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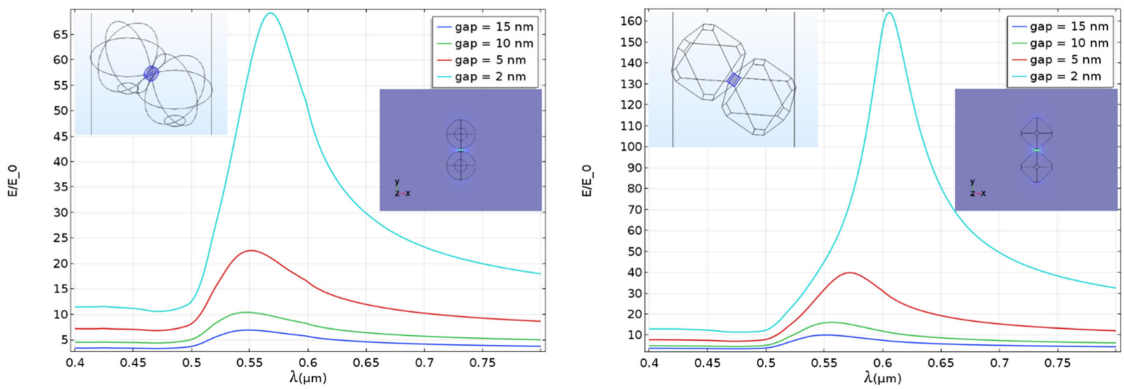
Simeon Trendafilov
Monica Allen, ***Senior Member, IEEE***
Jeffery Allen, ***Senior Member, IEEE***
Zhiqun Lin, ***Member, IEEE***



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Comparison of Octahedral and Spherical Nanoparticles for Plasmonics

(Invited Paper)

Simeon Trendafilov,[1] **Monica Allen**,[1] ***Senior Member, IEEE***, **Jeffery Allen**,[1] ***Senior Member, IEEE***, **and Zhiqun Lin**,[2] ***Member, IEEE***

[1]Air Force Research Laboratory, Munitions Directorate, Eglin Air Force Base, Okaloosa, FL 32542 USA
[2]School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332 USA

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Corresponding author: S. Trendafilov (e-mail: simeon.trendafilov.ctr@us.af.mil).

Abstract: Monocrystalline metallic nanoparticles are preferable for plasmonic applications, but grow only in polyhedral shapes, which deviate from the predominantly employed spherical shape. Through numerical simulations we have investigated possibilities for using octahedral instead of spherical Au nanoparticles in plasmonics. Our results show that the dimers of octahedral Au nanoparticles can provide higher field enhancement compared to spherical nanoparticles and that placing the octahedrons close to a metal plate can also have certain advantages compared to spheres.

Index Terms: Monocrystalline Au octahedron, nanoparticles, field enhancement, plasmonics.

1. Introduction

Recent years have seen much research dedicated to plasmonics especially focused on the optical properties of nanoparticles [1], [2] in order to provide enhancement and selectivity in applications such as sensing [3], biology [4], nanochemistry [5], etc. These benefits stem from the properties of localized surface plasmon (LSP) excitations of the unbound electrons in metallic nanoparticles, which result in large electromagnetic field enhancements by coupling to near fields at the resonant wavelength. Placing individual nanoparticles in close proximity to each other or to conductive metallic layers produces structures that can exhibit a rich variety of effects. This allows us to manipulate both resonant frequency and field amplitudes by varying interparticle spacing and geometrical arrangement of the particles. Nanoparticle dimers, while not the only ensembles that have been explored in the literature, have received extensive attention as they exhibit the salient features of local field enhancement in the gap and at the same time are simple enough to provide an understanding of the coupling of individual particle LSPs. Further, dimers can be easily assembled using appropriate surface functionalization chemistry in contrast to more exotic assemblies that are much more difficult to realize experimentally. On the theoretical front, plasmon hybridization models

[6], [7], have been used to successfully explain the formation of bonding and anti-bonding states in plasmonic nanoparticle dimers, in a manner similar to the formation of molecular electronic orbitals. Cross-linked Au nanoparticle dimers have been fabricated and characterized [8], [9], demonstrating them as promising candidates for plasmonic meta-materials.

2. Methods

Better plasmonic structures require better building blocks, i.e., nanoparticles. Spheres have been a natural choice, since they do not have orientation dependent features that complicate assembling consistent clusters and can be excited easily with simple light sources because of their insensitivity to polarization. However, spheres are not necessarily the easiest shape which to synthesize from monocrystals, since monocrystalline metallic nanoparticles naturally grow under equilibrium into polyhedral shapes and spherical crystals are not stable under standard growth conditions. One alternative is to grow polycrystalline spheres, but polycrystals have rough surfaces and grain boundaries that lead to defects and induce higher losses. Thus, polycrystalline nanoparticles are not an optimal solution for plasmonic applications. Another solution is to grow monocrystalline octahedral Au nanoparticles and render them spherical using etching as a post-processing step [10]. This method produces stable and highly spherical monocrystalline particles, but the additional etching step adds time and complexity to the fabrication process. In this paper, using detailed full wave electromagnetic simulations, we have delved into the question whether octahedral nanoparticles have certain advantages over spherical in some assemblies, thus removing the additional etching step.

The geometrical properties of nanoparticles influence their plasmonic response [11], [12]. For particle dimensions of less than 100 nm the dipole approximation holds well and size does not influence the response as much as aspect ratios and the presence of edges, which strongly affect both the spectral position of resonances as well as near field enhancements. A detailed comparative study of the near field enhancements in indium-doped cadmium oxide nanocrystal spheres, cubes and octahedrons and their respective dimers is presented in [12], demonstrating advantages of the octahedral shape in producing high field enhancement factors.

Moderately etched octahedrons, where the vertexes are smoothed out, can have the surfaces functionalization on the tips to consistently link them as dimers. Through numerical simulations the response of octahedrons and spheres of similar sizes and arranged as dimers are compared. A second configuration is considered where a nanoparticle is placed very close to a metal plate. The conductor will image the electric field emanating from the particle thus forming a “virtual” dimer. Results from this configuration for both octahedrons and spheres are also compared.

Solutions for LSPs on spheres can be found analytically and their coupling can be approximated, but for polyhedrons we have to perform numerical simulations in order to obtain useful results. Therefore, we resort to conducting full-wave 3-D electromagnetic simulations for our structures, using the finite element method (FEM)-based commercial software, Comsol Multiphysics, to model the real and virtual dimer configurations.

3. Dimers

The first set of simulations involves square arrays of dimers with the array period taken to be $P = 400$ nm. The array resides on a glass substrate and the dimers consist either of spherical or octahedral Au nanoparticles. Selecting what would be comparable dimensions for the spheres and octahedrons is somewhat arbitrary. If the diameter of the spheres is made equal to the maximum linear dimension of the octahedrons, i.e., the tip to tip distance, the spheres will have considerably larger volumes than the octahedrons. If, on the other hand, the volumes are set equal the disparity in maximum linear dimension is considerable. Therefore, we compromised by setting the sphere diameter to 50 nm and the octahedron edge length to 45 nm. Inevitable rounding of the edges and corners of actual synthesized particles results in deviation from the perfect octahedral shape and some particle variation. A mild etching step would improve particle uniformity but lead to removal of some tip material. To account for this the octahedrons have their tips truncated to squares with

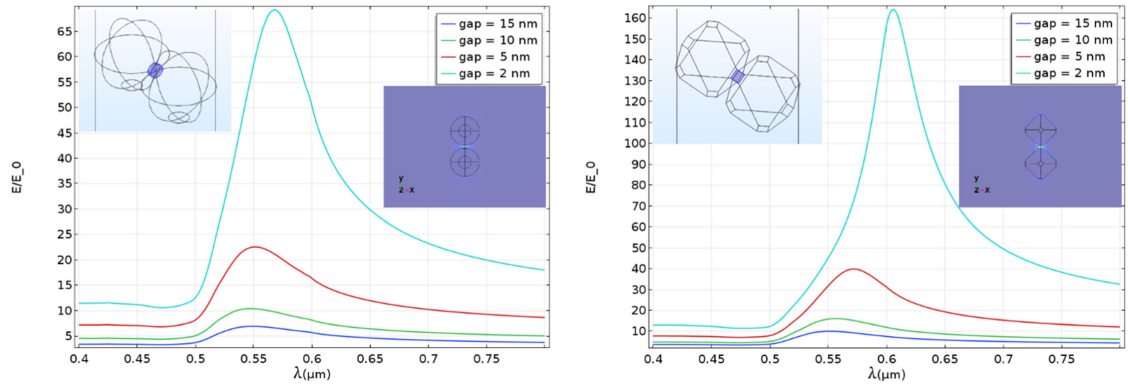

Fig. 1. Average electric field enhancement in the dimer gap, normalized to input field: (a) sphere dimer of varying gap; (b) octahedron dimer of varying gap. Electric field norm is averaged over a small volume around the dimer gap with averaging volumes shown in upper left corner insets.

diagonals of 10 nm. The overall result is slightly larger volume for the spheres and slightly larger maximum linear dimension for the octahedrons. The octahedrons are positioned oriented tip to tip in the dimer [top view is shown as an inset below the legend on Fig. 1 (b)].

The simulation domain is a single unit cell of the array. The domain is bounded by a port and a perfectly matched layer in the z-direction and periodic boundary conditions are set in the transverse dimensions. The port excites a plane wave propagating at normal incidence to the surface with the electric field linearly polarized along the dimer axis. The discretization mesh is refined near the surface of the Au nanoparticles and particularly around the dimer gap. FEM edge elements with second order shape functions are used. Au is modeled through complex permittivity interpolated as a function of wavelength for the spectral range of interest from the Johnson Christy [13] tabulated data and the glass substrate is modeled with constant refractive index of $n = 1.5$.

Field enhancement is averaged over the dimer gap for both types of dimers and the results are presented in Fig. 1 for various gaps ranging from 15 nm to 2 nm. The octahedron dimers exhibit higher electric field enhancements in the dimer gap and their relatively larger electric field is fairly uniform within the gap, in fact more so than in the case of spheres. The plasmonic resonance shows a red shift with decreasing gap, which is expected with light polarization along the dimer axis [7]. In order to better trace this resonance shift, results for dimer absorptance, as well as the single nanoparticle curves are plotted in Fig. 2. For the octahedron dimers the red shift is significantly more sensitive to the interparticle distance compared to the sphere dimers, which would make the octahedrons more attractive if the resonance position is used as a ruler for the inter-particle spacing.

4. Nanoparticles Near Metallic Plate – Virtual Dimers

In order to circumvent the problems with orienting and binding octahedral particles into dimers, we can obtain similar field enhancement effects sought after in applications by placing single particles over a metal plate [14], [15]. The principles of the interaction of a metalic surface with a metalic nanoparticle in close proximity can be understood through a simple dipole – metal surface model [14]. The electric field of the incident electromagnetic radiation will induce in the particle an electric dipole which will be imaged by a perfectly conducting surface. A dipole parallel to the surface is imaged antisymetrically and will thus be cancelled out by its image. A dipole normal to the surface however is imaged symetrically and will result in a field confuguration similar to that of a nanoparticle dimer. This simplified picture, valid for perfect conductors, is of course, strongly modified for real materials. At the wavelengths we are considering, Au in particular is not very ‘metallic’. Therefore,

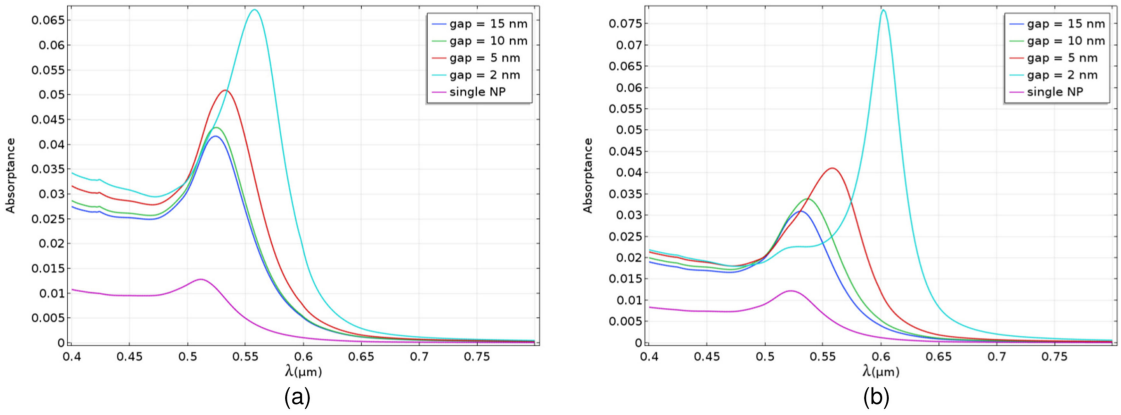

Fig. 2. Absorptance – (a) sphere dimer of varying gap plus single sphere; (b) octahedron dimer of varying gap plus single octahedron.

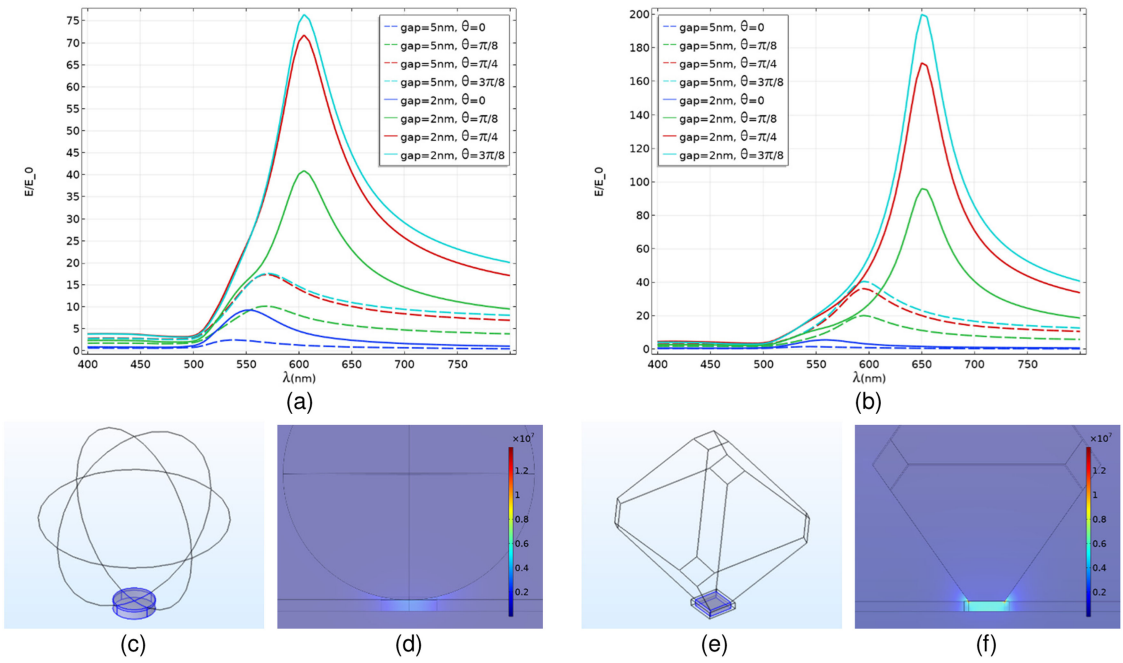

Fig. 3. Average field enhancement in the nanoparticle – metal plate gap, normalized to input field for different angles of incidence: (a) sphere; (b) octahedron. Electric field norm is averaged over a small volume around the nanoparticle – metal plate gap. The averaging volume is shown in (c) for sphere and (e) for octahedron. The diameter of the cylindrical volume in the case of sphere is equal to the diagonal of the octahedron truncation square. Side views of the respective electric field norm distributions in the gap at resonance peak are presented in (d) and (f) for the case of 2 nm gap and $3\pi/8$ angle of incidence.

we will need numerical simulations to explore the extent to which we can build virtual nanoparticle dimers from a metallic particle and its image in a metallic layer. In order to emulate a dimer response, we will need p-polarized light incident at an angle so that an electric dipole component normal to the surface can be excited.

Simulations in this case were conducted for single particles so that we can better exclude any SPP excitation effects due to the array. PMLs are used to terminate the computation domain in all directions and a scatterted field formulation is employed. The nanoparticle is separated from a

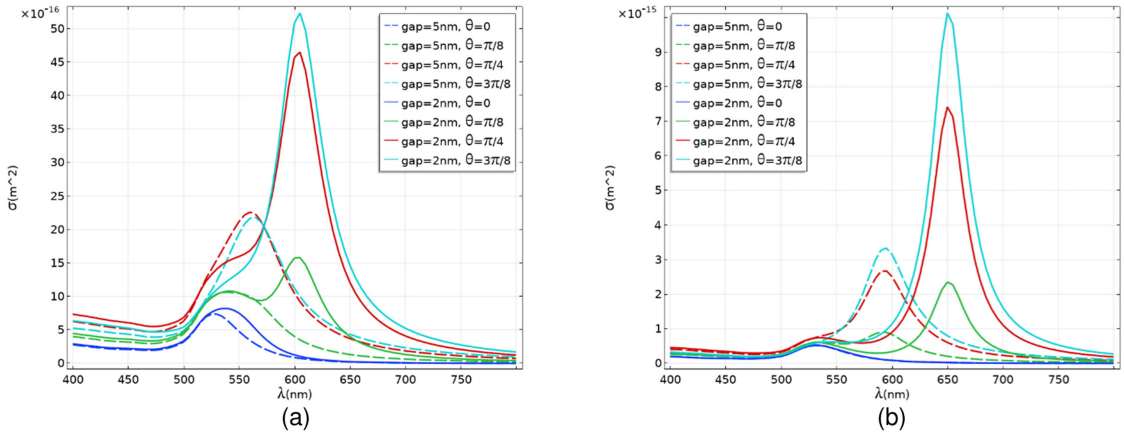

Fig. 4. Nanoparticle scattering cross section for different angles of incidence: (a) sphere; (b) octahedron.

45 nm thick gold layer by a polyelectrolyte film modelled as a lossless dielectric with refractive index n = 1.4, and the separation distance is set to either 5 nm or 2 nm. The impinging excitation is a p-polarized plane wave with varying angles of incidence θ.

Results for spherical and octahedral particle shapes are shown in Fig. 3 and show very similar trends to the results for dimers. The octahedral nanoparticle provides stronger field enhancement than the spherical as well a larger red shift of the response. In order to track better the resonant response scattering cross section results have been presented in Fig. 4. The scattering cross section is extracted as the power flux coming out of the nanoparticle. Due to the imperfect imaging, which is the result of the properties of Au in the spectral range under consideration, some scattering is present even at normal incidence. It is worth noting, that while for the spherical particle the field enhancement and the scattering cross section barely increase when the angle of incidence goes from $\pi/4$ to $3\pi/8$, for the octahedron there is a more substantial increase.

5. Conclusion

While selectively functionalizing the tips and building tip-to-tip connected dimers from very mildly etched octahedrons is challenging, nevertheless the octahedral particles have certain advantages for building dimers relative to their highly etched spherical counterparts. In applications where high field enhancement or sensitivity of the resonance shift to inter-particle distance are desirable the octahedrons are good building block candidates for LSP applications. In a configuration of a nanoparticle placed close to a metal plate the Au octahedrons also perform better than the Au spheres, in particular providing higher field enhancement for potential SERS applications.

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