Control of the quantum yield of a dipole emitter with coupled plasmonic modes

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Introduction

The fluorescence lifetime of a dipole emitter (e.g. atom, molecule, and quantum dot) can be modified close to plasmonic nanosystems [1-3]. However, the use of metallic structures induces the appearance of external non-radiative decay channels, that can substantially reduce the quantum yield. The interplay between local-field enhancement, and radiative and non-radiative decay channels can lead to an enhancement of the fluorescence signal or to quenching [4].

In addition, control of plasmon-resonance frequencies can be achieved by playing with the shape of metallic structures. Another way of tailoring the resonance frequency is the coupling of plasmonic modes in nanostructures. These **hybrid plasmonic modes** can lead to either radiative or non-radiative coupling [5].

In this work, we study the possibility of **controlling the fluorescence dynamics** of a single dipole emitter using coupled plasmonic modes. Plasmon hybridization offers spectral and spatial degrees of freedom that can be used to tune the spontaneous decay rate and the apparent quantum yield with high sensitivity.

These behaviours are common to all coupled-plasmonic structures and we show it for three different cases:

- The nanoparticle dimers.
- The thin film.
- The sphere-film systems.

Spontaneous decay rate

- Spontaneous decay happens at a rate Γ, which is the inverse of the lifetime of the excited state (τ).
- The decay rate depends on the structure of electromagnetic modes of the system through the imaginary part of the Green tensor at the position of the emitter.

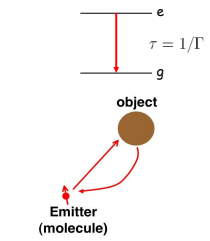
$$\Gamma \propto \Im m\left[\mathbf{u}.\mathbf{G}(\mathbf{r},\mathbf{r},\omega).\mathbf{u}\right]$$

LDOS

- In general, any change in the structure of electromagnetic modes will affect the decay rate. When absorption is present, non radiative channels are opened which contribute to the total decay rate.

$$\Gamma = \Gamma^{R} + \Gamma^{NR}$$

Radiative — Non-radiative

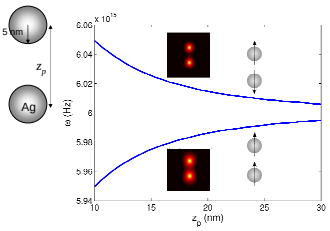


$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{G}(\mathbf{r},\mathbf{r}_p,\omega).\mathbf{p}(\mathbf{r}_p,\omega)$$

Nanoparticle dimers

Plasmon hybridization in dimers

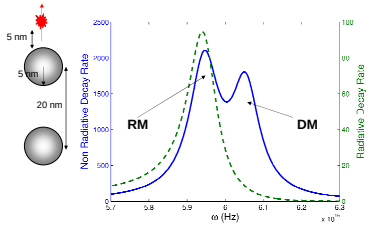
Individual nanoparticle plasmons hybridize to give two new modes : a bonding and a antibonding combination [5]. For large z_p, the shifts of the lowest modes of the dimer follow the interaction energy between two dipoles $(1/z_p)^3$.



Plasmon frequencies of a nanosphere dimer as a function of interparticle separation

Radiative and Dark Modes

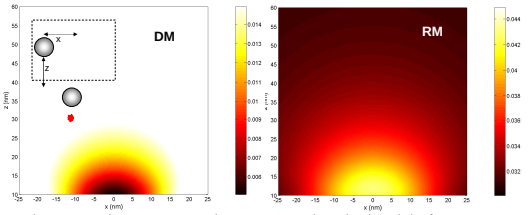
The net dipole moment of the antibonding configuration is zero, this mode is not easily excited by light [dark mode (DM)]. In contrast, the bonding configuration corresponds to two dipole moments moving in phase and is easily excited by light [radiative mode (RM)].



Γ^{NR} shows the two dimer-plasmon modes while Γ^{R} characterizes each mode (radiative or dark)

Apparent Quantum Yield

The apparent quantum yield η measures the number of photons emitted in the far field $\eta = \Gamma^{R}/(\Gamma^{R}+\Gamma^{NR})$. Close to metallic nano-objects, the apparent quantum yield tends to zero, leading to a quenching of the fluorescence [2]. However, in our case, due to plasmonic coupling in the dimer, a local increase of the quantum yield can be obtained for the radiative mode.

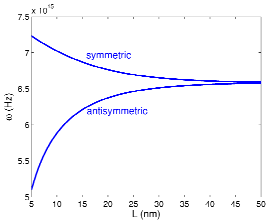


The nanoparticle scans a rectangular region above the molecule and the figure displays the value of η for each position of the nanoparticle in this rectangular region.

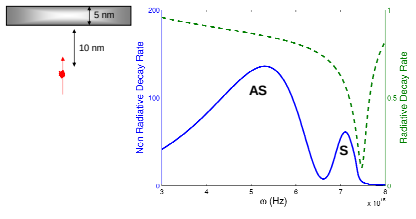
Thin metallic film

Dispersion relation

Surface plasmon waves (SPWs) propagate at each interfaces of a metallic film and a dielectric (here, vacuum). For a thick metal film (L>100 nm), each interface supports the same SPW (twofold degeneracy). When L decreases, the modes start to interact due to the overlapping of their evanescent contributions inside the metal, and a mode splitting is observed. The degenerate SPW splits into symmetric (S) and antisymmetric (AS) modes. The eigenfrequency of the S (AS) mode increases (decreases) as the film is made thinner.



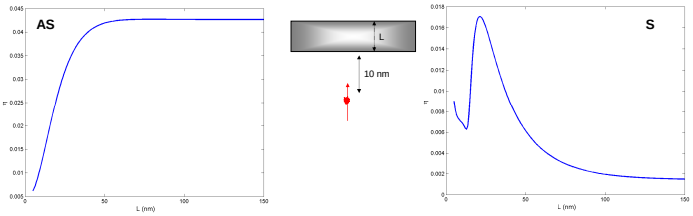
Eigenfrequencies of the plasmonic modes of a thin silver film versus the film thickness L.



Γ^{NR} and Γ^{R} of thin metallic film (L = 5 nm) illuminated by a dipole at 10 nm below the slab.

Apparent Quantum Yield

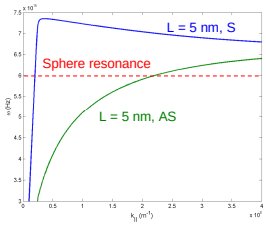
By analogy to the dimers, we change the film thickness in order to increase the SPW overlapping and calculate the apparent quantum yield. For the symmetrical mode, a reversed quantum yield contrast is obtained.



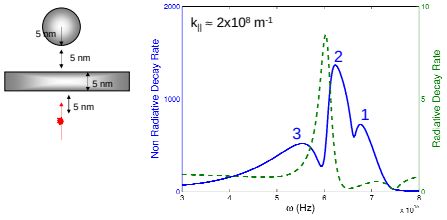
Sphere - film system

Mode coupling

Now, we examine the interaction between the discrete, localized plasmon of a metallic nanosphere (dipolar approximation) and the continuum of delocalized surface plasmons of a metallic thin film.



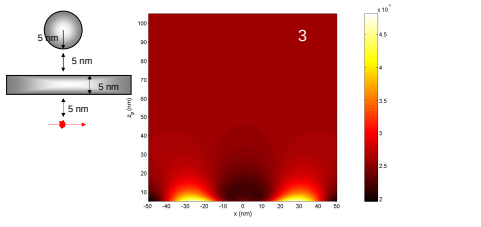
Dispersion relations of a thin metallic film and of the localized plasmon of a nanosphere.



Γ^{NR} and Γ^{R} of a sphere coupled to a metallic film illuminated by a dipole below the slab.

Dipole orientation

Quantum yield maps contain a signature of the transition dipole orientation of the emitter.

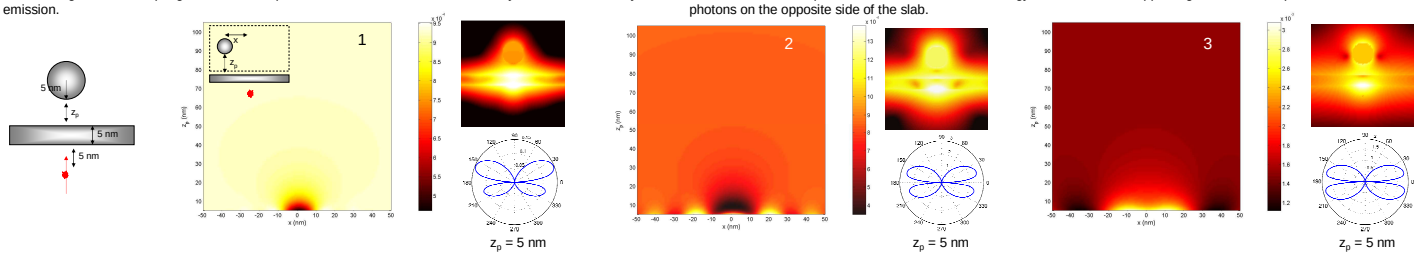


Apparent quantum yield map for a dipole oriented parallel to the slab interface.

Apparent Quantum Yield Maps and Radiation Patterns

Depending on the strength of the coupling between the sphere and the thin film, we can modify in a controlled way the spontaneous emission.

In addition, radiation patterns show that half of the energy is radiated in the upper region and makes possible the detection of photons on the opposite side of the slab.



z_p = 5 nm — z_p = 5 nm — z_p = 5 nm

Conclusions

Novel concept that permits a **control of the quantum yield with high spectral selectivity and spatial sensitivity.**

✓ The approach is based on the use of coupled plasmonic modes obtained by **plasmonic hybridization.**

✓ The coupling efficiency can be tuned using **the emission frequency and the emitter location as degrees of freedom.**

✓ The interplay between radiative and dark modes offers the possibility of **controlling the quantum yield by changing an internal parameter of the system.**

References

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This work was supported by the EU Integrated Project *Nanomagma* under contract NMP3-SL-2008-214107. C. V. acknowledges the Belgian National Fund for Scientific Research. L. S. F.-P. ackowledges support from the Spanish Ministry of Science and Innovation trhough its Juan de la Cierva program.