

Gold, Copper, Silver and Aluminum Nanoantennas to Enhance Spontaneous Emission

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We compute the decay rates of emitters coupled to spheroidal nanoantennas made of gold, copper, silver, and aluminum. The spectral position of the localized surface plasmon-polariton resonance, the enhancement factors and the quantum efficiency are investigated as a function of the aspect ratio, background index and the metal composing the nanoantenna. While copper yields results similar to gold, silver and aluminum exhibit different performances. Our results show that with a careful choice of the parameters these nanoantennas can enhance emitters ranging from the UV to the near-IR spectrum.

Keywords: Fluorescence, Decay Rates, Metal Nanostructures.

1. INTRODUCTION

Single molecules, nanocrystals and nanotubes are relevant light emitters for fundamental research and applications.^{1–6} However, many of these systems exhibit a low quantum yield and often photobleach. The latter issue can be solved by embedding the emitter into a matrix, such that reactive elements like oxygen cannot interact with the dye.^{7,8} Regarding the low quantum yield, a possible solution exploits the concept of radiative decay engineering with microcavities,⁹ photonic crystals¹⁰ or metal nanostructures.¹¹ It turns out that a faster radiative decay rate also reduces photobleaching, because the emitter is in the excited state for a shorter time. Even if microcavities and photonic crystals can be as small as a few microns, they still occupy a space much larger than the emitter. Furthermore, they require a well defined geometry, which gives constraints on the fabrication method and hence on the choice of the material.

Recently, we have experimentally demonstrated that a single gold nanoparticle enhances the fluorescence signal of a single molecule^{12,13} and found quantitative agreement with theory.¹⁴ Moreover, our calculations show that gold nanoparticles with designed shapes can increase the decay rates by three orders of magnitude.¹⁵ These so-called *nanoantennas*¹⁶ can thus be used to improve the quantum efficiency of emitters^{17,18} and reduce photobleaching¹⁹ with the advantage that they have nanoscale dimensions,

a simple shape, and a broad resonance that does not require fine tuning of the structure parameters. Furthermore, metal nanoparticles can be mass produced and surface functionalization allows controlled binding of the emitter.²⁰

Nanoantennas base their properties on the so-called localized surface plasmon-polariton resonance (LSPR), which is sustained by the collective oscillation of free electrons in the metal. This resonance can be tuned by changing shape, size, background index and material.²¹ Because emitters cover a broad spectral range, it is interesting to investigate which nanoantenna designs should be chosen for operation in a given frequency domain. Similar studies have been carried out for the field enhancement in surface-enhanced Raman scattering.^{22–24}

In this paper we study the decay rate enhancement and the quantum efficiency for an emitter coupled to nanoantennas made of one or two spheroids as a function of several parameters, including aspect ratio, background index and metal. We choose spheroidal nanoparticles because they have a simple geometry, yet with sufficient degrees of freedom to represent a model system for nanoantennas. Indeed, they have been extensively studied for field-enhanced spectroscopy^{22–24} and for fluorescence enhancement.^{15, 25–28} We discuss nanoantenna designs that cover the spectral range from the UV to the near-IR. Even if the LSPR can be easily tuned by changing the spheroid aspect ratio,²⁵ one has to consider that the decay rates might not be enhanced as much as desired. Therefore, both geometric effects and material properties have to be taken into account.

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2. RESULTS AND DISCUSSION

2.1. Theory and Computational Approach

When an emitter is placed in the near field of a nanoantenna, its radiative decay rate γ_{rad}^o is modified to $\gamma = \gamma_{\text{rad}} + \gamma_{\text{nrad}}$.¹⁴ γ_{rad} represents the energy that reaches the far field, while γ_{nrad} accounts for the radiated energy absorbed by the nanoantenna due to material losses. The ratio $\eta_a = \gamma_{\text{rad}}/\gamma$ can be considered as a quantum efficiency. If η_a is small, the emitter is quenched even if the radiative decay rate is large.¹⁴ Another important quantity is the Purcell factor defined as $F = \gamma_{\text{rad}}/\gamma_{\text{rad}}^o$, which represents the radiative decay rate enhancement. If the isolated emitter has a quantum efficiency η_o , when it is coupled to the nanoantenna, it acquires a quantum efficiency η that depends on F and η_a , which reads^{26,27}

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

Equation (1) shows that if the emitter possesses a poor quantum efficiency η_o , the nanoantenna can effectively enhance it to a value close to 100%, if $F \gg 1$ and $\eta_a \approx 100\%$. F and η_a strongly depends on the relative position and orientation of the emitter with respect to the nanoantenna¹⁴ and on the nanoantenna shape and size.¹⁵ Furthermore these quantities depend also on the material composing the nanoantenna and on the background medium. For simplicity, here we fix the emitter position and orientation and focus on the effect of size, shape and material properties. The emitter is positioned on the nanoantenna axis at a distance $d = 10$ nm from the spheroid surface and oriented along the spheroid major axis as shown in Figure 1(a). For the case of nanoantennas made of two spheroids, the emitter is at the center of a 20 nm gap formed between the two nanoparticles.

The decay rates are obtained from classical electrodynamics calculations by collecting the total P_{tot} and radiated P_{rad} powers of an oscillating dipole located at the position of the emitter.²⁹ These quantities are computed using the Finite-Difference Time-Domain (FDTD) method.^{30,31} Furthermore, we take advantage of the rotational symmetry of the system to reduce the problem to two dimensions, see Figure 1(b), and we employ the body-of-revolution FDTD approach.^{26,30} The experimental dielectric function of metals is fitted using Drude or Drude-Lorentz dispersion models.^{31,32} The FDTD mesh discretization is chosen to be 1 nm for gold and copper nanoantennas, while for silver and aluminum nanoantennas we use 0.5 nm to compensate for the shorter operating wavelength. We terminate the FDTD mesh with perfectly-matched-layer (PML) absorbing boundary conditions.³³

2.2. Gold and Copper Nanospheroids

To better understand the performances of nanoantennas we first review the optical properties of gold and copper.

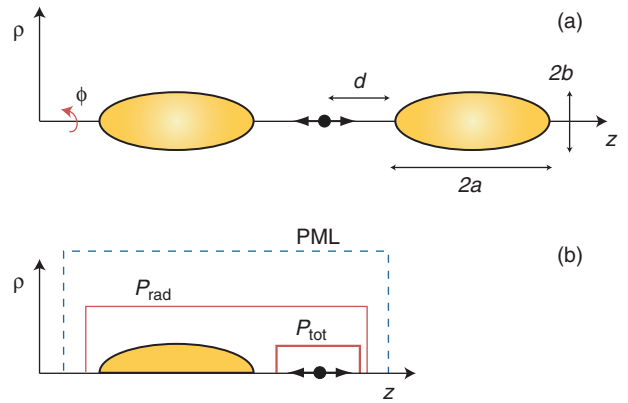


Fig. 1. A single emitter is coupled to a nanoantenna made of one or two metal spheroids. (a) The dipole is placed at a distance d and it is oriented along the z axis. The spheroid has dimensions a and b for the semi-major and semi-minor axes, respectively. When the nanoantenna consists of two spheroids, the emitter is at the center of the gap with width $2d$. The rotational symmetry with respect to the z axis makes the system a body of revolution that can be treated in two dimensions by considering its cross section. (b) The total P_{tot} and radiated P_{rad} powers are obtained using Poynting theorem (solid lines). The mesh is truncated using PML absorbing boundary conditions (dashed line).

Figure 2 shows the real and imaginary parts of the dielectric functions of gold and copper in the visible and near IR spectral range. The real part for the two materials is quite similar, whereas the imaginary part for copper is slightly

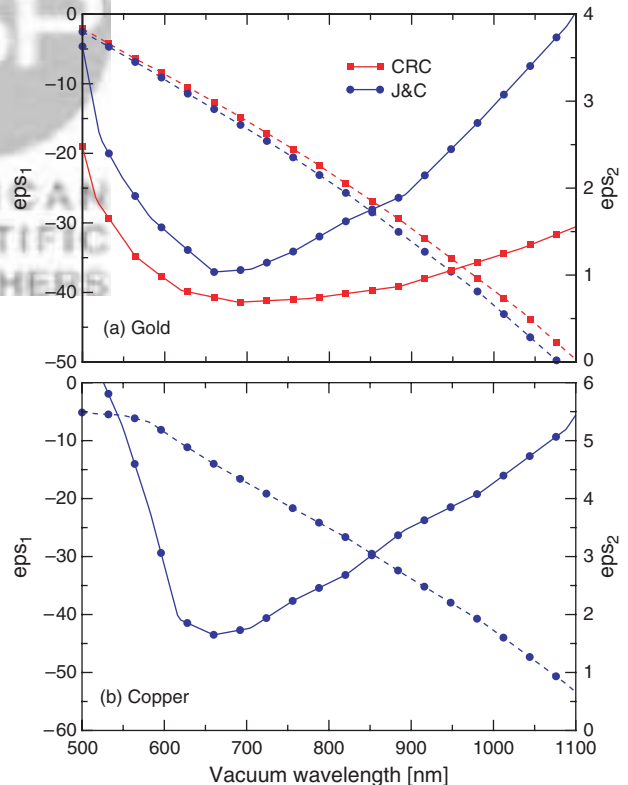


Fig. 2. Real (dashed curves) and imaginary parts (solid curves) of the dielectric functions of (a) gold and (b) copper. The experimental data are compiled from Refs. [37] (CRC) and [38] (J&C).

larger than for gold if the experimental data are taken from Ref. [38]. Therefore, we expect similar results for both materials. On the other hand, if for gold we consider the experimental values from Ref. [37], the imaginary part gets smaller and consequently gold nanoantennas should further improve with respect to copper. We choose the optical constants from Ref. [37] for gold and from Ref. [38] for copper.

Since we have already studied nanoantennas made of two gold spheroids,²⁶ here we focus the attention on single ones. This system can be also studied using an approximate method developed by Gersten and Nitzan²⁵ and recently improved by Mertens et al.^{28,34} to account for radiative damping³⁵ and depolarization effects.³⁶ Figure 3(a) elucidates how the Purcell factor and the quantum efficiency η_a depend on the background index for an emitter coupled to a gold spheroid with semi-axes $a = 70$ nm and $b = 25$ nm. Even a small change in the refractive index shifts the LSPR by more than hundred nanometers. At the same time, the resonance gets wider because radiative broadening increases with the refractive index.³⁵ That also explains the small decrease in the Purcell factor. As a consequence of material losses, the quantum efficiency drops to zero below 600 nm. However, the shift of the LSPR towards shorter wavelengths improves the quantum efficiency. For instance, it is larger than 70% around 650 nm if the nanoantenna is embedded in air, $n_b = 1$.

Figures 3(b and c) present the situation where the background index n_b is fixed to that of water, $n_b = 1.33$, and the spheroid axes are varied. In Figure 3(b) the semi-minor axis is constant, $b = 20$ nm, and the semi-major one spans from 40 to 70 nm. When the aspect ratio gets smaller the LSPR shifts towards shorter wavelengths and the Purcell factor drops.²⁶ Notice that even if a smaller aspect ratio implies a smaller volume and a dipolar LSPR closer to the higher order modes,²⁸ the quantum efficiency can still be large, as shown for $a = 40$ nm. Also decreasing the volume reduces the effect of radiative broadening and the LSPRs appear narrower. In Figure 3(c) we keep the semi-major axis constant, $a = 70$ nm, and vary the spheroid width. In this case, reducing the aspect ratio increases the volume such that radiative broadening increases and the LSPRs appear wider. For the same aspect ratio, the smaller spheroid in Figure 3(b) with $a = 40$ nm and $b = 20$ nm exhibits a stronger Purcell factor and a lower quantum efficiency than the larger one with $a = 70$ nm and $b = 35$ nm.

Figure 4 summarizes the results of a single gold spheroid in water for different values of the nanoantenna axes. In Figure 4(c) we plot the wavelengths at which the maximum Purcell factor is achieved, corresponding to the peak of the LSPR. These values are reported in Figure 4(b). For the same wavelengths we have also computed the quantum efficiency η_a , shown in Figure 4(a). The data for nanoantennas with resonances outside the wavelength range from

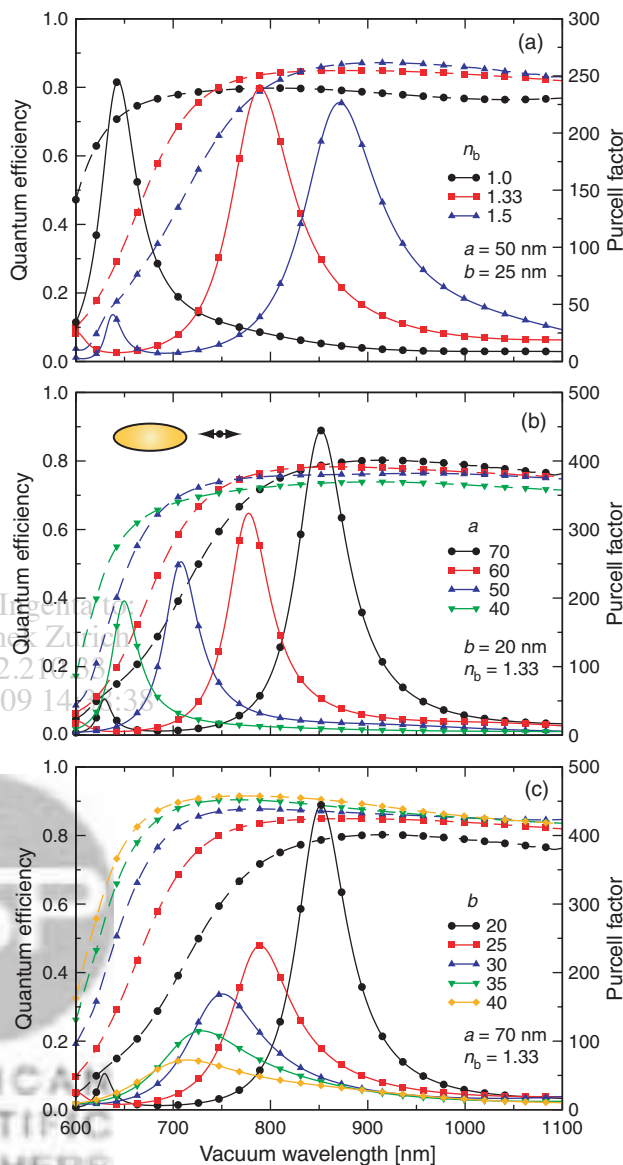


Fig. 3. Purcell factor (solid curves) and quantum efficiency η_a (dashed curves) for an emitter coupled to a gold spheroid for $d = 10$ nm (see Fig. 1(b)). (a) Dependence on the background index n_b for $a = 50$ nm and $b = 25$ nm. (b) Dependence on the semi-major axis a for $b = 20$ nm and $n_b = 1.33$. (c) Dependence on the semi-minor axis b for $a = 70$ nm and $n_b = 1.33$.

600 to 1100 nm have not been considered. While the quantum efficiency does not depend much on the spheroid parameters, the Purcell factor changes by almost an order of magnitude, as already seen in Figure 3.

We now move our attention to copper spheroids. Figure 5(a) shows the Purcell factor and the quantum efficiency η_a for an emitter coupled to a single spheroid in glass, $n_b = 1.5$, for $a = 60$ nm and variable b . Compared to gold (see Fig. 3(c)) the enhancement is smaller and the resonances are broader as expected by the fact that the imaginary part of copper is larger. On the other hand, the Purcell factor does not drop as rapidly when the

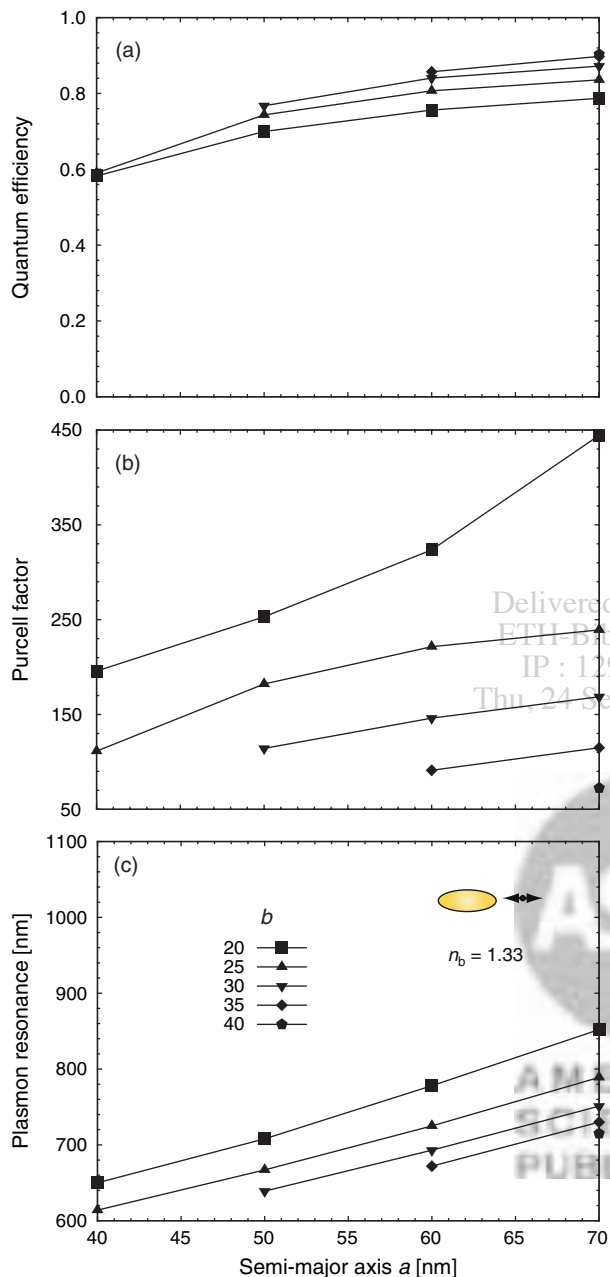


Fig. 4. (c) LSPR wavelength, corresponding to the maximum Purcell factor for an emitter coupled to a gold spheroid, as a function of a and b (see Fig. 1(b)). The distance to the spheroid is $d = 10$ nm and the background index is $n_b = 1.33$. (b) Purcell factor and (a) quantum efficiency η_a for the corresponding wavelengths and spheroid parameters given in (c).

aspect ratio decreases. The quantum efficiency is lower, but it shows the same trend. Namely, if the LSPR shifts to shorter wavelengths, the efficiency increases. For an aspect ratio equal to 2, for $a = 60$ nm and $b = 30$ nm, the Purcell factor is about 75 and the quantum efficiency is close to 70%. If we consider a nanoantenna made of two copper spheroids, we can improve both the Purcell factor and the quantum efficiency, but we also redshift the resonance wavelength, as shown in Figure 5(b).

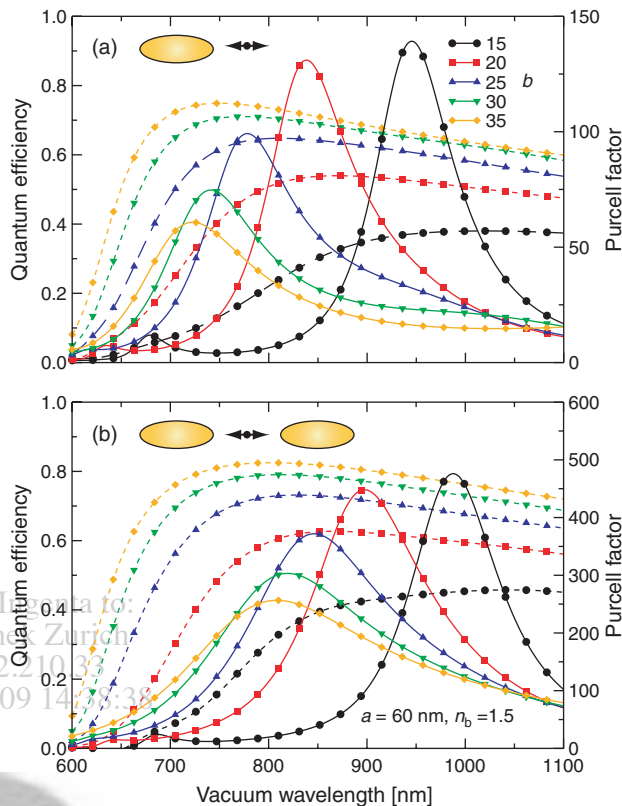


Fig. 5. Purcell factor (solid curves) and quantum efficiency η_a (dashed curves) for an emitter coupled to a nanoantenna made of (a) one or (b) two copper spheroids in glass, with $a = 60$ nm and $d = 10$ nm (see Fig. 1).

Collective data on the resonance wavelength, Purcell factor and quantum efficiency are displayed in Figure 6 for nanoantennas made of one or two copper spheroids in glass. In Figure 6(a) notice that the quantum efficiency is now more sensitive to the nanoantenna geometry than in the case of gold (see Fig. 4(a)), while the opposite holds for the Purcell factor, when comparing Figures 6(b) and 4(b). These differences stem from the imaginary part of the dielectric function, which is larger for copper. We should keep in mind that if for gold we used the optical constants from Ref. [38], gold and copper would exhibit even closer resemblance.

2.3. Silver and Aluminum Nanospheroids

We now consider nanoantennas made of silver or aluminum. As before, we start looking at the real and imaginary parts of the dielectric function, presented in Figure 7. Silver appears to be similar to gold if the experimental data are taken from Ref. [37] and from Ref. [38], respectively. The main difference is that silver has a higher plasma frequency so that the curves are shifted towards shorter wavelengths. Therefore, we expect that silver yields results similar to gold, but in a spectral range closer to UV light. However, if for silver we consider the experimental data of

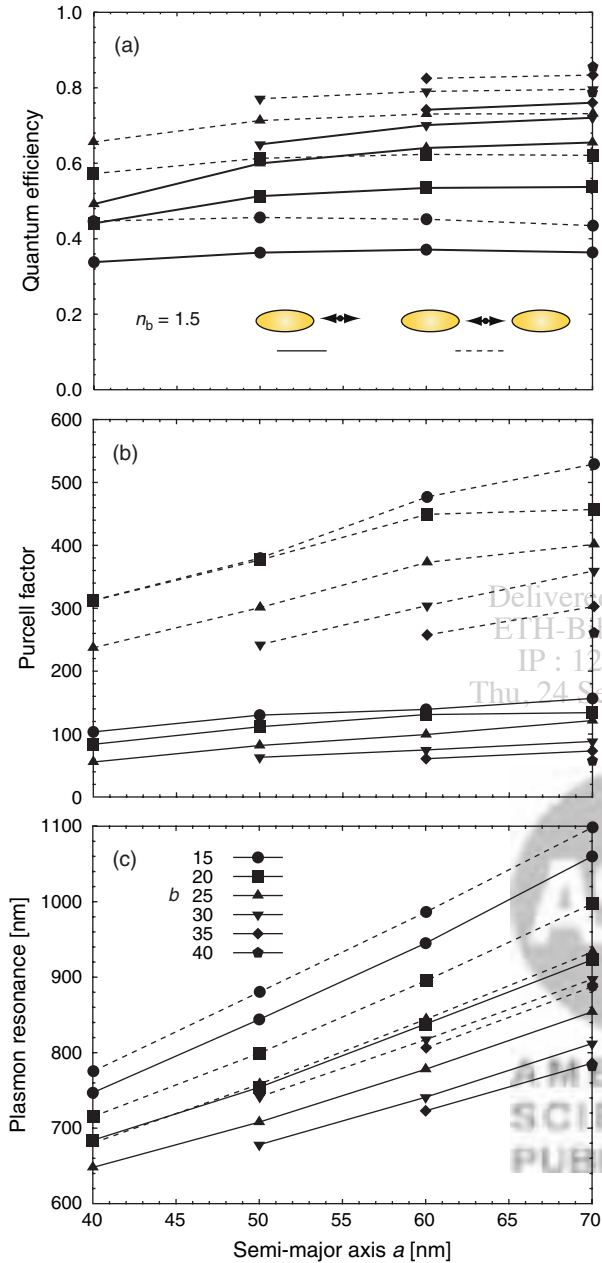


Fig. 6. (c) LSPR wavelength, corresponding to the maximum Purcell factor for an emitter coupled to one (solid curves), or two (dashed curves) copper spheroids, as a function of a and b (see Fig. 1). The distance to the spheroid is $d = 10$ nm and the background index is $n_b = 1.5$. (b) Purcell factor and (a) quantum efficiency η_a for the corresponding wavelengths and spheroid parameters given in (c).

Ref. [38], we notice that while the real part is almost the same, the imaginary part drops to much lower values. In this case, silver nanoantennas should perform much better than their gold counterparts. Because samples of silver nanoantennas might exhibit a lower optical quality than the bulk material, caused by imperfections in the crystalline structure and contamination occurring in the nanofabrication steps, we prefer to choose the experimental dielectric function with the largest imaginary part.³⁷

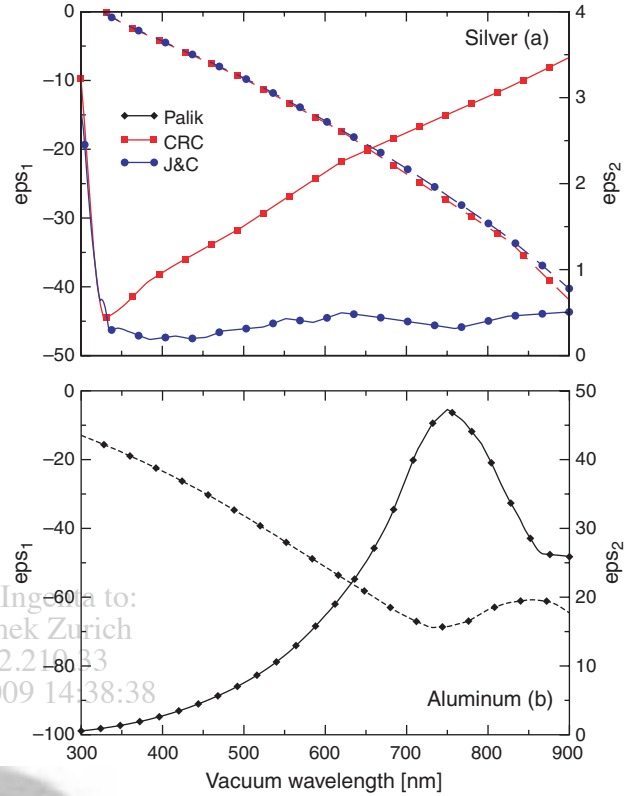


Fig. 7. Real (dashed curves) and imaginary parts (solid curves) of the dielectric functions of (a) silver and (b) aluminum. The experimental data are compiled from Refs. [37] (CRC), [38] (J&C), and [39] (Palik).

Figure 7(b) displays the optical constants of aluminum as given in Ref. [39]. Aluminum has a plasma frequency even higher than silver. Therefore the real part is larger in the same spectral range. On the other hand, there is an interband absorption peak located at 800 nm, which creates a dispersive profile in the real part of the dielectric function and, most importantly, a strong increase in the imaginary part. This makes aluminum less attractive for nanoantenna applications in the spectral range around 800 nm. Even if

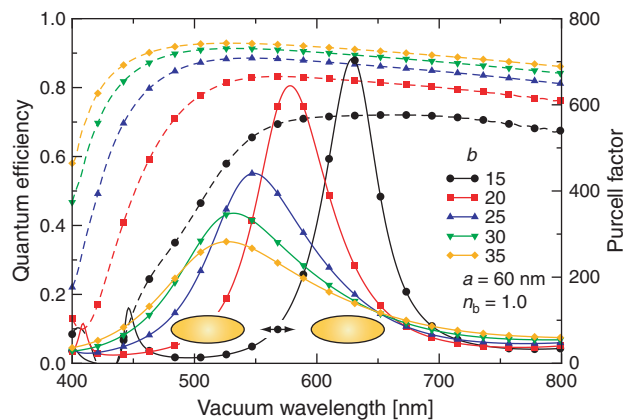


Fig. 8. Purcell factor (solid curves) and quantum efficiency η_a (dashed curves) for an emitter coupled to a nanoantenna made of two silver spheroids in air with $a = 60$ nm and $d = 10$ nm (see Fig. 1(a)).

the imaginary part is significantly larger than in the noble metals, in the region below 600 nm the large and negative real part ensures that the skin depth is sufficiently small to prevent significant losses.

Figure 8 shows the quantum efficiency η_a and the Purcell factor for an emitter coupled to a nanoantenna made of two silver spheroids in air. The general trend agrees with what we have previously discussed for gold in Figure 3(c), and for copper in Figure 5(b). Because

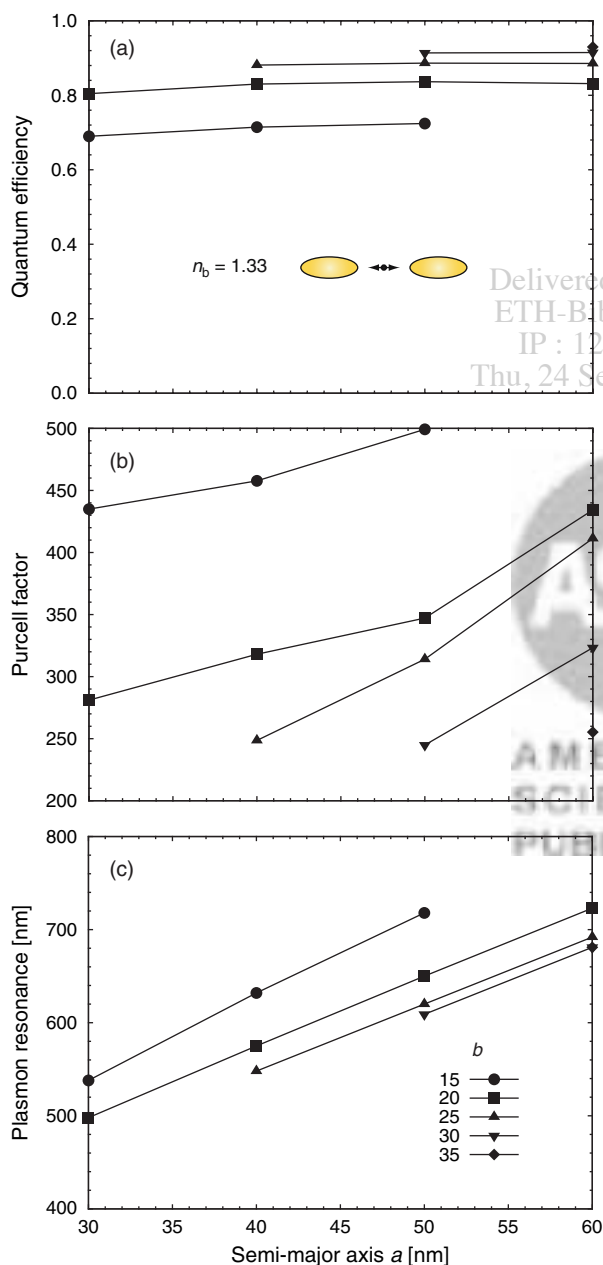


Fig. 9. (c) LSPR wavelength, corresponding to the maximum Purcell factor for an emitter coupled to two silver spheroids, as a function of a and b (see Fig. 1(a)). The distance to the spheroids is $d = 10$ nm and the background index is $n_b = 1.33$. (b) Purcell factor and (a) quantum efficiency η_a for the corresponding wavelengths and spheroid parameters given in (c).

the plasma frequency of silver is higher than that of gold and copper, the resonances are shifted by about 200 nm towards shorter wavelengths. Furthermore, the quantum efficiency and the Purcell factor are higher. Using the optical constants of Ref. [38] would have yielded even better results. A more complete set of results for silver nanoantennas embedded in water is given in Figure 9. In comparison to Figure 8, the LSPR is redshifted and the Purcell factor is slightly reduced due to the radiative broadening effect as seen for gold in Figure 3(a).

The quantum efficiency η_a and the Purcell factor for an emitter coupled to a nanoantenna made of two aluminum spheroids in air is provided in Figure 10. While the quantum efficiency, as expected, increases with the volume of the spheroid, the LSPR is not redshifted when the aspect ratio increases. The reason for that can be found in the electromagnetic interaction between the two spheroids. For a single aluminum spheroid, the LSPR exhibits a small redshift in agreement with the polarizability theory.^{24, 36} For the case of two aluminum spheroids separated by a gap $2d = 20$ nm, the interaction between the two LSPR modes is stronger for small aspect ratios than for larger ones because sharper particles have larger but more rapidly decaying near fields at their tips. The coupling between the two particles redshifts the LSPR.⁴⁰ The increased interaction explains also why the Purcell factor does not drop much when the aspect ratio decreases: the two spheroids act together more effectively to increase the near field. An indication of the same effect can be appreciated also for copper in Figure 5, where however the redshift caused by the single particle polarizability is so strong that makes it difficult to notice. The Purcell factors given by the aluminum nanoantennas of Figure 10 are not as large as found for the same system made from other materials. Because the quantum efficiency is large, the reason for that should be mainly attributed to radiative broadening rather than to losses.³⁵ For instance, since the radiative broadening is proportional to $1/\lambda^3$, the effect is 8 times

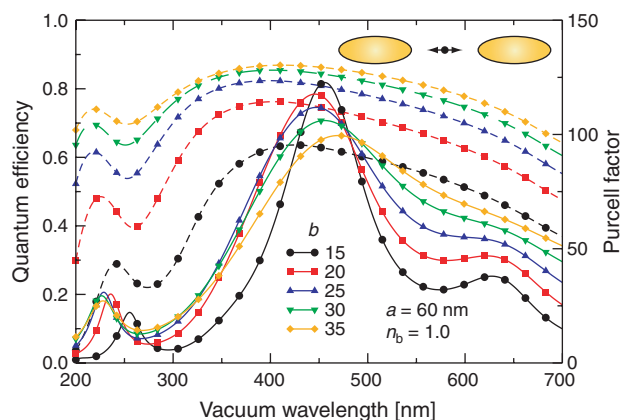


Fig. 10. Purcell factor (solid curves) and quantum efficiency η_a (dashed curves) for an emitter coupled to a nanoantenna made of two aluminum spheroids in air, with $a = 60$ nm and $d = 10$ nm (see Fig. 1(a)).

stronger at 400 nm than at 800 nm. Indeed calculations of the field enhancement have shown that the LSPR should be located around 200–300 nm and the semi-major axis of the spheroid should not be larger than 40 nm for optimal performances.²⁴ Therefore aluminum nanoantennas can be better exploited for the UV spectral region rather than for the visible and near IR range.

3. CONCLUSIONS

We have investigated the performances of nanoantennas for improving light emitters by considering different materials, namely gold, copper, silver and aluminum, aspect ratios and background media. While gold and copper can both operate in the near IR spectral range, silver is more suitable for the visible range and aluminum for the UV range. Therefore, various emitters can be enhanced by choosing appropriate nanoantenna parameters.

We have seen that contrary to conventional antennas, nanoantennas cannot be simply scaled to operate at different wavelengths. Here the material properties play a fundamental role. Also the choice of the experimentally determined optical constants available in the literature can be an issue of concern.⁴¹ In particular, these data have been obtained for bulk samples, while nanoantennas are truly nanoscale objects. Even if the volume of a nanoantenna is sufficiently large to ignore quantum-size effects,²¹ the fabrication methods might influence the actual optical properties by nanograins formation and material contamination.^{38,42}

Acknowledgments: We thank L. Rogobete, F. Kaminski, Y. Ekinci, N. Mojarad, H. Eghlidi, and S. Götzinger for helpful discussions. A. Mohammadi is thankful to the Persian Gulf University Research Council for partial support. This work was financed by the ETH Zurich initiative on Composite Doped Metamaterials (CDM).

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Received: 25 July 2008. Accepted: 6 October 2008.