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Comparative study of field enhancement between isolated and coupled metal nanoparticles: An analytical approach

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We present an analytical model that takes into account the coupling between the surface plasmon modes in complex metal nanostructures. We apply this model to evaluate the field enhancement in the gap of two coupled Au metal spheres embedded in GaN dielectric and compare the result with that obtained by the single sphere. The results show additional improvement can be obtained in the gap depending on the width of the gap. This approach offers a clear physical insight for the enhancement and a straightforward method for optimization. © *2010 American Institute of Physics*. [doi:10.1063/1.3532101]

The strong localized electric field induced by the surface plasmons (SPs) of nanostructured metals has been used to dramatically increase the sensitivity in Raman sensing as well as in fluorescence measurements,[1,2] and has been proposed as a method to increase the efficiency of solar cells[3] and detectors.[4] We have previously developed an analytical model for isolated metal nanoparticles that not only reveal the origin of the optical enhancement but also allow for optimization of the nanoparticle structure in order to maximize the enhancement effect.[5–7] One limiting factor has been the contradicting requirement on a single sphere that needs to be simultaneously a good resonator and an efficient antenna. This difficulty can be resolved with the use of two or more coupled metal nanoparticles. Building upon our earlier work on isolated metal nanoparticles, we develop an analytical model for complex metal nanostructures where the coupling between the SP modes of different metal spheres can result in further enhancement. We show that the field enhancement for the isolated sphere is proportional to the Q-factor of the metal, but for two closely coupled spheres, it is proportional to Q^2.

The electric potential of the lth SP mode associated with a single metal nanosphere in the coordinate system [Fig. 1(a)], under the electro-static approximation, can be given as[6,8]

$$\Phi_l = \begin{cases} \dfrac{a}{l+1} E_{\max,l} \left(\dfrac{r}{a}\right)^l P_l(\cos\theta), & r < a \\ \dfrac{a}{l+1} E_{\max,l} \left(\dfrac{a}{r}\right)^{l+1} P_l(\cos\theta), & r \geq a \end{cases} \tag{1}$$

where $P_l(\cos\theta)$ is the Legendre polynomial and $E_{\max,l}$ is the maximum field just outside of the metal sphere at $r=a$ and $\theta=0$. The lth mode frequency $\omega_l=\omega_p\sqrt{l/[l+(l+1)\varepsilon_D]}$, where ω_p is the metal plasmon frequency and ε_D is the dielectric constant of the surrounding media, ranges from $\hbar\omega_1=1.967$ eV to $\hbar\omega_\infty=2.261$ eV for Au nanosphere embedded in GaN ($\varepsilon_D=5.8$).[7] The surface charge density related to the normal component of the electric field can be determined to be $\sigma_l(\theta)=[(2l+1)/(l+1)]\varepsilon_0 E_{\max,l} P_l(\cos\theta)$ where ε_0 is the permittivity of free space. Such a charge distribution on the metal surface produces dipole moment that vanishes for all higher order modes ($l\geq 2$), except the $l=1$ mode whose dipole $p_1=2\pi a^3\varepsilon_0 E_{\max,1}$. This dipole mode is the only solution coupled to the external fields for as long as the nanosphere diameter is much smaller than the wavelength, while all higher order modes remain uncoupled to external radiation modes. As a result, this dipole mode decays radiatively at a rate proportional to the sphere volume, $\gamma_{\rm rad}=(2\omega/3\varepsilon_D)\chi^3$, in which $\chi=2\pi a/\lambda_D$ is the metal sphere radius normalized to the wavelength λ_D in the dielectric corresponding to the excitation frequency ω. Simultaneously, all the modes also experience nonradiative decay due to the imaginary part of the metal dielectric function at roughly the same rate equal to the metal loss, $\gamma_{{\rm nrad},l}\approx\gamma$.

The effective volume $V_{{\rm eff},l}$ of the lth mode can be defined through the mode energy that can be evaluated as an integral over the sphere surface $U_l=1/2\oiint\Phi_l\sigma_l d^2r=1/2\varepsilon_0\varepsilon_D E^2_{\max,l}V_{{\rm eff},l}$,[9] from which we obtain $V_{{\rm eff},l}=4\pi a^3/(l+1)^2\varepsilon_D$. This mode volume is always less than the volume of the nanosphere and decreases with $(l+1)^{-2}$ as the SP energy gets concentrated in a very small volume close to the surface of the nanosphere and is contained within a narrow angle around axis z.

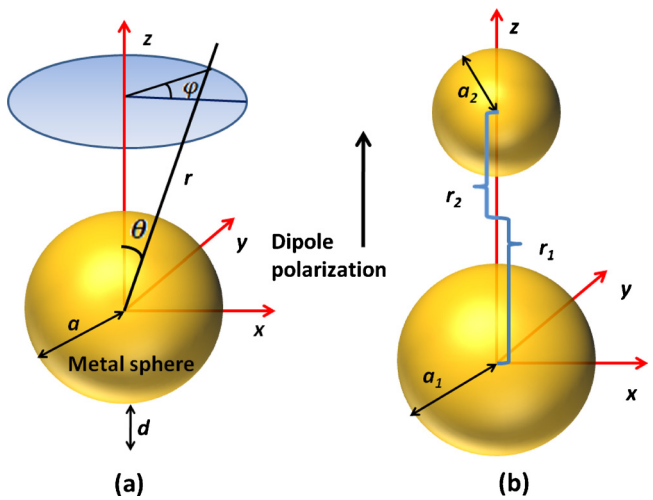

FIG. 1. (Color online) Illustration of (a) the spherical coordinate system used to describe the metal sphere dipole polarized along z-axis and (b) the geometry of two coupled metal spheres that are separated by $r_0=r_1+r_2$.

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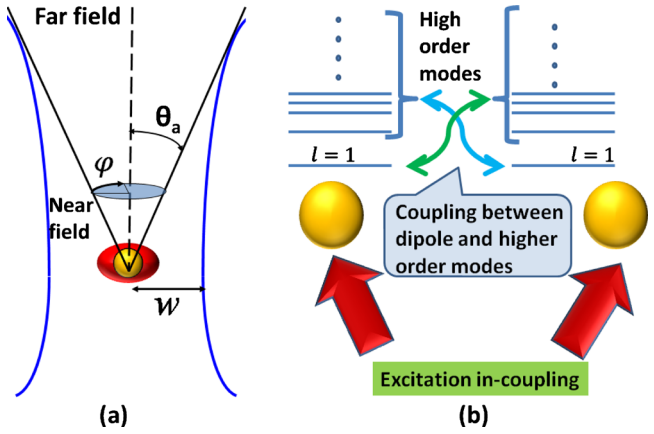

FIG. 2. (Color online) Illustration of (a) a metal nanosphere placed at the apex of a focused Gaussian beam with a numerical aperture characterized by the far-field half angle θ_a and (b) the coupling of optical excitation into the dipole modes of both spheres and their subsequent coupling into the higher order modes.

We shall now evaluate the field enhancement by a single metal sphere and then expand the model to coupled metal spheres. A fair comparison should be made with respect to a Gaussian beam tightly focused onto a diffraction limited spot of radius $w=\lambda_D/\pi\theta_a$ as shown in Fig. 2(a).[10] In the absence of metal, the field in the focal spot E_{foc} is related to the incident power $|s_+|^2=(\sqrt{\varepsilon_D}/Z_0)\pi(w/2)^2E_{\text{foc}}^2$ where Z_0 is the impedance of free space.[5] With a metal sphere placed at the focusing spot, the incident light can be coupled into the dipole mode ($l=1$) but not the higher order modes since all $l \geq 2$ modes are uncoupled with external fields. We arrive at the rate equation for the amplitude $A_1=\sqrt{U_1}$ of the dipole mode as[5]

$$\frac{dA_1}{dt}=j(\omega-\omega_1)A_1-\frac{\gamma_{\text{rad}}+\gamma}{2}A_1+\kappa_{\text{in}}s_+. \tag{2}$$

where the in-coupling coefficient $\kappa_{\text{in}}\approx(\theta_a/2)\sqrt{3\gamma_{\text{rad}}/2}$. At steady state, we obtain the field enhancement factor at a distance d (normalized $\chi_d=2\pi d/\lambda_D$) from the metal sphere[5]

$$F_S=\left|\frac{E_{\max,1}}{E_{\text{foc}}}\right|\left(\frac{a}{a+d}\right)^3=\frac{\sqrt{2}}{\sqrt{(Q^{-1}+2\chi^3/3\varepsilon_D)^2+\delta^2}}\left(\frac{\chi}{\chi+\chi_d}\right)^3, \tag{3}$$

where the Q-factor $Q=\omega/\gamma$ and the normalized excitation detuning $\delta=2(1-\omega_1/\omega)$. In the case of small sphere size, $Q^{-1}\gg\chi^3$, $F_S\approx\sqrt{2}Q\approx 14$ for $Q\approx 10$ for an Au sphere surrounded by GaN dielectric, when evaluated near sphere surface $\chi_d\ll\chi$ at resonance $\omega=\omega_1$. Actual field enhancement will be far less (see inset in Fig. 4). It is clear that in the case of isolated metal spheres, only dipole modes with relatively large effective mode volume contributes to the field enhancement since it is the only mode that couples to external fields, while all higher order modes capable of providing higher energy concentration with their smaller mode volumes play no part. Although it is desirable to have the dipole mode act as an efficient antenna and higher order modes as efficient resonators, it is simply impossible to realize with a single sphere since the different SP modes are orthogonal and decoupled from on another, thus a single sphere cannot be both a good resonator and an efficient antenna. This contradiction can, however, be resolved with the use of two or more closely spaced metal nanoparticles where the dipole mode of one sphere is coupled with the higher order modes of another to create the situation in which efficient antennas are coupled with the higher order modes of another to create the situation in which efficient antennas are coupled with the resonators to produce additional enhancement in the gap region [Fig. 2(b)]. The theory developed here can be applied to multiple spheres of different dimensions. But for simplicity, we examine exclusively the case of two spheres of equal size. The coupling energy between the two modes can be obtained as an integral of the electric potential $\phi_{l_1}^{(1)}$ of the l_1th mode of sphere 1 multiplied by the surface charge density $\sigma_{l_2}^{(2)}$ of the l_2th mode of sphere 2 evaluated over the surface of the sphere 2,

$$U_{l_1l_2}^{(12)}=\oiint\Phi_{l_1}^{(1)}\sigma_{l_2}^{(2)}ds^{(2)}=-4\kappa_{l_1l_2}^{(12)}A_{l_1}^{(1)}A_{l_2}^{(2)}, \tag{4}$$

where $A_l^{(i)}$ is the amplitude of the lth mode in the ith sphere. Of all the coupling coefficients $\kappa_{l_1l_2}^{(12)}$ we are mostly interested in the coupling between the dipole mode ($l=1$) in one sphere and all the modes with index l in the other sphere $\kappa_{1l}^{(12)}$ because they are the only ones associated with energy transfer between antennae and resonators, which can be obtained analytically as $\kappa_{1l}^{(12)}=[(l+1)/2](a_1/r_0)^{3/2}(a_2/r_0)^{l+1/2}$. The coupling between higher order modes of two spheres only shifts the resonant frequencies of those modes by a small amount, typically smaller than broadening γ and can be neglected in this analysis.

A rate equation similar to Eq. (2) can be established for the amplitude of each mode with additional terms that take into account of the coupling between the dipole mode in one sphere and all the modes in the other. At steady state, the total electric field at the location $r_1=r_0-r_2$ in the gap [Fig. 1(b)] is the summation of all modes from both spheres as

$$E(r_1)=E_{\max,1}^{(1)}\left[\left(\frac{a_1}{r_1}\right)^3+\sum_{l=2}^{\infty}\frac{\omega_{1l}\kappa_{1l}^{(12)}}{(\omega_l-\omega)+j\left(\frac{\gamma}{2}\right)}\frac{l+1}{2}\left(\frac{a_1}{r_2}\right)^{3/2}\left(\frac{a_2}{r_2}\right)^{l+1/2}\right]+E_{\max,1}^{(2)}\left[\left(\frac{a_2}{r_2}\right)^3+\sum_{l=2}^{\infty}\frac{\omega_{1l}\kappa_{1l}^{(21)}}{(\omega_l-\omega)+j\frac{\gamma}{2}}\frac{l+1}{2}\left(\frac{a_2}{r_1}\right)^{3/2}\left(\frac{a_1}{r_1}\right)^{l+1/2}\right], \tag{5}$$

where $\omega_{1l}=\sqrt{\omega_1\omega_l}$. The first term is the superposition of the dipole mode of sphere 1 and the higher order modes of sphere 2, and the energy of all these modes is coupled in through the $l=1$ mode of sphere 1, and vice versa for the second term. The field enhancement factor in the gap of two coupled spheres can then be obtained

$$F_C=\left|\frac{E(r_1)}{E_{\text{foc}}}\right|=\frac{\omega}{\sqrt{2}|M_{2\times2}|}\times\left|(m_{22}-m_{12})\left(\frac{a_1}{r_1}\right)^3\left[1+\frac{1}{4}\frac{a_2r_1^3}{r_0^2r_2^2}\sum_{l=2}^{\infty}\frac{\omega_{1l}(l+1)^2}{(\omega_l-\omega)+j\left(\frac{\gamma}{2}\right)}\left(\frac{a_2^2}{r_0r_2}\right)^l\right]+(m_{11}-m_{21})\left(\frac{a_2}{r_2}\right)^3\left[1+\frac{1}{4}\frac{a_1r_2^3}{r_0^2r_1^2}\sum_{l=2}^{\infty}\frac{\omega_{1l}(l+1)^2}{(\omega_l-\omega)+j\left(\frac{\gamma}{2}\right)}\left(\frac{a_1^2}{r_0r_1}\right)^l\right]\right|, \tag{6}$$

where the elements in the 2×2 matrix $M_{2\times2}$ are

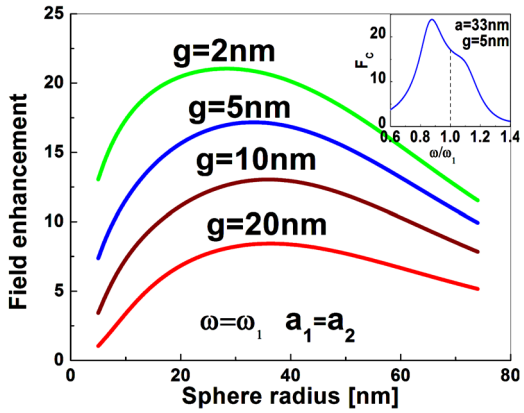

FIG. 3. (Color online) Field enhancement at the midgap of two equal Au spheres in GaN vs their radius at $\omega=\omega_1$. (Inset: frequency dependence of the midgap enhancement for the 5 nm gap with optimized sphere radius $a_{opt}=33$ nm.)

$$m_{11}=j(\omega-\omega_1)+\sum_{l=2}^{\infty}\frac{\omega_{1l}^2[\kappa_{1l}^{(12)}]^2}{j(\omega-\omega_l)+\frac{\gamma}{2}}+\frac{1}{2}\gamma_1^{(1)},\quad m_{12}=j\omega_1\left(\frac{a_2}{r_0}\right)^3$$

$$m_{21}=j\omega_1\left(\frac{a_1}{r_0}\right)^3,\quad m_{22}=j(\omega-\omega_1)+\sum_{l=2}^{\infty}\frac{\omega_{1l}^2[\kappa_{1l}^{(21)}]^2}{j(\omega-\omega_l)+\frac{\gamma}{2}}+\frac{1}{2}\gamma_1^{(2)}. \tag{7}$$

$\gamma_1^{(i)}=\gamma_{\text{rad}}^{(i)}+\gamma$ is the decay rate of the dipole mode of sphere i. Note the presence of different phases in the denominators—this is a direct consequence of delay associated with the energy transfer from one nanoparticle to another, i.e., the retardation effect. Therefore, this quasielectric-static model is valid for as long as the dimensions of each individual particle are small compared to the wavelength, while the total size of the system of nanoparticles can be of the order of wavelength and even larger.

The strong coupling between the dipole modes causes the resonances ω_1 to split, $\omega_{\pm}/\omega_1\approx 1\pm\sqrt{\kappa_{11}^2-(1/4Q_2)}$. Eq. (6) can be simplified at zero gap $r_0\approx 2a$ by the fact that coupling coefficients and metal spheres are small such that $[\kappa_{1l}^{(i)}]^2\approx 0$ for $l\geq 2$ and $Q^{-1}\gg\chi^3$, and that the higher order terms are significantly only for those lower indexes l whose frequency detuning is small, $Q^{-1}\gg 2(1-\omega_l/\omega)$. We thus obtain at the lower split $\omega-$, $F_C\approx 2\sqrt{2}Q|1-j9Q/8|\approx 9\sqrt{2}Q^2/4$.

We then realize that the terms from higher order modes ($l\geq 2$) in Eq. (6) are significant only for those lower indexes l whose frequency detuning from ω_1 is small, $Q^{-1}\gg 2(1-\omega_l/\omega_1)$, we thus obtain at the lower split $\omega=\omega_-$, $F_C\approx 2\sqrt{2}Q|1-j(9Q/8)|\approx(9\sqrt{2}Q^2/4)$. In comparison with the field enhancement by a single metal sphere which is proportional to Q, we now have additional contributions from higher order modes that have a relationship of Q^2. The result obtained at mid gap by Eq. (6) is shown in Fig. 3 for a range of gaps, $2<g<20$ nm at $\omega=\omega_1$. The shift of resonance to a lower frequency $\omega<\omega_1$ (inset of Fig. 3) is clearly demonstrated for the 5-nm gap optimized radius of $a_{opt}=33$ nm.

To have a fair comparison between single and coupled metal spheres, we obtain optimal enhancement for both cases

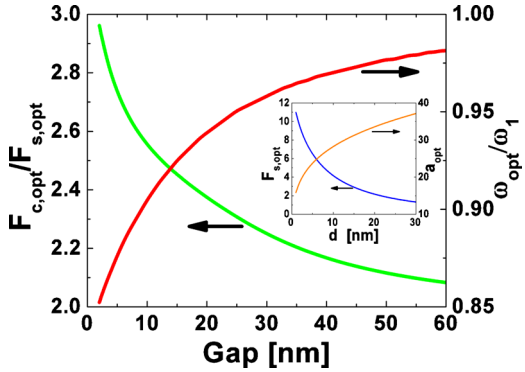

FIG. 4. (Color online) Ratio of optimal field enhancement by two coupled spheres to that by a single sphere, $F_{C,\text{opt}}/F_{s,\text{opt}}$, and the frequency shift $\omega_{\text{opt}}/\omega_1$ to yield $F_{C,\text{opt}}$ vs the gap. (Inset: maximum enhancement by a single sphere $F_{S,\text{opt}}$ achieved at a_{opt} vs separation equal to half gap $d=g/2$.)

at the locations of equal separation from metal surface. This means that for a single sphere we take the separation distance from its surface to be equal to half the gap, $d=g/2$, and obtain its peak enhancement $F_{S,opt}=\sqrt{2}Q/[1+(2Q\chi_D^3/3\epsilon_D)^{1/4}]^4$, by optimizing Eq. (3) at the normalized radius $\chi_{opt}=(3\epsilon_d\chi_d/2Q)^{1/4}$ at the dipole resonance $\omega=\omega_1$(inset in Fig. 4). In the case of coupled spheres, we not only optimize the radius of the two equal spheres but also the excitation frequency to take into account of the resonance shift. The ratio of the optimal field enhancement between the two cases, $F_{C,\text{opt}}/F_{s,\text{opt}}$, is presented in Fig. 4 where the frequency at which $F_{C,\text{opt}}$ is obtained is also shown. The improvement over single sphere is about a factor of 2–3. This factor is substantially smaller than the factor of additional $9Q/4$ obtained in the limit of zero gap because of the resonance detuning of different modes and the presence of the gap. However, by exploring multiple spheres of unequal dimensions, asymmetrical shapes, and off-center locations in the gaps, it is feasible to gain additional enhancement. For optical absorption and emission with properties directly proportional to the energy density, i.e., electric field squared (E^2), the improvement over single metal nanoparticles can be a factor of ~10. For the surface enhanced Raman scattering process whose intensity is proportional to E^4, an additional factor of 100 can be recovered.

Our analysis confirms the fact that more complex metallic nanostructures do offer advantage over the single nanoparticles and provides a simple "engineering" explanation in which the large enhancement is achieved in a smaller "cavity" mode that is coupled to a larger "antenna" mode.

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