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Fluorescence Enhancement with the Optical (Bi-) Conical Antenna[†]Ahmad Mohammadi,^{‡,§} Franziska Kaminski,^{‡,||} Vahid Sandoghdar,[‡] and Mario Agio^{*,‡}*Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland, and Department of Physics, Persian Gulf University, 75196 Bushehr, Iran**Received: September 30, 2009; Revised Manuscript Received: February 19, 2010*

We investigate the properties of finite gold nanocones as optical antennas for enhancing molecular fluorescence. We compute the modification of the excitation rate, spontaneous emission rate, and quantum efficiency as a function of the nanocone base and length, showing that the maximum field and fluorescence enhancements do not occur for the same nanocone parameters. We compare the results with those for nanorods and nanospheroids and find that nanocones perform better.

Introduction

A series of experiments in the late 1960s and in the 1970s discovered that molecular fluorescence and Raman scattering could be enhanced close to metal surfaces.^{1–5} These pioneering efforts spurred a flurry of theoretical works in subsequent years to understand and explain the phenomena encountered in surface-enhanced spectroscopy.^{6–10} Among various effects, these efforts identified field enhancement at sharp edges and surface roughness as a source of stronger fluorescence excitation and emission. It was also predicted that plasmon resonances in metallic films and nanostructures could enhance these effects further. Moreover, fluorescence quenching and the modification of the emission quantum yield due to the absorption in real metals were investigated theoretically. For all these effects, one discovered a very strong influence on the emitter orientation and position with respect to the metallic structure under study. These steep dependencies, which are inherent to near-field interactions, posed a great challenge to the experimental verification and quantitative understanding of surface-enhanced phenomena because they could not be controlled in ensemble measurements. As a result, only the large enhancement factors had to be deduced from averaging measurements.

The advent of scanning near-field optical microscopy (SNOM)^{11,12} and single molecule spectroscopy^{13,14} in the 1980s and their maturation in the 1990s provided the experimental tools for controlled laboratory investigation of surface-enhanced interactions. In 2004 we succeeded, for the first time, in examining the enhancement of fluorescence from a single oriented molecule as a function of its precise three-dimensional (3D) location close to a single gold nanoparticle. To do this, we placed a single gold nanosphere at the end of a glass fiber tip¹⁵ and used scanning probe microscopy to position it in the near field of single molecules embedded in a thin film. In an extended series of measurements we investigated the shortening of the fluorescence lifetime, the modification of the emission spectrum, the change in the emission pattern, the dependence of the excitation rate on the illumination wavelength within the plasmon resonance, and on the size of the gold nanoparticle.^{16–19}

These studies showed that a spherical gold particle acts as a nanoantenna that modifies the excitation rate, the spontaneous emission rate, the emission spectrum, and the radiation pattern of an emitter in its near field. Indeed, several other groups have also investigated single molecule fluorescence in the near field of well-defined scanning probes, which function as optical antennas.^{20–23}

The concept of optical antennas is closely linked to the physics of near-field microscopy, in which a tip mediates between a far-field illumination and the sample in its subwavelength vicinity.^{24,25} Progress in nanofabrication has motivated the realization of structures similar to radiowave antennas²⁶ for operating in the optical domain^{23,27–31} although various issues have to be considered. For example, metal nanoparticles support localized surface plasmon–polariton (LSP) modes that depend on the nanoparticle shape, composition, and surroundings.³² Moreover, losses due to absorption by real metals are not negligible at optical frequencies.³³ In addition, the molecule is coupled to the antenna via the displacement current, which is strongly position and orientation dependent.⁸ In this respect, there are ongoing efforts to reconcile these differences with standard antenna theory.^{34,35}

Recently, we proposed a few simple rules for designing optical antennas to enhance spontaneous emission by more than 3 orders of magnitude while avoiding quenching.³⁶ First, the plasmon resonance should be in a spectral region where dissipation in the metal is small. Second, the nanoparticle should have sharp corners to strongly increase the near field. Third, the antenna and the molecule dipole moment should be aligned in a head-to-tail configuration to maximize coupling and radiation. Fourth, the structure should be compatible with state-of-the-art nanofabrication. We then performed a detailed analysis of nanorods and nanospheroids for enhancing fluorescence by varying their aspect ratio and composition. We found that nanospheroids perform better than nanorods when the plasmon resonance needs to be shifted toward shorter wavelengths.³⁷ Moreover, by choosing different plasmonic materials, such as aluminum, silver, copper, and gold, we could obtain large Purcell effects and quantum efficiencies in a broad spectral region, from ultraviolet to near-infrared.³⁸ One of the issues that we identified is that the antenna efficiency η_a , which is the power that reaches the far field divided by the total emitter power, and the Purcell factor F , which represents the enhancement of the radiative decay rate, are maximal for different antenna parameters. In

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particular, we found that for gold nanorods and nanospheroids increasing η_a involves a rapid decrease of F in the visible and near-infrared range.³⁷

The question now is if one can improve the antenna design to increase F without decreasing η_a and losing control on the spectral position of the resonance. In this work, we propose that a simple solution based on using a nanocone, where one end can be sharp to increase the field enhancement and the Purcell factor, while the other larger end increases the volume and, thus, the antenna efficiency.^{7,39} The nanocone antenna is similar to the (bi-) conical antenna, which is the canonical example of a broad band antenna for applications in the VHF and UHF frequency bands.²⁶ However, for practical reasons such as the antenna weight, it is often realized in the form of a bow-tie.

Finite and semi-infinite metal nanocones are not a new concept in optics and SNOM.^{40–44} For example, conical SNOM probes could be exploited to focus surface plasmon–polaritons down to a spot size limited only by the tip curvature.^{45–48} Moreover, the field enhancement for semi-infinite⁴⁹ and finite^{50,51} silver nanocones has been studied as a function of the cone angle. In both situations, like for the bow-tie,²⁷ there exists an optimal angle that maximizes the enhancement. Moreover, it was pointed out that a finite nanocone can give rise to a stronger field than a semi-infinite one because of the LSPP resonance effect.^{52,53} Other groups investigated the modification of fluorescence lifetime by semi-infinite metal tips,^{54–56} where coupling to the surface plasmon–polariton mode leads to quenching. Also for finite nanocones, previous investigations concluded that quenching dominates at the LSPP resonance.⁵⁷

Here, we concentrate our attention on finite 3D gold nanocones to demonstrate that they can actually exhibit very interesting performances in terms of Purcell effect and antenna efficiency at the LSPP wavelength. In particular, we discuss the role of η_a in determining the optimal angle for enhancing fluorescence. First, we briefly review the theory and computational approach for studying spontaneous emission and molecular fluorescence with an optical antenna. Second, we investigate F and η_a of single and double gold nanocones as a function of cone angle. We then discuss the role of the emitter intrinsic quantum efficiency η_o , which together with F and η_a determines the effective quantum efficiency and the fluorescence enhancement. Lastly, we explore the effect of a supporting substrate and of rounding the tip.

Results and Discussion

Theory and Computational Details. We consider an isolated emitter with radiative decay rate γ_o^r , nonradiative decay rate γ_o^{nr} and quantum efficiency $\eta_o = \gamma_o^r / (\gamma_o^r + \gamma_o^{nr})$. The presence of a metal nanostructure modifies the spontaneous emission rate and introduces an additional nonradiative decay channel with rate γ^{nr} due to absorption in the metal.^{8,36} The new radiative decay rate γ^r and the quantum efficiency η can be related to the initial values by the following expression³⁷

$$\eta = \frac{\eta_o}{(1 - \eta_o)/F + \eta_o/\eta_a} \quad (1)$$

where $F = \gamma^r/\gamma_o^r$ is the Purcell factor and $\eta_a = \gamma^r/(\gamma^r + \gamma^{nr})$ is the antenna efficiency. Under weak excitation, the fluorescence signal of the isolated emitter is $S_o = \xi_o \eta_o |\mathbf{d} \cdot \mathbf{E}_o|^2$. Here, ξ_o represents the collection efficiency, \mathbf{d} is the transition electric dipole moment, and \mathbf{E}_o is the electric field at the emitter position.

With an optical antenna, the local electric field and the collection efficiency get also modified and the signal becomes $S = \xi \eta |\mathbf{d} \cdot \mathbf{E}|^2$.^{16,18} Assuming that the signal is collected over all angles, such that $\xi = \xi_o = 1$, the fluorescence enhancement reads

$$\frac{S}{S_o} = \frac{\eta}{\eta_o} \frac{|\mathbf{d} \cdot \mathbf{E}|^2}{|\mathbf{d} \cdot \mathbf{E}_o|^2} \quad (2)$$

Furthermore, if the metal nanostructure and the emitter are arranged in a configuration that almost preserves the dipolar radiation pattern of the isolated emitter,^{18,37} reciprocity implies that S/S_o can be well approximated by replacing the electric field enhancement $|\mathbf{d} \cdot \mathbf{E}|^2/|\mathbf{d} \cdot \mathbf{E}_o|^2$ with the Purcell factor F .⁵⁸ We thus write

$$\frac{S}{S_o} \simeq \frac{F}{(1 - \eta_o)/F + \eta_o/\eta_a} \quad (3)$$

From eqs 2 and 3 one immediately notes that the maximum fluorescence and the maximum field enhancements do not correspond because of η_o and η_a .

The calculation of F and η_a is performed here using the body-of-revolution (BOR) finite-difference time-domain (FDTD) method, which exploits the cylindrical symmetry of the nanocones to significantly reduce the computational burden in comparison to standard 3D-FDTD methods.⁵⁹ The computational details can be found in ref 37 and references therein. We focus our attention on gold³³ optical antennas made of one or two finite nanocones. The emitter is always at 10 nm from the sharp end of the nanocone, unless otherwise specified, and it is positioned and oriented along the nanocone axis. This distance is chosen in order to ignore effects due to nonlocality in the optical constants of the metal interface⁶⁰ and convergence issues in the FDTD method.⁶¹ The mesh pitch is 1 or 0.5 nm, depending on the nanocone geometry. For the case of an optical antenna made of two nanocones, the gap between them is fixed to 20 nm. The nanocone dimensions are chosen such that the LSPP is placed in the visible and near-infrared spectral range. The surrounding material is either glass (refractive index 1.5) or air.

Single and Double Conical Optical Antennas. Figure 1 displays the Purcell factor F and the antenna efficiency η_a for single and double nanocone antennas in glass as a function of the nanocone base b and the wavelength. The nanocone height is 80 nm, and the tip end is flat with a fixed diameter of 20 nm. The black curves correspond to the case of a nanorod.³⁷ Starting from this structure, the Purcell factor increases slightly and then decreases, confirming that there exists an optimal value for b .^{50,51} This trend is found for optical antennas made of one and two nanocones, as shown in Figure 1b and Figure 1d. However, Figure 1a and Figure 1c reveal that η_a steadily grows with b because the volume of the nanostructure increases. Intuitively, that occurs since scattering is proportional to the volume squared, while absorption is proportional only to the volume.³² Therefore, if both F and η_a have to be considered in the assessment of the antenna performances, one sees that b might be different than the optimal value found when only the field enhancement is taken into account. The dips in Figure 1a and Figure 1c are associated with the excitation of higher-order resonances, which increase the nonradiative decay rate more strongly than the radiative one.³⁶ An important advantage with

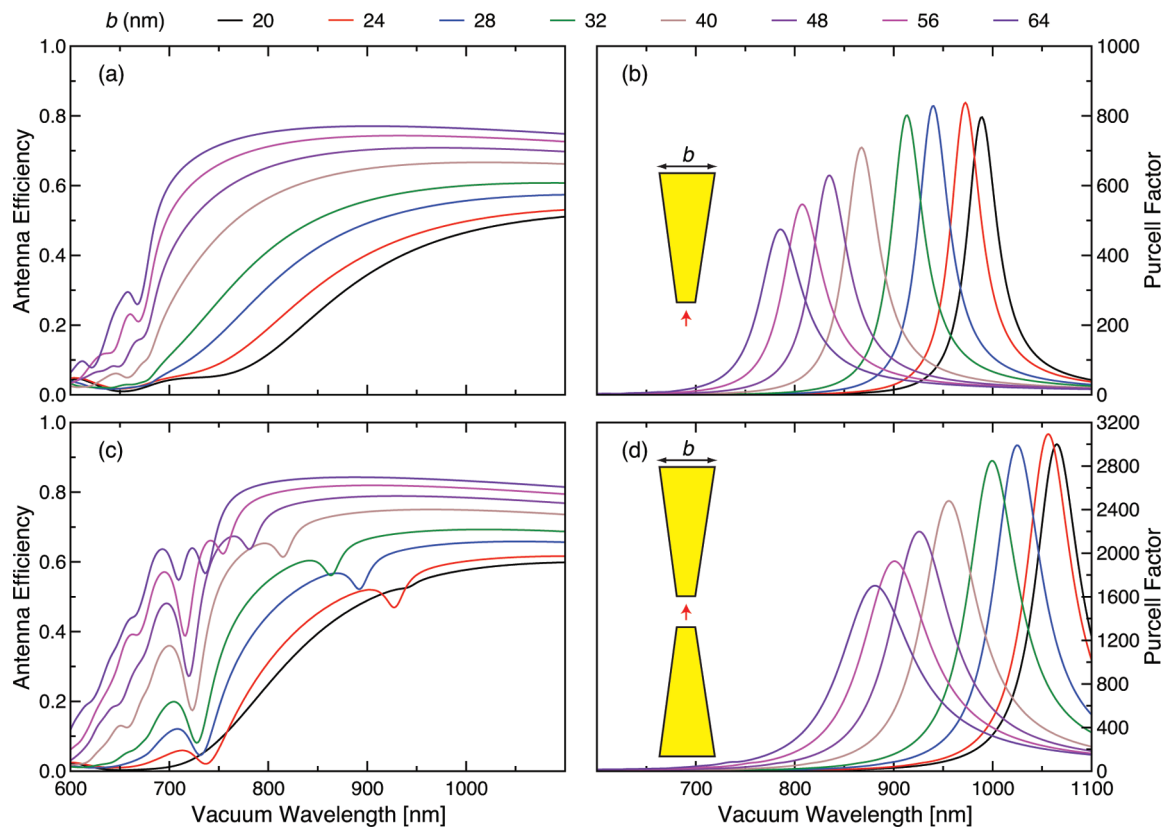


Figure 1. Single, (a) and (b), and double, (c) and (d), conical optical antennas in glass (refractive index 1.5). Purcell factor F , (b) and (d), and antenna efficiency η_a , (a) and (c), as a function of the base diameter b . The nanocone is 80 nm long and it has a fixed tip diameter of 20 nm. The optical antenna gap for the case of two nanocones is 20 nm. The insets in (b) and (d) sketch the antenna cross section, indicating the emitter position and orientation, and the nanocone parameter that is varied.

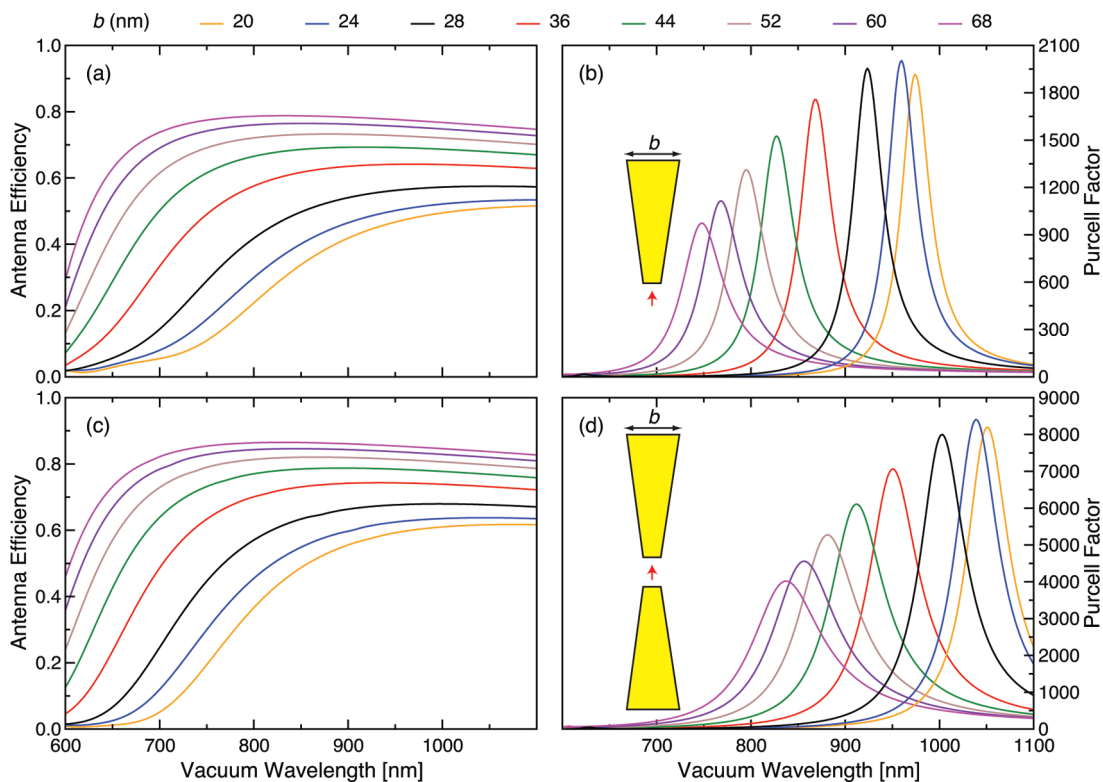


Figure 2. Single, (a) and (b), and double, (c) and (d), conical optical antennas in air (refractive index 1.0). Purcell factor F , (b) and (d), and antenna efficiency η_a , (a) and (c), as a function of the base diameter b . The nanocone is 140 nm long and it has a fixed tip diameter of 20 nm. The optical antenna gap for the case of two nanocones is 20 nm. The insets in (b) and (d) sketch the antenna cross section, indicating the emitter position and orientation, and the nanocone parameter that is varied.

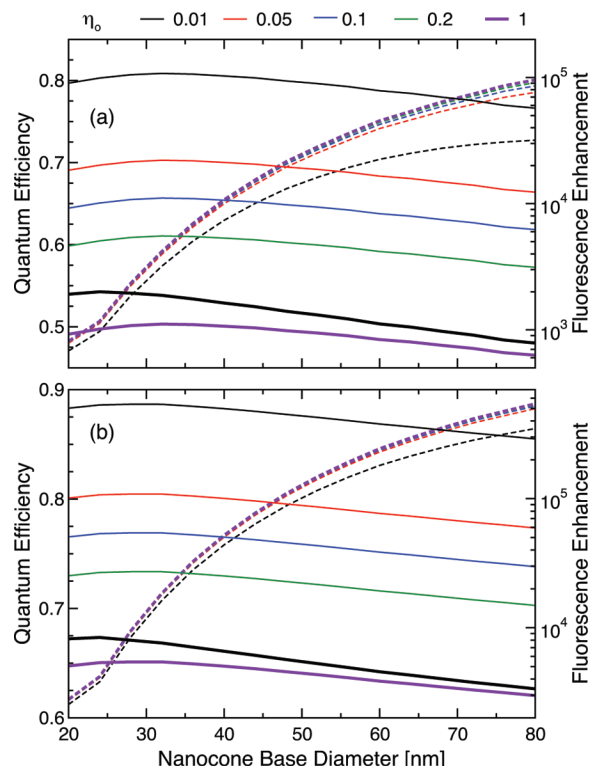


Figure 3. Single (a) and double (b) conical optical antennas in air (refractive index 1.0). Fluorescence enhancement S/S_0 (solid curves) and quantum efficiency η (dashed curves) as a function of the base diameter b at the wavelength corresponding to the maximal Purcell factor. The bold black solid curve represents the Purcell factor. The nanocone is 140 nm long and it has a fixed tip diameter of 20 nm. The optical antenna gap for the case of two nanocones is 20 nm. See the inset to Figure 2 for details on the coupling geometry.

respect to nanorods and nanospheroids is that here the resonance can be tuned toward the visible spectrum simply by changing the nanocone angle, without a significant loss of enhancement. Indeed, for nanorods we found that shifting the resonance by 100 nm can lead to a reduction of F by more than a factor of 2.³⁷

In Figure 2 we consider another set of optical antennas, where the surrounding medium is air and the nanocone height is 140 nm. The red shift due to a longer optical antenna is compensated by a lower refractive index so that the resonances are in the same spectral region of those shown in Figure 1. The overall behavior as a function of b is similar to the previous case. The main difference here is that the Purcell factor rises to as high as 2000 for a single nanocone and 8000 for a double nanocone antenna. Such large values combined with a very good antenna efficiency and a wide spectral tunability of the LSPP make them ideal systems for enhancing the radiative properties of solid-state quantum emitters.

Role of the Initial Quantum Efficiency. According to eq 3, the fluorescence enhancement depends on F , on η_a , and on the initial quantum efficiency η_0 . We anticipated that the value of b that maximizes F should not correspond to the value that maximizes S/S_0 . To discuss this point further, we plot in Figure 3 the fluorescence enhancement as a function of the nanocone base diameter b and η_0 . For each b we choose the wavelength associated with the maximum F . For the same wavelength, we also take η_a and use these quantities in eq 3. For a given η_0 , S/S_0 is maximal when b is about 30 nm in place of 24 nm obtained for F (see the bold black curve). The difference is small because F is so large that eq 3 can be well approximated by

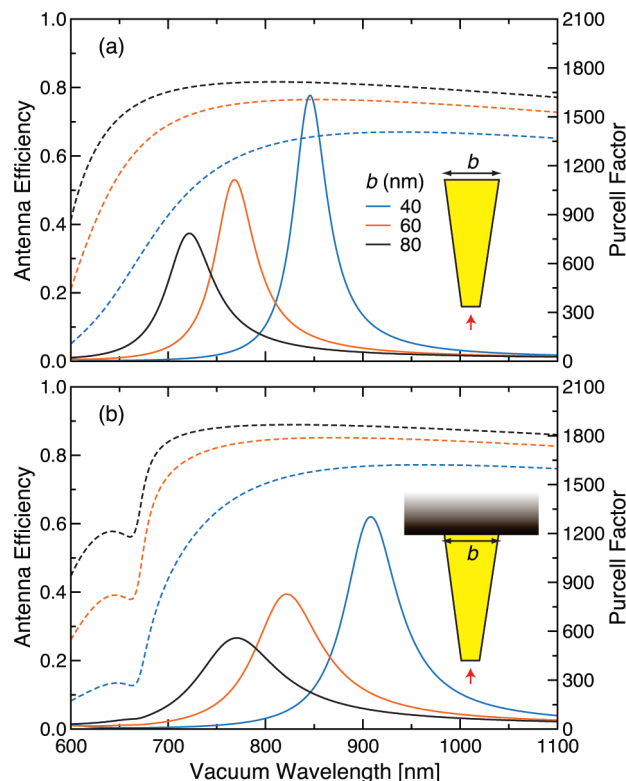


Figure 4. Effect of a supporting substrate on nanocone optical antennas in air. Purcell factor F (solid curves) and antenna efficiency η_a (dashed curves) without (a) and with (b) a glass substrate (refractive index 1.5). The nanocone is 140 nm long, it has a base diameter of 40, 60, or 80 nm and a fixed tip diameter of 20 nm. The insets in (a) and (b) sketch the antenna cross section, indicating the emitter position and orientation, and the nanocone parameter that is varied.

$S/S_0 = F\eta_a/\eta_0$. Since η_a does not change much compared to F , it turns out that maximizing F and S/S_0 give similar values for b . This can also be inferred from the quantum efficiency η , which is shown by dashed curves in Figure 3. η is close to η_a , corresponding to the curve for $\eta_0 = 100\%$, even when $\eta_0 = 5\%$. For smaller Purcell factors, the difference between the optimal b for F and for S/S_0 would be larger and vary with η_0 .

Effect of a Supporting Substrate. An important aspect for the experimental realization of nanoantennas is the effect of a supporting substrate. Often, the optical antenna is grown on a dielectric substrate^{62–65} or is attached to the end of a fiber.^{16,66–68} Previous works concluded that the presence of a substrate has a negligible effect on the field enhancement and on the spectral position of the LSPP for nanocones.^{50,51} Here, in Figure 4, we show that adding a glass substrate can shift the resonance by more than 50 nm. Furthermore, the LSPP exhibits a stronger radiative broadening, which decreases the Purcell factor F and the field enhancement,⁶⁹ and increases the antenna efficiency η_a . Note that the shift is smaller for the nanocone having the largest base diameter.

Effect of the Tip Termination. The last important aspect that we would like to address is the effect of the tip termination. Previous studies on the field enhancement in triangular nanoparticles have shown that changing the tip termination can affect the results.^{70,71} Here, we compare the case of a flat tip, shown in Figure 5a, with the case of a rounded tip having the same diameter, as shown in Figure 5b. We see that the resonance frequency and the antenna efficiency η_a are almost the same. The only noticeable difference occurs for the Purcell factor F , which is larger for the case of a flat tip. This holds also if the flat and rounded ends have a diameter of 10 nm in place of 20

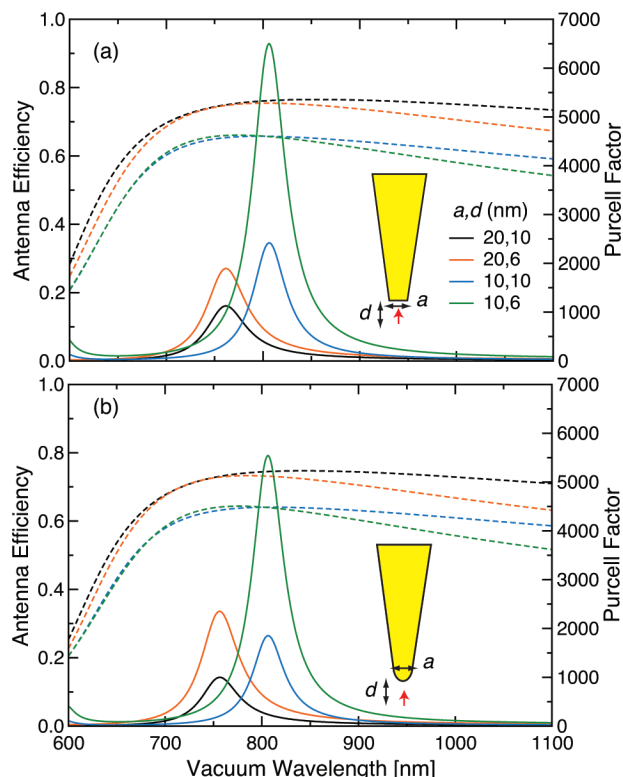


Figure 5. Effect of the tip termination on nanocone optical antennas in air. Purcell factor F (solid curves) and antenna efficiency η_a (dashed curves) for a flat (a) and rounded (b) tip. The nanocone is 140 nm long, it has a fixed base diameter of 60 nm and a tip diameter of 10 or 20 nm. The emitter is at a distance of 6 or 10 nm from the end of the tip. The insets in (a) and (b) sketch the antenna cross section, indicating the emitter position and orientation, and the varied nanocone parameters.

nm. Nevertheless, the difference between the two situations is not huge. Indeed, when the emitter is only 6 nm from the metal surface, the 20 nm rounded tip yields a stronger field enhancement in comparison to the flat one. These results stem essentially from the complex behavior of the electric field close to a metal tip.⁷²

Conclusion

We investigated the performance of gold nanocones as optical antennas for enhancing molecular fluorescence. Compared to nanorods and nanospheroids, the great advantage of nanocones is that the spectral position of the LSPP can be tuned toward shorter wavelengths by increasing the cone angle without compromising the Purcell factor and reducing the antenna efficiency. Another important practical aspect in favor of nanocones is the increased robustness and stability for vertical orientation because the base is larger than that for nanorods.^{62–68}

Moreover, we have shown that an optimal angle for the Purcell factor exists, which is directly related to the field enhancement studied in previous works.^{49–51} We have also studied the antenna efficiency, showing that quenching does not necessarily occur in correspondence with the LSPP.⁵⁷ While F increases and then decreases with increasing cone angle, η_a exhibits a monotonic growths. Therefore, because the fluorescence signal depends on the local electric field and on the quantum efficiency, the maximum field and fluorescence enhancements do not occur for the same cone angle. Nevertheless, we found that this difference is small if the Purcell factor is much larger than 1, which is easy to achieve using realistic nanocone parameters.

The strong fluorescence and field enhancement as well as the electric field localization at the nanocone tip holds great promise for high-resolution fluorescence, Raman, and other nonlinear nanoscopies.^{41–44} In fact, finite nanocones could be very efficiently butt-coupled to a dielectric nanofiber or interfaced with a weakly focused radially polarized beam for the realization of a high-throughput and large-bandwidth scanning near-field optical microscope.^{73,74} Considering the recent progress in the fabrication of single and double gold nanocone on substrates,^{62–65} cantilevers,^{67,68} and on the facet of optical fibers,⁶⁶ we anticipate a great deal of activity on this antenna system.

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