

Plasmonic in Metallic Nanostructures – Fabrication, Characterization and Applications in Surface-Enhanced Spectroscopy

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ABSTRACT

We are witnessing a rapid and ongoing expansion of nanoscience, driven by potential applications in advanced materials and nanotechnology. There is a race to develop techniques that may allow controlling the size, shape of nanostructures that can allow the tuning of their optical and electronic properties. Plasmonics is a field that encompasses and profits from the optical enhancement in nanostructures that support plasmon excitations. One of these new techniques is surface-enhanced Raman scattering (SERS), commonly used for nanostructure characterization. In the present report, we present a theoretical model for plasmon excitation and electric field enhancement that help to provide an explanation for the special features observed in experimental SERS. Two sets of experimental results are discussed illustrating the make out of the signature of the plasmonics producing the optical enhancement. The nanostructures used are silver colloids in dynamics experiments and spin coated metal island films

INTRODUCTION

Plasmonics is a term presently used to identify a branch of photonics¹ that harness the properties of surface plasmons. We speak of surface plasmons polaritons (SPP)² for planar surfaces and localized surface plasmon resonance (LSPR)³ for nanometer-sized metallic nanostructures, of which silver and gold are the most efficient for practical applications. Nanometric silver and gold particles that can support collective oscillations of the electrons strongly absorb and scatter light in the visible and near infrared spectral regions. The strong surface plasmon absorption is a delicate function of the dielectric function of the material, size and shape of the nanostructure, and dielectric properties of the surrounding media. Plasmon absorption are the source of the enhancement of optical properties.^{3,4} It is possible to fabricate nanoparticle shapes (spheres, rods, prisms,

wires or arrays of them) to attain the needed optical and electronic properties.^{5,6} In the present report we discuss the experimental results of optical enhancement of the inelastic scattering radiation of molecules placed at surface of the silver nanostructure or surface-enhanced Raman scattering (SERS).⁷ The SERS technique has been identified as optical techniques that can be used for characterization of nanomaterials. At the same time, the role of nanostructures in the amplification of optical fields has unleashed a flurry of activities since the first reports on single molecule detection (SMD).^{8,9} The experiments described here were intended to identify the role of the plasmon in the enhancement as it can be extracted from the properties of the observed SERS spectrum. First a simple model is presented for the calculation of the plasmon absorption and scattering based on the work of Shalaev and coworkers.¹⁰ The computational work helps to visualize the location of the plasmon along the electromagnetic spectrum and provides a clear scale for the enhancement factors that can be achieved in the SERS experiment, and is in agreement with more sophisticated computations.¹¹ Then we explore the electromagnetic enhancement by metal nanostructures (silver island films) and resonance Raman enhancement (SERRS) by excitation into molecular electronic absorption bands using a dye of the family of perylenes (commonly used in car paints). It is demonstrated that at very low concentrations (0.001 of a monolayer), the differences in plasmon contributions are detected in the relative intensity of the fundamentals compare to overtones and combinations Raman bands. In the second set of experiments the plasmon absorption is set working with colloidal solutions and a molecule that does not absorb in the spectral region of excitation. The dispersion of the enhancement is probed by changing the laser line of excitation. The results showed the plasmon signature, that have now been measured in the near field experiments.¹²

RESULTS AND DISCUSSION

THEORETICAL MODEL – The prediction of the absorption and scattering by a single particle has been known since the time of Maxwell-Garnett¹³ and were explicitly calculated for an sphere by Mie¹⁴. Since then, there have been many successful extensions to non-spherical shapes using the dipolar model.^{15, 16} Although the dipole model approximates the exact Mie solution to the sphere, it is appropriate when the particle is much smaller than the wavelength of light, which is often the case for small nanoparticles in the visible region of the electromagnetic spectrum.

The coupled dipole equations (CDE) have been used successfully in calculating the optical properties of composite media, including larger particles, where the dipoles are arranged to mimic a more complicated system, such as those used in DDA^{17, 18}, as well as fractal structures¹⁰, which could be applied to model aggregation, surface composition, or percolation. The general nature of the solution allows for calculation of optical properties, as well as enhanced Raman and electric fields at any point in space.

In this work, the CDE are used to calculate extinction, scattering, and as well, the enhanced field created by polarized light with up to 3 silver particles. This simple model illustrates the effect of aggregation on field dispersion and the distribution of the electric field in space.

The dipoles are arranged with spacing between them of 20nm. The incident light is chosen to come from the z direction, and the electric field polarized in the x direction. For the case of 2 particles, they are arranged in a line along the x axis. For 3 particles, there are two different configurations used: 3a is with the third particle added in a triangular fashion, while 3b adds the particle to the right of particle 2. These configurations are as seen in Figure 1.

The polarizability of each particle is given by:

$$\alpha = V \frac{\epsilon - 1}{\epsilon + 2}$$

Where α is the polarizability, ϵ is the frequency dependent dielectric function¹⁹, and V the volume of the dipole. Each dipole is treated as a sphere. The radius of each sphere is calculated using $a/R=1.612^{20}$, where a is the spacing between the dipoles, 20 nm in this case, and R the radius. This value is less than the expected $a/R=2$, as the dipole response will not be homogeneous: rather, it will be stronger in the region where the particles are in contact. This value of a/R causes the dipoles to overlap, and interact more strongly.

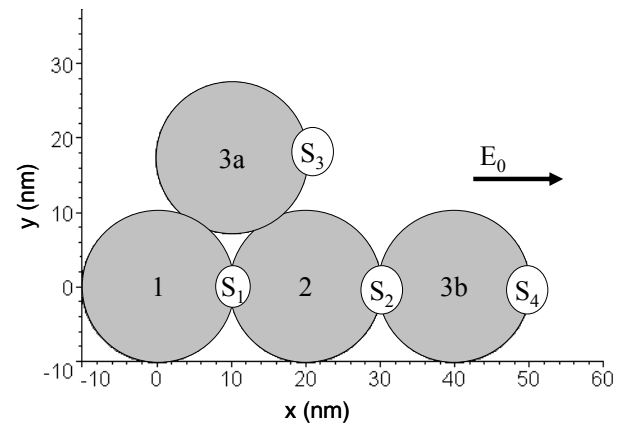


Figure 1 : Arrangements of particles. 1 and 2 represent the positions of a single particle, and dimer respectively, while 3a and 3b refer to the two different configurations of a 3 particle system.

The CDE, and equations for extinction and scattering cross sections as used by Markel et al.¹⁰ are applied, solved through the conjugate gradient method.¹⁷ The electric field is calculated through the addition of a non-interacting particle at the desired position, and the sum of the dipole moment vectors divided by the polarizability of each particle is taken at this point. The enhancement of the electric field, A , is calculated by:

$$A = \left| \frac{\vec{E}_{inc} + \sum_i \vec{E}_i}{\vec{E}_{inc}} \right|$$

A is used in two different ways: First, the dependence of the electric field at a variety of points is taken with respect to frequency. Secondly, contour maps of the electric field at peak frequencies are generated over the region of space surrounding the particles.

The extinction for particles 1, 2, and 3, interacting as described above, is shown in Figure 2.

The extinction for the single particle peaks at 354 nm, as expected for a 20 nm silver particle. Two particles along the line of the incident electric field polarization show strong coupling to both the electric field and each other, resulting in a much stronger extinction that is red shifted to 426 nm. Due to the selected polarization along the x axis, the addition of the third particle in configuration 3a causes a slight blue shift, to 422 nm, with a negligible increase in extinction. Examination of the dipole moment vectors in this case shows the creation of components in the y-direction, where in the 2 particle case, the response to the electric field is only in the x. As these y components do not couple to the electric field, which is only in the x, they do not contribute to the extinction. In a sense, the 3rd particle causes a damping of the system by inducing dipole moments which do not couple to the incident field. In configuration 3b, the trend from the 2

particle system is continued, with a shift more to the red, to 528 nm, as well as a substantial increase in extinction. As 3a and 3b occupy the same volume, and have the same surface area, these very different spectra illustrate the sensitivity to geometry in nano particle extinction.

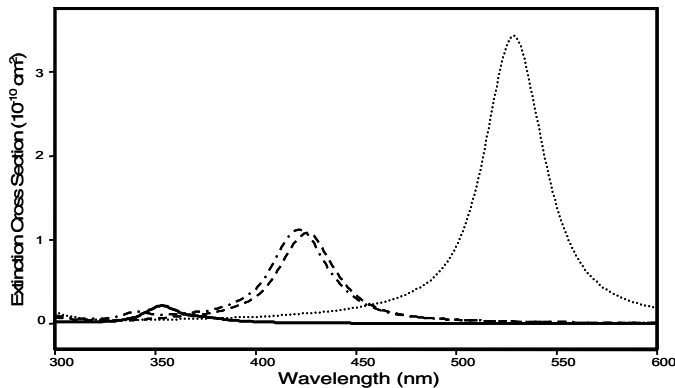


Figure 2: Extinction cross section vs. Incident Wavelength for 1 (solid), 2 (dashed), and 3 particles, in configuration 3a (dot-dash) and 3b (dotted).

The scattering results follow a similar trend, with the scattering peaking at the same wavelength as the extinction for 1 and 2 particles. For configuration 3a, the scattering is strongest at 424 nm, and for 3b at 529 nm. The scattering contribution to the total extinction also demonstrates an interesting trend. For 1 particle, the scattering is only 3.7% of the extinction, while for 2 it contributes 12.7%. The scattering contributions for the two different configurations of 3 particles are 13.6% and 25.6% for 3a and 3b respectively, demonstrating that both extinction and scattering are strongly dependent on geometry.

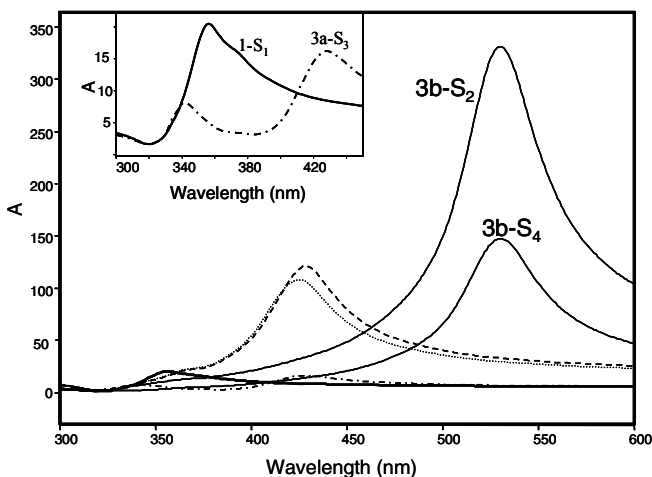


Figure 3. Electric field enhancement vs. Wavelength for 1 particle sampled at S_1 (solid), 2 particles sampled at S_1 (dashed), and 3 particles (dotted line), in configuration 3a sampled at S_1 , and 3b sampled at S_2 and S_4 . The inset shows detail of the single particle and configuration 3a from 300 to 450nm.

The electric field as a function of incident wavelength is shown in Figure 3. In general, the peak wavelengths are slightly red shifted compared to the extinction, and the tails to the red extend out much further. The single particle shows a peak at 356 nm. The maximum enhancement has a magnitude of 20. For two particles, the peak is at 428 nm both at the center (S_1), where the magnitude of the field enhancement is 121, and at the side (S_2), where $A=63$. The field is approximately three times as high to the right of both particles then for a single particle, due to the increased dipole moment due to the interaction. In the center, the field is approximately doubled again relative to the outside, as the dipole moments of both particles are strongly felt. For 3 particles, in configuration 3a, due to the damping mentioned above, the peak is blue shifted to 426 nm. The intensity drops slightly, compared to the enhancement for two particles, at the same positions. The field enhancement for the 3rd particle shows why: A peak at 342 nm appears, as seen in the inset of Figure 3, corresponding to a response that is not fully coupled to the other two particles. In this case, modes are created that correspond to both the single particle and the dimer. In configuration 3b, however, the strongest enhancement is observed at 530 nm, with a magnitude of 331 at one of the inside positions (S_2), and 147 to the right of all three particles (S_4). There is a clear dependence on geometry again for field strengths as well.

Figure 4, 5, and 6 show contour maps of the electric field enhancement over the region of space surrounding the particles, at the peak frequencies calculated in Figure 3. The color scale follows visible light, with violet and blue being lowest enhancement, and red being the highest in each case. The particle radius as shown in the figures is slightly smaller than 10 nm, to allow visibility of the fields at the surface, and between the particles. The single particle shows the strongest enhancement in the direction of the field polarization, as expected. For two particles, the enhancement is strongest in the region between the particles, with an intermediate enhancement around the outside of the system in the direction of incident field polarization.

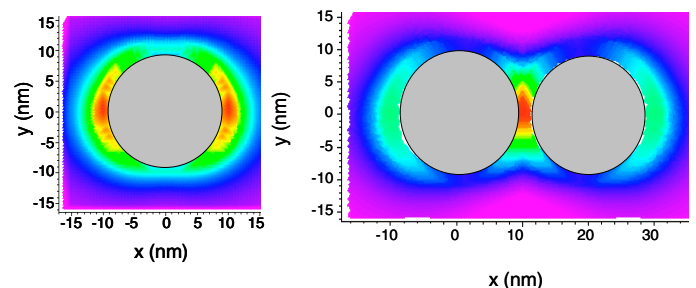


Figure 4: Electric field enhancement for 1 particle at 356 nm (left) and 2 particles at 428 nm (right). The scale is described in the text.