Fluorescence enhancement in the vicinity of complex plasmonic nanostructures: A transformation optics approach

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Abstract

In this paper, the interaction of a dipole emitter (*e.g* molecule or quantum dot) with complex plasmonic nanostructures is investigated by means of transformation optics. The fluorescence enhancement as well as the quantum efficiency are derived analytically. Their spectral and spatial properties are analyzed in the perspective of future experiments.

1. Introduction

Surface plasmons have drawn a considerable attention for the last decade because of their ability to route and manipulate light at the nanoscale [1, 2, 3, 4]. Squeezing light into nanoscale volumes greatly boosts light-matter interactions as shown by surface enhanced Raman scattering (SERS) [5, 6] or enhanced fluorescent emission [7, 8]. There have been tremendous efforts to design and optimize nanostructures and obtain the best efficiency in light harvesting and nanofocusing. Until now, this optimization has mainly relied on numerical simulations [9, 10]. Recently, a more powerful approach based on transformation optics has been proposed to derive analytically the optical response of complex nanostructures [11, 12, 13]. It consists in finding a conformal map that transforms the plasmonic nanostructure under investigation into a simpler plasmonic system that can be solved analytically. Transformation optics closely links the physics at work in each of the different geometries and gives a unique physical insight on the propagation of surface plasmons in complex nanostructures. Here, we apply this strategy to predict analytically the fluorescence enhancement of molecules placed in the vicinity of metallic nanostructures. As the absorption and emission process occur at different frequencies, a perfect knowledge of the spectral and spatial properties of the field enhancement might be decisive for the implementation of new types of biosensors. In this study, we will consider the interaction of a fluorophore with a dimer of nanowires (Fig.1(a)). To solve this problem, this configuration will be mapped onto a much simpler one consisting of a dipole sandwiched between two semi-infinite metal slabs (Fig.1(b)). The solution in the latter geometry will allow us to derive analytically different quantities such that the fluorescence enhancement as well as the quantum efficiency in presence of the metallic nanostructure. Note that previous works have investigated theoretically similar problems [14, 15, 16] but none of them have led to a full analytical solution.

2. Purcell factor, quantum yield and fluorescence enhancement

The quantum yield is an important parameter that drives the fluorescence signal. It is defined by,

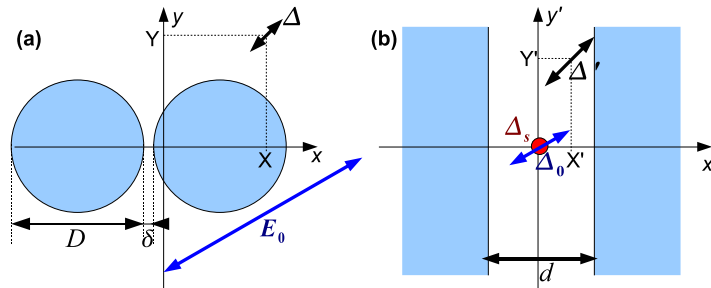$$\eta = \gamma^R / (\gamma^R + \gamma_{int}^{NR} + \gamma^{NR}) \tag{1}$$

Fig. 1: (a) A pair of metallic nanowires of diameter D and separated by a distance δ is illuminated by an incident plane wave $\mathbf{E_0'}$. The dipole $\mathbf{\Delta'}$ accounts for a fluorescent molecule placed in gthe vicinity of the nanostructure. (b) Using the transformation already described in Ref.[12], the latter system is transformed into two semi-infinite metallic slabs separated by a thin dielectric film. $\mathbf{E_0'}$ and $\mathbf{\Delta}$ are transformed into two dipoles $\mathbf{\Delta_0}$ and $\mathbf{\Delta'}$, respectively. An absorbing particle $\mathbf{\Delta_s}$ accounts for the radiative losses in the initial frame [18].

where γ^R is the radiative decay rate that gives rise to the emission of a photon in the far field, γ_{int}^{NR} is an intrinsic nonradiative decay rate that accounts for internal losses, and γ^{NR} is the external nonradiative decay rate induced by dissipation in the metal. The other key quantity is the fluorescence enhancement. Under weak excitation, the fluorescence signal of an isolated emitter is $S_0 = \eta_0 \left| \mathbf{\Delta}.\mathbf{E_0} \right|^2$. In the presence of the plasmonic nanostructure that behaves as an optical nanoantenna, the local electric field $\mathbf{E}$ is modified and the signal becomes $S = \eta \left| \mathbf{\Delta}.\mathbf{E} \right|^2$. The fluorescence enhancement then reads

$$S/S_0 = \left(\eta \left| \mathbf{\Delta}.\mathbf{E} \right|^2 \right) / \left(\eta_0 \left| \mathbf{\Delta}.\mathbf{E_0} \right|^2 \right) \tag{2}$$

The conformal transformation described in Fig.1 leads to tractable analytical expressions of the quantum yield and of the fluorescent enhancement. Fig.2 shows the frequency and spatial dependence of this enhancement. The maximum of the fluorescence enhancement (*i.e* in the middle of the narrow gap) is displayed as a function of frequency and of the distance δ between the two nanowires (see Fig.2(a)). Several peaks arise and red-shift when the two nanoparticles approach each other: they correspond to localized surface plasmon resonances that arise for $\left(\sqrt{\delta/(2D)} + \sqrt{1 + \delta/(2D)} \right)^{4n} = \mathrm{Re} \left\{ (\epsilon - 1)/(\epsilon + 1) \right\}$ [12]. Our theory predicts that the fluorescence of a molecule can be enhanced by 5 orders of magnitude in the gap. Fig.2(b) and (c) show the spatial dependence of the fluorescence enhancement for different orientation of the dipole. The fluorescence enhancement highly depends on the position of the molecule. Hence, plasmon hybridization offers spectral and spatial degrees of freedom that can be used to tune the fluorescence and the apparent quantum yield with high sensitivity.

5. Conclusion

To conclude, note that the conformal transformation approach can be extended to a wide range of nanostructures (crescents [11], 3D dimers [13], nanoshells, etc.). More than simply elegant, this strategy is powerful since it provides a fully analytical solution to describe the physics of the interaction between a fluorophore and a plasmonic nanostructure. Unlike a numerical approach, an efficient and rapid optimization of the nanostructures can be performed. Our analytical model predicts quantitatively the quantum yield and the fluorescence enhancement induced by these metallic structures for nanowire diameters below 100 nm. As the absorption and emission process occur at different frequencies, a perfect knowledge of the spectral and spatial properties of the field enhancement might be decisive for the implementation of experimental setup aiming at single molecule detection.
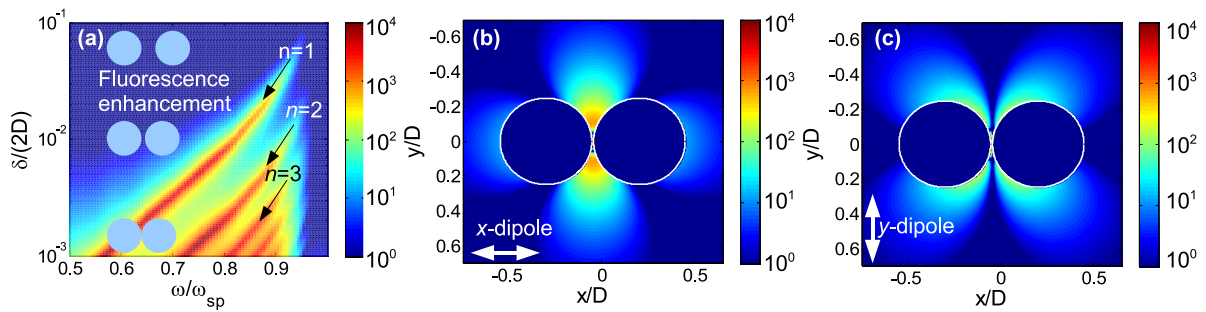
Fig. 2: Fluorescence enhancement for a dimer of silver nanowires (with $D = 20nm$, permittivity taken from Ref.[17] and assuming $\eta_0 = 1$). (a) S/S_0 as a function of $\delta/(2D)$ and frequency for a dipole oriented along x. (b) and (c) S/S_0 at the first resonance ($n = 1$) and for $\delta = D/50$.

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