FINITE ELEMENT METHOD BASED INVESTIGATION OF SUBSTRATES EFFEKT ON SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Abstract:

Surface-enhanced Raman spectroscopy (SERS) is a widely used method for the detection of molecules of environmental concern such as pesticides. One of the key factors to achieve high sensitivity in SERS is the high electromagnetic enhancement formed between plasmonic nanoparticles which is dependent on the wavelength used, shape, size, distance, and type of nanoparticles. In this regard, the scope of this paper is to investigate the enhancement factor achieved between adjacent silver or gold nanoparticles of different geometrical configurations by changing the shapes and sizes of the particles. Simulations based on finite element methods (FEM) were carried out to investigate the effect of different excitation laser wavelengths. The obtained results show the dependency of the enhancement factor, size, type of nanoparticles, excitation wavelength of the laser, dielectric properties of the surrounding medium and the type of substrate used.

Keywords: SERS; FEM; plasmonics; metals; COMSOL

1. INTRODUCTION

The currently available conventional measurement methodologies for the detection in biomedical or environmental applications are aligned toward chromatography, mass spectroscopy, capillary electrophoresis, or ELISA [1]. These methods, however, require complicated measurement setups and qualified personnel at the expense of time. In this regard, electrochemical sensors have been a viable alternative to the above methods as they are sensitive, portable, easy, and fast. However, specificity in complex matrices is one of the major hurdles to overcome for electrochemical sensors [2]. Surface-enhanced Raman spectroscopy (SERS) has been a promising vibrational spectroscopy technique to acquire the molecular fingerprint of the molecules of interest. SERS is based on the amplification of weak Raman intensity by using plasmonic nanoparticles. The phenomena was first observed by Fleischmann *et. al.* wherein the Raman signal was amplified by 10^6 times on a rough silver surface [3]. The enhancement could be explained by the excitation of localized surface plasmon [1][4] which is dependent on the type of wavelength, nature of substrate, size, shape of the nanoparticles, and the type of surrounding media. The higher the enhancement factor, the better the sensitivity of SERS measurement. However, the lack of quantitative information about the contaminant is one of the issues with SERS.

In this paper, FEM simulations have been implemented to investigate the role of wavelength used, size and shape of nanoparticles on the enhancement factor achieved between the nanoparticles. Typically, finite difference time domain (FDTD) is used for solving the electromagnetic equations and resolving the gradients. However, FDTD simulations require a large computational time compared to FEM due to the extremely fine mesh sizes required to resolve the electric field gradients near to the nanoparticles [5]. Considering the computational expenses, FEM was selected for the simulations within this paper. Circular shapes were considered with different geometry configurations. The current work in the simulations related to SERS have been largely focussed on the effect of size and shape of nanoparticles on the spectral sensitivity and investigations on the effect of surrounding medium on the spectral sensitivity and the formation of new peaks as a function of the refractive index of the surrounding medium has been very limited. In addition, the role of substrate in subsequent enhancement between the nanoparticles has not been elaborated previously. The work would enable the design of experiments in such a way that the SERS enhancement could be maximized by selection of appropriate wavelength and size of the nanoparticles and aid in achieving high sensitivity towards environmental contaminants such as pesticides.

2. DESCRIPTION OF THE FEM MODEL

COMSOL Multiphysics, a finite element software was used for the simulation of SERS phenomena. The physics was implemented through a wave optics module which solves the equation for the electromagnetic field. Frequency domain analysis was carried out at different wavelengths for the developed model. All the simulations were carried out in 2D unless stated otherwise.

Figure 1 shows the geometry of the model simulated in COMSOL. As can be seen in the enlarged view, the nanoparticles were modelled as circles with diameters ranging from 10 to 100 nm. The geometry of nanoparticles is considered as circles instead of spheres for the sake of simplicity and further the achieved results in 2D for circles can be extrapolated along the three dimensions in 3D when modelled as spheres. The geometry is also termed as a dimer. The dimers were enclosed in a perfectly matched layer (PML) domain in order to absorb all the electromagnetic radiations in order to avoid any reflections back toward the nanoparticles that may interfere with the scattered radiations. Manual meshing with size 1/5 times the wavelength was assigned to the nanoparticles so that the electromagnetic field components are well resolved. PML meshed with normal size distribution and the same mesh was swept to the outer boundary with the distribution of five elements. Appropriate thickness was selected for efficient absorption of the scattered fields without any spurious reflections back to the domain of interest.
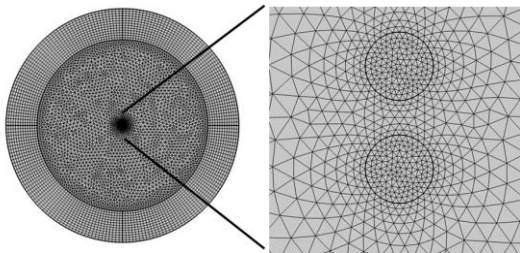

Figure 1: Schematic of the modelled geometry with the meshing taken from COMSOL

The laser beam was approximated as a plane wave and the beam was polarized in y-direction and the direction of propagation was assigned from -x to +x. The wave optics module solves equation (1) for computing the scattered electric fields everywhere inside the modelled geometry.

$$\nabla * (\mu^{-1}\nabla * E) - \omega^2\varepsilon_c E = 0 \qquad (1)$$

Where ε and μ are the relative permeability and permittivity, ω is the angular frequency and E is the total electric field. The polarization and propagation direction of the electromagnetic wave substantially affect the enhancement factor between the nanoparticles. The effect is demonstrated in figure 2 wherein the plane wave is excited with polarization perpendicular and parallel to the orientation of nanoparticles.
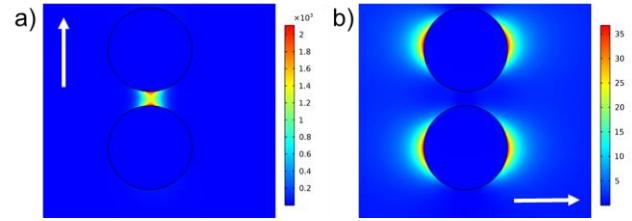
Figure 2: The effect of enhancement factor and formation of hotspot on a) parallel and b) perpendicular polarization of the electromagnetic wave.

As can be seen, from figure 2b, the polarization perpendicular to the orientation substantially reduces the enhancement factor and further the hotspots are not created between the nanoparticles, which is of paramount importance for detection.

The size of the nanoparticles plays a substantial role in the enhancement factor observed between the nanoparticles. Figure 3 shows the plot of the enhancement factor as a function of different sizes for gold nanoparticles across different excitation wavelengths. The nanoparticles were separated by a distance of 10 nm and the size of the nanoparticles varied from 10 to 50 nm. The enhancement factor is considered as the fourth power of the normal electric field (normE⁴) as the incident electric field and scattered field are both enhanced in the vicinity of the nanoparticles [6]. As can be seen, in figure 3, the enhancement factor increases as the size of the nanoparticles increases. The reason could be attributed to the increase in presence of plasmons as the size of the nanoparticles increases. Further, the enhancement factor is centred around 540 nm for gold nanoparticles of different sizes which are in accordance with the previous studies [7-8]. However, the increase in the enhancement factor is not high as the size increases due to the surface effects which arises due to the size and the distance between the two adjacent nanoparticles.
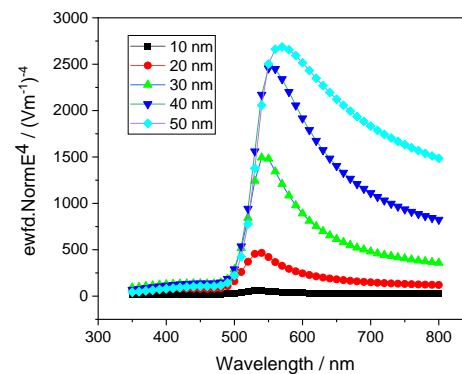
Figure 3: Plot of the enhancement factor of gold nanoparticles with different sizes as function of wavelength
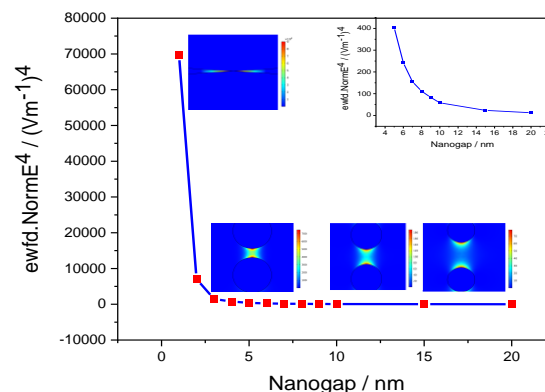
Figure 4 shows the images of the hotspots formed between two gold nanoparticles of different sizes and the distance of 10 nm between them. As can be seen, the intensity of hotspots is very less for smaller sizes at a distance of 10 nm. However, as the size increases, due to the large surface area that creates a confined space between the nanoparticles, leading to high intensity of hotspots. It can be concluded that the larger the size of the particles, the density of the particles on the surface will be higher to obtain a better enhancement factor between the particles. Further, as the size increases the position of the hotspots shifts to the outer surface of the nanoparticles as observed at 50 nm which would enhance the detection capability as the molecule of interest does not need to be present precisely between the nanoparticles and would further provide valuable information about surface adsorption of the molecules.
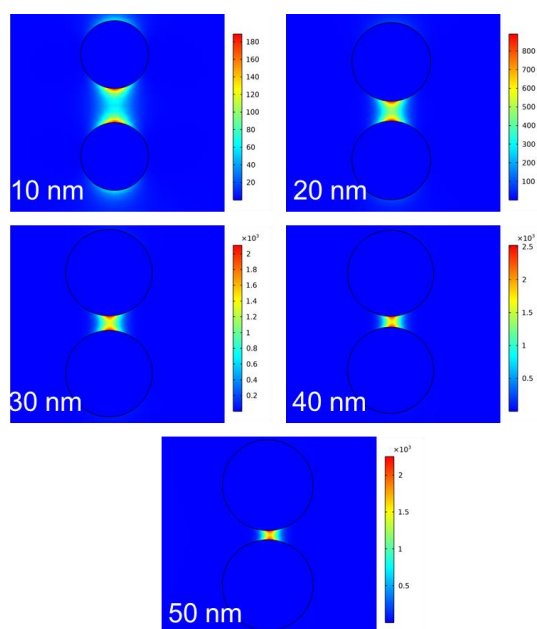
Figure 4: Images of the hotspots formed between the nanoparticles and the corresponding scale of the electric field enhancement

Figure 5 shows plot of the electric field enhancement for gold nanoparticles of 10 nm radius as a function of the nanogap between the two nanoparticles. The formation of hot spots in between is not visible when both the nanoparticles touch each other. However, the enlarged view shows the hotspots are created at the sides of the spheres with a very high enhancement factor. Further, the enhancement factor is reduced considerably as the distance between the two nanoparticles increases due to the weakening of the plasmonic interaction. The inset shows the reduction from 5 nm to 20 nm and the images show the hotspot formed between the nanoparticles as function of distances. At very large distances such

as 10 to 20 nm, the enhancement is considerably lower and the surfaces with such distribution are less suitable for the detection of very low concentrations of molecules.

Figure 5: Electric field enhancement as function of the distance with the corresponding images of the hotspots and inset shows the reduction in enhancement from 5 to 20 nm

Apart from gold, silver nanoparticles have also been extensively used for SERS-based detection of molecules. Herein, we investigated the effect of size of silver nanoparticles as function of wavelength on the enhancement factor. As can be seen from figure 6, the localized surface plasmon resonance occurs at around 350 nm for a size of 10 nm. The resonance and indirectly the enhancement factor shifts slightly to higher wavelength (360 nm) as the size increases to 20 nm. In addition, upon further increase in the size, the enhancement factor reduces, and the resonance shifts to higher wavelength (370 nm) unlike gold nanoparticles wherein the size and enhancement factor are directly proportional to each other. An increase in enhancement factor is observed at high wavelengths starting from a particle size of 30 nm and a very broad peak could be observed for a particle size of 50 nm at around the wavelength of 550 to 600 nm. The unique behaviour of silver nanoparticles could be attributed to the interaction of the electric field with the nanoparticles. As the particle size is comparatively much smaller than the wavelength, below 30 nm, the electrons experience a uniform electric field. In the contrary, as the size increases, the nanoparticles experience non uniform electric fields leading to red shift of resonance peaks and broadening of the peaks [9]. Further, the difference in resonance spectra for gold and silver nanoparticles is due to the overlap of surface plasmon resonance of silver nanoparticles with the interband transitions at around 350 nm [10-11]. In the case of gold nanoparticles, the overlap is very minimal leading to a broader peak at higher wavelengths compared to silver nanoparticles. It can be concluded that silver nanoparticles show high spectral sensitivity with size due to its high plasmon resonance and the

formation of multiple peaks are observed at large particle sizes due to the occurrence of multipolar excitations [9] in silver as compared to gold nanoparticles.
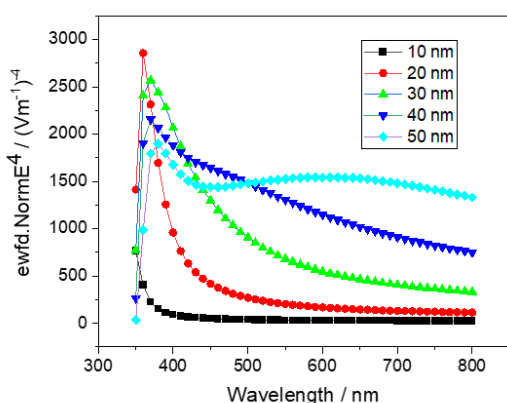
Figure 6: Plasmonic resonance and enhancement of silver nanoparticles at different sizes as a function of wavelength.

The detection by SERS is influenced by changes in the refractive index of the surrounding medium depending on the type of analyte molecules present in the sample. The changes in the refractive index of the surrounding medium change the plasmonic properties of the metallic nanoparticles. Figure 7 represents the changes in the plasmonic resonance as function of changes in the refractive index of the surrounding medium from 1 to 3 for 30 nm gold dimers. As can be observed from figure 7, the peak at 540 nm for refractive index 1 is present at 1.5. However, the peak at 540 nm is sharper and higher order components of resonance occurs at 610 and 700 nm. Further increase in refractive index to 2 leads to diminishing of the peak at 540 nm and the enhancement factor increases at 640 and 700 nm. As the refractive index increases even further, the peak at 640 nm becomes smaller and at 700 nm is enlarged. At refractive index 3, the peak at 640 nm is completely diminished and new peaks are formed at much higher wavelengths in the infrared regime. The changes in the plasmonic behaviour leads to the red shift and formation of multi order component peaks and extinction of the lower order peaks for gold dimers as refractive index of the surrounding medium increases.

As the refractive index changes, the dielectric properties of the medium change making it more polarizable which attenuates the electric charge on the surface of metallic particles. This attenuation leads to a reduction in restoring force which leads the resonance to occur at lower frequency or higher wavelengths.
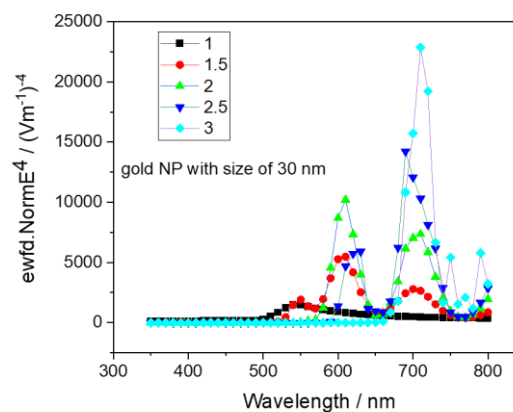
Figure 7: Plot showing the dependency of the enhancement factor and plasmonic resonance on the refractive index of surrounding medium

Apart from the type, size, distance and surrounding medium, the substrate used plays a vital role in the SERS enhancement factor. Figure 8 shows the electric field enhancement for the gold dimers on gold and graphite-based substrates. As can be seen, the gold substrates create a pathway for higher enhancement compared to graphene-based substrates in between the dimers. Further, the red shift in the peak position is observed for gold substrates and higher order peaks are present at approximately 700 and 800 nm for the gold substrates. Further, the peak at 540 nm for dimers suspended in air is red shifted for both substrates. The reason could be attributed to the propagation of evanescent wave on the surface of gold substrate due to the laser excitation which creates a plasmonic coupling between the nanoparticles. However, the enhancement achieved with the dimers suspended in air is quite higher than the dimers present on the substrate.
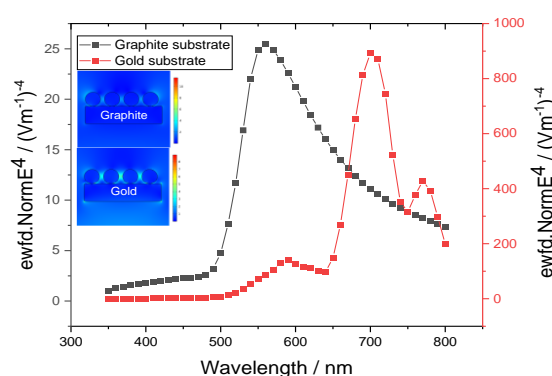
Figure 8: Images showing the enhancement of gold nanoparticles on gold and graphite substrates

3. SUMMARY

The importance of the nanoparticle size, type, distance, the dielectric properties of the surrounding medium and excitation wavelength in the plasmonic enhancement have been investigated. For gold nanoparticles, the enhancement of the electric field increases as size increases. In contrast, for silver nanoparticles, the enhancement increases up to 20 nm and a further increase in size leads to reduction and the enhancement at higher wavelength increases. Further, at 50 nm for silver nanoparticles, a broad peak is formed at around 600 nm. The distance between the nanoparticles and the corresponding enhancement has been investigated and it has been found that the enhancement reduces as the distance between the particles increases due to the low level of plasmonic interaction. The effect of changes in the refractive index of surrounding media showed that higher refractive index leads to red shift of the plasmonic resonance and the formation of peaks related to higher order components. The results demonstrate the effect of different parameters on SERS enhancement and appropriate wavelength can be selected based on the developed SERS substrates by surface morphology, nanoparticle type, size, and shape characterization to improve the sensitivity of the measurement for the detection of contaminants at very low concentrations.

4. REFERENCES

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