

Cascaded plasmon resonances multi-material nanoparticle trimers for extreme field enhancement

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ABSTRACT

Optical field enhancement in coupled plasmonic nanostructures has attracted significant attention because of field enhancement factors that significantly exceed those observed in isolated nanostructures. While previous studies demonstrated the existence of such cascaded field enhancement in coupled nanospheres with identical composition, this effect has not yet been studied in systems containing multiple materials. Here, we investigate the polarization-dependent optical response of multi-material trimer nanostructures composed of Au nanoparticles surrounded by two Ag nanoparticles as a function of nanoparticle size and inter-particle spacing. We observe field enhancement factors that are ten times larger than observed in isolated Au nanoparticles.

Keywords: Cascaded plasmon resonance, Field enhancement, Heterotrimers, Asymmetric plasmons, Trimer

1. INTRODUCTION

Metallic nanostructures have attracted enormous interest in nanoscience and nanophotonics due to their ability to enhance and confine optical fields in subwavelength regions. Many important properties of complex plasmonic structures arise from near-field coupling between adjacent nanostructures. Coupled plasmon resonances can produce stronger optical field enhancement factors than observed in isolated plasmonic resonators, allowing these nanostructures to improve the sensitivity of surface-enhanced Raman spectroscopy (SERS)^{1,2}, improve the performance of certain nonlinear optical processes³ and enhance spontaneous emission and stimulated emission rates⁴.

Li and *et al.* showed that a self-similar chain of plasmon resonant metal nanoparticles with identical composition is able to produce significantly higher field enhancement factors than observed in common coupled plasmonic structures⁵ such as metal nanoparticle dimers. The strong field enhancement observed in self-similar chains of nanoparticles is due to a phenomenon sometimes called cascaded field enhancement, which occurs when small nanoparticles with lower polarizability are driven by the strong near-field of its larger neighbor nanoparticle. The effect has been studied experimentally and theoretically, with most studies focusing on cascaded field enhancement in plasmonic nanostructures composed of one material. Recently, optical properties of compositionally asymmetric dimers, heterodimers, were numerically and experimentally investigated^{6,7,8,9}. In these studies, the near field and far field behavior of Ag-Au nanosphere dimers was investigated with a focus on the coupling between free electron oscillations of the silver nanoparticle and bound electron transitions in the gold nanoparticle.

Here, we numerically investigate the optical response of compositionally and geometrically asymmetric trimer nanostructures composed of a small Au nanoparticle surrounded by two large Ag nanoparticles. In this structure, the dipolar plasmon resonance of silver dimer produces the strong optical near field required to drive small gold nanoparticle in the cascaded field enhancement scheme. The field enhancement spectra of the trimers were calculated numerically as a function of nanoparticle size and inter-particle spacing. Results show that different cascading regimes can exist depending on the dimensions and particle size differences.

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2. TRIMER GEOMETRY

In order to achieve cascaded field enhancement two plasmon resonant systems with different polarizability and similar plasmon resonance energy are needed. Figure 1 shows a schematic of multi-material Ag-Au-Ag trimer used in the present study to achieve these conditions. The trimer structure is composed of a small Au nanoparticle symmetrically surrounded by two large silver nanoparticles. The isolated gold nanosphere has lower plasmon resonance energy than an isolated silver nanosphere assuming identical dielectric environment, which seems to preclude cascaded coupling between silver and gold particles. To avoid this problem, here we use the red-shifted plasmon resonance of a silver dimer excited along the dimer axis as the 'large resonator' that provides the strong near-field required to drive the small Au resonator. The spectral plasmon resonance of the silver dimer can be matched to the plasmon resonance of the gold nanosphere by varying the Ag-Ag inter-particle spacing as well as the silver nanoparticles size.

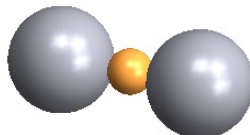


Figure 1: Schematic of Ag-Au-Ag trimer structure.

Three-dimensional frequency domain electromagnetic simulations were performed using CST Microwave Studio¹⁰. We considered multi-material Ag-Au-Ag trimers embedded in a host with a frequency independent real refractive index of 1.33, similar to that of water at visible frequencies. The structure is excited using a plane wave propagating in the direction normal to trimer axis and polarized along the trimer axis. The silver dielectric function is described by a Drude model fit to literature data given by $\epsilon_{Ag} = \epsilon_{\infty} - \omega_p^2 / (\omega^2 + i\omega\Gamma)$ where $\epsilon_{\infty} = 5.451$, $\omega_p = 1.474 \times 10^{16}$ rad/s, and the electron scattering rate is $\Gamma = 8.354 \times 10^{13}$ s⁻¹. Literature data was used for gold dielectric function¹¹. For simplicity surface scattering is neglected in these simulations.

3. RESULTS

3.1 Silver nanoparticle size effect

Figure 2 shows the calculated field enhancement inside the gap of silver dimers in the absence of a central Au nanoparticle for Ag nanoparticle diameters of 60 nm, 80 nm and 100 nm at a fixed edge-to-edge spacing of 20 nm. All three spectra show a broad plasmon resonance as well as a sharp multipolar peak at high frequencies. The broad resonance is related to the dipolar plasmon resonance of two silver nanoparticles which redshifts as the particle size increases. This is due to the larger polarizability of the large nanoparticles which leads to stronger dipole-dipole interaction. The dashed line shows the internal field enhancement of an isolated 10 nm gold nanoparticle for comparison. Note that the dipole resonance of the silver dimer can be tuned to overlap with the Au nanoparticle resonance peak by using different size for silver nanoparticles.

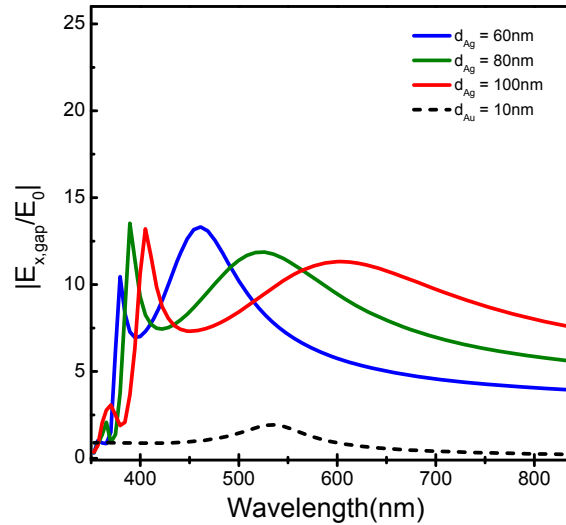


Figure 2: Field enhancement in the gap of silver dimers at fixed edge-to-edge spacing of 20nm with silver nanoparticle diameter of 60nm, 80nm and 100nm, and internal field enhancement of an isolated 10nm diameter Au nanoparticle (dashed line).

Figure 3 shows the internal field enhancement of a 10 nm diameter gold nanoparticle located at the center of the silver dimers from Fig. 2. The largest field enhancement occurs when the plasmon resonance of the isolated gold nanoparticle matches that of the red-shifted resonance of the silver dimer, which occurs for a silver particle diameter of 80 nm. In case of small size difference, blue line, two dipolar modes at 470 nm and 535 nm are related to the silver dimer resonance and the isolated gold plasmon resonance, correspondingly.

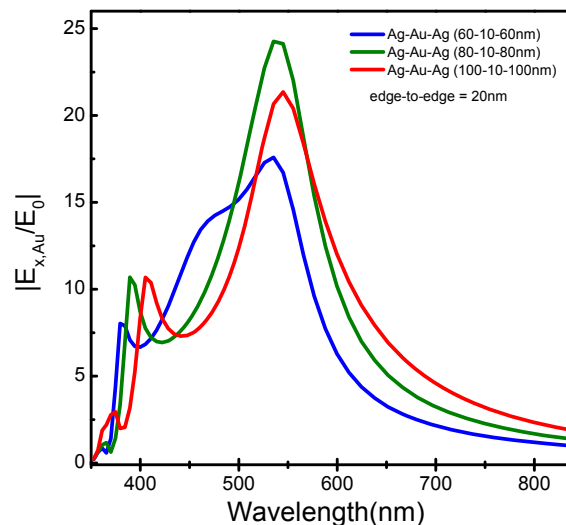


Figure 3: Internal field enhancement of a 10nm gold nanoparticle located at the center of the silver dimer structures from Fig. 2.

3.2 Interparticle spacing effect

Figure 4 shows the internal field enhancement in the gap of a silver dimer with a fixed Ag nanoparticle diameter of 100 nm for edge-to-edge spacings of 40 nm, 30 nm and 20 nm. Spectra demonstrate that the dipolar plasmon resonance redshifts as the edge-to-edge spacing decreases, which is a well-known phenomenon when a dimer is longitudinally excited. In addition, the strength of the confined electric field in the gap increases when the edge-to-edge spacing decreases.

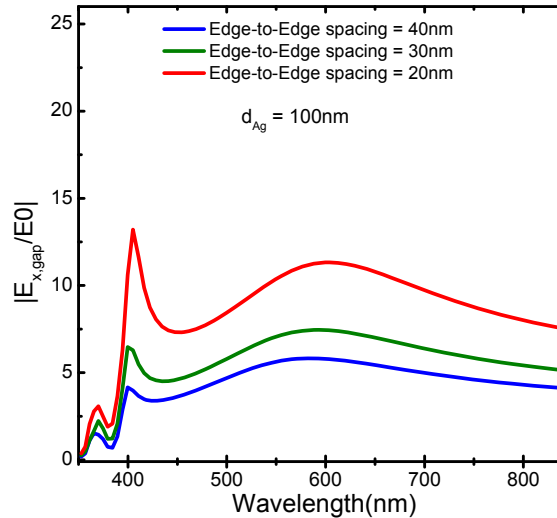


Figure 4: Field enhancement in the gap of silver dimers for a fixed Ag nanoparticle diameter of 100nm and an edge-to-edge spacing of 40nm, 30nm and 20nm.

Figure 5 shows the internal field enhancement of a 10 nm diameter gold nanoparticle placed at the center of the silver dimers from Fig. 4. The field enhancement inside gold nanoparticle is approximately equal to the multiplication of the field enhancement inside the isolated gold nanoparticle, Fig. 2 (dashed line), and the field enhancement in the gap of silver dimer, Fig. 4, as expected in the presence of cascaded plasmon resonance¹².

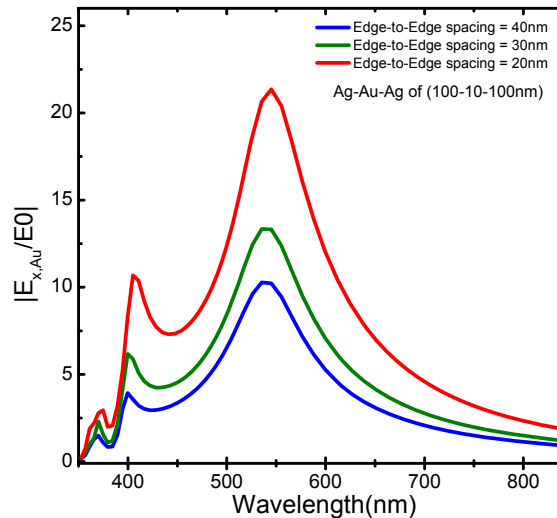


Figure 5: Internal field enhancement of a 10nm gold nanoparticle located at the center of the silver dimer structures from Fig. 4.

The results in Figs. 2 and 3 show that for mismatched resonances of the Ag dimer and the Au monomer that make up the multi-material trimer structure, relatively small field enhancement values are obtained, Fig. 3 (red and blue curves). In the case of matched dimer-monomer resonance frequencies, multiplicative cascaded field enhancement is observed, leading to a field enhancement factor of 24, 12 times larger than observed in isolated Au nanoparticles, Fig. 3 (green curve). Results show that mutual coupling system in a multi-material trimer enables strong field enhancement inside and around gold nanoparticles.

4. CONCLUSIONS

Optical field enhancement inside a gold nanoparticle in multi-material Ag-Au-Ag nanoparticle trimers has been numerically studied. It was shown that for small size differences, clear mode splitting and declined field enhancement occurs. Results show that for specific size differences and a specific geometry (interparticle spacing) multiplicative cascaded field enhancement occurs in which the internal field enhancement inside the gold nanoparticle exceeds that of isolated Au nanoparticles by up to a factor 12. The presented structure appears compatible with chemical synthesis and assembly methods, suggesting that cascaded heterotrimers could form the basis of biochemical sensors that require large electric field enhancement.

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