3-17-2011

Theory of optical emission enhancement by coupled metal nanoparticles: An analytical approach

Greg Sun
University of Massachusetts Boston, greg.sun@umb.edu

Jacob B. Khurgin
Johns Hopkins University

AIP | Applied Physics Letters

Theory of optical emission enhancement by coupled metal nanoparticles: An analytical approach

G. Sun and J. B. Khurgin

Citation: Appl. Phys. Lett. **98**, 113116 (2011); doi: 10.1063/1.3565170
View online: http://dx.doi.org/10.1063/1.3565170
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v98/i11
Published by the American Institute of Physics.

Theory of optical emission enhancement by coupled metal nanoparticles: An analytical approach

G. Sun[1,a)] and J. B. Khurgin[2]
[1]*University of Massachusetts Boston, Massachusetts 02125, USA*
[2]*Johns Hopkins University, Baltimore, Maryland 21218, USA*

(Received 15 December 2010; accepted 20 February 2011; published online 17 March 2011)

We present an analytical "coupled mode" model explaining enhancement of emission by an emitter placed within complexes of metal nanoparticles and apply it for an important case of an emitter placed inside the gap of two coupled Au nanospheres. This approach has dual advantages of exposing the underling physics of the enhancement and revealing a straightforward path toward optimization. © *2011 American Institute of Physics*. [doi:10.1063/1.3565170]

Modification of optical properties of atoms and molecules in the vicinity of nanostructured metal surfaces has been known for a long time,[1] and has more recently been applied to enhancement of Raman scattering,[2] fluorescence,[3] and photovoltaic processes.[4] While many theoretical models relied upon extensive numerical calculations, we have developed a simple analytical model for isolated metal nanoparticles that revealed the origin of enhancement for various optical properties, allowed for optimization of nanoparticle parameters, and notably, established the enhancement limits and figures of merits.[5–7] In a nutshell, to enhance luminescence the surface plasmon (SP) mode in a nanostructure must be tightly confined to ensue a large Purcell factor[8] so that energy can be efficiently transferred from the active molecule into the SP mode before it gets lost via nonradiative decay inside the molecule. At the same time this SP mode should be efficiently coupled to the free space so that energy can get radiated out before it gets lost via Ohmic loss inside the metal. In other words, the nanostructure should present at once a good cavity and an efficient antenna. A single nanoparticle can never satisfy this "best of both worlds" demand and more complex structures must be explored.

Clusters of coupled nanoparticles have been indeed shown to provide larger field enhancement than a single particle by numerous experimental[9,10] and theoretical[11,12] works. However, most of the latter relied upon complex and time-consuming numerical models missing a clear physical picture which do not allow for quick optimization. Furthermore, as we have already mentioned, the enhancement of electric field does not always correlate directly to that of optical emission which has a strong dependence on the original radiative efficiency of the emitters placed at the "hot spots" of a nanocluster. Recently we have expanded our "eigenmode" approach to the system of coupled nanoparticles and offered a simple explanation of field enhancement as progressive coupling of energy from free space via the dipole modes acting as antennae to the higher order modes acting as tight cavities where the hot spots are engendered.[13] This coupled mode approach is well suited to analyze the reverse process of coupling the energy from active molecules to the free space via succession of SP modes and in this work we apply it to the nanoparticle dimer, which has not been analyzed for the enhancement of emission.

To emphasize the role played by the coupling of SP modes we shall commence with the properties of SP modes supported by a single metal nanosphere of radius a placed in the dielectric with relative permittivity ε_D. The frequency of the lth SP mode $\omega_l=\omega_p\sqrt{l/[l+(l+1)\varepsilon_D]}$,[7] where ω_p is the metal Plasmon frequency. For Au spheres surrounded by GaN, these mode frequencies range from $\hbar\omega_1=1.967$ eV to $\hbar\omega_\infty=2.261$ eV. Among all the SP modes, only the dipole ($l=1$ mode produces a non-vanishing dipole moment that couples to radiation modes, i.e., acting as an antenna and subject to the radiative decay at a rate proportional to the sphere volume, $\gamma_{rad}=2\omega\chi^3/3\varepsilon_D$,[13] where $\chi=2\pi a/\lambda_D$ is the radius normalized to the wavelength λ_D in the dielectric corresponding to the emission frequency ω. At the same time, all the modes experience nonradiative decay due to the imaginary part of the metal dielectric constant ($\varepsilon=\varepsilon'+j\varepsilon''$) at roughly the same rate, $\gamma\sim\omega\varepsilon''/\varepsilon'$ ($\hbar\gamma\approx0.20$ eV at the dipole mode resonance). Each SP mode of the lth order is well characterized by its effective mode volume $V_{eff,l}=4\pi a^3/[(l+1)^2\varepsilon_D]$.[13] Thus the higher order modes can indeed be very efficient cavities, yet they remain uncoupled to radiation modes. And the only SP mode that is rather efficiently coupled to the outside, is anything but a good cavity due to both its larger volume and additional radiative loss.

This harmful state of affairs can be remedied if the outlet can be found for the energy trapped in the higher order modes. For the example of two coupled Au nanospheres (Fig. 1) where the polarization of the molecule is along the connecting line between the two spheres, energy captured by the higher order modes of one sphere can now be coupled into the dipole mode of the other, providing a channel for it to turn into free space radiation. In other words, with the use of coupled metal nanoparticles, it is possible to combine the dipole mode of one particle acting as an efficient antenna with a combination of higher order modes of another particle acting as efficient cavities. Here we develop an analytical model for the energy transfer between the SP modes of closely spaced metal spheres and use it to estimate its efficiency. The theory can be applied to multiple particles of different shapes and dimensions but for the sake of simplicity, we examine exclusively the case of two spheres separated by $r_0=r_1+r_2$ [Fig. 1].

a)Electronic mail: greg.sun@umb.edu.

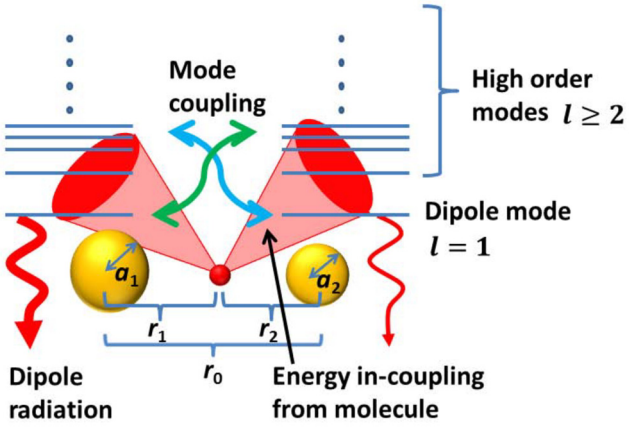

FIG. 1. (Color online) Illustration of the energy coupling from the emitter to SP modes as well as their subsequent coupling between two closely spaced metal spheres that are separated by $r_0=r_1+r_2$. The polarization is along the line that connects the centers of the two spheres.

In order to properly address the energy balance between the molecule, SP modes in the nanospheres and the free-space radiation we introduce the amplitudes for the lth SP mode of sphere i as $A_l^{(i)}=\sqrt{U_l^{(i)}}$, where $U_l^{(i)}$ is the mode energy, and similarly, the amplitude of the dipole of the excited emitter as $B=\sqrt{U_m}$ where U_m is the energy of the molecule. We can now write the set of coupled equations as

$$\begin{aligned}
\frac{dA_1^{(i)}}{dt} &= j(\omega_1-\omega)A_1^{(i)} - \frac{1}{2}(\gamma+\gamma_{rad}^{(i)})A_1^{(i)} - \frac{1}{2}\sqrt{\gamma_{rad}^{(i)}\gamma_{rad}^{(j)}}A_1^{(j)} \\
&\quad - j\sum_{l=1}^{\infty}\omega_{1l}\kappa_{1l}^{(ij)}A_l^{(j)} - j\omega_{1B}\kappa_1^{(i)}B, \\
\frac{dA_l^{(i)}}{dt} &= j(\omega_l-\omega)A_l^{(i)} - \frac{1}{2}\gamma A_l^{(i)} - j\omega_{1l}\kappa_{1l}^{(ji)}A_1^{(j)} \\
&\quad - j\omega_{lB}\kappa_l^{(i)}B, \quad l\geq 2, \\
\frac{dB}{dt} &= \frac{\sqrt{\gamma_m P}}{2} - \frac{1}{2}\gamma_m B - j\sum_{l=1}^{\infty}\omega_{lB}(\kappa_l^{(1)}A_l^{(1)}+\kappa_l^{(2)}A_l^{(2)}),
\end{aligned} \tag{1}$$

where $\omega_{lB}=\sqrt{\omega\omega_l}$ and $\omega_{1l}=\sqrt{\omega_1\omega_l}$. Included in Eq. (1) are the usual detuning and decay terms for all SP modes, and the super-radiance term $\frac{1}{2}\sqrt{\gamma_{rad}^{(i)}\gamma_{rad}^{(j)}}A_1^{(j)}$ that accounts for the coherent character of emission by two dipoles, as well as the excitation term that contains the pumping power P that excites the molecule (but not the SP modes directly) with an original decay rate of $\gamma_m=\tau_{rad}^{-1}+\tau_{nrad}^{-1}$. There are also two kinds of coupling terms. The coupling between the molecule and the lth mode of sphere i is described by the coupling coefficient

$$\kappa_l^{(i)} = \frac{l+1}{2\sqrt{\gamma_{rad}^{(i)}\tau_{rad}}}\left(\frac{a_i}{r_i}\right)^{l+2}. \tag{2}$$

The presence of $\gamma_{rad}^{(i)}$ indicates that coupling is stronger for smaller spheres, and the $(l+1)$ relationship suggests more efficient coupling to higher order modes which, unfortunately, are uncoupled to the outside—the aforementioned antenna-cavity incongruity. There is also coupling between all the modes with index l in sphere j and the radiating dipole mode $(l=1)$ of sphere i and can also be obtained analytically as[13]

$$\kappa_{1l}^{(ij)} = \frac{l+1}{2}\left(\frac{a_i}{r_0}\right)^{3/2}\left(\frac{a_j}{r_0}\right)^{l+1/2}. \tag{3}$$

The coupling between higher order (i.e., nonradiative) modes of two spheres does not contribute to the energy transfer and will be neglected in this analysis.

At steady state, the first two equations in Eq. (1) can be written in a matrix form as

$$\boldsymbol{M}_{2N\times 2N}\begin{bmatrix}\mathbb{A}^{(1)}\\ \mathbb{A}^{(2)}\end{bmatrix} = \begin{bmatrix}\mathbb{K}^{(1)}/\sqrt{\gamma_{rad}^{(1)}}\\ \mathbb{K}^{(2)}/\sqrt{\gamma_{rad}^{(2)}}\end{bmatrix}\frac{B}{\sqrt{\tau_{rad}}}. \tag{4}$$

Here $\mathbb{A}^{(i)}$ is a vector of N components consisting of mode amplitudes $A_l^{(i)}$, $l=1\ldots N$, $i=1,2$, $\boldsymbol{M}_{2N\times 2N}$ is a $2N\times 2N$ complex matrix containing all the intersphere coupling terms, detuning and decay terms, and $\mathbb{K}^{(i)}$ is a coupling vector whose lth component is $K_l^{(i)}=j\omega_{lB}[(l+1)(a_i/r_i)^{l+2}/2]$. Inverting the matrix in Eq. (4) we obtain for the SP mode amplitude vector, $\mathbb{A}^{(i)}=[jB/\sqrt{\gamma_{rad}^{(i)}\tau_{rad}}]\mathbb{T}^{(i)}$ where the complex vector $\mathbb{T}^{(i)}=\boldsymbol{M}_{2N\times 2N}^{-1}\mathbb{K}^{(i)}$, which allows us to determine the total radiating power as,

$$P_{SP} = |\sqrt{\gamma_{rad}^{(1)}}A_1^{(1)} + \sqrt{\gamma_{rad}^{(2)}}A_1^{(2)}|^2 = |T_1^{(1)}+T_1^{(2)}|^2\frac{B^2}{\tau_{rad}}. \tag{5}$$

At steady state, we can use the third equation in Eq. (1) to write the excitation power as

$$P = \left|\gamma_m - 2\sum_{l=1}^{\infty}\omega_{lB}\left(\frac{\kappa_l^{(1)}T_l^{(1)}}{\sqrt{\gamma_{rad}^{(1)}\tau_{rad}}} + \frac{\kappa_l^{(2)}T_l^{(2)}}{\sqrt{\gamma_{rad}^{(2)}\tau_{rad}}}\right)\right|^2\frac{B^2}{\gamma_m}. \tag{6}$$

Taking the ratio of the radiative efficiency in the presence of coupled metal nanospheres, $\eta_{SP}=P_{SP}/P$, to the original radiative efficiency of the molecule, $\eta_{rad}=\tau_{rad}^{-1}/(\tau_{rad}^{-1}+\tau_{nrad}^{-1})=1/\tau_{rad}\gamma_m$, we find the enhancement of efficiency $F=\eta_{SP}/\eta_{rad}$ as

$$F = \frac{1+|T_1^{(1)}+T_2^{(2)}|^2}{\left|1-\eta_{rad}\Sigma_{l=1}^{\infty}\omega_{lB}(l+1)\left[\left(\frac{a_1}{r_1}\right)^{l+2}\frac{T_l^{(1)}}{\gamma_{rad}^{(1)}} + \left(\frac{a_2}{r_2}\right)^{l+2}\frac{T_l^{(2)}}{\gamma_{rad}^{(2)}}\right]\right|^2}. \tag{7}$$

Equation (7) can be applied to any emitter placed in the vicinity of two coupled nanospheres of different sizes. Obviously, there is a large parameter space including the sizes of the gap and spheres, the original radiative efficiency and frequency, over which we can analyze the enhancement. For simplicity, we only examine here the symmetric case of a molecule placed at the mid gap of two equal spheres ($r_1=r_2=r_0/2$), and leave other geometric scenarios for future study. We consider Au nanospheres with its dispersion given in Ref. 14 embedded in GaN matrix. For optimization, we only consider the gaps greater than 2 nm since quantum effects such as electron tunneling significantly reduce the enhancement when the gap is below 2 nm.[15]

The dependence of enhancement on sphere radius is shown in Fig. 2 for a molecule with a negligible original radiative efficiency $\eta_{rad}\sim 0$ emitting at the dipole-mode resonance $\omega=\omega_1$. The peaks are consistently obtained near the sphere radius ~ 30 nm for a rather wide range of gaps. This can be explained by the fact that at this radius radiative and nonradiative decay rates of dipole modes approach each other which results in matched out-coupling. The enhance-

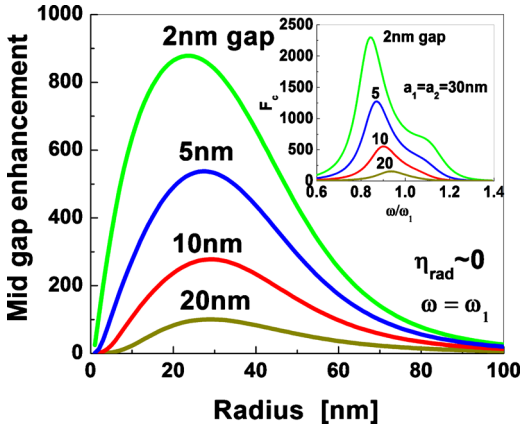

FIG. 2. (Color online) Mid gap enhancement vs the radius of two identical Au spheres that are embedded in the GaN matrix and are separated by a range of gaps. The emitter is assumed to have negligible radiative efficiency $\eta_{rad} \sim 0$ emitting at $\omega=\omega_1$. Insert: frequency dependence of the enhancement for the sphere radius of 30 nm with gaps of 2, 5, 10, and 20 nm.

ment shown in Fig. 2 is not optimum, as the coupling splits the dipole resonance into two modes so that maximum enhancement is obtained at frequencies below SP resonance (inset in Fig. 2).

So far the results closely follow those for the field enhancement obtained in Ref. 13, but the situation does change when we consider a more practical case of emitters with non-negligible original radiative efficiency η_{rad} as we have done in Fig. 3 where the enhancement at the optimized frequency ω_{opt} is plotted versus the gap width for a fixed sphere radius of 30 nm. As η_{rad} increases the enhancement gets weaker and practically vanishes when η_{rad} reaches 10%—a rather obvious result since the out-coupling efficiency of the SP dipole modes of the two 30 nm spheres $2\gamma_{rad}/(2\gamma_{rad}+\gamma) \approx 0.30$, is not much better than η_{rad}. For all $\eta_{rad} < 10\%$ the enhancement initially grows as the gap narrows but then the "luminescence quenching" sets in as more energy gets efficiently transferred into the increasingly higher order modes where it decays nonradiatively instead of being coupled into the dipole mode.[7] The onset of quenching occurs at smaller gaps for the less efficient emitters, because it is more critical to couple their energy into the SP modes as fast as possible, before it decays nonradiatively inside the emitter, even if most of the energy ends up trapped in these high order modes. In the extreme case of $\eta_{rad} \sim 0$, the object can be placed right next to the spheres without experiencing

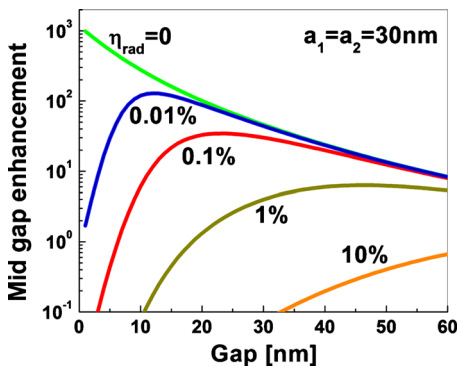

FIG. 3. (Color online) Mid gap enhancement optimized at ω_{opt} by two 30-nm-radius Au spheres vs their separation gap for a range of emitter efficiency.

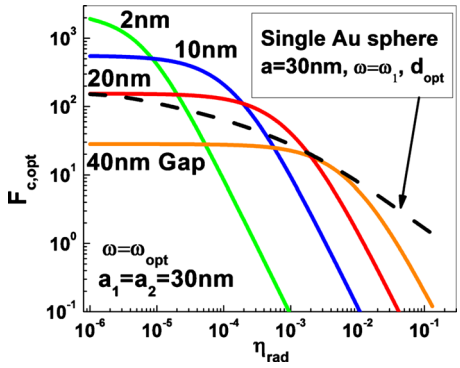

FIG. 4. (Color online) Enhancement $F_{c,opt}$ optimized at redshifted frequency ω_{opt} by two identical coupled Au nanospheres of 30 nm separated by gaps of 2, 10, 20, and 40 nm, over a wide range of emitter's original radiative efficiency. The dashed curve is the enhancement by a single Au sphere of 30 nm with optimal separation d_{opt} from a molecule emitting at $\omega=\omega_1$.

any quenching. Indeed for Raman scattering that can be treated as the photoluminescence with a vanishing efficiency no quenching ever occurs as testified by numerous experiments.

In Fig. 4, the mid-gap enhancement for 30-nm-radius spheres separated by a range of gaps at the optimized frequency ω_{opt} is plotted and compared with that by a single Au sphere of 30 nm obtained at the optimal separation from a molecule emitting at the dipole-mode resonance $\omega=\omega_1$.[7] Interestingly, improvement over a single sphere appears only for really small η_{rad}. Evidently, relatively good emitters enhanced by a single sphere already possess high enough radiative efficiency and the introduction of the second sphere only increases the Ohmic losses. But for less efficient emitters the two sphere scheme does have a clear advantage.

In conclusion, our analysis indicates that symmetrical metal nanostructures do offer advantage over the single nanoparticles, but only for weak emitters. Further improvement can potentially be achieved by exploring asymmetric structures in which emitters are placed in off-center positions in between two unequal spheres, allowing the smaller sphere to act as a cavity and larger one as an antenna. Last but not least, our approach provides a simple "engineering" explanation for the whole emission enhancement process according to which large Purcell enhancement is achieved in smaller "cavity" modes that are coupled to larger dipole "antenna" modes.

[1]M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).
[2]S. Nie and S. R. Emory, Science **275**, 1102 (1997).
[3]L. Novotny, Appl. Phys. Lett. **69**, 3806 (1996).
[4]S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, J. Appl. Phys. **101**, 093105 (2007).
[5]J. B. Khurgin, G. Sun, and R. A. Soref, Appl. Phys. Lett. **94**, 071103 (2009).
[6]J. B. Khurgin and G. Sun, J. Opt. Soc. Am. B **26**, B83 (2009).
[7]G. Sun, J. B. Khurgin, and C. C. Yang, Appl. Phys. Lett. **95**, 171103 (2009).
[8]M. Purcell, Phys. Rev. **69**, 681 (1946).
[9]V. M. Shalaev, Phys. Rep. **272**, 61 (1996).
[10]Y. Zou, P. Steinvurzel, T. Yang, and K. B. Crozier, Appl. Phys. Lett. **94**, 171107 (2009).
[11]P. Nordlander, C. Oubre, E. Prodan, K. Li, and M. I. Stockman, Nano Lett. **4**, 899 (2004).
[12]K. Li, M. I. Stockman, and D. J. Bergman, Phys. Rev. Lett. **91**, 227402 (2003).
[13]G. Sun and J. B. Khurgin, Appl. Phys. Lett. **97**, 263110 (2010).
[14]P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).
[15]J. Zuloaga, E. Prodan, and P. Nordlander, Nano Lett. **9**, 887 (2009).