plasmon band seems to be related to the E-field enhancement at A and could be due to the confinement in the x-direction of the Nanowave substrate (in the direction of incident E-field polarization). As the shell thickness increases, the plasmon is confined to the top junction of the metal shell, possibly because the incident wave is unable, at these incident wavelengths, to penetrate the thick shell to couple the two metal nanoparticles at junction B.

Surface-averaged SERS enhancement

Nanowave structures were first fabricated to be used as SERS substrates for trace analysis, so it is important to investigate the expected SERS enhancement, $SERS_{EF}$, that they are able to provide, and how this quantity varies with shell thickness. The $SERS_{EF}$ is calculated by evaluating the absolute electric field, $|E|$, and then raising it to the fourth power.¹⁶ However, rather than evaluate $SERS_{EF}$ at a single point in space (a popular method that presents the highest possible $SERS_{EF}$ at a hot spot but ignores the rest of the substrate), a more meaningful measure of the theoretical $SERS_{EF}$ is obtained by integrating $|E|^4$ over the probed area of interest.¹⁷ Experimentally, the measured SERS signal is effectively proportional to the average $|E|^4$ signal emitted by the molecules over the entire probe area, normalized to the number of molecules (monolayer-coverage assumed) being excited by the incident source. Depending on the microscope objective magnification power and numerical aperture, the probe area typically ranges from a few of μm^2 to tens of μm^2 ; this implies that the probe area consists of both hot spots (regions of strong EM enhancement) and flat surfaces (regions of weak EM enhancement). Therefore, from a purely geometrical standpoint and for a given type of analyte molecules, it can be envisaged that the measured SERS intensity strongly depends on the spatial density of hot spots, the achievable EM enhancement in those hot spots, and the ratio of molecules adhered in hot spots to those adhered elsewhere.

Thus, the average $SERS_{EF}$ that Nanowaves can provide is estimated by first calculating the surface-area-averaged E-field, $|E_{avg}|$, and then raising it to the fourth power to obtain an approximate $SERS_{EF}$. This was performed by integrating the E-field over the 3-dimensional Nanowave top-surface, which is depicted in blue in Figure 10(a) and the areas of which are

reported in Table 1. The surface-averaged E-field as a function of wavelength is reported in Figure 10(b,c), and the general trends observed in Figure 7 - the number of peaks and the shift of the peaks towards the respective plasmon bands of gold and silver - are also apparent here. Interestingly, however, the maximum E-fields of the gold and silver Nanowaves are comparable, for each shell thickness, even though silver showed consistently stronger $|E|$ relative to gold, Figure 6. This is due to the small inter-particle hotspot area relative to the total top-surface area, such that averaging diminishes the importance of the intense E-fields present in the hotspots compared to the low E-fields everywhere else.

The SA-average E-field is low, with a maximum calculated SERS EF of approximately $5^4 = 625$ for gold or silver, at both $\lambda = 1000nm$ and $\lambda = 940nm$, respectively. Although this finding does not validate the significantly higher experimental data reported by Vo-Dinh *et al.*,³ a number of possible explanations could be offered to understand the difference. Firstly, capillary effect when drying that concentrates the analyte into the crevices where it then dries and experiences the high local E-fields (hot spot concentration effect); secondly unaccounted surface roughness covering the entire metal surface, which would increase the local E-field such that the average E-field experienced by metal-bound analytes would be significantly higher; thirdly, the crevices are actually sharper in reality than they were simulated, which would translate to an increased average E-field, but more importantly, to much more significant E-field enhancement in the inter-particle hotspots. Assuming the analyte is concentrated in those junctions, this could explain the stronger measured signal. Nevertheless, all variables held constant, we propose that this methodology is a fairer comparison of the SERS EF potential of substrate, rather than merely presenting the highest achievable value at a single point in space.

It is noteworthy that a decrease in the diameter of the underlying silica nanoparticle, which would lead to higher density of hotspots, would not yield an increase of the SA-averaged E-field. For example, a 10—*nm*-thick Nanowave constructed with 30*nm* silica nanoparticles (characterized by a $10\times$ decrease in area to $3\times 10^{-15}m^2$) did not yield any significant difference in SA-averaged E-field. This is possibly due to the relatively small contribution from the hotspot enhancements compared to the total averaged area, combined with an intrinsically complex dependence of E-field enhancement on nanoparticle size; in this case, the 30*nm* nanoparticles exhibited lower E-field enhancements than the 100*nm* nanoparticles.

The intriguing appearance of longer-wavelength (or lower-energy) peaks in the Figure 6 absorption spectra was investigated by probing the 3-D solutions at those wavelengths, which are depicted in Figure 11. It is noteworthy that the 40*nm* and 50*nm* Nanowaves of both gold and silver do not exhibit distinct long-wavelength peaks. As depicted in Figure 11, at these excitation wavelengths, the E-field enhancement is strongest at, and mostly confined to, the side junctions B.

As the shell thickness increases, the ratio $|E_A|/|E_B|$ decreases as $|E_B|$ remains high but $|E_A|$ weakens; this contrasts to the trend exhibited in Figure 9 for the short-wavelength plasmon band. It is interesting that for 40*nm* and 50*nm* shells, the enhancement at B is not significant, possibly due to the incident field not being able to effectively penetrate into the shell to that depth.

When considered jointly, Figure 9 and Figure 11 suggest an explanation for the dual-plasmon peak nature exhibited by the Nanowave structure: the short-wavelength plasmon band is a manifestation of the E-field enhancement in the top crevice of the metal shell (junction A), and the long-wavelength plasmon band can be attributed to the E-field enhancement on either side of the interparticle gaps (junctions B). More generally, the short-wavelength plasmon band is a result of the spatial confinement in the x-direction, and the long-wavelength plasmon band is due to spatial confinement in the y-direction. This hypothesis was verified by relaxing the physical confinement along the y-direction such that the Nanowave structures became metal-coated cylindrical nanowires that extended to infinity in y, generically depicted in Figure 12. With an x-polarized incident excitation, the E-field enhancement occurs along the entire nanowire ridge, unconfined in the y-direction, Figure 12(c).

The absorption spectra of these nanowires are presented in Figure 13, for both gold and silver, and only exhibit a single plasmon band, which approximately co-registers with the corresponding short wavelength plasmon bands of the Nanowaves in Figure 6: for 10nm- and 20nm-thick gold shells, the peaks are located at 780nm and 600nm for Nanowires, respectively, compared to 710nm and 610nm for Nanowaves, respectively. For 10nm- and 20nm-thick silver shells, these peaks are positioned at 700nm and 520nm for the Nanowires, respectively, compared to 640nm and 520nm for the Nanowaves, respectively. The absorption spectra also possess similar magnitudes (1×10^{-14}) and FWHM as those in Figure 6.

Figure 14 depicts the surface-averaged E-field, which is comparable magnitude to the Nanowave geometry, but yet again, only a single main plasmon peak is seen here for each metal thickness. To further investigate the hypothesis that increasing the spatial confinement of the structure leads to additional plasmon bands, the Nanowave structure was further confined in the $x-y$ plane by removing the periodic boundary condition in that same plane, such that the E-field of a cluster of only seven nanoparticles was evaluated. Indeed, this extra confinement led to the emergence of a longer wavelength plasmon peak in the 1100 — 1200nm wavelength range, depicted in Figure 15 for silver; confined gold Nanowaves also introduced an extra, long-wavelength plasmon band.

The non-periodic Nanowave structure consistently reproduces the three short-wavelength plasmon bands, albeit sharper and of larger magnitude; this more confined structure, however, exhibits an additional, broad plasmon band appears at 1150nm, whereas the unconfined, periodic Nanowave geometry does not. The dampening and broadening of the plasmon peaks for the unconfined Nanowave is probably due to the contribution from long-range, delocalized surface plasmons originating from the adjacent nanoparticles at infinity, which are absent in the confined structure; the investigation of this phenomenon is beyond the scope of this manuscript.

Conclusion

This study investigates the plasmon behavior in the vicinity of Nanowave substrates of various thicknesses, which has been sought after for over 25 years since this idea was first

conceived. To the best of our knowledge, we report the first numerical study of the Nanowave structure in 3-D, taking into account infinite boundaries and interparticle rounding in order to reproduce the experimental behavior as faithfully as possible. Rather than probing the substrate at a single point, the local E-field was averaged over the substrate's top surface, where molecules would adhere, to determine the surface-averaged SERS and thus provide a more realistic study.

For thin metal shells, the Nanowave structure exhibits two plasmons bands in the case of gold, and three in the case of silver. As the shell thickness increases, the long wavelength band vanishes possibly due to the incident field not being able to penetrate to the base of the shell to excite the long-wavelength plasmon. SERS was evaluated by surface-area averaging the E-field. The lower-than-expected average E-field resulted from low surface area ratio of hotspots to flat surfaces, implying that the highest SERS EF is obtainable by concentrating the molecules of interest into the periodic hotspots, where the local E-field is the strongest. Indeed, compared to a maximum E-field enhancement approximating 30 for both silver and gold, when evaluated at a single point in space, the maximum average E-field was merely 5.

Finally, this study provides insight into the appearance of multiple plasmon bands. Specifically for the Nanowave structure, the short-wavelength peak is attributed to the plasmonic coupling at the top of junction (site A), and the long-wavelength peak to the crescent-shaped base of the metal-dielectric function (sites B). By relaxing the periodic boundaries in the x-y plane, a third peak is exhibited in the NIR due to the even more confined structure under incident

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Figure 1. SEM of a typical Nanowave substrate: monolayer of close-packed 100nm silica nanospheres assembled on coverslip, onto which 50nm silver or gold is evaporated: (a) The Nanowave 3D structure is demonstrated by tilting the SEM stage to 45 degrees. The inset depicts an enlarged portion of the Nanowave, where the unit cell employed for numerical simulation is delineated.

Figure 2.

Schematic of the geometry used for theoretical modeling of the Nanowave substrate. The unit cell, delineated in the SEM from Figure 1, is reproduced as a 3-D FEM model comprising 100nm silica nanospheres coated with metal of varying thicknesses. The top view conveys the rectangular unit cell, whose dimensions were selected such as to enclose one complete particle; the infinite extent of the unit cell in the x-y plane is modeled by employing periodic boundary conditions, consisting of PEC's in the x-direction, and PMC's in the y-direction. The incident, x-polarized E-field propagates perpendicular to the Nanowave array in the $-k_z$ direction. The x-z slice through $y = 0$ conveys that the structure is simulated in air and that the computational boundaries in the z-direction consist of PML's that prevent any back reflections of the scattered field onto the structure. The smoothing in 3-D schematic illustrates the method employed to smooth the interstitial space between adjacent nanoparticles. Two orthogonal planes, $x-z$ and $y-z$, describe the flat smoothing of thickness that encircles the entire 3-D junction; this was achieved by forcing a combination of geometrical variables, heights h and radii r , depicted here and detailed in Table 1

Figure 3.

Top and cross-sectional views of the Nanowave models for shell thicknesses 10 — 50 nm, demonstrating the geometrical effect of the inter-particle rounding parameters in Table 1. As the shell thickness increases, the triangular opening between Nanowave particles #1, 2 and 3 decreases (top view), and the junction between adjacent particles (side view) thickens, consistent with experimental observation

Figure 4.

Simulation data of unit cell of Nanowave structure consisting of 100nm silica nanospheres coated with 50nm gold; (a) geometric setup for FEM solving, detailing the 50nm gold coating (red) and the 100nm silica nanoparticles (clear). The PEC, PMC and PML boundaries are all denoted. A projection of the 3-D smoothing between adjacent particles can clearly be perceived on the PMC face in the x-z plane; (b) 3-D isosurfaces of the E-field, $|E_x|$, in the vicinity of the Nanowave structure. The incident plane wave, $\mathbf{E}(\mathbf{r}, t) = E_x e^{j(\omega t + k_z z)}$, is polarized along the x-axis, propagates in the -z direction, has amplitude of 1 and a wavelength $\lambda = 580\text{nm}$. The strongest E-field is confined to the interstitial spaces aligned with the x-polarization direction, making the Nanowave an array of controllable hot-spots. The periodicity of the unit cell is evident by the presence of identical E-field patterns at the x-oriented interstitial spaces that are cut by PEC or PMC boundaries

Figure 5.

Further analysis of the 3D solution of $|E_x|$ in Figure 3(b): (a) Side view projection of the unit cell, depicting that $|E_x|$ is strongest in the junctions formed between adjacent nanoparticles, $|E_x|_{max} 12V/m$, and that for this metal thickness, the field remains confined within the metal shell, not penetrating much into the silica nanoparticles; (b) Top view projection of the unit cell, with white dotted circles delineating the underlying metal-coated silica nanoparticles. For both (a) and (b), identical $|E_x|$ isosurface patterns are generated at the x-oriented interstitial spaces, confirming successful boundary periodicity in both the x- and y-direction. The dimensions of the structures are denoted by labeled axes in both figures.

Figure 6.

Absorption spectra of the Nanowave structures for (a) gold and (b) silver metal shells. The discrete data points represent the calculated values from the simulation, and computed at a small enough λ -interval to capture the rapid variations of the plasmon bands. They are then interpolated using a spline function to smooth out the curves. The gold spectra convey two main absorption bands for the thinner shells 10 — 30nm, and only a hint of a shoulder for the 40nm thickness Nanowave. The 50nm shell has a single distinct absorption band. Silver Nanowaves have two, and sometimes three, absorption peaks for all metal thicknesses.

Figure 7. E-field enhancement at positions defined in the last column of Table 1 as a function of excitation wavelength λ for (a) gold and (b) silver Nanowaves of varying metal thicknesses.

Figure 8. Analysis of the short-wavelength plasmon peak (a) and corresponding E-field enhancement (b) of gold and silver Nanowave substrates, as a function of metal thicknesses.

Figure 9.

Spatial analysis of E of the short-wavelength plasmon peak of gold Nanowaves of varying shell thicknesses. The diagrams are kept to scale relative to each other, clearly illustrating the thickening of the gold shell from 10nm to 50nm. The encircled letters A and B denote locations where E-field enhancement occurs and will be used to simplify the analysis.

Figure 10.

Spectra of the surface-averaged $|\mathbf{E}|$; (a) the top surface of the metal coating (blue) is where molecules would attach and experience the local E-field, and is the surface over which the E-field is integrated to obtain the average E-field over the entire structure for the wavelengths of interest. This is repeated for every shell thickness to yield the $|\mathbf{E}|_{avg}$ spectra for gold and silver in (b) and (c); (b) $|\mathbf{E}|_{avg}$ for the gold nanowaves; (c) $|\mathbf{E}|_{avg}$ for the silver nanowaves.

Figure 11. Spatial analysis of $|E|$ of the long-wavelength plasmon peak of gold Nanowaves for shell thicknesses 10nm , 20nm and 30nm . The diagrams are to scale relative to each other. The encircled letters A and B denote locations where E-field enhancement occurs and will be used to simplify the analysis.

Figure 12.

Metal-coated cylindrical nanowires that extend to infinity in the x -direction, but are periodic in the y -direction: (a) as a generic model, 20nm of metal (red) is deposited onto the 100nm diameter cylindrical wires, and the finite rounding between adjacent wires is kept identical to its corresponding nanowave of equal metal coating, given in Table 1; (b) the top surface of the metal coating (blue) is where molecules would attach and experience the local E -field, and is the surface over which the E -field is integrated to obtain the average E -field, $\langle E \rangle_{\text{avg}}$, over the entire structure; (c) a representative isosurface solution of $|E|$ for the 20nm silver-capped wire @ $\lambda = 510\text{nm}$ (plasmon peak), conveys that the strongest E -field enhancement occurs in the groove and is invariable along the y -direction, as expected.

Figure 13.

Absorption spectra of the Nanowire structures for (a) gold and (b) silver metal shells. The discrete data points, representing calculated values from the simulation, are interpolated using a spline function to smooth out the curves. Compared to the Nanowave structure that exhibits two plasmon bands for both gold and silver, only one plasmon band is excited in the Nanowire structure, for both metals.

Figure 14.

Spectra of the surface-averaged $|E|$ of (a) gold and (b) silver Nanowires, integrated over the blue surface shown in Figure 12(b) for shell thicknesses 10nm to 50nm.

Figure 15.

E-field spectrum of *periodic* v.s. *non-periodic* Nanowave unit cell for 20nm silver Nanowave. The non-periodic structure was achieved by removing the x-axis PEC and y-axis PMC boundaries, extending the computational domain to completely enclose the 7 metal-capped nanoparticles, and enclosing the structure with PML boundaries. The difference is depicted in the schematics to the right of the graph. (Note: the distance between the outer spheres and the PMLs for the non-periodic Nanowave structure is not to scale)

Table 1

Geometrical properties of the Gold and Silver Nanowaves and Nanowires, corresponding to the parameters in Figure 2. The Nanowires are designed with the same parameters as the Nanowaves, except that they extend to infinity in the y-direction. The last column represent the position coordinates at which $\mathbf{E}/$ is measured in to plot the spectra in Figure 6. The measurement points are located in the inter-particle crevices and can be co-registered in 3-D with Figure 5.

Shell Thickness z (nm)	Nanowave					Nanowire Top SA (nm ²)		$ \mathbf{E} $ meas. 1 [x,y,z] coord. (nm)
	r_{metal} (nm)	r_{SiO_2} (nm)	h_{metal} (nm)	h_{SiO_2} (nm)	w (nm)	δ (nm)	Top SA (nm ²)	
10	9.0	9.0	0	10	18.0	2.0	3.02×10^{-14}	2.44×10^{-14} [50,0,22]
20	11.0	11.0	6	14	22.0	2.5	3.20×10^{-14}	2.38×10^{-14} [50,0,33]
30	12.0	12.0	16	14	24.0	3.0	3.53×10^{-14}	2.35×10^{-14} [50,0,45]
40	13.0	13.0	26	14	26.0	3.5	3.83×10^{-14}	2.33×10^{-14} [50,0,55]
50	13.5	13.5	36	14	27.0	4.0	4.13×10^{-14}	2.31×10^{-14} [50,0,65]