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Engineering Hotspots in an ESP-LSP Configuration for Ultra-high SERS Enhancement based Sensors

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Abstract: The critical importance of inter-particle gap on SERS enhancement was established both theoretically and experimentally to achieve enhancement of 10^{10} in an ESP-LSP configuration. Highly sensitive detection of glycerin was presented as model sensing.

OCIS codes: 240.6695, 250.5403, 260.6970, 280.4788

1. Introduction

Plasmons are the quanta of longitudinal oscillations of free electrons in free electron rich materials, such as metals or some semiconductors. Based on the dimensions of the metal and the configuration of the structure, various kinds of plasmonic excitations are feasible. For example, plasmons at an interface of a metal surface and a dielectric medium are called propagating or extended surface plasmons (ESPs), while those in subwavelength metallic nanoparticles are called localized surface plasmons (LSPs).

Several attempts have been made to study the coupling between ESPs and LSPs [1, 2]. Most of the efforts in studying such configurations have been towards exciting ESPs via LSPs excitation [3]. The configurations of metal nanoparticles (MNPs) separated by few nanometers from a metal film were solved as a mirror image problem and the hotspots were considered to lie in between the NP and its mirror image [4]. These studies did not consider the excitation of ESPs, which requires matching of the wave vector of the incident light to that of the ESPs. Some groups did report the excitation of LSPs via ESPs coupling, as it was understood very recently that this mode of coupling has potential for ultra-high electromagnetic enhancements [5, 6]. None of the studies available in literature could reach the optimum conditions of LSP excitation using ESPs for ultra-high electromagnetic enhancements. Moreover, the inter-particle distance (IPD, ' d ') between the NPs plays a critical role in ESP-LSP coupling and needs more serious observations. Very recently, our group realized the excitation of LSPs via ESPs to achieve ultra-high enhancements of electromagnetic (EM) fields [7]. To realize such a coupling, one needs to excite ESPs to couple them to LSPs under appropriate conditions. This was achieved by exciting ESPs in a Kretschmann-Raether (K-R) configuration, and coupling these ESPs to the LSPs of MNPs placed in the vicinity. The space between the continuous metal film and the metallic nanostructure is called hot spot, as the EM field in this space is manifold to that of the incident light. In a preliminary work from our group [7], surface enhanced fluorescence (SEF) signal from Rhodamine 6G was demonstrated in hotspots formed between 40 nm AuNPs and a continuous silver (Ag) film in a K-R configuration. Even though the concept of ultra-high field enhancement was proven, the optimum enhancement limit was not yet achieved. Further, precise quantitative experimental confirmation of the findings of the simulations was a challenge as the determination and control of the number of molecules in the hot spot was difficult. Furthermore, the SEF signal is influenced by bleaching and other interactions between the fluorophore and the metal. Hence, the configuration needed more investigation, which we studied both theoretically and experimentally using SERS; because, it is now well established method to represent the EM enhancement. To make it more precise and controlled, simulations were performed to optimize the size and IPD, ' d ' of AuNPs for maximum field enhancements. Further, the ultra-sensitive detection of glycerin was demonstrated as a model sensing application.

2. Experimental Setup

Fig. 1(a) represents a K-R configuration schematic of the excitation of LSPs via ESPs, while the molecule of interest sandwiched in between the metal film and the NP. In a K-R configuration, the base of a high index prism is coated with a thin layer of metal and the light incident at the interface of the metal and surrounding medium through the prism excites ESPs under phase matching condition. Now, when metallic nanostructures (such as nano-particles, -holes, or -rods) are kept in the neighborhood of the metallic film, at certain favorable conditions, the ESPs may couple to LSP modes of the MNPs, which leads to huge EM enhancement, called hot spot. A molecule placed in the

Fig. 1. Schematic of the (a) ESP-LSP excitation and hotspots, (c) experimental setup for SERS measurements; (b) SEM image of Ag/4-ATP/80nmAuNP configuration (inset shows the IPD evaluation using ImageJ software from NIH [8])

hotspot responds with enhanced spectroscopic signals. The SERS signals from such hotspots were studied using an experimental setup, whose schematic is drawn in Fig.1(c). A SF11 glass substrate coated with 47 nm of silver film was immobilized with a monolayer of 4-aminothiophenol (4-ATP) molecules and then spherical AuNPs of 80 nm diameter were attached on it via electrostatic attraction. The concentration of the AuNP colloids was varied to obtain the SF11/Ag/4-ATP/AuNP substrates with varying d . The scanning electron microscope (SEM) image of a Ag/4-ATP/80 nm AuNP configuration is presented in Fig. 1(b). The value of d estimated using ImageJ software from NIH [8] was around $1 \mu\text{m}$. Such substrates were attached to a SF11 prism with index matching fluid. The ESPs were excited via TM polarized light from a 785 nm laser. The ESPs couple to LSPs of AuNPs to enhance the Raman signals from the 4-ATP molecules. The SERS signals were collected from the top of the configuration via a collection optics and passed through a long pass filter to let only Stokes Raman signals pass before feeding it to a Raman spectrometer. SERS spectra from Ag/4-ATP/AuNP configurations with varying d were recorded. Later, ultra-small limit of detection for the varying concentrations of glycerin was obtained on the optimal configuration.

2. Results and discussion

Fig.2 (a) presents the simulated results on the EM enhancement as a function of d . It can be observed that both the maximum field in the hotspots as well as the average field for the structure both increase with increase in d , reach to a maximum around $d = 1300 \text{ nm}$ and then start decreasing. The optimum value of d depends on various parameters such as the particle size, the spectral regime, mutual interaction among MNPs and the total geometrical area. The simulated results were reconfirmed with experiments. Fig. 2(b) shows the SERS spectra for Ag/4-ATP/AuNP configurations with varying d . It can be seen that with an increase in d , the SERS power first increases, reaches to a maximum and then starts decreasing with further increase in d . A more quantitative prediction of effect of d on

Fig. 2. Effects of IPD ' d ' on (a) the maximum (left), and average (right) electric field enhancement in Au NPs array over Ag film at 785 nm with 34.645° incidence angle inside the prism, (b) SERS spectra of Ag/4-ATP/AuNP structure. Inset shows the quantitative variation

SERS signal can be seen in the inset, where the SERS power @ 1077 cm^{-1} band with all the SERS spectra referenced to zero have been plotted with varying d (spacing), obtained from the estimated from processing the SEM images with ImageJ software, as shown in Fig. 1(b). It can be concluded from the inset that the maximum SERS signal is obtained close to 1300 nm . This configuration was used for glycerin detection experiments. The SERS spectra for varying concentrations of glycerin in ethanol have been plotted in Fig. 3. The inset shows the SERS peak power @ 1077 cm^{-1} band. It can be observed that with an increase in the glycerin concentration, the SERS signal increases. We could detect concentrations as small as $10^{-10}\%$. With a Signal to noise ratio of 450:1 of the spectrometer, the LOD can further be improved by a factor of 10^{-2} .

Fig.6. SERS spectra for varying Wt. % of glycerin in ethanol. The inset shows the SERS signal @ 1077 cm^{-1} band vs Log_{10} (Wt. %) variations

Estimation of enhancement factor:

Enhancement factor is given by the following relation:

$$EF = \frac{I_{SERS} / N_{Ads}}{I_{Bulk} / N_{Bulk}}$$

With the help of density, mol. wt., and size of solid 4-ATP being 1.18 g/cc , 125.19 g/mol and 0.2 nm^2 , respectively, N_{ads} and N_{Bulk} were estimated. The I_{SERS} and I_{Bulk} parameters were obtained from the experimental Raman spectra. The estimated enhancement factor was 1.66×10^{10} per molecule in the hotspots. A more detailed explanation can be found elsewhere [9].

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