Practical limits of absorption enhancement near metal nanoparticles

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Practical limits of absorption enhancement near metal nanoparticles

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We consider the enhanced absorption of optical radiation by molecules placed in the vicinity of spherical metal nanoparticles in the realistic situation that includes perturbation of the optical field by the absorbing molecules. We show that there is an optimal nanosphere radius that gives the strongest enhancement for each combination of the number of absorbing molecules, their absorption strength, and their distance from the nanosphere surface and that the enhancement is strong only for relatively weak and diluted absorbers. © *2009 American Institute of Physics.*
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Recent years have witnessed an increased interest in "nanoplasmonics" relevant to sensor applications. In this paper, we discuss such applications and focus upon the increased optical absorption that results when molecules are placed near metal nanoparticles. This enhancement is part of the general study of field modification obtained in the vicinity of nanostructured metallic objects[1,2] whose characteristic features are much smaller than the optical wavelength. It has been well understood that the enhancement of optical field is associated with excitation of localized surface plasmon (LSP) modes, and it has been established that diverse optical effects can be enhanced near the resonantly excited metal nanoparticles. Enhancements of radiative decay rates,[3] fluorescence,[4,5] Raman scattering,[6] and others have been demonstrated by numerous groups, and these experiments have been supported by a large body of theoretical work.[7,8] However, the actual numerical values of enhancement reported in different experiments differ by orders of magnitude and are often inconsistent with the theoretical or numerical results. Furthermore, no clear understanding exists on how a given effect can be maximized by optimizing the size and/or shape of nanoparticles for a specified optically active atom, molecule, or quantum-confined object such as quantum dot. For the sake of generality, we refer to all these objects as "molecules." Often an electrostatic approach is used in which the radiative decay is neglected, and this cannot be valid in applications where highly efficient radiative coupling is required. Following our previously developed model for the surface plasmon polariton enhancement of electroluminescence,[9] we have started to develop a consistent analytical approach to the plasmonic enhancement of optical effects by considering the most basic phenomena of radiative decay in the vicinity of metal nanoparticles.[10] Our approach, based on effective volume method pioneered by Maier,[11] considers the process of emission as a two-step progression; the first step being Purcell-enhanced emission of energy into the LSP mode followed by the second step of energy emission out of the LSP mode into free space. The quantum efficiency of the first step requires the LSP mode to be essentially a small volume high-Q cavity, while the quan-

tum efficiency of the second requires the same mode to be nothing but a relatively large (up to $\lambda/2$) low-Q optical antenna. These two demands are difficult to reconcile; thus, for each specified emitting molecule characterized by its own original unenhanced radiative efficiency η_0, one can find the optimum size of nanoparticles that maximizes the radiative efficiency enhancement. We have also shown that only for those relatively inefficient $\eta_0 < 10\%$ molecules, one can achieve substantial efficiency enhancement, while for the relatively efficient emitters the losses in the metal negate whatever Purcell gain can be achieved.

We now turn our attention to the reverse problem, i.e., enhancement of the absorption by molecules placed in the vicinity of metal nanoparticles. This issue is important for two reasons. First of all, it had been proposed to use metal nanoparticles to enhance the efficiency of photo-detectors[12,13] and solar panels,[14,15] and second, absorption is the first step in the photoluminescence (PL) emission of PL sensors and thus enhanced absorption means improved sensitivity. The main goal of our work is to provide a rigorous yet simple analytic estimate of the attainable enhancement of absorption that takes into account all the radiative and nonradiative losses and, most essential, provides the optimization routine for a given absorber characterized by its original absorption strength. Rather unsurprisingly, we show that the stronger the original absorption the less enhancement is attainable and this fact leads to important practical consequences.

Consider the absorption by a molecule located near a metal nanosphere (here we consider only the spherical nanoparticles but our treatment can be easily expanded to take account of different shapes). The nanosphere is placed at the waist of a Gaussian light beam focused onto the profile, as shown in Fig. 1, with a numerical aperture characterized by a far field half angle θ. In the absence of the metal sphere, the beam of small angle θ will simply be focused onto a diffraction limited spot at the apex of the cone whose radius at the waist $w_0 = \lambda_d/\pi\theta$, where λ_d is the wavelength in the dielectric.

In the absence of the nanosphere, the field in the focal spot E_{foc} can be related to the power $|s_+|^2$ carried by the incident wave as follows, using the notation in Ref. 16,
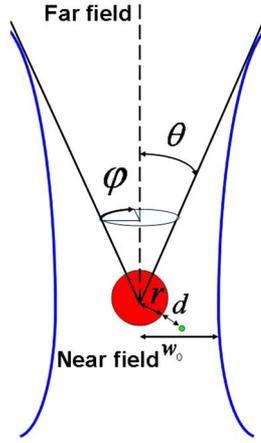
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FIG. 1. (Color online) Illustration of a metal nanosphere with a radius r placed at the apex of a focused Gaussian beam with a numerical aperture characterized by the far-field half angle θ. In the absence of the metal sphere, the beam will be focused onto a diffraction-limited spot with radius w_0 at the waist.

$$|s_+|^2 = \frac{n}{Z_0}\pi\left(\frac{w_0}{2}\right)^2 E_{\text{foc}}^2, \tag{1}$$

where Z_0 is the impedance of free space and n is the index of refraction in the dielectric. In the presence of a metal sphere with radius r, the incident light can be coupled into the LSP mode with resonant frequency ω_0 and with an effective mode volume[10] $V_{\text{eff}}=4\pi r^3(1+1/2\varepsilon_D)/3$ that produces maximum field E_{max} at the surface of the sphere which is related to the LSP mode energy $|a|^2$ as

$$|a|^2 = \tfrac{1}{2}\varepsilon_0\varepsilon_D E_{\text{max}}^2 V_{\text{eff}}, \tag{2}$$

where ε_0 is the permittivity of free space and ε_D is the dielectric constant of the medium.

In the two-step process of absorption, the first step is coupling of energy from free space modes contained in the focused beam into the LSP mode. This is a process reciprocal to the radiative decay of the LSP mode into the free space modes that are contained within the far field solid angle Ω, which is characterized by the angle dependent decay rate $\gamma_{\text{rad}}^{\Omega}=\gamma_{\text{rad}}\int_0^\Omega f(\theta,\varphi)d\Omega$, where the angular frequency dependence $f(\theta,\varphi)=3(1-\sin^2\theta\cos^2\varphi)/8\pi$ in the spherical system (Fig. 1), and the radiative decay rate into all radiation modes at resonant frequency ω_0 is[10]

$$\gamma_{\text{rad}} \equiv \gamma_{\text{rad}}^{4\pi} = \left(\frac{2\pi r}{\lambda_D}\right)^3\frac{\omega_0}{1+2\varepsilon_D}. \tag{3}$$

For small angles θ we obtain $\gamma_{\text{rad}}^{\Omega}\approx\frac{3}{8}\gamma_{\text{rad}}\theta^2$, and then using the reciprocity discussed by Haus[16] that relates the in-coupling coefficient $\kappa_{\text{in}}^{\Omega}$ from the light cone to the radiative decay rate $\gamma_{\text{rad}}^{\Omega}$ of the LSP mode, we obtain $\kappa_{\text{in}}^{\Omega}=\sqrt{\gamma_{\text{rad}}^{\Omega}}\approx(\theta/2)\sqrt{3\gamma_{\text{rad}}/2}$. Now we arrive at the rate equation for the amplitude a of the LSP,

$$\frac{da}{dt}=j(\omega-\omega_0)a-\frac{\gamma_{\text{nrad}}+\gamma_{\text{rad}}}{2}a+\frac{\theta}{2}\sqrt{\frac{3\gamma_{\text{rad}}}{2}}s_+, \tag{4}$$

where the nonradiative decay rate of the LSP mode $\gamma_{\text{nrad}}=\gamma$ with γ being the metal loss in the Drude-model approximation for the metal dielectric dispersion. The steady state solution of Eq. (4) at resonance yields
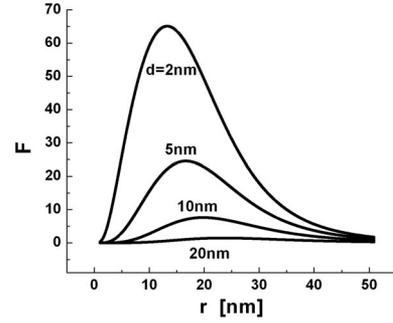

FIG. 2. Absorption enhancement factor as a function of Ag sphere radius embedded in GaN for different values of spacing d.

$$a = \sqrt{\frac{3}{2}}\frac{\gamma_{\text{rad}}^{1/2}\theta}{(\gamma_{\text{nrad}}+\gamma_{\text{rad}})}s_+. \tag{5}$$

Using relations (1) and (2), we obtain the field intensity enhancement (and thus the absorption enhancement) factor

$$F = \frac{E_{\text{max}}^2}{E_{\text{foc}}^2} = \frac{3\lambda_D^3}{8\pi^2 V_{\text{eff}}}\frac{Q_{\text{rad}}^{-1}}{(Q_{\text{nrad}}^{-1}+Q_{\text{rad}}^{-1})^2}, \tag{6}$$

where we have introduced the Q-factors $Q_{\text{rad(nrad)}}=\omega_0/\gamma_{\text{rad(nrad)}}$. Note that Eq. (6) does not contain the angle θ—thus the enhancement does not depend on the focusing scheme. From Eq. (3), we have $Q_{\text{rad}}^{-1}=\chi^3/(1+2\varepsilon_D)$, where the normalized radius $\chi=2\pi r/\lambda_D$. If we further normalize Q_{nrad} to $Q=Q_{\text{nrad}}/(1+2\varepsilon_D)$ and take into account that the actual atom or molecule is situated at a distance d from the metal sphere, we then obtain

$$F = \frac{E_{\text{max}}^2}{E_{\text{foc}}^2} = \frac{9\varepsilon_D}{2}\frac{1}{(\chi^3+Q^{-1})^2}\left(\frac{\chi}{\chi+\chi_d}\right)^6, \tag{7}$$

where $\chi_d=2\pi d/\lambda_D$. Clearly, in the limit of a very small nanosphere the intensity enhancement becomes proportional to Q^2 as expected from simple electrostatic considerations. In fact, the maximum enhancement in Eq. (7) occurs at optimum radius $\chi_{\text{opt}}=(\chi_d/Q)^{1/4}$, which yields $F_{\text{max}}=Q^2(9\varepsilon_D/2)\times(Q^{1/4}\chi_d^{3/4}+1)^{-8}$. The field intensity enhancement factor for an Ag nanosphere embedded in GaN ($Q=2.77$, $\hbar\omega_0=2.344$ eV) is shown in Fig. 2 as a function of the sphere radius r for several values of distance d. The enhancement is rather significant for small spacing ($d<10$ nm) between the metal sphere and absorbing atom or molecule and diminishes quickly when $d>20$ nm.

The origin of a strong dependence of F on sphere radius in Eq. (7) lies in the importance of a radiative decay term that is not taken account in the simple electrostatic calculations. One should also take into account the energy loss due to absorption in the active molecules, especially since strong absorption is what is desired. The rate of decay due to absorption is

$$\gamma_{\text{abs}}=\frac{c}{n}\frac{N_a\sigma_a}{V_{\text{eff}}}\left(\frac{\chi}{\chi+\chi_d}\right)^6, \tag{8}$$

where c is the speed of light in free space, σ_a is the absorption cross section of the molecule, and N_a is the number of molecules per sphere. We can now introduce an additional Q-factor due to absorption as
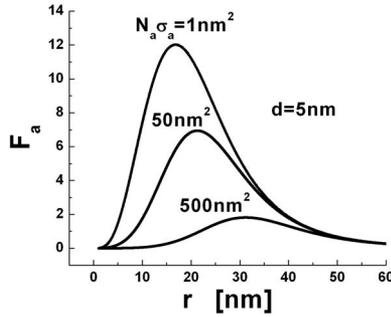
FIG. 3. Absorption enhancement as a function of sphere radius r for the Ag/GaN system wherein the absorbing molecules with a range of total absorption cross section are placed at $d=5$ nm from the Ag sphere.

$$Q_a = \frac{\omega_0}{\gamma_{\text{abs}}(1+2\varepsilon_D)} = \frac{\lambda_D^2}{N_a\sigma_a}\frac{\chi^3}{6\pi\varepsilon_D}\left(\frac{\chi+\chi_d}{\chi}\right)^6. \quad (9)$$

This finally brings us to

$$F_a = \frac{9\varepsilon_D}{2}\frac{1}{(\chi^3+Q^{-1}+Q_a^{-1})^2}\left(\frac{\chi}{\chi+\chi_d}\right)^6. \quad (10)$$

The result of enhancement is shown in Fig. 3 as a function of sphere radius r for the Ag/GaN system by fixing $d=5$ nm for several values of the total absorption cross section $N_a\sigma_a$. It is clear that the absorption of the active molecules becomes important when it approaches the loss in the metal. This can be confirmed by optimizing Eq. (10) for small $d\sim 0$. Then we find the optimum normalized metal sphere radius $\chi_{\text{opt}}=(6\pi\varepsilon_D N_a\sigma_a/\lambda_D^2)^{1/6}$ and $F_{a,opt}\approx (9\varepsilon_D Q^2/2)$ $\times[2Q(6\pi\varepsilon_D N_a\sigma_a/\lambda_D^2)^{1/2}+1]^{-2}$. Thus absorption in the active molecules themselves will become main limiting factor when $N_a\sigma_a \gtrsim \lambda_D^2/24\pi\varepsilon_D Q^2 \approx 14$ nm^2 for the Ag/GaN system and would not change substantially over the most of visible and near IR spectrum because an increase in wavelength would be balanced by a corresponding increase in Q-factor as metals become less absorptive at longer wavelengths. For a relatively small number of organic molecules, even with absorption cross sections as high as 0.1 nm^2 in the case of Rhodamine 6G,[17] the absorption on active molecules will play no role in determining the limit of field enhancement. At the same time, if one considers detectors based on semiconductors, specifically semiconductor quantum dots, their cross-sections are on the scale of a few nm^2,[18] thus the factor $N_a\sigma_a$ can easily approach 100 nm^2 and absorption becomes more relevant. As one can see from Fig. 3 for $N_a\sigma_a \sim 100$ nm^2, only a factor-of-few absorption enhancement is attainable and even then only for relatively small distance from the metal surface.

To better emphasize the points made in this work, we have performed optimization of the absorption enhancement for a wide range of total absorption cross section and spacing between the molecules and metal spheres. The optimized results shown in Fig. 4 clearly indicate that the strongest absorption enhancement (by almost two orders of magnitude) is attainable for the small number of weakly absorbing molecules placed close to the metal spheres, while for the large number of strong absorbers spread out only a dozen nanometers further away from the spheres the absorption enhancement is far more modest if it exists at all.
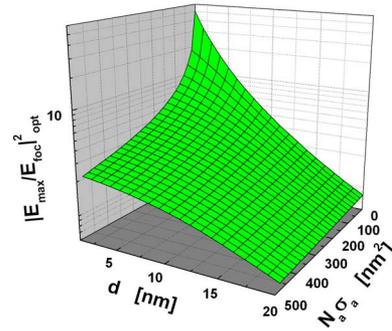

FIG. 4. (Color online) Absorption enhancement in the Ag/GaN system optimized for absorbing molecules with a total absorption cross section $N_a\sigma_a$ placed at a distance d from the Ag sphere.

In conclusion, we have developed an analytical model of absorption enhancement in the vicinity of metal nanoparticles and have shown that the degree of enhancement strongly depends on the particle dimension, thereby providing a straightforward route to optimizing the absorption enhancement. The main conclusion is that metal nanoparticles can dramatically improve the performance of optical sensors in which the analyte molecules are few and their original absorption is low. At the same time, when the original absorption is already significant, as is the case of most optical detectors and photovoltaic devices, the enhancement is weak or nonexistent due to metal loss.

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