

Gold-Coated Fumed Silica Monolayer for Efficient Large-Scale SERS Substrates with High Density Nanogaps

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Abstract:

Surface enhance Raman spectroscopy (SERS) capacitates applications in chemical and biological sensing and detection. It provides highly-sensitive sensing tool able to detect even at single molecule level. Therefore, large-scale fabrication of SERS substrates becomes an increasing interest, especially for those with high sensitivity at near-infrared (NIR) spectrum. In this study, we propose a highly porous silica-gold core-shell network structure as a possible efficient NIR-active SERS substrate with high density nanogaps to induce strong field localization. This structure can be simply produced in large scale using ultrathin gold layer deposition on a fumes silica nanolayer template. The localized surface plasmon resonance (LSPR) properties of such structure were investigated numerically by solving Maxwell's equation performed in COMSOL Multiphysics®. The randomized geometry of gold-coated fumed silica was generated using an algorithm with code written in a built-in model method. The plasmonic resonance was observed through absorption spectrum as well as the localized electric field in the SERS structure. It was found that the proposed plasmonic structures provide large SERS enhancement factor with high spatial density of hot spots, particularly at the nanogaps. Furthermore, the plasmon resonances of most geometry cases are broadband at NIR range.

Keywords: Surface Enhance Raman Spectroscopy (SERS), plasmonic resonance, large-scale SERS substrate, gold-coated fumed silica, high density nanogaps

1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is a surface-sensitive technique that makes use of rough metallic surfaces or nanoparticles, such as gold nanospheres, or silver nanoprisms, to substantially enhance Raman scattering signal from trace molecules adsorbed on them. This label-free and non-invasive detection technique has great advantages, ideal for a

wide variety of applications such as biological sciences, where SERS can be used to analyze medical materials [1], biological and organic materials [2]. This technique is sensitive enough to afford detection at single molecule level. For SERS mechanism, rough metal surface is required to interact with an incident electromagnetic wave and induce strong field localization within a sub-wavelength dimension. The squeeze of electromagnetic wave or so-called 'hot spot' is generated by a phenomenon called localized surface plasmon resonance (LSPR), where the conduction electrons coherently oscillate in response to the driving electric field of the incident wave [3].

In recent years, the uses of laser beam at near infrared (NIR) wavelengths for SERS gains the increasing popularity. The major advantage of performing SERS in the NIR region is the reduction of fluorescence background from the sample that can swamp out the Raman features. By far, the most popular Raman excitation wavelength is 785 nm as it provides good balance between Raman cross-section and low fluorescence level. However, some other NIR wavelengths, e.g. 830 nm or 1064 nm can be found for works in which further fluorescence suppression is required. SERS substrates, active in NIR region, generally involve new classes of plasmonic materials, e.g. metal oxides, or chalcogenides. Nevertheless, common metals like silver or gold can also support NIR plasmon resonance when their size has high aspect ratio, e.g. nanorods or with core-shell structures [4].

It is also known that the electric field near plasmonic nanoparticles becomes intensified at the sharp edges of the nanoparticles. Therefore, SERS intensity obtained from star-shaped nanoparticles is much higher than spherical particles due to lightning rod effect [5]. However, it is normally difficult to fabricate such metallic nanoparticles with sharp tips. Another approach employs nanogaps within metal nanostructure as a good strategy to generate highly enhanced electric field intensity [6]. Besides, this

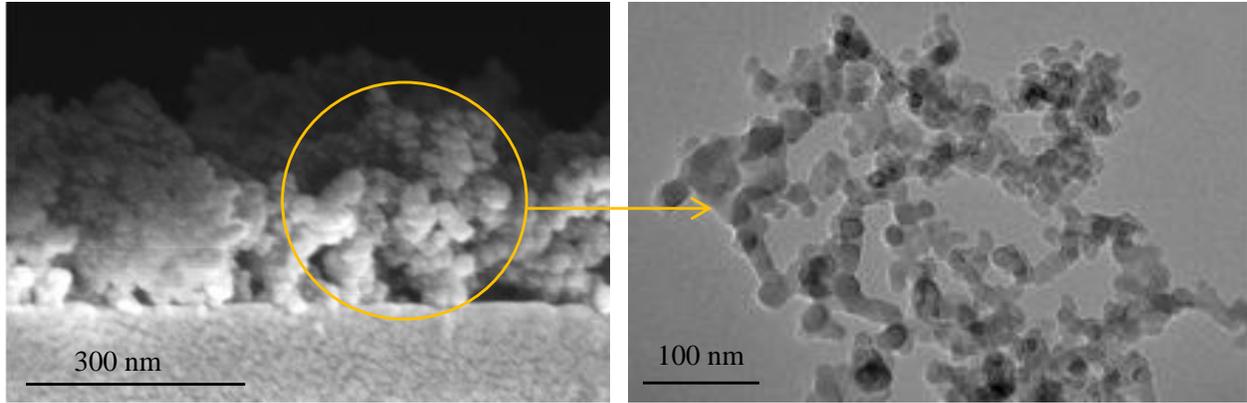


Figure 1. A monolayer of fumed silica composed of 3D random network structure, which provides intrinsically high density of nanogaps.

nanogap can be more cost effective to fabricate large scale SERS substrates, as it can be simply formed by nanoparticle assembly, or the use of particles with intrinsic nanogaps as a template for metal coating.

Fumed silica is a class of nanomaterials with highly porous structure and high density nanogaps, composed of primary particles assembled in a gel-like 3D network. It is also a low-cost nanomaterial that provides very high specific surface area up to 400 m²/g. The primary particle is virtually spherical in shape with diameter 10-20 nm [7]. Fumed silica has low refractive index as it contains large percentage of air in its structure. This low index will push electric field extension toward the surface. Furthermore, fumed silica particles can be easily formed a nanolayer by using, e.g. layer-by-layer technique as shown in Figure 1, ready for gold deposition to produce silica-gold core-shell SERS templates for NIR Raman spectroscopy. The fabrication of gold shell can be done either by physics vapor deposition or by solution processing [4].

In this work, we used COMSOL Multiphysics® to perform electromagnetic wave simulation to investigate LSPR properties of SERS substrate, formed by highly porous silica-gold core-shell network structures. The unique geometry of fumed silica core coated with thin gold shell was created by algorithm implemented in a model method coding. The effects of geometric parameters, including silica particle size, gold thickness and particle density, on the resulting plasmonic resonance behaviors were studied, as well as the field enhancement at the nanogaps.

2. Theory

Localized surface plasmon resonance is an electromagnetic mode that strongly confides near the

interface of metallic nanoparticles and the surrounded dielectric medium. The distribution of electric field confinement associated with plasmon resonance can be determined by the Maxell's wave equation, which is expressed as,

$$\nabla \times \mu_r^{-1}(\nabla \times \mathbf{E}) - k_0^2 \left(\epsilon_r - \frac{j\sigma}{\omega\epsilon_0} \right) \mathbf{E} = 0, \quad (1)$$

where σ is the electrical conductivity, μ_r and ϵ_r are the relative permeability and the relative permittivity (or dielectric function) of material respectively. The time-independent term of the \mathbf{E} field is defined as $\mathbf{E}(x, y, z) = \tilde{\mathbf{E}}(x, y) e^{-jk_z z}$. Here, we consider for time-harmonic electromagnetic wave oscillating at frequency ω . The optical medium is assumed non-magnetic, such that the relative permeability can be approximated by $\mu_r \approx 1$. For metallic nanoparticles with $\sigma \neq 0$, the term $\epsilon_r - j\sigma/\omega\epsilon_0$ can be regarded as a complex dielectric function of the medium, that is [8]

$$\tilde{\epsilon}_r = \epsilon_r - \frac{j\sigma}{\omega\epsilon_0}. \quad (2)$$

According to the Drude-Lorentz model of electrical conduction, where both bound and free electrons contribute to the optical properties of a general metallic nanoparticle, the complex dielectric function is given by the following equation [9],

$$\tilde{\epsilon}_r(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 - j\gamma\omega} + \frac{\omega_p^2}{\omega^2 + j\gamma_d\omega}, \quad (3)$$

where ϵ_∞ is the bulk dielectric function, ω_p is the plasma frequency of free electron gas, and γ_d is the damping constant of bulk metal. Here, γ is the modified damping constant, which is dependent on the geometry of the metallic nanoparticle, i.e.

$$\gamma = \gamma_d + A \frac{v_f}{a_{eff}}, \quad (4)$$

where v_f is the Fermi velocity of electron in metal and A is the geometrical parameter. For a core-shell system, a_{eff} represent the effective radius.

At optical frequency, however, the value of $\tilde{\epsilon}_r$ can be experimentally determined from the complex refractive index $\tilde{n}(\omega) = n(\omega) + j\kappa(\omega)$ of a medium. Sometimes, it is more convenient and more accurate to give the description of dielectric function for metallic nanoparticles throughout $\tilde{n}(\omega)$. The relationship between the complex refractive index and the complex dielectric function is given by $\tilde{n} = \sqrt{\tilde{\epsilon}_r}$. For a dielectric medium surrounded metallic nanoparticle, it is assumed lossless; therefore, the imaginary part of the refractive index vanishes.

By solving the Maxwell's wave equation for a plasmonic medium, the localized electric field distribution can be determined. In general, surface plasmon resonance squeezes electromagnetic wave energy within a very small mode volume, which greatly increases the local electric field strength. The targeted analyte molecules that adsorb at metallic nanoparticles surface will be excited by the intense incident field, giving rise to significantly enhanced Raman signal. Furthermore, the electric field of the output Raman component is also enhanced as well by the same effect. The SERS enhancement factor can be approximated by the following equation,

$$EF \cong |E(\omega)|^2 |E(\omega')|^2, \quad (5)$$

where $E = E_{loc}/E_{inc}$ (E_{loc} is the amplitude of local electric field at the hot spot, E_{inc} is the amplitude of the incident field), ω is the frequency of the incident lights, and ω' is the Stokes-shifted frequency. The plasmon resonance is slowly-varying in response to the frequency within typical Raman shift range; thus, it can be assumed that $|E(\omega)| \cong |E(\omega')|$. With this assumption, the SERS enhancement factor follows the so-called $EF \sim |E|^4$ law.

3. COMSOL Multiphysics® Simulation

In this section, we implemented 2D numerical simulation of electromagnetic wave propagating in a highly porous structure of fumed silica template homogeneously coated by a gold nanolayer. To simplify the creation of such geometry, we assumed that the desired structure is equivalent to the connecting network of silica-gold core-shell nanospheres. We introduced an algorithm, coded using a built-in feature of model methods in COMSOL to generate silica-gold core-shell primary particles and connect them to form a gel-like network structure. The whole particles were placed in a rectangular domain with area $2600 \text{ nm} \times 300 \text{ nm}$ representing a cross-sectional regime of SERS porous thin film. The silica core sizes from 10-20 nm, gold shell nanofilm thickness from 1-5 nm, and particle fill factor between 0.1-0.5 were used as input parameters to generate the geometries in this study.

Figure 2 displays the schematic of the developed algorithm to generate a highly porous SERS substrate with silica-gold core-shell nanospheres random network. The total number of particles to be created is determined from the given fill factor, defined as the ratio of all particles' area and the rectangular regime area. It begins with the generation of an initial core-shell particle with given core size and shell thickness, put at a random position inside the regime. To account for particle aggregation in fumed silica, the next core-shell particle must be randomly connected to one of the existing particles. To prevent the overlapping of silica cores, the distance between the centers of any adjacent silica particle should be equal to its diameter, i.e. silica cores make a point contact to each other. Also, the whole particles of must be placed completely inside the rectangular regime. A typical geometry is illustrated in *Figure 3*.

The plasmonic structure was set in air, and modeled using the COMSOL Wave Optics module with electromagnetic wave propagation in frequency domain. It solved for the in-plane electric field components. The electromagnetic wave was launched vertically from port 1 at the top boundary, exiting port 2 at the bottom. The sides were set as scattering boundaries. The SERS enhancement factor, e.g. $|E|^4$, mapping was evaluated to visualize the hot spots created by the plasmonic structure. From the input wave power at port 1 and the output wave power at port 2, the absorption spectrum of SERS substrate was also determined for a wavelength range swept from 300 nm to 1500 nm. Another study was done by solving mode analysis for planar structure.

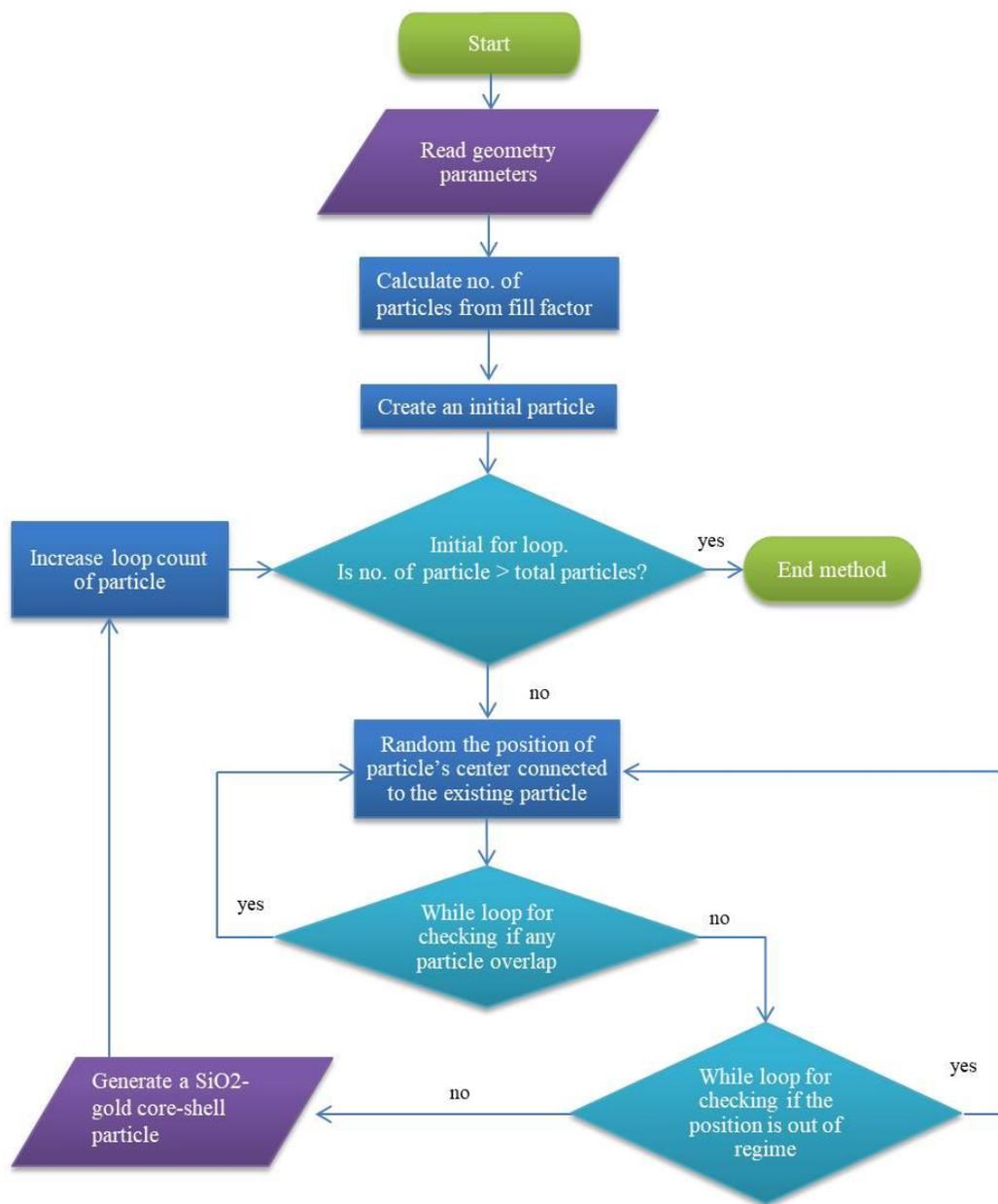


Figure 2. Flowchart of the model method with algorithm to create gold-coated fumed silica structure

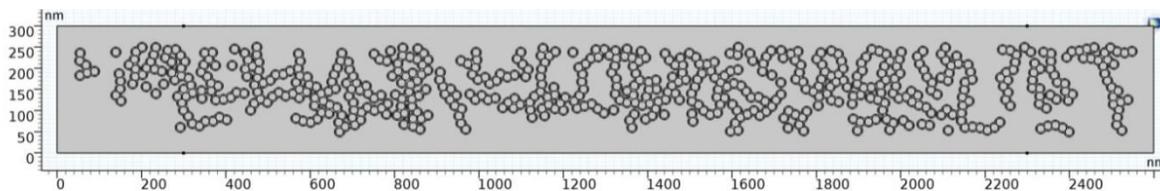


Figure 3. The geometry of gold-coated fumed silica network in a rectangular regime as SERS substrate

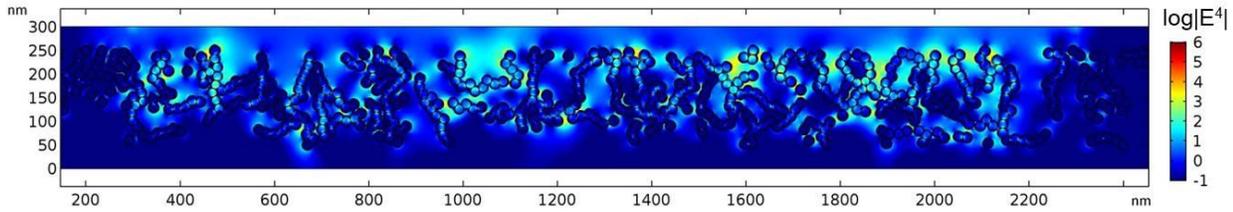


Figure 4. The simulation result shows $|E|^4$ distribution on a SERS substrate, excited by a vertical wave incident.

4. Results and Discussions

The simulation results are elaborated in this section. The in-plane components of electric field were solved for various conditions of SERS substrate, and the enhancement factor $|E|^4$ was determined as shown, for instance, in Figure 4. It was found strong localization of electric field around the primary particles and the plasmonic field is even stronger at the nanoscale gaps between clusters. Those hot spots correspond to maximum SERS enhancement factor. The wave is incident normally from the top which experience plasmonic resonance, leading to strong absorption and scattering along the propagation distance to the bottom. Therefore, the field enhancement factor near the top surface is greater than that inside the fumed silica film.

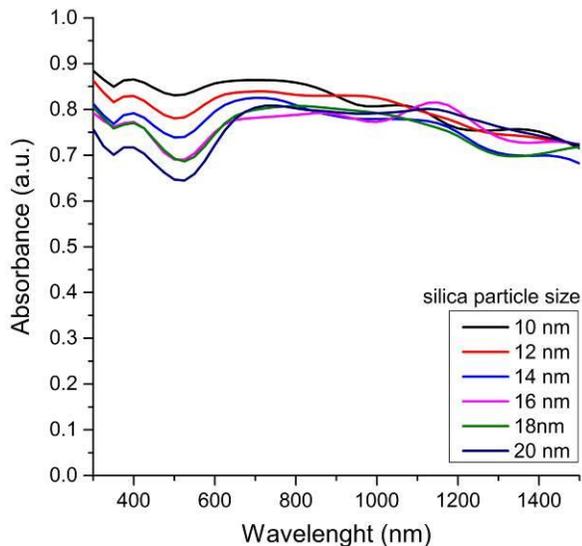


Figure 5. Absorption spectra of SERS substrate with various silica primary particles sizes.

The spectral behaviors of plasmonic resonance upon silica primary particles sizes were investigated for particle diameter between 10 nm and 20 nm. All silica size conditions are coated with uniform gold layer with constant thickness of 3 nm. The simulation spectra are shown Figure 5. In general, all cases of silica primary

particle sizes yield broadband and strong plasmonic resonance covered for the entire UV, visible and near infrared spectrum. We attribute this feature to the random configurations of the nanoparticle cluster, which give rise to different size of nanogaps for both inter and intra particle chain networks. Furthermore, the silica core does not play the active role for plasmonic properties of the structures. However, there is an observable difference in the absorption spectrum, where the larger silica particle sizes result in slightly weaker plasmonic resonance. The change of silica particles size slightly changes the geometry of the coating gold layer that marginally perturbs the plasmonic behavior.

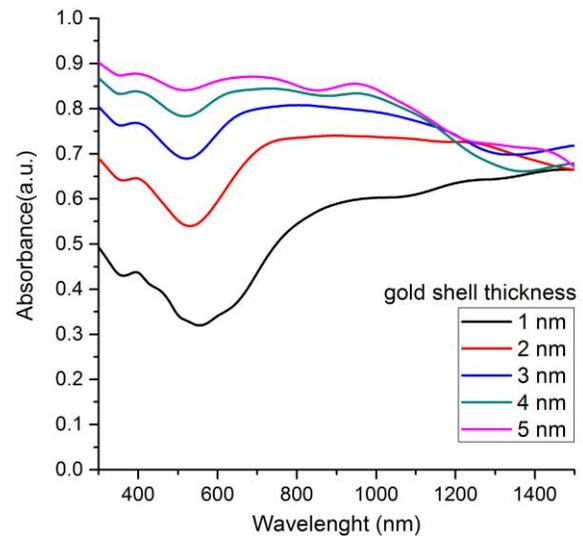


Figure 6. Absorption spectra of SERS substrate with various thickness of coated gold layer.

The effect of gold shell layer on fumed silica template was also numerically studied for silica core particles of fixed primary size at 18 nm, and the results are displayed in Figure 6. It is clearly found that the gold shell layer thickness has stronger effect on the plasmonic resonance frequency when compared with the effect of silica core size. The resonance wavelength tends to shift further toward near infrared region for thin layer of gold coating.

The increasing gold thickness leads to greater absorption for broadband spectrum range.

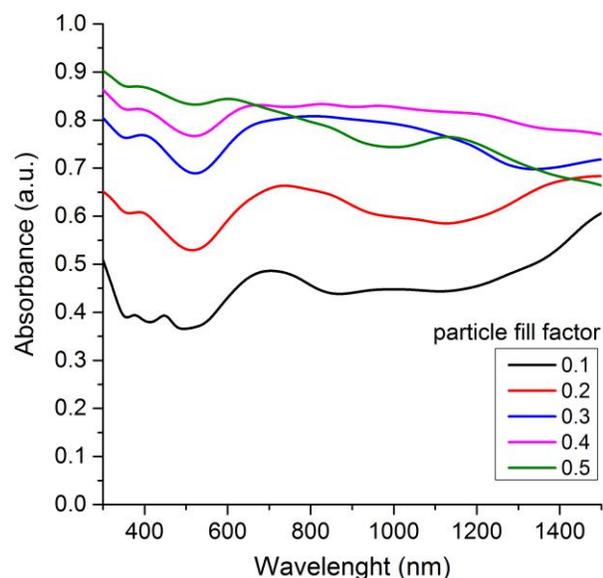


Figure 7. Absorption spectra of SERS substrate with various packing density of silica particles.

We also investigated for the effect of the packing density of fumed silica template on the resulting plasmonic resonance wavelength. In this particular simulation, the silica core size was set at 18 nm with gold shell layer thickness of 3 nm. The particle density was quantified through a 2D fill factor. As shown in Figure 7, the increasing particle density, in the range 0.1 to 0.4, generally raise the plasmonic strength and hence absorption, as the particle gaps becomes closer. However, at the high fill factor value of 0.5, the plasmonic effect witnesses a modest drop especially at NIR region. As the particles are more compact and highly aggregated, the effective particle radius reaches the bulk regime so the damping constant. Therefore, the plasmonic resonance at the studied wavelength range is not satisfied. In fact, it should have an optimum particles density that maximizes the number of nanogaps to support strong field localization. In this case, the fill factor of 0.3-0.4 are among the best particle densities which yield good plasmonic effect.

In addition, mode analysis simulation was also performed to calculate for the eigenmodes of an electromagnetic wave propagating perpendicularly to the screen and through SERS structure. The enhancement factor associated with an eigenmode is shown in Figure 8. There is no absorption or scattering loss along the propagation distance for this configuration, so that the strong plasmonic resonance can be observed. Particularly, the structure shows high SERS

enhancement factor up to 10^7 , and high density of nanogaps that accommodate much enhanced optical field. This high density of plasmonic hot spots in the SERS substrate is very favorable for Raman signal boost as it increases the probability that the analyte will fall into the hot spot region. Furthermore, as the structure is highly porous and the silica particles have low refractive index, the electric field extends more to the surface and the surrounding air medium.

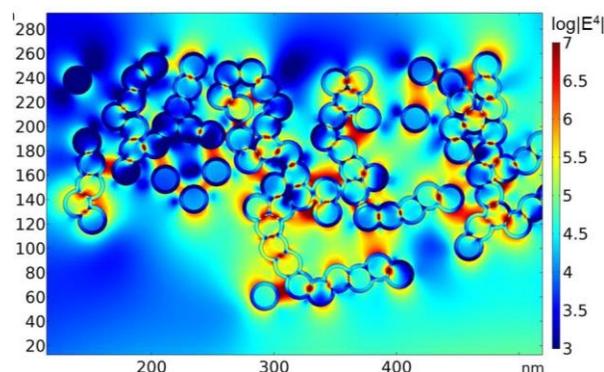


Figure 8. SERS enhancement factor map shows strong field localization at high density of nanogaps.

5. Conclusions

In summary, we performed simulation to investigate the potential of SERS substrate with high nanogap density made from silica-gold core-shell random network structure inspired by the structure of fumed silica particles. The numerical results confirm that most of the geometry structures support strong LSPR in the NIR spectrum range. The layer thickness of the gold shell has more profound effects on the resulting plasmonic resonance, when compared to the silica core size. The particle density is also an important parameter affecting the strength of plasmonic resonance as it associates with nanogap dimension. Lastly, the random plasmonic structure provides high SERS enhancement factor up to 10^7 with high hot spot density and electric field extension.

6. References

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7. Acknowledgements

This work was funded by Development and Promotion of Science Technology Talents (DPST) Research Grant. We also would like to thanks the NanoPhotonics research group for continual supports.