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Near-fields in Arrays of Triangular Particles: Coupling Effects and Field Enhancements

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Abstract: Field enhancements are mainly due to surface plasmon resonances and near-field coupling between particles. High near-field enhancements can be exploited in surface enhanced Raman spectroscopy and other sensing methods. COMSOL Multiphysics was used to investigate coupling effects between noble metal particles. At inter-particle distances of few nanometers near-fields can be enhanced to values exceeding 100 under adequate polarization conditions. Red shifts in the near-field spectra occur in gold nanorods as the separation between particle decreases. Coupled trimers of silver particles generate Fano-like resonances due to destructive interference between electric and magnetic dipoles.

Keywords: Near-field optics, surface-plasmons, surface enhanced Raman scattering, Fano resonance.

1. Introduction

Nanoparticles of noble metals (Ag, Au) can strongly enhance near-fields due to light focusing at nanoscale and surface-plasmon resonances. One of the applications of the strong field enhancements is surface enhanced Raman scattering (SERS) [1]. Raman spectra of molecules attached, or in close neighborhood to the metal nanoparticles, increase their Raman scattering cross section by several orders of magnitude. Raman scattering enhancements are approximately proportional to $G = |E|^4$. Raman enhancements of at least $G \sim 10^{10}$ are necessary to obtain single molecule SERS [2]. Calculations show that molecules between spherical silver spheres could reach such enhancements [2].

Nanosphere lithography has been often used to fabricate nanoparticle templates for SERS [3]. It consists evaporation of metal films on top of close-packed 2D arrays of polymer spheres. Polymer spheres in diameter range from 100 nm to several microns are commercially available. After removal of the coated spheres, an hexagonal array of triangular-shaped metal particles remains on the substrate. Figure 1 (a) shows an example of gold particles fabricated using polystyrene (PS) spheres of 3 µm diameter. Though the AFM image shows sharp edges of the Au particles, the transmission electron micrograph of figure 1 (b) reveals small metal particles surrounding the triangles. These particles are formed by coalescence during the thermal evaporation of the thin film and do join the compact film of the triangular ones. However, the localized surface-plasmons of these small particles are excited by light as well and due to the small distance to the triangular ones near-field coupling effects can occur.

More recently, it was found that plasmonic nanostructures may present Fano-like resonances [4-6]. Fano resonances arise, namely, from destructive interference between radiative (bright) and non-radiative (dark) plasmon modes. These resonances of non-Lorentzian shape have been found in different plasmonic structures, as non-concentric nanoshells [5] and hexagonal arrays of gold spheres [6].

Using the RF module of COMSOL Multiphysics, we have investigated the coupling effect on gold rods and its dependence on the inter-particle gap length and the Fano-like resonance on a trimer of silver nanospheres.

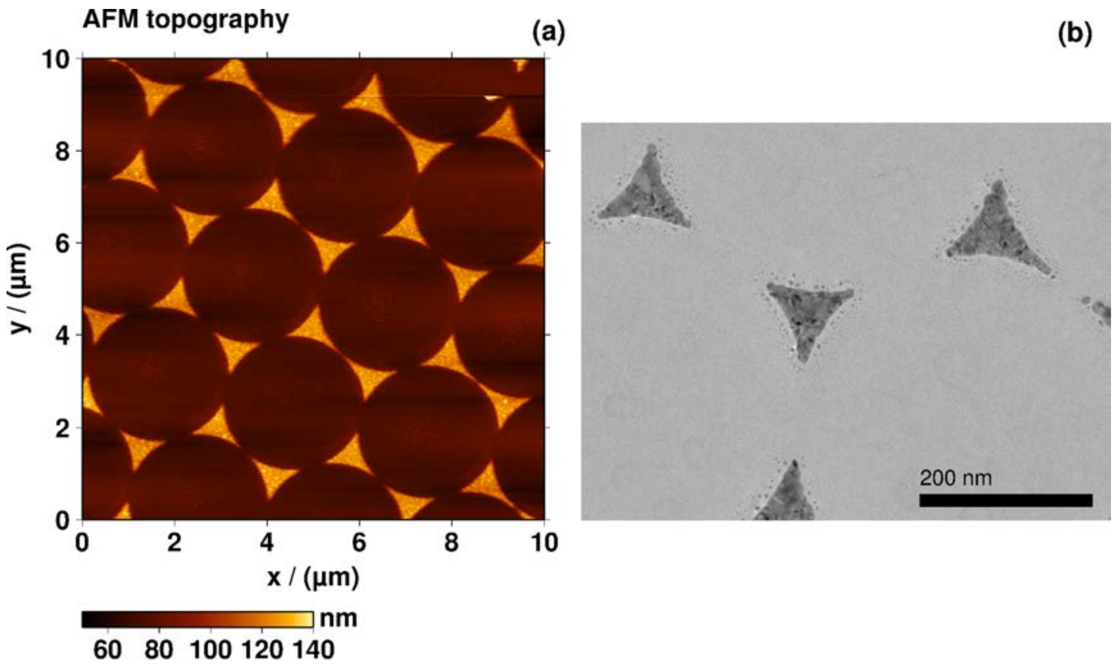

Figure 1: (a) AFM topography of gold nanoparticles fabricated by NF. (b) TEM micrograph of gold nanoparticles fabricated using PS spheres of 400 nm diameter. Small particles of round shape are in periphery of the triangular ones.

1.1 SERS on triangular particles

SERS measurements of methylene blue (MB) on silver particles were done using a confocal Raman microscope [3]. Experimental results show that the strongest spectra occur at the corners, or edges of the triangular particles (see figure 2 (b)). The position of the strongest Raman spectra can be obtained by comparison with pixel position of the corresponding the Rayleigh scattering image (fig. 2 (a)).

In figure 2 (c) are presented spectra obtained at single pixels marked in figure 2 (a). At the corners of the silver particles (points P1 and P2) strong SERS spectra where obtained, whereas in the middle of the hexagonal array (point P3) no methylene blue Raman spectrum could be found. The location of the strongest SERS spectra indicates where the near-field reaches the largest enhancement. Taking into account the size of the silver triangles no resonance is expected at visible wavelengths close to 532 nm. Thus, very strong near-fields are probably due to coupling between small clusters and the larger particles.

1.2 Coupling effects on gold nanorods and silver trimers

The surface-plasmons on pairs of gold nanorods at close distance also can couple and lead to strong near-fields at their gap. Investigations of the extinction cross section and calculations done with discrete dipole approximation (DDA) software package DDSCAT show red shifts in resonance of linear arranged gold rods. The shift increases as the gap between the particles decreases [7].

Fano-like resonances were found in silver sphere trimers. The resonances arises from coupling between an electric dipole and a magnetic dipole, excited when the incident electric field is parallel to the plane contained the centers of the spheres. However, a symmetry breaking is necessary for the interference between magnetic and electric modes [8]. The calculations were done using the generalized multiparticle Mie method (GMM). We tried to reproduce some of the calculations using COMSOL Multiphysics.

2. Using COMSOL Multiphysics (RF) to investigate plasmonic structures

We have used the RF module to define the plasmonic nanostructures and their boundary conditions. Scattering boundary conditions were used for the computational domain and Cartesian coordinate PML layers applied. The incoming field was defined as plane harmonic wave and the solver PARDISO was used for fields computation.

Refractive index of Au and Ag was defined based interpolated values of experimental data of Johnson and Christy [9].

configurations were investigated: linear arrangement and T-arrangement. In the former, the pair of rods was aligned in the x-direction. The gap between the top ends of the rods was chosen 3 nm and 5 nm. The field was either polarized along the symmetry axis of the rods or perpendicular to it. In the later arrangement, the rods were placed in the plane XY in T-configuration with a gap length s = 3 nm.

Three spherical silver particles of diameter 60 nm were placed at the corners of an equilateral triangle of side length 122 nm. Thus, the spheres are separated by a gap of 2 nm. A second arrangement is obtained by

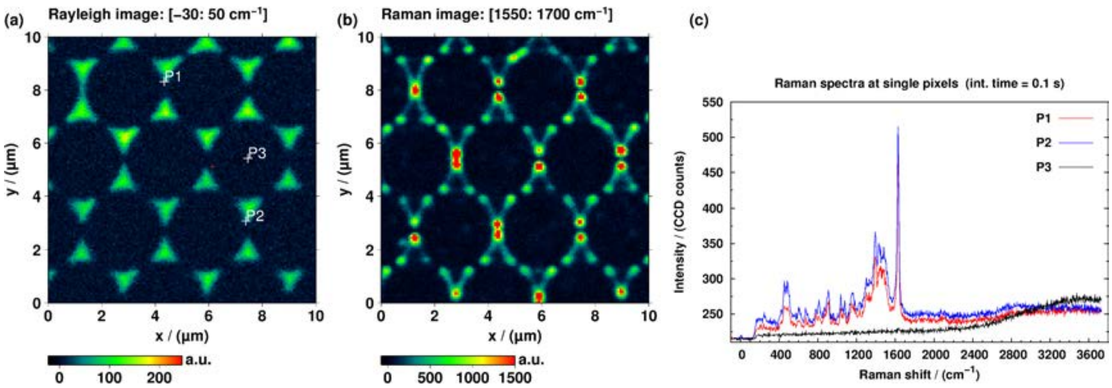

Figure 2: SERS images of a sample with triangular Ag particles coated by methylene blue, obtained with a confocal Raman microscope. (a) Rayleigh scattering image. (b) Raman image of the strongest Raman peak. (c) Single Raman spectra extracted from pixels marked in (a). λexc = 532 nm, Pexc = 12 µW.

Triangular particles were modeled with shape and size similar to those obtained by NL. For example, triangular particles with a side length of 120 nm are obtained using nanospheres of 400 nm diameter as lithography masks.

Two polarization direction were investigated: E_x and E_y . The propagation direction was chosen perpendicular to the plane of the particles and the field modulus was set to 1 V/m. For the sake of simplicity, particles were embedded in dielectric medium of refractive index n = 1.5 . Several geometries were investigated, namely triangular particle with spherical particle located close to one of the corners and a symmetric triangular particle dimmer. The spherical particle has diameter 30 nm (the thickness of the triangular particle) and is 2 nm away from the corner of the triangular one. The gap in the dimmer is 10 nm.

Gold rods were modeled as cylinders of length 30 nm with two hemispherical ends of radius 15 nm. They have an aspect ration of 2.0, with total length 60 nm and diameter 30 nm. The refractive index of the medium was the same an in [7], n = 1.56. Two spacial

moving one the spheres r = 3 nm away from its original position, in the outward symmetric direction. For both structure geometries two incident field polarization were investigated: orthogonal plane wave illumination, with electric field parallel to the triangle side along the Y-axis, and tangential illumination with the same electric field direction, but propagation along the X-axis. The spheres are in medium of refractive index n = 1.33

3. Coupling and field enhancements in triangular particles

Couplings in near-field can be easily seen in slices of the electric field modulus $|E|$, when a spherical particle is placed close to one of the corners of the larger triangular particle (figure 3). The size of the spherical is influences the maximum of the near-field at the gap, but the gap length plays a major role in the coupling when the polarization is parallel to the symmetry axis of both particles. On the other side the maximum field enhancement achieved depends on the wavelength. While, for $\lambda = 532$ nm field enhancements of 199 are reached, for $\lambda = 800$ nm they can exceed 500.

The coupling between triangular particles with the nearest corners in the polarization direction is also visible (fig. 3 (c) and (f)). However, as in the of the sphere, a increase of the gap attenuates drastically the near field. For 10 nm gap, the field enhancement reaches only 35 (fig. 3 (c)).

4. Resonance shifts in pairs of gold nanorods

As well as in the previous case increasing gap length reduces the field enhancement. However, there are other coupling effects, like frequency shifts in the extinction cross section. Decreasing the gap in linear oriented rods leads of plasmon resonance shifts (figure 4). These shifts can be understood using the classical model of coupled oscillators. An increase in the coupling constant increases the shift in the resonance frequency and a splitting into two resonant modes. Experimental results confirmed the theoretical prediction of hybridization of surface-plasmon modes [5,7].

We have investigated two of geometries discussed by Funston et al. [7]: the linear arrangement and the T-arrangement. Though we do not have calculations of the extinction cross section so far, we have found a shift in maximum of the near-field of the resonance toward longer wavelength as the gap length decreases: The near-field maximum for $s = 5$ nm was located around 760 nm while for $s = 3$ nm it shifts to 780 nm . The far-field extinction efficiency spectra have resonances below 700 nm . However, there are shifts between the near-field maxima and the extinction maxima.

On the other hand, although the near-field maximum is correlated with its mean value at the gap some errors can happen in FEM calculation leading to uncorrelated maximum of mean values. In the T-configuration the near-field maxima approach the extinction maxima of [7]. However, for one of the

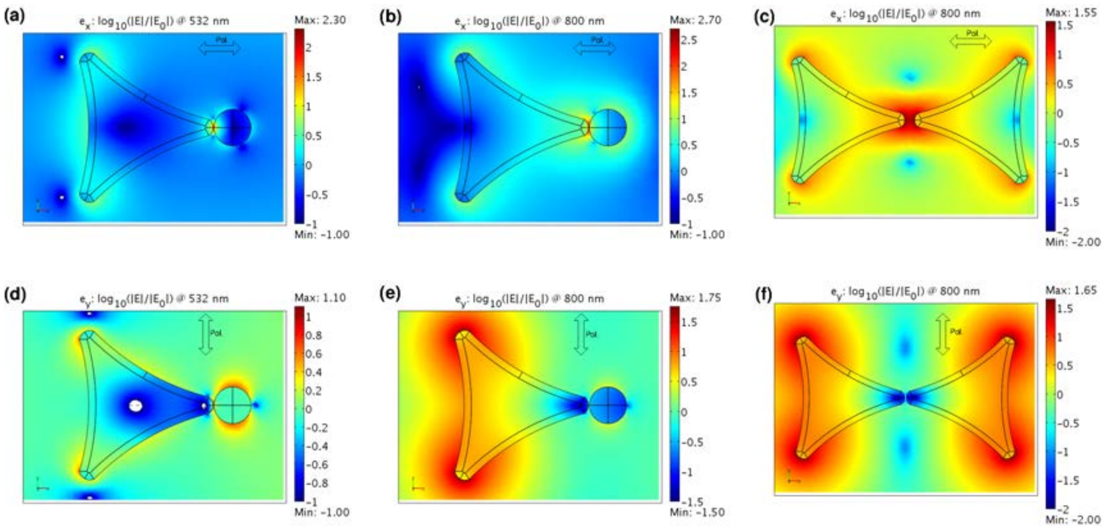

Figure 3: Electric field slices in logarithmic scale of the symmetry plane of a triangular Ag particle with a Ag sphere (a), (b), (d) and (e), and triangular Ag dimers (c) and (f). The incident field propagates perpendicularly to the plane of the particles. Gap length between sphere and triangular particle: 2 nm. Gap length in dimmer: 10 nm.

polarizations (along the X-axis) we obtained a broad near-field resonance.

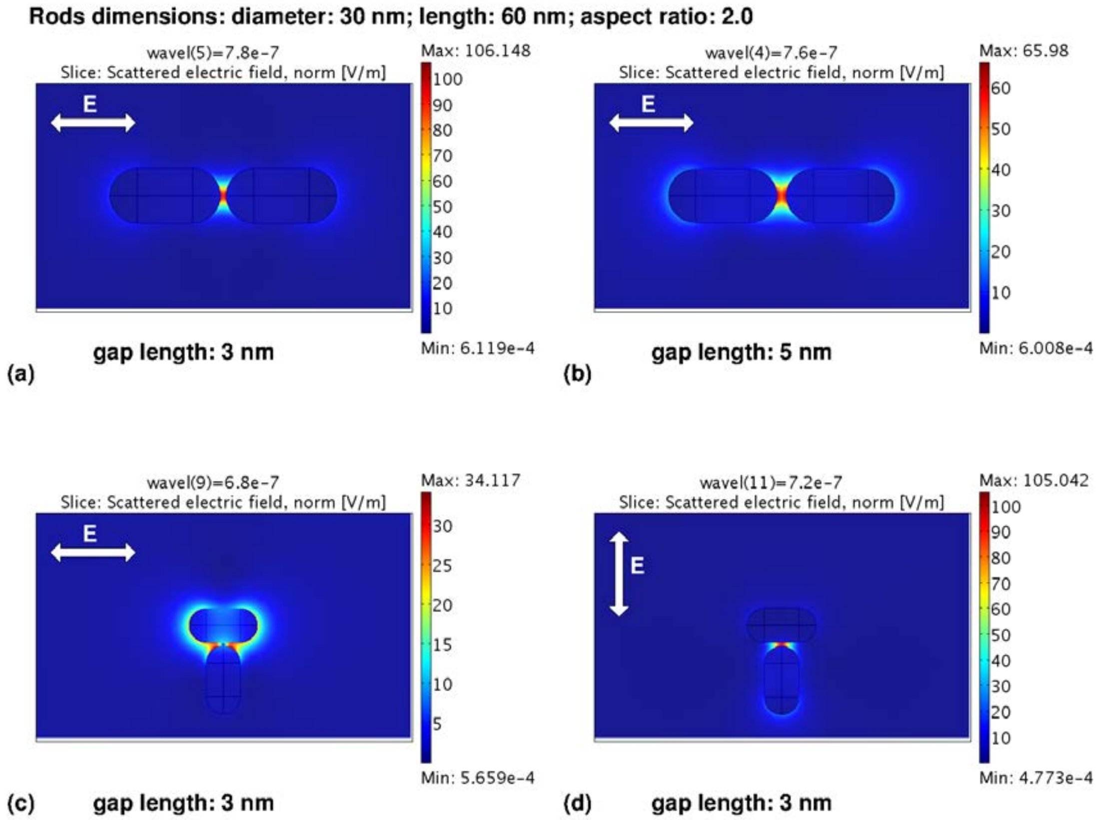

Figure 4: Modulus of the electric field of Au rods in linear and T-arrangement. Gap length in (a), (c), and (d): 3 nm, and in (b): 5 nm.

5. Fano-like resonances in coupled silver sphere trimers

Sheikholeslami et al. investigated the Fano-like resonances in Ag sphere trimer [8]. These Fano resonances arise from the destructive coupling between electric and magnetic dipole modes excited in the trimer. For that, a symmetry breaking is necessary changing the equilateral arrangement into an isosceles (figure 5). In the later both orthogonal and tangential incidence lead to similar resonances of the near-field maximum. As well the extinction cross-section results obtained with GMM present two resonances separated by a dip [8]. The spectral position of the far-field is similar to the maximum found in COMSOL near-field calculations, respectively 590 nm and 560 nm (figures 6 and 7).

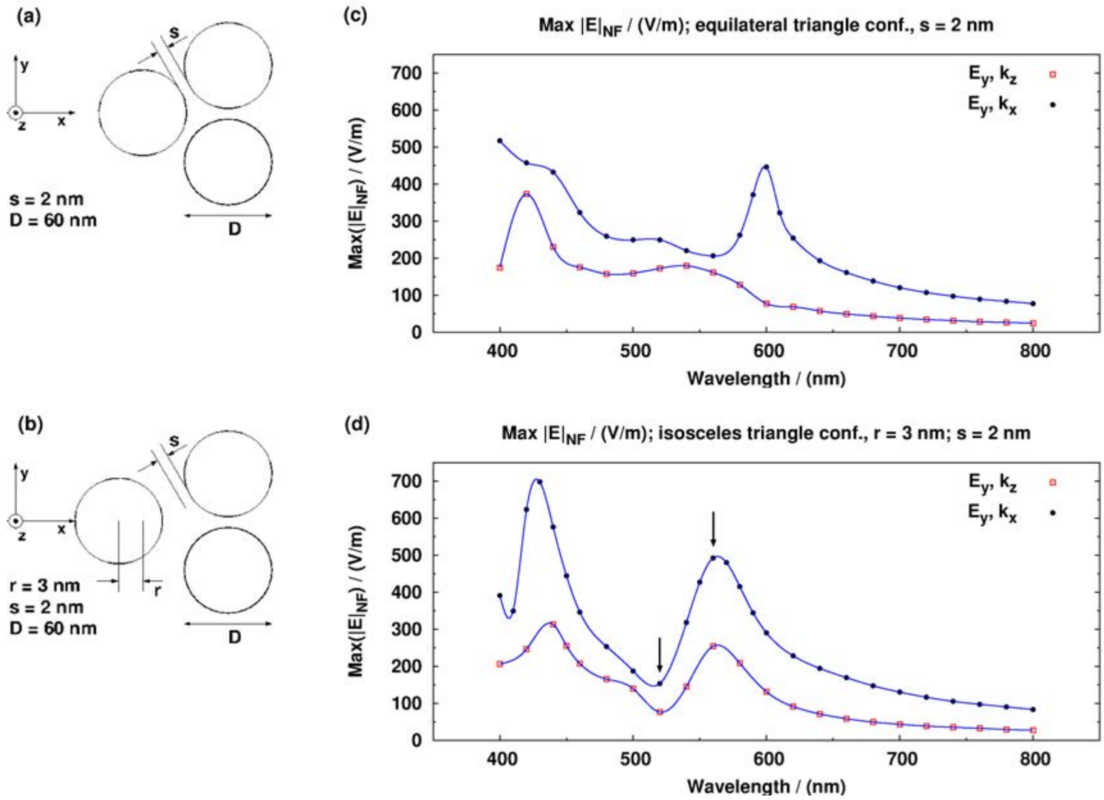

Figure 5: Equilateral (a) and isosceles (b) triangle arrangements of Ag 60 nm diameter spheres. The gap between the spheres in (a) is 2 nm. In (b) the sphere at left was shifted to the left along the X-axis 3 nm. (c) and (d) present plots of the maximum of the electric obtained from the COMSOL calculations.

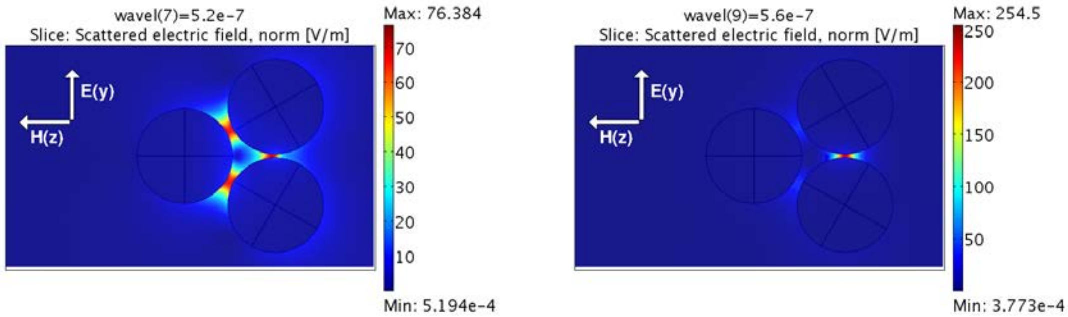

Figure 6: Electric field slice at the center of the spheres for orthogonal illumination.

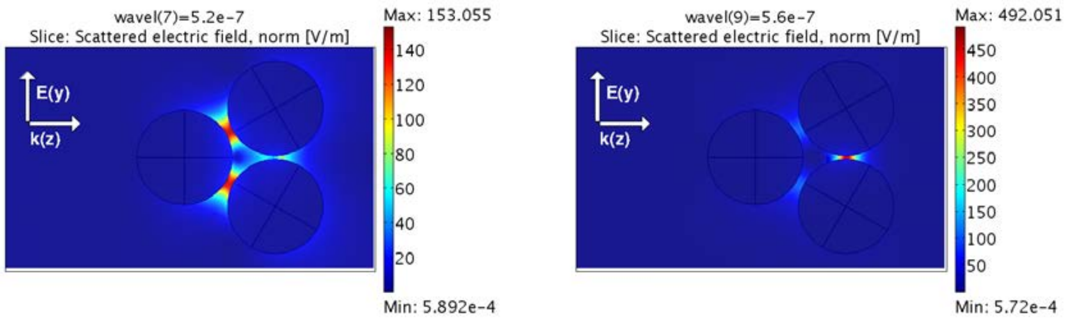

Figure 7: Electric field slices at the center of the spheres for tangential illumination.

6. Conclusions

Simulations done with COMSOL Multiphysics using th RF module permit to obtain the magnitude of near-fields in plasmonic particles. The field enhancements achieved, as result of coupling between two silver triangular particles, or between a triangular particle and a small sphere, reach more than 100 for some wavelengths. These field enhancements give rise to Raman enhancements of the order of 10^8. SERS measurements of methylene blue molecules attached to silver particles indicate that strong Raman scattering occurs at the corners and edges of the silver particles, where near-field coupling between the triangular particles and small particle clusters could occur. Although high field enhancements are usually obtained for wavelengths close to λ = 800 nm (plasmon resonance of the triangular particle), very high near-field (500) are found between the corner of the triangular particle corner and the sphere, for polarization along the axis of the center of mass.

Simulations done on gold rods give rise to near-field results which can be compared with extinction spectra obtained in [7]. Resonance shifts to the red were found in the near-field maximum spectra as inter-particle distance decreases. Similar effect was observed in measurements of the far-field extinction spectra and in calculations with DDSCAT [8]. However, we have found a broad resonance for the T-configuration with polarization along the symmetry axis of the top particle. By contrary, narrower resonance was obtained in DDA calculations.

COMSOL simulations on coupled silver spheres confirm the results obtained in [8], using GMM calculations. There is a Fano-like resonance as function of interference due to the coupling of electric dipole and the magnetic dipole excited in the trimer.

7. References

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8. Acknowledgements

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