Strong coupling between a dipole emitter and localized plasmons: enhancement by sharp silver tips

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Abstract: In this work sharp silver nanotips are analyzed and proposed as useful plasmonic tools to reduce the threshold for the onset of strong coupling in the electromagnetic interaction of a point-like emitter with localized surface plasmons. If compared to similarly-sized spherical nanoparticles, conically-shaped nanoparticles turn out to be extremely useful to reduce the oscillator strength requirements for the emitting dipole, a reduction of the threshold by one sixth being obtained in a double cone configuration. Moreover the transition to the strong coupling regime is analyzed for several cone apertures, revealing a nonmonotonic behavior with the appearance of an optimal cone geometry. The emitted-light spectrum is obtained from the classical framework of the Discrete Dipole Approximation. This combined classical-quantum electrodynamics treatment is useful for the theoretical investigation on nonperturbative light-matter interactions involving complex shaped nanoparticles or aggregates.

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1. Introduction

In the study of the spontaneous emission of light by an excited dipolar emitter, several different regimes can be recognized [1]. In the perturbative or *weak-coupling* regime, deexcitation of the dipole is described by means of a decay rate calculated with Fermi golden rule. On the other hand, when the strength of interaction overcomes radiative and nonradiative losses, the system

could enter the non-perturbative or *strong coupling* regime, where the excitation is reversibly exchanged between the emitter and the electromagnetic field. A third recently investigated scenario is the *ultrastrong coupling* regime [2–4], characterized by an interaction strength comparable with the dipole transition energy and a relevant role played by the nonresonant terms of the Hamiltonian.

In the strong-coupling regime, the lowest excited states of light and matter, which are degenerate in the absence of interaction, are split into a pair of new states, separated by the so-called Rabi energy $\hbar\Omega$. This phenomenon is reflected by the recognizable formation of a doublet of peaks in the emitted-light spectrum around the dipole frequency, known with the name of *vac-uum Rabi splitting*. The strong coupling regime has been originally observed for single atoms in high-finesse optical resonators [1]; in the last few years, however, the rapid progress of epitaxial growth and nanolithography techniques, as well as the development of near-field optical spectroscopy, has made the strong-coupling regime of quantum dots coupled to optical microcavities a hot area of research [5–8]. Another framework for the search of nonperturbative effects is represented by circuit quantum electrodynamics with Josephson resonators [9].

As a general rule, the strong coupling regime can be entered when the interaction of the emitter with radiation is significantly increased due to photonic density localization and enhancement phenomena. For this reason, localized surface plasmons of metal nanosystems represent promising candidates for the investigation of strong coupling effects, thanks to the possibility of concentrating optical energy on the sub-wavelength scale and to enhance the local density of states of radiation, producing an increase of the spontaneous decay rate sometimes comparable with high-Q optical cavities. The reversible exchange of energy between the emitter and electromagnetic modes has interesting potentialities for several applications which span from quantum information to bio-sensors; for this reason, nonperturbative light-matter interaction continues to attract much interest in the nanophotonics community. Strong coupling effects in proximity to metal nanostructures have been the subject of several theoretical [10–17] and experimental works [18–23].

A qualitative description of the crossover from weak to strong coupling regimes for an emitter in resonance with a single radiation mode can be attained by estimating the coupling strength g. This quantity increases with the oscillator strength f of the emitter and decreases with the effective volume V_{eff} of the mode (which quantifies the degree of localization of the field). The threshold for entering the strong coupling regime can be expressed as $g > |\gamma - \gamma_0|/4$, where γ and γ_0 are the linewidths of the electromagnetic mode and the emitter, respectively [24]. In dielectric systems, such as high-Q optical microcavities, since modal effective volumes are constrained by the diffraction limit, nonperturbative effects are generally reached by reducing the cavity γ and the emitter γ_0 decay rates, for instance with low temperatures in order to get very long nonradiative exciton decay times. In plasmonic systems, on the contrary, the linewidth of plasmon modes is usually very large, due to Ohmic losses inside the metal, but the criterion could be equally satisfied as an effect of the subwavelength effective volumes which characterize surface plasmons. As a side advantage, higher temperatures are sufficient with respect to traditional dielectric systems.

In this work, the possibility to achieve a vacuum Rabi splitting in the emission spectrum of a single dipolar emitter coupled to a finite-size silver nanocone is analyzed within the framework of the Discrete Dipole Approximation (DDA) [25, 26]. Recently, it has been shown that DDA allows to calculate the perturbation induced by the metal nanostructure onto the decay dynamics of a point-like emitter with a good level of accuracy [27]. Here, we consider metallic nanoparticles with the shape of a truncated cone, a height of 20 nm, and variable semi-aperture angles. We suppose that an oscillating dipole is located 2 nm far from the tip of the cone, along the symmetry axis. This geometry favors the excitation of plasmonic modes strongly localized around the tip of the cone, as confirmed by the fact that modal frequencies and coupling strengths are weakly dependent on the height of the particle, but significantly dependent on the semi-aperture angle [28].

In order to maximize the coupling between the dipole and plasmonic modes, we consider a dipole located very close to an ideally sharp conical tip, since it has been shown that the enhancement of the dipole decay rate (and, in general, the strength of light–matter interaction) is greatly lowered with the increasing of the particle–dipole distance and the radius of curvature of the tip [27]. Continuous development of fabrication techniques has brought the investigated configuration within the range of state-of-art technology [29–31]; some discussion of non-ideal configurations is also given. Our computational results reveal the possibility to enter the strong coupling regime with a dipole oscillator strength as low as a few units for the double cone configuration, a value which is compatible with those of organic molecules or quantum dots. Moreover, it represents one of the lowest thresholds in the current literature [10, 11, 13–15, 17]. The effects of nonradiative losses are discussed in view of real far-field spectroscopy measurements.

We stress that the results are subject only to the approximation of macroscopic electrodynamics, since the experimental dielectric function of silver [32] is used and retardation effects are taken into account. Combining the computational DDA method with a quantum electrodynamical treatment of radiation-matter interaction results in a powerful approach, that can be applied to nanoparticles of any shape and for any given dispersive dielectric function.

2. Method

In the rotating wave approximation (RWA), the power spectrum (averaged over the solid angle) emitted to the far-field by a point-like dipole located at position \mathbf{r}_0 in proximity to a metal nanostructure is given by the expression [16]

$$S(\omega) = \frac{\hbar\omega}{2\pi} q(\omega) \Gamma(\omega) S'(\omega), \tag{1}$$

$$S'(\omega) = \left| \frac{1}{i [\omega_0 - \omega - \delta \omega(\omega)] + \frac{1}{2} \Gamma(\omega)} \right|^2,$$
(2)

where ω is the emitted frequency, ω_0 the dipole transition frequency, $q(\omega)$ the quantum yield of the system, $\Gamma(\omega)$ the perturbative dipole decay rate (calculated from the Fermi golden rule), and $\delta\omega(\omega)$ the photonic (anomalous) Lamb shift. The quantum yield is defined as the ratio between the radiative decay rate $\Gamma_R(\omega)$ and the total decay rate $\Gamma(\omega)$. Nonperturbative dynamical effects are entirely contained in the term $S'(\omega)$, here named *dipole spectrum*, which depends on both radiative and non-radiative plasmonic decay channels. In principle, the dipole spectrum can be directly measured with near field experiments. On the other hand, the prefactor containing the quantum yield depends only on the radiative decay channel and accounts for the propagation of light from the emitter to the far-field detector.

The decay rate and Lamb shift are both functions of the frequency and assume the forms

$$\Gamma(\omega) = \frac{2\omega^2}{\hbar\epsilon_0 c^2} \, \tilde{\mathbf{p}}_0 \cdot \operatorname{Im} \overleftrightarrow{\mathbf{G}}_{tot}(\mathbf{r}_0, \mathbf{r}_0, \omega) \cdot \tilde{\mathbf{p}}_0; \qquad (3)$$

$$\delta\omega(\omega) = \frac{1}{\pi\hbar\epsilon_0 c^2} \, \mathscr{P} \int_0^{\infty} d\omega' \frac{\omega'^2 \tilde{\mathbf{p}}_0 \cdot \operatorname{Im} \overleftrightarrow{\mathbf{G}}_{sc}(\mathbf{r}_0, \mathbf{r}_0, \omega') \cdot \tilde{\mathbf{p}}_0}{\omega' - \omega}$$

$$\simeq \frac{\omega^2}{\hbar\epsilon_0 c^2} \, \tilde{\mathbf{p}}_0 \cdot \operatorname{Re} \overleftarrow{\mathbf{G}}_{sc}(\mathbf{r}_0, \mathbf{r}_0, \omega) \cdot \tilde{\mathbf{p}}_0, \qquad (4)$$

where we have extended the lower integration limit to $-\infty$ and used Kramers–Kronig relations. $\overrightarrow{\mathbf{G}}_{\text{tot}} = \overrightarrow{\mathbf{G}}_{\text{free}} + \overrightarrow{\mathbf{G}}_{\text{sc}}$ is the dyadic Green function containing the free–space term and the scattering term originating from the electromagnetic response of the metal. As it can be inferred from Eqs. (3) and (4), our expression for the far-field spectrum in Eq. (1) is the RWA equivalent of that reported in [33], the main notation difference being that we explicitly write the perturbative decay rate and the Lamb shift instead of the dyadic Green function. The magnitude of Γ and $\delta \omega$ depends on the dipole moment of the emitter \tilde{p}_0 ; in this work, however, we equivalently employ the dipole oscillator strength $f = 2m_e \omega_0 \tilde{p}_0^2/(e^2\hbar)$. Notice that Γ and $\delta \omega$, being quadratic with \tilde{p}_0 , become linear with the oscillator strength f.

In the computational framework of the DDA, the dyadic Green function can be calculated from the field scattered back by the nanoparticle to the dipole location:

$$\overleftrightarrow{\mathbf{G}}_{\mathrm{sc}}\left(\mathbf{r}_{0},\mathbf{r}_{0},\boldsymbol{\omega}'\right)\cdot\tilde{\mathbf{p}}_{0}=\frac{c^{2}}{4\omega^{2}}\,\tilde{\mathbf{E}}_{\mathrm{sc}}\left(\mathbf{r}_{0}\right).$$
(5)

Thus, we can use Eq. (5) to obtain the decay rate and the Lamb shift and calculate the full emission spectrum with Eq. (1). All the simulations done in this work have been realized with an interdipole distance of d = 1/16 nm for the metallic scatterers, this discretization being enough to ensure a good convergence level [27].

3. Results

Before moving to the full computational results, we present a qualitative estimation of the magnitude of light-matter interaction. In Fig. 1(a) the decay rates Γ (calculated with the DDA for a f = 1 dipole) are plotted for Ag cones with five different tip apertures as a function of the dipole frequency and compared to the one obtained for an Ag sphere of the same size. For these sharp cones excited in an extremely near region, total decay rates are strongly peaked around a single surface plasmon resonance and result about 10 times larger than those which can be achieved with rounded tips with a curvature radius of 3 nm [27]. If we suppose, for simplicity, that the peaks are of Lorentzian lineshape, the spectrum in Eq. (1) can be worked out analytically and it is found that the threshold condition for the onset of a vacuum Rabi splitting is [16] $\gamma < 4f\Gamma_{max}$, where γ and Γ_{max} are the full width at half maximum and the maximum height of the peak, respectively, this being due to the linear dependence of the total decay rate on f. Thus, for each plasmonic system characterized by γ and Γ_{max} , we can define the *threshold oscillator strength* $f_{th} = \gamma/(4\Gamma_{max})$, which provides a good starting estimate of the minimal coupling required to enter the nonperturbative regime.

The threshold oscillator strengths for the systems under consideration are reported in Fig. 1(b). The $\theta = \pi/13$ tip shows an important decrease of the oscillator strength with respect to the spherical geometry. However, a non-monotonic behavior of f_{th} as a function of the aperture can be noticed: the oscillator strength decreases with decreasing aperture until an optimal value of $\pi/13$ is reached, but further reducing the aperture reverses the trend and increases again the threshold oscillator strength. The trend of Fig. 1(b) is mostly determined by the behavior of the linewidth γ , which has a minimum for the $\pi/13$ aperture, as shown in Fig. 1(a). This is in relation with the fact that small-aperture cones, in spite of presenting a stronger localization of the electric field (the well-known *superfocusing effect*), are characterized also by a wider frequency distribution of the plasmonic modes, which results in a broader lineshape. For large-aperture cones, on the other hand, the linewidth increases towards the limiting value for a flat surface.

The present treatment allows a qualitative estimation of the effect of varying the distance between the dipole and the conical tip. As it can be inferred from [27], the maximum of the total decay rate depends on the dipole–tip distance d with an approximate d^{-4} dependence,



Fig. 1. (a) Perturbative decay rates Γ calculated with the DDA for 20 nm Ag cones with several tip angles θ (sketch in inset), ranging from $\pi/21$ to $\pi/3$, and for a silver nanosphere with the diameter of 20 nm. The dipole (f = 1) is put 2 nm away from the metal–vacuum interface and it is oriented along the symmetry axis for the cones and radially for the sphere. (b) Threshold values for the oscillator strength required to enter the strong-coupling regime (calculated by fitting curves in (a) with Lorentzian lineshapes, as explained in text) for the different geometries.

i.e., a simple doubling of the dipole–tip distance increases the threshold oscillator strength by a factor ~ 16 . As a consequence, very close proximity of the emitter to the metallic nanostructure is crucial for the investigation of nonperturbative effects. From this point of view, the conical geometry has a clear advantage, as it is naturally suitable to a raster scanning configuration [30].

The onset of the strong-coupling regime for the systems under consideration is also confirmed by the results obtained from Eqs. (1) and (2) with the full computational expressions for the decay rate and the Lamb shift, without assuming Lorentzian lineshape. In Fig. 2 the dipole spectrum $S'(\omega)$ is plotted as a function of the emitted frequency and of the oscillator strength for a dipole in resonance with the surface plasmon frequency. The upper panel (a) refers to a silver nanosphere, whereas the lower panel (b) refers to a $\theta = \pi/13$ nanocone. In both cases the onset of vacuum Rabi splitting is clearly visible, but the minimal oscillator strength required for the sphere is far higher than for the cone, in agreement with our previous considerations. The threshold oscillator strength f_{th} is a mathematical quantity that essentially characterizes the transition between the over-damping and the under-damping regimes in the decay probability of the dipole. However, notice that, due to the finite width of the peaks, the oscillator strength should be somewhat larger than the threshold value to obtain an appreciable splitting in the spectrum. Nevertheless, f_{th} is taken as a well-defined lower bound for the dipole coupling



Fig. 2. The dipole spectrum $S'(\omega)$ as a function of the oscillator strength, for (a) 20 nm diameter sphere and (b) cone with a $\theta = \pi/13$ semi-aperture, for an emitter frequency ω_0 fixed respectively to 3.66 eV and 1.60 eV. Insets on the left represent the analyzed systems in which the dipole is put at 2 nm from the nanoparticles.

strength needed to achieve strong-coupling interaction.

In Fig. 3 the results obtained for a double cone configuration are reported. More in detail, the dipole is assumed to emit between two identical tips whose aperture is $\theta = \pi/13$, which corresponds to the optimal one (sketch in Fig. 3). The dipole is 2 nm distant from each cone and oriented along the symmetry axis. Numerical simulations, reported elsewhere [27], revealed the excitation of plasmonic resonances that are stronger and red-shifted with respect to the single cone one, this being probably due being due to a *bonding* combination of the resonances reported in Fig. 1. The higher decay rate registered in this case is responsible for a much lower threshold in the oscillator strength ($f_{th} \simeq 6$) with respect to the single cone configuration ($f_{th} \simeq 13$) with an anti-crossing behavior of the peak maxima in the emitted spectrum well visible at f = 20 [Fig. 3(b)]. The double-cone effect depends on the distance between the two cones, as discussed in [27]: when the second cone is more than a few nanometers apart, the single-cone effect is recovered.

Finally, in Fig. 4 we report the far-field emitted-power spectra $S(\omega)$ and compare them with the dipole spectra $S'(\omega)$ for the three different structures here analyzed (sphere, cone and double cone) and for several oscillator strengths, in the range 10 - 50. This comparison is presented in order to shed light on the effect of the plasmonic quantum yield, in view of real far-field spectroscopy measurements. As in most plasmonic systems, the quantum yield for the systems under consideration is low, due to the prevalence of non-radiative modes at short distance. This effect competes with the strong enhancement of light–matter coupling induced by the localization of the plasmonic field. The resulting radiative decay rate, however, remains significantly higher than the free-space decay rate — up to a few orders of magnitude for the double cone configuration [27], — allowing in principle the experimental detection of the emission spectrum with a sufficient signal-to-noise ratio.

On the other hand, although the onset of the strong coupling regime depends on the total strength of plasmon-dipole interaction in both channels, radiative and non-radiative, the quan-



Fig. 3. The dipole spectrum $S'(\omega)$ as a function (a) of the emitter frequency ω_0 and (b) of the oscillator strength *f* for a double cone configuration, represented in the inset on the left. The oscillator strength in (a) is f = 20, while the dipole transition energy used in (b) is $\omega_0 = 1.57 \,\text{eV}$.



Fig. 4. The far-field emitted-power spectrum $S(\omega)$ [solid line] compared with the dipole spectrum $S'(\omega)$ [red dashed line], for different geometries treated in the work: (a) a 20 nm-diameter silver sphere, (b) a $\theta = \pi/13$ silver nanocone, (c) the double cone configuration of Fig. 3. Each curve has been calculated for a different oscillator strength (in the range 10-50) and normalized independently of the other. Dipole frequencies are the same as in Figs. 2 and 3.

tum yield induces a modulation of the far-field emission spectrum [see Eq. (1)], which can result in a significant suppression of strong coupling effects. This is evident in the case of the nanosphere (a), where the maximum of the radiative emission is centered onto the l = 1 dipolar surface plasmon at $\omega \simeq 3.5 \text{ eV}$. However, the optimal resonance frequency for the transition to the strong coupling regime is around $\omega \simeq 3.66 \text{ eV}$, as an effect of the excitation of higher-order strongly non-radiative plasmon modes. As a consequence, the vacuum Rabi splitting results strongly quenched in the far-field for the spherical geometry. This is not the case of the cone (b) and double cone (c) systems, for which the maximum of the radiative decay rate coincides with the maximum of the field enhancement, as a result of the excitation of the strongly radiative mode. In these cases, the fingerprint of vacuum Rabi splitting, even if partially modulated by the quantum yield, survives even in the far field spectrum.

The present results in terms of threshold oscillator strength are much closer to experimental realization than those reported in [16], on two respects: first, the calculations of this work are performed by taking realistic dielectric functions of Ag, which have a much higher dissipation (almost an order of magnitude) than for the Drude model assumed in [16]. Second, the conical shape of the nanoparticles results nowadays well accessible by an experimental point of view [29] and the configuration with the dipole *outside* the nanoparticle is also favourable for experimental probing by raster scanning of a nanotip [30]. Thus, the present calculations are believed to represent a significant step in the direction of tailoring the interaction between a dipole and a metal nanoparticle, in view of achieving the strong coupling regime.

4. Conclusion

In conclusion, we have numerically predicted the onset of strong electromagnetic coupling for low oscillator strength dipole emitters put in proximity of sharp silver nanotips. 20 nm Ag cones, either in a single or double configuration, turn out to be much more advantageous with respect to a 20 nm diameter Ag sphere, if an optimal aperture is selected. Despite the intuitive idea that decreasing the tip angle would lead to better localization of the surface plasmonic field, the threshold oscillator strength for the occurrence of strong coupling has a nonmonotonic behavior as a function of the aperture angle, with an optimal semi-aperture angle around $\pi/13$. This is in relation with the fact that small-aperture cones are characterized by surface plasmon modes with a broader frequency distribution and the threshold oscillator strength is mainly related to the modal width of surface plasmons.

Employing the numerical DDA approach together with quantum electrodynamics turns out to be a powerful predictive method, that can be applied to metal nanoparticles of any shapes. The systems here analyzed involve emitters and nanoparticles which can be realized with state-of-art techniques, and this could open new avenues towards the real observation of the reversible exchange of energy between a dipole emitter and the electromagnetic field in plasmonic nanosystems.

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