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Impact of high-order surface plasmon modes of metal nanoparticles on enhancement of optical emission

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We consider the impact of high-order surface plasmon modes supported by the metal nanoparticles on the efficiency enhancement of optical emission. Using the example of Au nanosphere embedded in the GaN dielectric, we show that for an emitter with certain original radiative efficiency, placing the emitter too close to the metal sphere does not always produce additional enhancement. Thus our model provides analytical treatment of the luminescence quenching and can be used to optimize both nanoparticle size and its separation from the emitter to yield maximum enhancement. © 2009 American Institute of Physics. [doi:10.1063/1.3250160]

The properties of optically active objects of nanometer dimensions can be dramatically modified by metal nanoparticles.¹⁻⁶ These nanoscaled objects could be either molecules, atoms, or quantum dots (QDs) (here we shall use the generic term “molecule” to denote them all). The phenomenon that has a particularly important practical application in luminescence is the enhancement of optical emission when these molecules are placed in close proximity to the metal nanoparticles. Depending on the metal, molecule, dielectric, and geometry, the actual values of enhancement reported in different experiments differ by orders of magnitude and are often inconsistent with the theoretical or numerical results. Most theoretical works do not venture far beyond calculating the local electric field enhancement, which may be perfectly fine for the case of surface enhanced Raman scattering, but for the cases of photo and electroluminescence (EL) the relation is more complex and depends on the properties of the emitting molecule itself. Recently, we have developed an analytical model that provided the theoretical understanding with a clear underlining physics of plasmonic enhancement of optical absorption and emission by metal nanoparticles.⁷⁻⁹ The theory takes into account the radiative decay of the SP modes that is often neglected in the electrostatic approach, and thus adequately describes the modification of the behavior of the molecules. Using this model we have demonstrated the route for optimization of the nanoparticle size and established the limits of enhancement of optical absorption and emission for molecules of given absorption cross section and radiative efficiency. However, one parameter that remains to be optimized is the separation of the molecule from the metal nanoparticle since the enhancement continues to increase until the separation becomes small enough where luminescence quenching takes place.¹⁰ The quenching effect in the literature has been associated with direct nonradiative transfer of energy from the molecule to the metal excitation, but no adequate theory of this phenomenon has been developed. In this letter, we show that luminescence quenching can be described as excitation of higher order nonradiative SP modes and can be quantitatively analyzed as such.

Consider the geometry of a single metal nanosphere being placed in a dielectric media shown in Fig. 1(a) where a spherical polar coordinate system with the z -axis parallel to the dipole polarization is employed. In the absence of external fields and charges, the eigenmodes should satisfy the Laplace equation $\nabla^2\Phi=0$ with a solution of the l th mode¹¹

$$\Phi_l = \begin{cases} C \left(\frac{r}{a}\right)^l P_l(\cos \theta), & r < a \\ C \left(\frac{a}{r}\right)^{l+1} P_l(\cos \theta), & r \geq a \end{cases} \quad (1)$$

where $P_l(\cos \theta)$ is the Legendre polynomial and C is a normalization constant. The continuity of the normal electrical displacement $D_r = -\epsilon \frac{\partial \Phi_l}{\partial r}$ requires that the dielectric functions of the metal $\epsilon_M(\omega)$ and the dielectric $\epsilon_D(\omega)$ must be related as $l\epsilon_M(\omega_l) + (l+1)\epsilon_D(\omega_l) = 0$, where ω_l is the resonance frequency of the l th mode. We shall refer to these solutions as multipoles with the lowest ($l=1$) solution being a familiar dipole solution $\epsilon_M(\omega_1) + 2\epsilon_D(\omega_1) = 0$ —the only solution that couples to the external fields for as long as the nanosphere diameter is much smaller than wavelength. As the order increases, the multipole solutions gradually approach the resonance of the surface plasmon polariton (SPP) on the flat metal-dielectric interface, $\epsilon_M(\omega_\infty) + \epsilon_D(\omega_\infty) = 0$, where $\omega_\infty = \omega_{\text{SPP}}$ is the resonance SPP frequency. It can be shown that

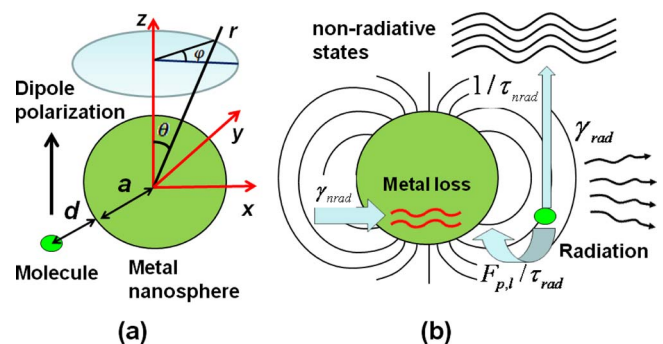


FIG. 1. (Color online) (a) The spherical coordinate system used to describe the metal sphere dipole polarized along z -axis with a radius a separated from a molecule by a distance d and (b) illustration of luminescence enhancement from the molecule placed near the metal sphere.

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the charge distributions on the metal surface are such that all $l \geq 2$ modes have zero dipole moments and thus remain uncoupled to external radiating fields. Using the Drude model approximation for the metal dielectric function and assuming a frequency-independent ϵ_D for the dielectric, we obtain the expression for the resonant frequencies $\omega_l = \omega_p \sqrt{\frac{l}{l+(l+1)\epsilon_D}}$, where ω_p is the plasma frequency. We shall use Au nano-

spheres embedded in GaN as an example to illustrate our optimization procedure since unlike Ag which gets oxidized, Au is routinely used to obtain plasmonic enhancement, and InGaN QDs formed in GaN emit in the frequency range ($\hbar\omega_1 = 1.967$ eV to $\hbar\omega_\infty = 2.261$ eV) of the SP modes supported by the Au/GaN combination.

The electric field of the l th mode can now be written as

$$\mathbf{E}_l(r, \theta) = \begin{cases} \mathbf{E}_{in,l} \\ \mathbf{E}_{out,l} \end{cases} = \begin{cases} E_{max,l} \left(\frac{r}{a}\right)^{l-1} \left[-\frac{l}{l+1} P_l(\cos \theta) \hat{r} + \frac{1}{\sin \theta} [P_{l+1}(\cos \theta) - \cos \theta P_l(\cos \theta)] \hat{\theta} \right], & r < a \\ E_{max,l} \left(\frac{a}{r}\right)^{l+2} \left[P_l(\cos \theta) \hat{r} + \frac{1}{\sin \theta} [P_{l+1}(\cos \theta) - \cos \theta P_l(\cos \theta)] \hat{\theta} \right], & r \geq a \end{cases} \quad (2)$$

where $E_{max,l} = \frac{c}{a}(l+1)$ is the maximum field just outside of the metal sphere at $r=a$ and $\theta=0$. As the mode order increases the field gets more and more “compressed” closer to the surface of a nanoparticle. Such a concentration of energy near the metal surface is best reflected by the effective mode volume $V_{eff,l}$ which is defined through the SP mode energy $U_l = \frac{1}{4} \epsilon_0 \epsilon_D E_{max,l}^2 V_{eff,l}$ which can be evaluated as¹³

$$U_l = \frac{1}{4} \epsilon_0 \frac{\partial \omega \epsilon_M}{\partial \omega} \int_{r < a} |E_{in,l}|^2 d^3 r + \frac{1}{4} \epsilon_0 \epsilon_D \int_{r > a} |E_{out,l}|^2 d^3 r \quad (3)$$

to yield

$$V_{eff,l} = \frac{8\pi a^3}{(l+1)(2l+1)} \left[1 + \frac{l}{(l+1)\epsilon_D} \right]. \quad (4)$$

Note that the effective volume of the dipole mode ($l=1$), $V_{eff,1} = \frac{4\pi a^3}{3} \left(1 + \frac{1}{2\epsilon_D}\right)$ is slightly larger than the volume of the nanosphere, but as the mode order index l increases, the effective volume decreases roughly with l^{-2} as the SP energy gets concentrated in a very small volume very close to the surface of the nanosphere and is contained within a narrow angle around axis z . The dipole mode ($l=1$) couples into radiating field, so it decays both radiatively and nonradiatively with the rate $\gamma_l = \gamma_{rad} + \gamma$, while all other high order modes ($l \geq 2$) decay only nonradiatively with the same rate that is equal to the metal loss $\gamma_l = \gamma$, and the dipole radiative decay rate $\gamma_{rad} = \frac{2\omega_1}{1+2\epsilon_D} \left(\frac{2\pi a}{\lambda_1}\right)^3$ (Ref. 7), where λ_1 is the wavelength of the radiating SP dipole in the dielectric. The small effective volumes of the high order modes indicate that the energy can be coupled rather efficiently into these modes—an additional energy loss mechanism that must be taken into account. The enhancement can be treated as a two-step process shown in Fig. 1(b)—first the electrically excited molecule with an original radiative decay rate τ_{rad}^{-1} relaxes by emitting energy at a frequency ω into all SP modes at the rate of $F_{p,l} \tau_{rad}^{-1}$ for the l th mode which is enhanced by the Purcell factor $F_{p,l}$ ¹⁴ among them only the dipole mode ($l=1$) will subsequently couple out to radiation modes at the rate γ_{rad} while all higher order modes ($l \geq 2$) dissipate energy nonradiatively. Simultaneously, the molecule itself also relaxes nonradiatively with a rate of τ_n^{-1} .

The Purcell factor can be estimated as a ratio of the effective density of the l th modes $\rho_l(\omega, d) = \frac{L_l(\omega)}{V_{eff,l}} \left(1 + \frac{d}{a}\right)^{-2l-4}$, where $L_l(\omega) = \frac{\gamma_l/2\pi}{(\omega-\omega_l)^2 + \gamma_l^2/4}$ is the normalized Lorentzian line-width of the l th mode, to that of the radiation continuum with wavelength λ in the dielectric, $\rho_{rad}(\omega) = \frac{1}{3\pi^2} \left(\frac{2\pi}{\lambda}\right)^3 \frac{1}{\omega}$ whose polarization is lined up with the SP dipole,

$$F_{p,l}(\omega) = \frac{3\pi\epsilon_D\omega L_l(\omega)(2l+1)(l+1)^2}{8\chi^3} \left(\frac{\chi}{\chi + \chi_d}\right)^{2l+4} \quad (5)$$

where $\chi = 2\pi a/\lambda$ and $\chi_d = 2\pi d/\lambda$. The Purcell factors at $\omega = \omega_1$ (Fig. 2 inset) clearly demonstrate the physical origin of luminescence quenching, as separation d decreases, progressively larger fraction of energy stored in the molecule gets coupled into to the higher order modes ($l \geq 2$), where it gets subsequently dissipated.

This phenomenon is better illustrated with the cumulative effect of the higher order modes known as the “luminescence quenching ratio”

$$f_q = \frac{\sum_{l=2}^{\infty} F_{p,l}}{F_{p,1}} = \sum_{l=2}^{\infty} \frac{\pi\gamma_l L_l(\omega_1)(2\epsilon_D + 1)(2l+1)(l+1)^2}{24(1 + \chi_d/\chi)^{2l-2}(l+1)\epsilon_D + l}, \quad (6)$$

where the molecule is taken to be at resonance with the dipole mode $\omega = \omega_1$ —the only mode that couples out to radia-

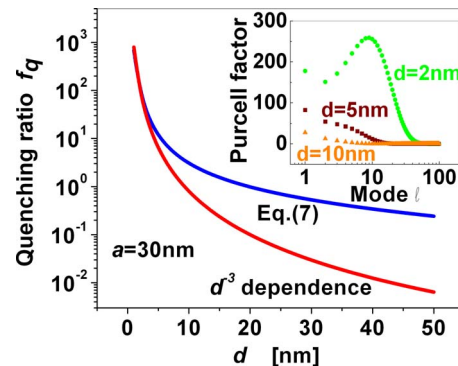


FIG. 2. (Color online) EL Quenching ratios obtained exactly by Eq. (7) and approximately with the d^{-3} dependence vs molecule-metal sphere separation for an Au sphere of radius $a=30$ nm and average detuning $\delta_{l \geq 2} = 2.82$. (Inset: Purcell factors associated with various SP modes for the molecule placed at $d=2, 5, 10$ nm from the Au nanosphere.)

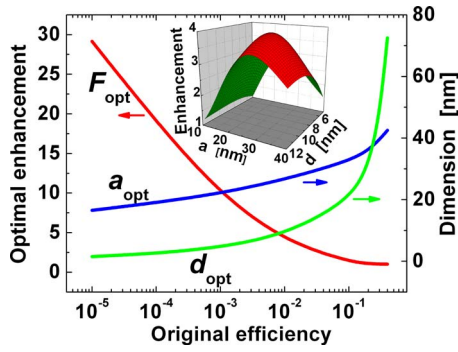


FIG. 3. (Color online) Optimized enhancement, Au nanosphere radius, and molecule-sphere separation over a range of original radiative efficiency. (Inset: Enhancement dependence on the Au nanosphere radius and on the molecule-sphere separation for emitting at the dipole mode resonance $\omega = \omega_1$ with $\eta_{rad} = 0.01$.)

tion. If we use some average mode frequency $\bar{\omega}_{l \geq 2}$ of these nonradiative modes in the Lorentzian linewidth $L_l(\omega_1)$ and assume large enough dielectric constant $2\epsilon_D \gg 1$, the above summation Eq. (7) can be approximated analytically to show a d^{-3} dependence of the quenching ratio that can also be obtained in the vicinity of flat metal surface by the method of image charges, $f_q \approx \frac{1}{6} \left(\frac{x}{x_d}\right)^3 (1 + Q_n \chi^3) \frac{1}{1 + \delta_{l \geq 2}^2}$, where the Q -factor $Q_n = \frac{2\omega_1}{\gamma(1+2\epsilon_D)}$, and the average detuning, $\delta_{l \geq 2} = \frac{2(\bar{\omega}_{l \geq 2} - \omega_1)}{\gamma}$. The result is shown in Fig. 2 for EL quenching ratios obtained exactly using Eq. (6) and approximately with the d^{-3} dependence for an Au sphere with a radius of $a = 30$ nm and average frequency detuning $\hbar(\bar{\omega}_{l \geq 2} - \omega_1) \approx 0.28$ eV ($\delta_{l \geq 2} = 2.82$). The approximation is reasonably accurate for small separations but consistently underestimates the quenching effect of the high order modes for $d \geq 10$ nm. Clearly, in order to limit the quenching ratio, the molecule cannot be placed too close to the metal nanoparticle.

In comparison with the case in which the high order modes are neglected,⁷ the luminescence enhancement factor should be modified to include the quenching ratio f_q as

$$F = \frac{1 + F_{p,1} \eta_{dp}}{1 + F_{p,1} (1 + f_q) \eta_{rad}}, \quad (7)$$

where the dipole mode out-coupling efficiency $\eta_{dp} = \gamma_{rad} / (\gamma_{rad} + \gamma)$ and the original radiative efficiency of the molecule $\eta_{rad} = \tau_{rad}^{-1} / (\tau_{rad}^{-1} + \tau_{nr}^{-1})$. We have calculated the enhancement factor for a molecule emitting at $\omega = \omega_1$ with $\eta_{rad} = 0.01$ for an Au sphere in GaN (Fig. 3 inset). The enhancement factor exhibits strong dependence not only upon the nanosphere size but also upon the separation. The optimal nanosphere size a_{opt} occurs at the radius where it is small enough to yield small effective mode volume for an enhanced Purcell factor, yet is still sufficiently large to assure strong radiative out-coupling of the dipole mode. If high order modes can be neglected, it is always better to have molecules positioned as close as possible to the metal sphere in order to take advantage of the large Purcell factor of the dipole mode. But with high order modes, the energy of the molecules placed too close to the metal sphere also gets coupled into these nonradiative (or dark) modes, and simply

dissipates as metal loss. As a result, an optimized separation d_{opt} can be located to allow for significant coupling into the dipole mode while adequately suppresses the luminescence quenching by high order modes.

The optimized enhancement F_{opt} for a wide range of original radiative efficiencies obtained at a_{opt} and d_{opt} is shown in Fig. 3. For molecules with low η_{rad} the matter of most concern is to compete with the high nonradiative decay rate of the molecule by transferring energy into the dipole mode even at the expense of simultaneous coupling into high order modes, which clearly favors small nanosphere volumes and close separations. For higher η_{rad} , the less critical is the concern of energy transfer from the molecule to the dipole mode, but rather from the dipole mode to free-space radiation and the energy loss caused by coupling into the high order modes. Obviously, this situation prefers larger nanoparticles that have greater radiative decay rate γ_{rad} , as well as larger separations that reduce the energy coupling into the high order modes.

In summary, we have developed an analytical model of luminescence quenching by properly treating the interaction between the excited molecules and high order “dark” modes of nanoparticles. The net effect of these nonradiative modes is rapid decrease of emission efficiency enhancement when the molecule is placed close to the metal surface. We have shown that the maximum enhancement can be obtained by optimizing both the size of metal nanosphere and its separation from the molecule. We have confirmed our prior results⁷—enhancement can be quite strong for inefficient molecules, but not for those emitters that are already fairly good. It is easy to see that once the symmetry is broken even the higher order modes would acquire some dipole moment and become partially radiative which may reduce the quenching, which is indeed what happens at rough surfaces.¹⁵

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