Taking cascaded plasmonic field enhancement to the ultimate limit in silver nanoparticle dimers

S. Toroghi*[a], P. G. Kik[a,b]
[a]CREOL, The College of Optics and Photonics, University of Central Florida, 4000 Central Florida Blvd, Orlando, FL 32816, USA; [b]Department of Physics, University of Central Florida, 4000 Central Florida Blvd, Orlando, FL 32816, USA

ABSTRACT

Cascaded optical field enhancement in coupled plasmonic nanostructures has attracted significant attention because of field enhancement factors that dramatically exceed those observed in isolated nanostructures. While previous studies demonstrated the existence of cascaded enhancement, little work has been done to identify the requirements for achieving maximum field enhancement. Here, we investigate cascaded field enhancement in silver nanosphere dimers as a function of volume ratio and center-to-center separation, and show the requirements for achieving the ultimate cascading limit in nanoparticle dimers. We observe field enhancements that are a factor 75 larger than observed in isolated silver nanoparticles.

Keywords: Cascaded field enhancement, Mutual interaction, Dimers, Multiplicative cascading, Ultimate cascading

1. INTRODUCTION

In recent years, the coupling between metal nanoparticles in plasmonic nanostructures has attracted enormous interest due to the strong field enhancement factors that can be achieved and the possibility of tuning the plasmon resonance frequency in these structures[1-8]. Recently, it has been shown that a specific type of coupled nanoparticles, a self-similar chain of plasmon resonant metal nanoparticles, is able to produce much higher field enhancement factors compared to isolated plasmonic structures[1]. The strong field enhancement in a self-similar chain of nanoparticles is due to a phenomenon called cascaded field enhancement. In this effect, a small particle in the chain is driven by the resonantly enhanced near field of a large neighboring particle, leading to extreme field confinement inside and around the small particle. The strong cascaded field enhancement enables the use of these nanostructures in a wide variety of plasmon related experiments such as enhanced Raman scattering[2,8], enhanced nonlinear optical response[9], and enhanced stimulated emission[10].

Cascaded plasmonic field enhancement has been studied experimentally and theoretically. In a recent study, Sun *et al.* used a fully analytical coupled-mode model to investigate the optical properties of plasmonic metal dimers[11,12]. The optical field enhancement inside the small nanoparticle and in the gap between two nanoparticles was studied taking into account dipolar and multipolar plasmon resonances. Their model shows how the various modes interact to produce the optical field enhancement in cascaded plasmonic structures; however, the inclusion of multipolar modes, while necessary in some situations, complicates the picture substantially.

In this paper, we use a dipole-dipole interaction model to investigate the effect of size difference and the center-to-center separation in silver nanoparticle dimers on the cascaded field enhancement. We introduce three different cascading regimes, '*hindered*', '*multiplicative*' and '*ultimate*', for nanoparticle dimers, depending on the mutual interaction strength. We show that the presented model allows us to rapidly evaluate the effect of the particle size differences and inter-particle spacing on the attainable cascaded field enhancement.

*storoghi@creol.ucf.edu; phone 1 407-823-6899; fax 1 407-823-6875

Plasmonics: Metallic Nanostructures and Their Optical Properties X, edited by Mark I. Stockman,
Proc. of SPIE Vol. 8457, 84570D · © 2012 SPIE · CCC code: 0277-786/12/$18 · doi: 10.1117/12.930333

2. NUMERICAL METHOD

2.1 Dipole-Dipole interaction model

We consider each nanosphere as a point dipole with a polarizability α_i given by

$$\alpha_i = 3\varepsilon_0\varepsilon_h V_i \frac{\varepsilon_m - \varepsilon_h}{\varepsilon_m + 2\varepsilon_h} \tag{1}$$

where V_i, is the volume of nanosphere i. ε_0, ε_m and ε_h are the vacuum permittivity, the dielectric function of the metal and the dielectric function of the host, respectively. The dipole moment of a nanosphere located at position r_i, can be written as

$$\mathbf{p}_i = \alpha_i \mathbf{E}_{loc}(\mathbf{r}_i) \tag{2}$$

where $\mathbf{E}_{loc}(\mathbf{r}_i)$ is the sum of the incident field $\mathbf{E}_{inc}(\mathbf{r}_i)$ and the local electric fields generated by all the neighbor dipoles at locations $\mathbf{r}_i$, which itself is given by

$$\mathbf{E}_{loc}(\mathbf{r}_i) = \mathbf{E}_{inc}(\mathbf{r}_i) + \mathbf{E}_{dipole,j}(\mathbf{r}_i) = \mathbf{E}_0 e^{i\mathbf{k}_i \cdot \mathbf{r}_i} - \sum_{i \neq j} \mathbf{A}_{ij}\mathbf{p}_j \tag{3}$$

where $\mathbf{A}_{ij}\,\mathbf{p}_j$ is the electric field contribution of dipole j at the position of dipole i and is given by

$$\mathbf{A}_{ij}\mathbf{p}_j = \frac{e^{ikr_{ij}}}{4\pi\varepsilon_0\varepsilon_h r_{ij}^3}\left[k^2\mathbf{r}_{ij} \times (\mathbf{r}_{ij} \times \mathbf{p}_j) + \frac{(1-ikr_{ij})}{r_{ij}^2}\left(r_{ij}^2\mathbf{p}_j - 3\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{p}_j)\right)\right] \qquad \text{for } i \neq j \tag{4}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$ and k is the magnitude of the wavevector in the host medium.

For a dimer structure illuminated with an electromagnetic wave polarized along the dimer axis, as shown in Fig. 1, the dipole-dipole interaction matrix, A_{ij}, can be written as

$$A_{12} = A_{21} = \frac{e^{ikd}}{2\pi\varepsilon_0\varepsilon_h}\left(\frac{ik}{d^2} - \frac{1}{d^3}\right) \tag{5}$$

where d is the center-to-center separation of the two nanospheres in the dimer structure. Substitution of Eq. 3 into Eq. 2 and considering a dimer structure excited with longitudinal polarization in the quasi-electrostatic regime, leads to

$$\begin{aligned} p_1 &= \alpha_1[E_{inc} - A_{12}p_2] \\ p_2 &= \alpha_2[E_{inc} - A_{21}p_1] \end{aligned} \tag{6}$$

The dipole moment of both nanoparticles can be obtained by solving these two linear equations, leading to

$$\begin{aligned} p_1 &= \alpha_1 \frac{1 - \alpha_2 A_{12}}{1 - \alpha_1\alpha_2 A_{12}^2} E_{inc} \\ p_2 &= \alpha_2 \frac{1 - \alpha_1 A_{12}}{1 - \alpha_1\alpha_2 A_{12}^2} E_{inc} \end{aligned} \tag{7}$$

The second term in the denominator, $\alpha_1\ \alpha_2\ A_{12}{}^2$, represents a coupling parameter that describes the effective mutual interaction strength between the dipoles. With the known dipole moment for each nanoparticle, the electric field in every position can be evaluated.

2.2 Field Enhancement factor

Assuming that the structures remain in the quasi-electrostatic limit, the internal electric field of the nanoparticles can be obtained using the following formula.

$$E_{in} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} E_{loc} \tag{8}$$

The local electric field in Eq. 8 can be obtained using the obtained dipole moment in Eq. 7 together with Eq. 2 which states $E_{loc} = p/\alpha$. The internal electric field of the small nanoparticle in the dimer structure thus becomes:

$$E_{in,1} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} E_{loc,1} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} \frac{1 - \alpha_2 A_{12}}{1 - \alpha_1\alpha_2 A_{12}^2} E_{inc}. \tag{9}$$

The internal field enhancement factor is defined as $g_{in} = E_{in}/E_{inc}$, which for particle 1 becomes:

$$g_{in,1} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} \frac{1 - \alpha_2 A_{12}}{1 - \alpha_1 \alpha_2 A_{12}^2}. \quad (10)$$

Using the continuity of the normal electric displacement at the metal surface, $\varepsilon_h E_{out} = \varepsilon_m E_{in}$, and Eq. 10, the external field enhancement factor at the surface of the small nanoparticle in the dimer structure can be written as

$$g_{out,1} = \frac{\varepsilon_m}{\varepsilon_h} g_{in,1} \quad (11)$$

We introduce a parameter called the multiplicative field enhancement factor g_{MFE} which is the product of the external field enhancement factor of an isolated large nanoparticle measured at the position of the small nanoparticle (i.e. at a distance d from the center of the large nanoparticle) and the internal field enhancement of the isolated small nanoparticle, *i.e.*

$$g_{MFE,1} = g_{out,2}(d)\, g_{in,1} \quad (12)$$

where $g_{out,2}$ (d) represents the field contribution of the large nanoparticle at a distance d from the center of that nanoparticle. Comparison of multiplicative field enhancement spectra and the field enhancement spectra as obtained through the coupled dipole model reveals the various interaction regimes governing the field enhancement of the dimer structures. A large deviation from multiplicative field enhancement indicates a strong mutual interaction regime while a small deviation indicates weak mutual interaction. The latter condition can lead to field enhancement values approaching the ultimate cascading limit. The ultimate cascading limit is a specific situation of multiplicative cascading in which the smaller particle is sufficiently close to the large nanoparticle to experience its maximum external field enhancement of $|3\varepsilon_m(\omega_{LSP})/(\varepsilon_m(\omega_{LSP})+2\varepsilon_h)|$, while the polarizability of that is small enough to not disturb the dipole moment of the large nanoparticle. Therefore, the multiplicative cascading would produce an ultimate internal field enhancement of magnitude $|g_{ucl,in}| = |g_{1,in}(\omega_{LSP}) \times 3\varepsilon_m(\omega_{LSP})/(\varepsilon_m(\omega_{LSP})+2\varepsilon_h)| = 2\,(3\varepsilon_h/\mathrm{Im}(\varepsilon_m))^2$.

3. RESULTS

An asymmetric silver nanosphere dimer is used to investigate cascaded field enhancement. A schematic of this dimer structure is shown in Fig. 1. Literature data were used for the dielectric function of silver[13] and we consider that these structures are embedded in a host medium with $\varepsilon_h = 2.25$. The size of large nanoparticle is kept constant, R_2=5nm, in all parametrical studies in this paper.

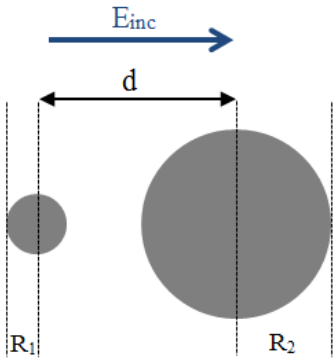

Figure 1: Schematic of the asymmetric dimer with two nanospheres with radii R_1 and R_2 at a center-to-center spacing d.

Figure 2 shows the internal field enhancement spectra, $|g_{in,1}| = |E_{in,1}/E_{inc}|$, in the small particle for four silver nanoparticle dimers with different volume ratios, V_2/V_1, of 1, 5, 20 and 100 while the center-to-center separation, d, is fixed at 15nm. The radius of the small nanoparticle, R_1, in the four different dimers is 5nm, 2.92nm, 1.84nm and 1.07nm, respectively, while that of the large nanoparticle is kept constant at 5nm. The internal field enhancement of the small nanoparticle in the dimer with volume ratio of 1 (red solid line) shows a redshift of the plasmon resonance compared to that of the isolated nanoparticle (dashed line). The internal field enhancement of the small nanoparticle for structures with volume ratios of 5 (orange solid line) and 20 (green solid line) show plasmon resonance mode splitting while the field enhancement is lower than the expected multiplicative field enhancement $|g_{MFE,1}|$ (dotted line). Under longitudinal

excitation the low energy mode is a symmetric mode while the higher energy mode is an anti-symmetric mode. The small nanoparticle in a dimer with a volume ratio of 100 (blue solid line) shows the largest field enhancement factor compared to other dimer structures with lower volume ratios. In this case the enhancement is comparable to the multiplicative field enhancement spectrum (dotted line) which indicates that the mutual interaction between the two nanoparticles at this specific volume ratio and inter-particle spacing is weak.

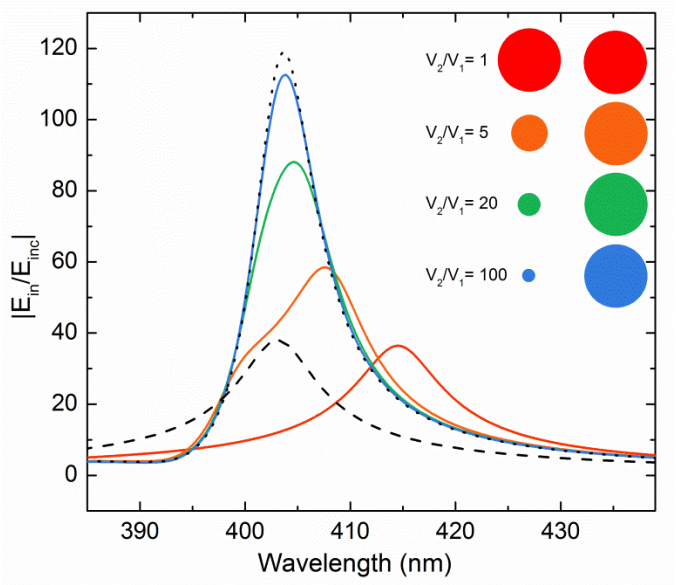

Figure 2: Internal field enhancement spectra of four dimer structures with different volume ratios and constant center-to-center separation of 15nm. The dashed line shows the isolated nanoparticle field enhancement spectra. The dotted line shows the multiplicative field enhancement spectrum of the dimer structure.

Figure 3 shows the internal field enhancement spectra, $|g_{in,1}| = |E_{in,1}/E_{inc}|$, in the small particle for four silver nanoparticle dimers with different center-to-center spacing, d, of 40nm, 15nm, 12nm and 10nm with a fixed volume ratio of 100. The internal field enhancement for the center-to-center separation of 40nm, Fig. 3(a), shows a small improvement of the field enhancement (solid line) compared to that of the isolated nanoparticle (dotted line) while the spectrum is nearly identical to the multiplicative field enhancement spectra (dashed line). This indicates that the mutual interaction between the well-separated nanoparticles in this dimer structure is weak. The result for a center-to-center separation of 15nm, Fig. 3(b), shows that the smaller separation leads to a higher field enhancement in the small nanoparticle due to the larger near-field contribution of the large nanoparticle at this distance. The nearly identical spectra of the internal field enhancement of the small nanoparticle (solid line) and the multiplicative field enhancement (dashed line) demonstrates that the structure is still in the weak mutual interaction regime. At a center-to-center separation of 12 nm, Fig. 3(c), the peak value of the field enhancement of the small nanoparticle (solid line) is significantly below the expected multiplicative field enhancement (dashed line) indicating significant mutual coupling between two nanoparticles at this distance. Results for a center-to-center separation of 10 nm, Fig. 3(d), show a large mode splitting in the internal field enhancement of the small nanoparticle (solid line) along with a field enhancement factor that is well below the multiplicative field enhancement (dashed line) indicative of strong mutual interaction at this distance.

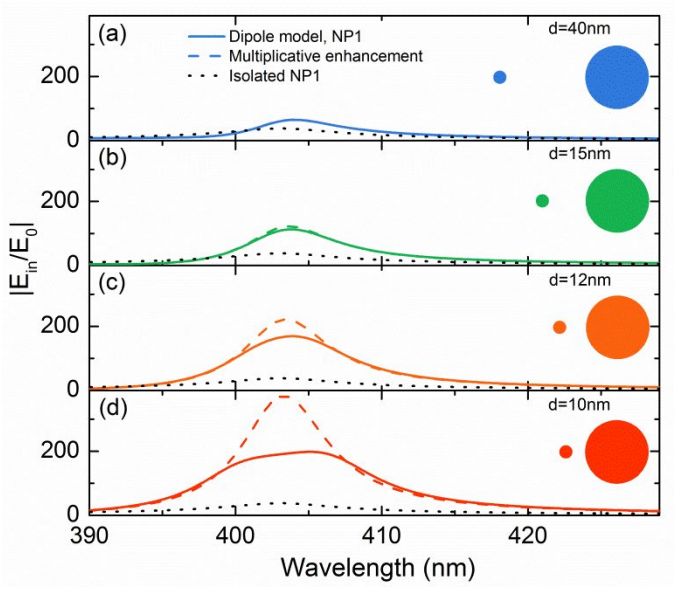

Figure 3: Internal field enhancement spectra of the small nanoparticle for 4 different dimer structures with different center-to-center spacing and constant volume ratio of 100. Dashed lines show the multiplicative field enhancement spectra while dotted lines show the internal field enhancement of the isolated nanoparticle.

The results above demonstrate that asymmetric silver nanoparticle dimers produce peak field enhancement factors that are increased compared to that of an isolated silver nanoparticle for a wide range of center-to-center spacings and particle size differences. In addition, the largest field enhancement factors are observed at large size differences and small center-to-center spacings. For extremely large volume ratios and small center-to-center separation, the calculated internal field enhancement factors are predicted to reach the ultimate cascading limit $|g_{ucl,in}| = 2.9\times10^3$ for these materials. One should note that the dipole-dipole method used to calculate these field enhancements does not take into account surface scattering which is known to introduce a substantial increase in resonance linewidth and a reduction in peak field enhancement values for particles smaller than a few nanometers in diameter. The dipole interaction model also does not include multipolar plasmon modes expected to arise for small inter-particle spacing at intermediate volume ratios where the inhomogeneous near-fields are strong. However, the largest field enhancement factors occur in the multiplicative cascading regime in which the mutual interaction is necessarily weak, reducing the importance of multipolar modes. Consequently, our simplified point dipole model predicts surprisingly precise results for systems producing multiplicative cascading, including systems operating near the ultimate cascading limit.

4. CONCLUSIONS

We used a point dipole-dipole interaction model to evaluate cascaded field enhancement in asymmetric silver nanosphere dimers. We showed three different cascading regimes, '*hindered*', '*multiplicative*' and '*ultimate*', that can occur depending on the mutual interaction strength. The evolution of the field enhancement factor as a function of particle volume ratio and the center-to-center separation was analyzed. The structures were shown to enable an ultimate internal cascaded field enhancement of a factor 2.9×10^3 for dimers with large size difference and small inter-particle spacing.

REFERENCES

[1] Li, K.; Stockman, M. I.; Bergman, D. J., "Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens," Phys Rev Lett 91(22), 227402 (2003).

[2] Kravets, V. G.; Zoriniants, G.; Burrows, C. P.; Schedin, F.; Casiraghi, C.; Klar, P.; Geim, A. K.; Barnes, W. L.; Grigorenko, A. N., "Cascaded Optical Field Enhancement in Composite Plasmonic Nanostructures," Phys Rev Lett 105(24), 246806 (2010).
[3] Nordlander, P.; Oubre, C.; Prodan, E.; Li, K.; Stockman, M. I., "Plasmon hybridizaton in nanoparticle dimers," Nano Lett 4(5), 899-903 (2004).
[4] Aizpurua, J.; Bryant, G. W.; Richter, L. J.; de Abajo, F. J. G.; Kelley, B. K.; Mallouk, T., "Optical properties of coupled metallic nanorods for field-enhanced spectroscopy," Phys Rev B 71(23), 235420 (2005).
[5] Aubry, A.; Lei, D. Y.; Maier, S. A.; Pendry, J. B., "Interaction between Plasmonic Nanoparticles Revisited with Transformation Optics," Phys Rev Lett 105(23), 233901 (2010).
[6] Nurmikko, A. V.; Atay, T.; Song, J. H., "Strongly interacting plasmon nanoparticle pairs: From dipole-dipole interaction to conductively coupled regime," Nano Lett 4(9), 1627-1631 (2004).
[7] Zhang, X.; Su, K. H.; Wei, Q. H.; Mock, J. J.; Smith, D. R.; Schultz, S., "Interparticle coupling effects on plasmon resonances of nanogold particles," Nano Lett 3(8), 1087-1090 (2003).
[8] Gopinath, A.; Boriskina, S. V.; Premasiri, W. R.; Ziegler, L.; Reinhard, B. M.; Dal Negro, L., "Plasmonic Nanogalaxies: Multiscale Aperiodic Arrays for Surface-Enhanced Raman Sensing," Nano Lett 9(11), 3922-3929 (2009).
[9] Li, K. R.; Stockman, M. I.; Bergman, D. J., "Enhanced second harmonic generation in a self-similar chain of metal nanospheres," Phys Rev B 72(15), 153401 (2005).
[10] Li, K. R.; Li, X. T.; Stockman, M. I.; Bergman, D. J., "Surface plasmon amplification by stimulated emission in nanolenses," Phys Rev B 71(11), 115409 (2005).
[11] Sun, G.; Khurgin, J. B.; Bratkovsky, A., "Coupled-mode theory of field enhancement in complex metal nanostructures," Phys Rev B 84(4), 045415 (2011).
[12] Sun, G.; Khurgin, J. B., "Optimization of the nanolens consisting of coupled metal nanoparticles: An analytical approach," Appl Phys Lett 98(15), 153115 (2011).
[13] Johnson, P. B.; Christy, R. W., "Optical-Constants Of Noble-Metals," Phys Rev B 6(12), 4370-4379 (1972).