

Désordre contrôlé sur des nanostructures métalliques pour des applications en plasmonique

Thi Phuong Lien Ung

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UNIVERSITE PARIS-SACLAY

Control disorder for electromagnetic localization in plasmonic devices for nanophotonic application

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Titre : Désordre contrôlé sur des nanostructures métalliques pour des applications en plasmonique

Mots clés : Plasmonique, nanostructures, nanocristaux, microscopie

Résumé: Les nanostructures métalliques permettent de confiner la lumière à des échelles sub-longueur d'onde grâce à l'excitation de plasmons de surface. Elles ouvrent la voie à de nombreuses applications que ce soit en imagerie, en élaboration de composants photoniques ou en information quantique.

Cette thèse porte sur l'étude de nanostructures métalliques, semi-continues ou constituées par des réseaux de trous au désordre contrôlé, et à leur interaction avec des nanocristaux semi-conducteurs colloïdaux particulièrement photostables.

En associant plusieurs approches expérimentales complémentaires (spectroscopie en champ lointain, microscopie de champ proche optique, microscopie avec une sonde active de champ proche, caractérisation par microscopie confocale de l'émission de nanocristaux couplés surfaces aux métalliques), nous avons pu mettre en évidence les caractéristiques spécifiques des modes plasmons de ces différentes structures. Pour les réseaux au désordre contrôlé, nous avons en particulier analysé l'apparition progressive de modes localisés intenses et déterminé l'influence de paramètres tels que l'épaisseur de la couche d'or. le diamètre des trous ou la périodicité initiale du réseau. Les résultats expérimentaux obtenus se sont révélés en très bon accord avec les simulations numériques réalisées par FDTD.

Title : Control disorder for electromagnetic localization in plasmonic devices for nanophotonic application

Keywords : Plasmonic, nanostructures, nanocrystals, microscopy

Abstract: Metallic nanostructures allow us to confine light at sub-wavelength scales by the excitation of surface plasmon. They open the way for many applications in imaging, photonic components development and quantum information.

This thesis deals with the study of metallic nanostructures, semi-continuous or based on holes gratings with a controlled disorder, and their interaction with colloidal semiconductor nanocrystals that are very photostable.

Combining several complementary experimental approaches (far-field spectroscopy, near-field optical microscopy, near-field active probe microscopy, characterization by confocal microscopy of

emission of nanocrystals coupled to the metallic surfaces), we were able to highlight specific characteristics of the plasmon modes of these different structures. For the gratings with a controlled disorder, we have in particular analyzed the emergence of intense localized modes and determined the influence of parameters such as the thickness of the gold layer, the diameter of the holes or the initial periodicity of the grating. The experimental results are in very good agreement with the numerical simulations carried out by FDTD.



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GENERAL INTRODUCTION

For the development of many devices, reducing the size of components is a crucial requirement. In the field of optics, efforts are also focused on miniaturization and have spawned to the domain of nanophotonics which gathers optics and nanotechnology. Photonic nanostructures are now fabricated more and more easily and precisely by techniques such as electron-beam lithography or focused ion-beam etching.

Nanophotonics supplies specifically the means of enhancing and control lightmatter interaction [1]. Low-dimensional nanostructures (2D or 1D), such as photonic crystals, microcavities or waveguides have been designed [1]. They exhibit interesting properties like strong modification of the density of optical states [2–5] which is the basic for quantum-optic applications.

Light-matter interaction at the nanometer scale is also at the heart of plasmonics that explores the optical response of metals under the interaction with the electromagnetic field. Plasmons have been studied in the very early of 19th century [6,7]. Basically, the collective electronic excitations formed at the metal-dielectric interface generate propagative surface plasmon polaritons (SPPs) or localized surface plasmons (LSPs) associated to electromagnetic field enhancements. SPs modes can carry out the electromagnetic energy [8] but, above all, these modes offer the unique possibility to overcome the limit induced by diffraction. Light can be confined at the nanoscale which provides the opportunity to transfer informations in nanostructured surface [9] and have opened up a wide range of applications for nanooptics [10–16].

In the field of plasmonics, one of the most attractive system used from the early of last century consists in hole gratings which exhibit SPPs and Rayleigh anomalies. For this kind of structures, a very significant discovery belongs to Ebbesen about the extraordinary optical transmission (EOT) through a periodic sub-wavelength hole arrays in a very thick metallic film [17]. Thanks to the idea of Ebbesen, many other sub-wavelength nanostructures have been exploited such as triangular aluminum plates on a glass slide [18] or rectangular gold and silver patterns [19,20]. Recently, some researchers have focused on the SPPs and LSPs of very thin metallic films which display high absorption at the surface plasmon resonance wavelength [21–24].

If many nanophotonic structures are based on orderely patterns, metallic nanostructures as dielectric ones are also a great example of what can be made of disorder in physics. In a photonic crystals, the transition from order to disorder can introduce strong light confinement due to multiple light scattering and induce the well-known phenomenon of Anderson localization [25,26]. The energy can be localized in small volumes leading to strong electric field enhancements. Therefore, random structures can be used as an alternative to ordered nano-structures because of the strong light localization. Furthermore, many applications which need broadband operation can take advantage of the absence of spatial periodicity in such random structures.

In the domain of nanophotonics, besides photonic nanostructures, many semiconductor nanostructures have been developed as nanosources of light. They have contributed gradually in the miniaturization of the devices. When the material is reduced to nanoscale dimensions, electrons are confined so that quantum size effects prevail. Nowadays, it is possible to synthesize objects for which quantum confinement occurs in one direction (nanoplaquettes or nanorubans) [27,28], two directions (nanowires or nanobatons) [29,30] or three directions of space (nanocrystals (NCs) and quantum dots) [31,32]. For the lastest, the energy levels in the conduction or valence bands exhibit a discrete structure like those of individual atoms [33–35]. Quantum dots can be grown by molecular beam epitaxy but also by colloidal synthesis (they are then referred as colloidal NCs). The synthesis of inorganic nanostructures is a new branch of synthetic chemistry that has grown fast and is now moving towards more and more sophisticated objects. By playing on the different elaboration conditions, such as injected precursors, the temperature during growth or the different additives used, it is possible to obtain objects of various sizes and shapes [27,36]. NCs are now available in aqueous or organic solutions or polymer [37-39] and the surface of these semiconductor nanostructures can be easily functionalized. Their high flexibility make them very attractive for many application such as biological marking [40, 41], the realization of optoelectronics devices [42–44] or lasers [45, 46], and also for single photons generation in the field of quantum optics [47, 48].

Improvement of the NCs synthesis has enabled to achieve quantum efficiencies greater than 90 % for CdSe NCs which are the most elaborated NCs. It is well known that the fluorescence properties of the NCs are not intrinsic to the emitters but correspond to the coupling between the emitters and surrounding electromagnetic field [49, 50]. Following the approach first suggested by E. M. Purcell, the spontaneous emission of these nano-emitters can then be tailored using photonic cavities. Most of the studies on the modification of quantum dots fluorescence first focused on the use of various dielectric cavities such as planar cavities [51, 52] or photonic crystals [53, 54]. However broadband plasmonic cavities are particularly well suited to control the fluorescence of NCs that operate at room temperature and are characterized by a large wavelength bandwidth.

Reciprocally, photonic nanostructures can be probed by decay rate, polarization or intensity measurements using NCs. As an an example, the photonics crystal modes can be localized by recording the fluorescence of the NCs coupled to the photonic crystal [55]. Indeed, the coupling is described by the projected local density of state (LDOS) which is used to quantify the magnitude of vacuum fluctuations at the origin of the spontaneous emission of photons [1].

The work presented in this manuscript fits into the framework of the study of disordered metallic nanostructures. The "Optics at the Nanoscale" group has investigated for some several years semi-continuous gold films close to the percolation threshold. Using Finite Difference Time Domain (FDTD) simulations, a near-field optical microscopy but also the coupling of these films with colloidal NCs, hot spots were investigated in details. During my PhD, my key purpose was to study new plasmonic structures for which the disorder can be controlled. I benefited from the experience of the group and implemented new experimental methods (like far-field spectroscopic transmission and reflection experiments with a confocal microscope) to get relevant results with many complementary approaches about the optical characteristics in near-field and far-field of plasmonic structures with different spatial ordering.

The outline of the manuscript is the following:

- In the first chapter, I will introduce the basic concepts concerning surface plasmons and the opportunities opened by their coupling with a single NC placed nearby. A brief description of the CdSe NCs synthesis methods are next provided. The structure of the carrier levels and the optical properties of these nano-emitters are then presented, highlighting the role played by Auger recombinations. The specificity of thick-shell CdSe/CdSe NCs in terms of reduced flickering is finally described.
- In the second chapter, the optical properties of semi-continuous gold film (random gold) are introduced. They show very localized surface plasmons modes referred as "hot spots", for which the electromagnetic field is much higher than the excitation field. To investigate the modes, the films were coupled to single NCs acting as probes. By simultaneously measuring the photoluminescence (PL) decay rate and the linear polarization ratio, we get new insights about the structures of these modes on this kind of structures and their variation in the near-field.
- The third chapter is focused on the designing of the hole gratings I used as an alternative to semi-continuous gold films for the study of the effect of disorder in metallic nanostructures. To start with, ordered hole gratings are characterized. They will be used as a reference for the last chapter. Simulations have been performed with a FDTD software in order to understand the dependence of the plasmon resonances with different parameters of the hole grating (periodicity, hole diameter, thickness of the metal layer). The results obtained about the coupling between different gratings with single NCs are presented. The NCs are deposited directly on the grating or attached at the end of a Scanning near-field optical microscopy (SNOM) tip.
- The last chapter first introduces the way in which disorder is generated in the ordered hole grating. FDTD simulations are used to map the near electric field and study the effect of the disorder. The influence of the gold film thickness, the excitation wavelength are also detailed. By changing the number of holes considered to carry out the simulations, we also investigate the delocalization of the plasmon modes. Experiments based on a scanning near-field optical microscope (SNOM) show a good agreement with the FDTD results. In addition, the far-field optical properties are explored with a transmission-reflection setup which is developed from a confocal microscope and a spectrophotometer. Following the same method as in chapter 2 and 3, the coupling of the disordered holes with single colloidal NCs is the last step to study the effect of the disorder on the electromagnetic field in the nano-hole structures.

Finally, the main results presented in the manuscript are summarized and some outlooks and future directions for these studies are given.

FUNDAMENTALS OF PLASMONICS AND METAL/EMITTERS COUPLING.

Plasmon resonances have been studied for more than a century. The story of plasmons has begun in the very early of 19th century when Faraday studied the colors of gold particles [6]. Since this time, the optical properties of metal have attracted great attention of the science community. A detailed theory was first developed by Gustav Mie [56] who explained the optical properties of scattering particles. In 1952, David Pines and David Bohm demonstrated the relation between the individual and collective particle aspects of the electron gas [57] and developed a first Hamiltonian approach for the long-range electron-electron correlations [57,58].

Plasmons are at the core of the optical properties of metals. In more detail, the study of plasmons enables to characterize the interaction between the electromagnetic field and the free electrons in metal, specially at the surface of the metal. The surface plasmon (SP) modes were first predicted by R. Ritchie in 1957 [59].

With the development of the material science at the nanoscale, plasmonics offers very promising possibilities for transferring informations in nano-structured surface [9]. The crucial point is that plasmons provide a unique method of manipulating and confining the light in nanoscale geometries [60]. They have opened up a wide range of applications for nano-optics [10–16]. Due to the low quality factors, plasmonic resonators are very well suited for the control of nano-emitters operating at room temperature since they exhibit large linewidth.

From this point of view, semiconductor nanoparticles are a prime example of such fluorophores. Since the 80s, semiconductor particles have attracted great attention and have become more and more popular in different fields of chemistry and physics. Through the improvement of the fabrication techniques, the size of the semiconductor structures have been reduced from the microscale [33, 34, 61–63] to the nanoscale [64, 65]. They are now studied by a large number of laboratories over the world.

At this scale, quantum size effects prevail. Nowadays, it is possible to synthesize objects for which quantum confinement occurs in one direction (nanoplaquettes or nanorubans) [27,28], two directions (nanowires or nanobatons) [29,30] or three directions of space (NCs) [31,32]. The quantum size effects in semiconductor NCs results in the spatial confinement of electrons and holes [62] with the discretization of the electronic states [64]. The energy levels of the excitonic states can be controlled by adjusting the size of the nanoparticles and the optical properties such as the absorption spectra [66–68] or the fluorescence wavelength can be tuned. The possibility to design these nanostructures has opened the opportunity for a wide range of applications such as fluorescence imaging for molecule tracking in biology [40,41],

1.

the realization of optoelectronics devices [42–44] or lasers [45,46], and more recently for the generation of single photons in the field of quantum information [69].

In this manuscript, we will focus on the CdSe NCs that are the most advanced structures in terms of optical properties. They are approximately spherical [62] and benefit from low-cost processing. They are very bright, photostable and exhibit a high photoluminescence (PL) quantum yield (85 %) at room temperature [70]. From 2008, the synthesis of a thick CdS shell encapsulating the CdSe has enabled to achieve a good passivation of core surface and a good confinment of the exciton in the NC. It is well known that the fluorescence properties of the NCs such as the PL decay rate polarization are not intrinsic to the emitters but correspond to the coupling between the emitter and the surrounding electromagnetic field [50]. These nano-emitters can then be used as probes to investigate the optical properties of plasmonic structures as the ones I studied during my PhD.

The basic theory of plasmonics is discussed in the first part of this chapter. The optical properties of bulk metal are introduced to describe the fundamental excitation of the conduction electron sea in bulk material. This corresponds to volume plasmons. Then the propagation of SPP and LPP are explained in detail. Several experimental approaches for the optical excitation of SPP are then presented. Finally, the coupling between a plasmon resonance and a nano-emitter is described.

In the second part, I will first briefly introduce the synthesis method of CdSe NCs. The effects of the quantum confinement on the electronic structure of these nano-objects are then presented. These effects are very important to understand the optical properties which are shown after. The next part describes the Auger effect which corresponds to an energy transfer between charge carriers that is very effective in nano-structures. It is at the root of many optical properties of individual NCs such as blinking or single photon emission. Finally, we will insist on the opportunities opened by the recent realization of thick CdS shells.

1.1 Optical properties of bulk metal

The interaction of metals with the electromagnetic fields can be fundamentally understood by resolving Maxwell's equations [71]. The optical properties of the bulk metal can be first described microscopically by its dispersive properties, that is by a complex electric function $\varepsilon(\omega)$. The complex electric function is defined as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ where the imaginary part $\varepsilon_2(\omega)$ corresponds to the amount of absorption inside the medium while the real part $\varepsilon_1(\omega)$ gives the amount of polarization of the material.

To determine $\varepsilon(\omega)$ in a basic approach, the metal can be microscopically modeled as a gas of free electrons moving around a fixed background of positive ion cores [71].

Consider first a thin metallic film, described simply by a number n of free electrons per unit of volume. Let's put this film in a uniformly and positively charged environment and describe this system with an approach classic of the electron (figure 1.1).

The motion of the free electrons gas under an external electric field E is described by the equation:

$$m\frac{d^2x}{dt^2} + m\gamma\frac{dx}{dt} = -eE \tag{1.1}$$



Fig. 1.1: Configuration of oscillation of electrons in a metal [72].

where e is charge of the electron and m its mass. γ is the characteristic collision frequency determined by the invert of the relaxation time of the free electron gas $1/\tau$. Representing the waves via complex numbers and supposing that the external field shows a harmonic time dependence $E(t) = E_0 e^{-i\omega t}$ with a temporal angular pulsation ω , the solution of the equation 1.1 writes:

$$x(t) = \frac{e}{m(\omega^2 + i\gamma\omega)}E(t)$$
(1.2)

The polarization P generated by the displaced electrons is expressed as:

$$P = -nex = -\frac{ne}{m(\omega^2 + i\gamma\omega)}E(t)$$
(1.3)

with n is the density of the free electron gas. The link between the dielectric displacement D and P is:

$$D = \varepsilon_0 E + P \tag{1.4}$$

By inserting the expression for P in Eq.1.3 and Eq.1.4, we obtain the following result for the dielectric function of the free electron gas:

$$D = \varepsilon_0 E(t) - \frac{ne}{m(\omega^2 + i\gamma\omega)} E(t) = \varepsilon_0 (1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}) E(t)$$
(1.5)

where $\omega_p^2 = \frac{ne^2}{\varepsilon_0 m}$ is the plasma frequency of the free electron gas. From Eq.1.5 we can deduce the dielectric function as:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \tag{1.6}$$

The real and imaginary parts of this complex dielectric function are determined by:

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \tag{1.7a}$$

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau}{\omega(1+\omega^2 \tau^2)} \tag{1.7b}$$

In the case of large frequencies close to ω_p ($\omega \gg \gamma$), these equations lead to negligible damping and $\varepsilon(\omega)$ reduces to:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{1.8}$$

which can be considered as the dielectric function of the undamped free electron plasma. In noble metals like gold or silver, the behavior in this region is completely changed leading to an increase of ε_2 .

On the contrary, when $\omega \ll \gamma$, the free electrons gas is in the regime of very low frequency. The metal mainly absorbs with a coefficient:

$$\alpha = \sqrt{\frac{2\omega_p^2 \tau \omega}{c^2}} \tag{1.9}$$

Now lets us return to the large frequencies regime. The dispersion relation of traveling waves evaluates to:

$$\omega^2 = \omega_p^2 + K^2 c^2 \tag{1.10}$$

This dispersion relation is plotted in figure 1.2 in which the propagation of transverse electromagnetic waves is forbidden for $\omega < \omega_p$. Above the plasma frequencies, waves propagate with a group velocity $v_g = \frac{d\omega}{dK} < c$.



Fig. 1.2: Dispersion relation of transverse electromagnetic waves for bulk plasmons [73]. Electromagnetic wave propagation is only allowed for $\omega > \omega_p$ [71].

When the oscillations of electrons are localized at the interface between a metal and dielectric material (or air), they are called surface plasmons (SPs). They were first predicted in 1957 by R. Ritchie [59]. In this case, the real part of the dielectric function changes sign across the interface between the metal and the dielectric. When SPs appear on a large planar interface, they are called surface plasmon polaritons (SPPs). On the closed surface of a small particle, they are called LPP. In the next section, we will discuss these two kinds of SPs.

1.2 Surface plasmon polariton (SPP)

1.2.1 Surfaces plasmon polariton at a metal/insulator interface

SPPs are the solutions of the Maxwell's equation for a metal/insulator interface. They include the charge motion on the metal surface (called surface plasmon) and the electromagnetic surface waves propagating along the interface (called polariton). In order to address the optical properties of SPPs, let us consider a system consisting in an interface between a metal and a dielectric medium with respective dielectric constants ε_m and ε_d .



Fig. 1.3: Surface plasmon polariton at a dielectric-metal interface.

The resolution of the Maxwell's equations shows that the electric and magnetic fields of a SPP are transverse magnetic (TM) waves propagating along the interface in a direction denoted x (figure 1.3). They decay exponentially in the x and z direction. We have:

$$E = E_0 e^{i(k_x x \pm k_y y - \omega t)} \tag{1.11a}$$

$$H = H_0 e^{i(k_x x \pm k_y y - \omega t)} \tag{1.11b}$$

in which k_x and k_z are the wave vectors in x and z direction. k_z determines the decays of the electromagnetic field with increasing distance from the surface. It writes:

$$k_{z,d} = \sqrt{k^2 - \varepsilon_d \frac{\omega^2}{c^2}} \tag{1.12a}$$

$$k_{z,m} = \sqrt{k^2 - \varepsilon_m \frac{\omega^2}{c^2}} \tag{1.12b}$$

The boundary condition at the plane z = 0 is:

$$\frac{k_{z,m}}{k_{z,d}} = -\frac{\varepsilon_m}{\varepsilon_d} \tag{1.13}$$

Combining Eq.1.12 and Eq.1.13, we obtain an explicit expression of the dispersion relation of a SPP propagating at the interface between the two media:

$$k_{SPP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \tag{1.14}$$

The metal has a complex dielectric constant $\varepsilon_m = \varepsilon'_m + i\varepsilon^m_m$. The real part relates to the conductivity of the metal and the penetration depth of the electric field in the metal, meanwhile the imaginary part represents the losses in the material. The real part is often much larger than the imaginary part, so the SPP wave vector is approximated by:

$$k_{SPP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d \varepsilon'_m}{\varepsilon_d + \varepsilon'_m}}$$
(1.15)



Fig. 1.4: Dispersion relation of SPP at a dielectric-metal interface in comparison with the dispersion relation of light in the dielectric medium [74].

The corresponding dispersion curve is shown in figure 1.4. The electromagnetic field of the SPP decays exponentially into the dielectric medium in contact with the metal. At very low frequency ω , we have:

$$k_{SPP} = \frac{\omega}{c} \lim_{\varepsilon_m \to -\infty} \left(\sqrt{\frac{\varepsilon_d \varepsilon'_m}{\varepsilon_d + \varepsilon'_m}} \right) \approx \frac{\omega}{c} \sqrt{\varepsilon_d}$$
(1.16)

and the SPP curve approaches to the light line. In the free space, there is no coupling of propagating free space light with the electrons in the metal. In the opposite regime of large wave vectors, the frequency of SPP is drawing near the plasmon frequency $\omega_{SP} = \frac{\omega_p}{\sqrt{1+\varepsilon_d}}$. Due to the limit of the negligible damping of the conduction electrons oscillation, the wave vector $k_{SPP} \to \infty$.

Consequently, the SPP dispersion is in the right side of the dispersion curve of light in the dielectric medium. The wave vectors of SPPs are always bigger than the wave vector of the light propagating in the dielectric medium at the same energy, as shown in figure 1.4. As a result, SPPs cannot radiate light into the dielectric medium and, reciprocally, cannot be excited by conventional illumination [75]. In order to match the wave vector of the incident light with the wave vector of SPP at the interface, several methods have been developed. They are explained in details in the next section. Finally, when compared to propagating modes in the dielectric medium, SPPs show higher wave vectors corresponding to very small wavelength, even in the nanometer range.

An evanescent field created by a SPP propagates into the dielectric medium but also into the metal [76]. Due to the Ohmic losses in the metal, the energy carried by a SPP decays exponentially with a characteristic propagation length L_{SPP} which is determined by the imaginary part of the SPP wave number:

$$k_{SPP} = k'_{SP} + ik''_{SP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}} + i\frac{\omega}{c} \sqrt{\left(\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}\right)^3} \frac{\varepsilon''_m}{2(\varepsilon'_m)^2}$$
(1.17)

$$\Rightarrow \frac{1}{L_{SPP}} = 2 \text{Im} k_{SPP} = \frac{\omega}{c} \sqrt{\left(\frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d}\right)^3 \frac{\varepsilon_m^{"}}{(\varepsilon'_m)^2}}$$
(1.18)

Similarly, the SPP trapped at the metal-dielectric interface creates an electromagnetic field which is attenuated perpendicularly into the metal. The penetration of SPP into metal is characterized by a skin depth δ . The skin depth formula in the metal can be expressed as [77]:

$$\delta = \frac{\lambda}{2\pi} \sqrt{\frac{|\varepsilon'_m| + \varepsilon_d}{\varepsilon_m^2}} \tag{1.19}$$

and is typically a few tens of nanometers [78].

In the dielectric medium, the field will fall off far more slowly with the propagation length, typically between 10 μ m and 100 μ m. Eq.1.18 and Eq.1.19 point out that the two characteristic lengths depend not only on the materials used but also on the wavelength. Because of this very strong sensitivity to slight perturbations within the skin depth, SPP has been considered as a useful tool to probe inhomogeneities of a surface.

1.2.2 Optical excitation of surface plasmon polaritons

As explained in the previous section, we cannot excite the SPPs by the conventional illumination of the metal because, for a given energy, the wave vector k of the incident light is always smaller than k_{SP} , the wave vector of the propagation at the flat interface metal/dielectric. However, there are several optical coupling techniques to create matching between the momentum of the incident photons and the SPP at the given photon energy [75]. We now detail the following strategies: the prism coupling, the grating coupling, the near-field excitation, the diffraction on a structured surface and using highly focused optical beams.

Prism coupling

SPP excitation using the prism coupling is based on a high refractive index prism to achieve attenuated total reflection. The prism shortens the wavelength of the incident light. The wavevector k of the incident light is typically increased by 10 % [76]. In the Kretschmann configuration (figure 1.5a), the metal film is illuminated by the incident light through a dielectric prism (reflective index n_p) under an angle greater than the critical angle to have total internal reflection [79]. When the light passes through the prism, its wave vector (k_p) is increased by a factor n_p :

$$k_p = n_p k_0 = n_p \frac{\omega}{c} \tag{1.20}$$

At the angle θ_{SP} of the incident light (θ_{SP} is the angle measured from the normal), the *x*-component of k_p in the prism coincides with the k_{SP} at the air/metal interface. For a thin metal film, resonance light tunneling through the metal film occurs and results in a wave vector matching at the air/metal interface:

$$k_{SPP} = n_p \frac{\omega}{c} \sin \theta_{sp} = \sqrt{\varepsilon_{prism}} \frac{\omega}{c} \sin \theta_{sp}$$
(1.21)



Fig. 1.5: SPP excitation configuration using prism coupling with total internal reflection in the Kretschmann geometry (a) [74]. (b) Dispersion relation of an electromagnetic wave in air (black), prism (blue) and air/metal/prism interface (red).

The SPP excitation occurs when the angle of incidence satisfies Eq.1.15 and Eq.1.21:

$$\sin \theta_{Sp} = \frac{1}{\sqrt{\varepsilon_{prism}}} \sqrt{\frac{\varepsilon_d \varepsilon'_m}{\varepsilon_d + \varepsilon'_m}}$$
(1.22)

Under these conditions, the light can be coupled to SPPs with nearly 100 % efficiency [74]. Figure 1.5b presents the dispersion relations for the excitation of SPP at the air/metal/prism interface by means of prism coupling. The slope of the light in the prism is slower than in the air. So for the same excited photon energy, we always have $k_{air} < k_{sp} < k_{prism}$, that allows the coupling of the SPP with the incident light at air/metal interface. However, the SPP generation is no longer possible if the the metal film becomes thicker and prevents tunneling. The solution in this case consists in using the Otto configuration scheme. The SPP is also achieved this way when we want to work with indirect contact with the metal.

A variant of prism coupling is the excitation using highly focused optical beams as shown by Bouhelier and Wiederrecht in 2005 [80]. A high numerical aperture microscope objective is used to excite SPP (figure 1.6). The metal film deposited on a glass substrate which is brought into contact with an oil-immersion objective. The high numerical aperture makes sure that the focused excitation beam comes to the metal film with a very large angle, including $\theta > \theta_c$, the critical angle of total internal reflection at glass-air interface. The matching wave vector at metal-air interface at the angle is:

$$\theta_{SPP} = \operatorname{arsin}\left(\frac{\omega}{c}\frac{1}{nk_0}\right) > \theta_c$$
(1.23)

The excited SPP can radiate back to the glass substrate at an angle $\theta_{SPP} > \theta_c$ and be collected by the objective through the immersion oil layer. Figure 1.7 presents images of leakage radiation of SPP excited by a continuous white-light in TM polarization. The propagation length of the SPP can be measured by this radiation intensity distribution conveniently.



Fig. 1.6: Schematic of SPPs excitation by continuous white-light using an index-matched oil immersion lens [71, 80].



Fig. 1.7: (a) Leakage radiation intensity distribution for a TM polarized white-light continuum excitation beam, showing SPPs propagating away from the excitation spot. (b) No SPP excitation is observed for TE polarization. [80].

Grating coupling

The mismatch between the in-plane components of the wave vector k_x of the incident photons and k_{sp} can be overcome via surface gratings. For simplicity, onedimensional periodic grating is depicted in figure 1.8a with period a. A light beam of wavelength λ is incident at an angle θ . The propagation of the wave in the periodic grating is described by Bloch modes and the phase-matching goes on whenever the following condition is fulfilled:

$$k_{SPP} = k\sin\theta + mk_{qrating} \tag{1.24}$$

where $k = 2\pi/\lambda$ is the wave vector of the impinging beam and $k_{grating} = 2\pi/a$ is the grating effective wave vector. m = 1, 2, 3... is an integer value corresponding to the diffraction order. Experimentally, the excitation of the SPP by the grating is detected as a minimum in the intensity of the reflected light [71]. The prerequisite of grating coupling is that the incident beam must be polarized perpendicularly to the grating grooves, that is *p*-polarized (TM).

If the excitation of the SPP by the grating can be achieved, reciprocally, the SPP that propagates along the surface is diffracted by the grating and can be radiatively coupled into the far-field. It is interesting to note that the SPP can be excited in both air-metal and substrate-metal interfaces.

More generally, we can excite SPP on films with a random surface roughness



Fig. 1.8: (a)Phase-matching of light and SPPs using a grating [71]. (b) Dispersion curve for SPP [72].

or manufactured localized scatters which are described in this thesis in the chapter about the plasmonic structures. The phase-matching condition is given by:

$$k_{SPP} = k\sin\theta \pm \Delta k_x \tag{1.25}$$

where Δk_x is the momentum component provided by the scattering structure. Eq.1.25 points out that random surface roughness also creates an additional loss channel for SPP propagation [71]. Another point of view for the grating coupling approach is presented in figure 1.8b. The dispersion relation of SPP folds into the first Brillouin zone of the periodic structure and coupling is obtained for wave vector corresponding to the intersection of the the SPP dispersion curve and the photonic one.

Near-Filed excitation with a tip

In contrast with the prism coupling or grating coupling which excite the SPPs over a macroscopic area, the excitation of SPPs by irradiating a surface in the near-field allows the local excitation of SPPs over an area $a \ll \lambda$ [71]. When illumination through a scanning near-field optical microscopy (SNOM) fiber tip (figure 1.9a) is used, the tip can be considered as a SPP point source [81]. Based on the small aperture size of the probe tip, the light comes out from the tip with wave vector components k_{out} following $k_{out} \ge k_{sp} \ge k_0$.

Figure 1.9b shows an example of the results that can be obtained. It exhibits the intensity distribution of two lights jets emerging from the illumination spot on a silver film. Due to the longitudinal nature of the SPP field, it is in the direction of the polarized electric field [74]. The intensity variation of the SPPs is fitted by:

$$I_{SPP} = \frac{e^{-\rho/L}}{\rho} \cos^2\phi \tag{1.26}$$

where ρ and ϕ are the polar coordinates in the interface plane, and L is the intensity decay constant of the propagating SPP. Techniques using SNOM will be



Fig. 1.9: (a) Excitation of SPPs using near-field illumination with a sub-wavelength aperture [71,74]. (b) Spatial intensity distribution of SPPs on a silver film, $\lambda = 633$ nm [81].

described in more details in the next section corresponding to the experimental setup I used in Groupe d'Étude de la Matière Condensée (GEMaC).

Near-Filed excitation with a nano-emitter

In a first approach, a single excited emitter close to a metal surface can be investigated as the interaction of an oscillating dipole with the metal. Two interaction components have to considered: the near-field and the far-field radiation ones (figure 1.10).



Fig. 1.10: Excited fluorophore interacting wiht a thick metal surface in the near-field and far-field [76].

If the fluorophore is far from the metal $(d \gg \lambda)$, it interacts with the metal only by the far-field radiation for which the dispersion relation of SPP cannot be satisfied. The fluorescence of the emitter is reflected and its lifetime versus distance is the well-known oscillating function first discribed by K.H. Drexhage [82,83]. In contrast, when the excited fluorophore is close to the metal film $(d \ll \lambda)$, the components of the near-field surrounding the emitter can match the in-plane wave vector k_x of the SPP that can then be excited.



Fig. 1.11: Schematic of in-plane wave vector matching for SPPs [76].

This description allows also to understand the quenching of the fluorescence of an emitter located very close to a metal interface [76]. Let us analyze the excited charges separation that exists at the metal/dielectric interface induced by the light nearby a fluorophore (figure 1.11). If the distance between charges is large, i.e. the in-plane wave vector k_x of the incident light is small, a radiative wave can be created (figure 1.11a). This corresponds to a radiative plasmon (RP) with a wave vector k_1 . When the distance between charges decreases, k_x increases (figure 1.11b). The electric field continuity across the interface involves that the angle of wave vector k_1 with respect to the normal direction is larger. When the distance between charges becomes shorter and shorter, k_x is the norm of k_1 (figure 1.11c). In this case, the SPPs are non-radiative plasmons (NRP) that decay into heat. The emission of a fluorophore is then quenched.

Diffraction on surface features

Another strategy for the optical excitation of SPPs is based on the diffraction of light on surface structures (figure 1.12). The sub-wavelength of the surface features make the incident light generate SPPs propagating on the surface; in the meantime, the scattered light goes back into free space. Depending on the material, the size and the shape of the structures, the SPP scattering can be changed and give us various information of optical properties of SPPs. The roughness of the metallic films can also be studied through angle resolved diffraction measurements and Fourier analysis [84–86].



Fig. 1.12: Schematic of the SPP excitation using diffraction on surface features [74].

1.3 Localized surface plasmon (LSP)

Surface plasmon resonance exists not only on continuous metal surface but also on metal particles. They are called localized surface plasmon (LSP). LSP is the result of oscillations of the collective free electrons at the boundaries of small metal particles [87, 88], see figure 1.13. In contrast to SPP, LSP can be excited directly by an incoming electromagnetic field without any special phase matching technique. The phase matching conditions are suppressed due to the absence of translation invariance. The incident excitation light needs only to match the energy of the oscillation [89]. The combination of both absorption and scattering light processes then results in an intense surface plasmon extinction band [71]. Thus, metal nanoparticles display intense colors which is completely different from a continuous metal film. In general, the LSP can enhance the electromagnetic field confinement and is very sensitive to the refractive index of the surrounding medium. The improvement of metal nanoparticles synthesis have recently opened numerous potential applications such as reflective index sensors, photovoltaics, molecular fluorescence, etc...



Fig. 1.13: Illustration of the electron charge displacement in a metallic particle that creates a localized plasmon resonance [90].

In order to understand the properties of LSPs, let us consider the case of a metallic sphere inserted into a dielectric matrix (figure 1.13). The size of the particle is in the range of the penetration depth of the electromagnetic field into the metal [75]. As previously, the incident electromagnetic field causes the excited electrons to get displaced with respect to the ions lattice in the nano-particle. The moving

distances of the electrons in a metallic particle are limited by the size of particles themselves. The lattice ions and the free electron charges are in excess in the surfaces facing each other and generate a dipole and higher order moment components. To characterize the interaction of a particle of size d with the electromagnetic field, a simple quasi-static approximation can be applied provided that $d \ll \lambda$.

We start with the simple geometry represented in figure 1.14: an isotropic homogeneous sphere is located in a uniform static electric field $E = E_0 \hat{z}$. The dielectric response of the sphere is described as a function of the frequency of the electric field $\epsilon(\omega) = \varepsilon' + i\varepsilon$, which is simplified as a complex number ϵ .



Fig. 1.14: Sketch of a homogeneous metallic sphere placed into an electrostatic field [71].

The optical properties of LSP are in good agreement with the Mie theory for the calculation of the scattering and absorption of electromagnetic radiation by a sphere [7, 71]. Under the above hypothesis, the nano-particle acts as an electric dipole that absorbs and scatters the electromagnetic field resonantly. The electric dipole moment of the particle is given by:

$$P = 4\pi\varepsilon_0\varepsilon_m a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 \tag{1.27}$$

where ϵ_m is the dielectric permittivity of the surrounding medium and E_0 the incident electric field. The dipole of the particle is defined through the polarizability α by the equation $P = \varepsilon_0 \varepsilon_m \alpha E_0$, so the complex polarizability of a small sphere writes:

$$\alpha = \frac{P}{\varepsilon_0 \varepsilon_m E_0} = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$
(1.28)

The distribution of the electric field inside (E_{in}) and outside (E_{out}) the spherical particle can be evaluated from [71]:

$$E_{in} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 \tag{1.29a}$$

$$E_{out} = E_0 + \frac{3n(n \cdot P) - P}{4\pi\varepsilon_0\varepsilon_m} \frac{1}{r^3}$$
(1.29b)

n, r are the unit vector and magnitude of the position vector. To quantify the energy absorbed by the sphere particle, the definition of absorption and scattering cross-section (C_{abs} and C_{scat} respectively) are expressed by:

$$C_{abs} = k \operatorname{Im} \left[\alpha \right] = 4\pi k a^{3} \operatorname{Im} \left[\frac{\varepsilon - \varepsilon_{m}}{\varepsilon + 2\varepsilon_{m}} \right]$$
(1.30a)

$$C_{sca} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2$$
(1.30b)

Both of them are dependent on the ratio a/λ where λ is the wavelength of the incident light. In the quasi-static limit, the cross section for the extinction $C_{ext} = C_{abs} + C_{sca}$ is given by:

$$C_{ext} = 9\frac{\omega}{c}\sqrt{\varepsilon_m^3}V\frac{\varepsilon^{"}}{\left[\varepsilon' + 2\varepsilon_m\right]^2 + \varepsilon^{"2}}$$
(1.31)

When metal-enhanced fluorescence is considered, the absorption term C_{abs} gives rise to quenching and the scattering term C_{sca} to emission enhancement [76].

The electric field of the dipole is induced from the oscillation of the electrons:

$$E_{dipole} = k^2 e^{ikr} \frac{r \times (r \times P)}{r^3} + e^{ikr(1-ikr)} \frac{[r^2 P - 3r(r \cdot p)]}{r^5}$$
(1.32)

The electric field effect can be modeled by FDTD simulation (a numerical approach that will be presented in details in chapter 3). Figure 1.15 displays the intensity distribution of the electric field around a silver nanoparticle of 80 nm diameter for a wavelength of 355 nm. In this case, the electric field enhancement comes only from a dipolar resonant mode.



Fig. 1.15: Electric field enhancements of silver nanoparticles of 80 nm diameter at $\lambda = 355$ nm [91].

If there are two particles close one from the other, a coupling between the oscillations of the electrons in the two particles is observed. Therefore, it is possible to obtain the localization of the field in the space between the two particles. Figure 1.16 presents the localization of electric field which depends crucially on the polarization of the incident wave and the distance between two particles. These results



Fig. 1.16: Electric field distribution generated by 2 particles of 60 nm diameter separated by 4 nm (a and b), 6 nn (c) and 8 nm (d) at 600 nm. [72]

are simulated by the FDTD method with the parallel (a) or perpendicular polarized illumination (b) at 600 nm for gold particles. Figure 1.16 (a) and (b) show that the coupling between two spheres only exists when the polarization of illumination is parallel to the dimer. On the contrary, only the dipolar resonance in single particles is generated with perpendicular polarization.

The distance between the two spheres plays an important role in the intensity of the coupling field (see figure 1.16 c and d). Very strong enhancement of the electromagnetic field is also observed. These phenomena are involved for the case of a semi-continuous film which consist of small metal islands in various forms and sizes. However, many studies showed that the properties of the semi-continuous films are explained by the coexistence of localized and delocalized plasmons [92]. The properties of the very localized fields will be described in detail in chapter 2.

1.4 Plasmon / nano-mitter coupling

The description of SPP and LSP in the previous parts shows that SPs in metal nanostructures exhibit specific features such as very localized and enhanced electromagnetic modes. The question is: how can we investigate theses optical properties ? One current strategy consists in using near-field microscopy. Another approach is based on the modification of the fluorescence properties of a single nano-emitter coupled to the plasmonic structure, that is the change in the spontaneous emission process.

1.4.1 Spontaneous emission

The spontaneous emission is the process which correponds to the transition from an excited energy state to a lower energy state of a quantum mechanical system such as an atom or a molecule with the emission of a photon. The spontaneous emission is fundamentally explained by the quantum theory. Dirac was first to develop a quantum theory of radiation to derive the spontaneous emission rate accurately in 1927 [93]. After this pioneer work, the interaction between light and matter, more and more elaborated theories were developed to address the spontaneous emission [94–96], as part of the rise of the quantum electrodynamics (QED) theory [97], the relativistic quantum field theory of electrodynamics.



Fig. 1.17: Spontaneous emission process.

In the weak coupling regime, the coupling interaction between a dipole and the electromagnetic field appears as a perturbation in the two-level system Hamiltonian. An emitter in the excited stated E_2 spontaneously decays to the ground state E_1 and emits an energy quantum in the form of a photon (firgure 1.17). This spontaneous emission is called fluorescence and the energy of the released photon is determined by the energy gap between the two states:

$$\hbar\omega = E_2 - E_1 \tag{1.33}$$

The evolution of the quantum state versus time is governed by the Schrodinger equation:

$$i\hbar \frac{d}{dt} \left| \phi(t) \right\rangle = \left(H_0 + H_p \right) \left| \phi(t) \right\rangle \tag{1.34}$$

where H_0 is the Hamiltonian of the two-single level system and H_p describes the interaction between the emitter and the electromagnetic field. In the dipolar and resonant approximation, we have: $H_p = \vec{E} \cdot \vec{D} \cdot \vec{D}$. The detailed solution of Eq.1.34 is demonstrated in [98]. The radiative transition rate in free space from state $|2\rangle$ to state $|1\rangle$ is given by:

$$\Gamma_0 = \frac{2\pi}{\hbar^2} \left| \langle 1 | \hat{\mu}_{12} \cdot \hat{E}_0 | 2 \rangle \right|^2 \rho_0(\hbar\omega)$$
(1.35)

in which $\hat{\mu}_{12}$ is electric dipole operator and E_0 is the vacuum field. $\rho_0(\hbar\omega_0)$ is the free space density of state calculated by considering the electromagnetic modes in a

cube of volume V:

$$\rho_0(\hbar\omega) = \frac{\omega^2 V}{\pi^2 c^3} \tag{1.36}$$

The transition matrix element in Eq.1.35 is expressed by:

$$\left| \langle 1 | \hat{\mu}_{12} \cdot \hat{E}_0 | 2 \rangle \right|^2 = \frac{1}{3} \mu_{12}^2 E_0^2 = \frac{1}{3} \mu_{12}^2 \frac{\hbar \omega}{2\varepsilon_0 V}$$
(1.37)

Combining Eq.1.35, Eq.1.36 and Eq.1.37, we obtain the decay rate of the spontaneous emission of an emitter in free space:

$$\Gamma_0 = \frac{\omega^3 \mu_{12}^2}{3\pi\varepsilon_0 \hbar c^3} \tag{1.38}$$

If the emitter is inserted into a medium with an index n, the LDOS and then the spontaneous emission rate are n times higher.

1.4.2 Purcell factor

Purcell effect was first described by Edward Mills Purcell in 1946 [49]. It accounts for the enhancement or inhibition of the spontaneous emission of an emitter that is inserted into a cavity.

For a single mode of a cavity with a pulsation ω_m and with a linewidth $\Delta \omega$, $\rho(\omega)$ can be modeled by the following Lorentzian distribution:

$$\rho(\omega) = \frac{\Delta\omega}{2\pi V} \frac{1}{\left(\frac{\Delta\omega}{2}\right)^2 + \left(\omega_m - \omega\right)^2} \tag{1.39}$$

The increasing of the LDOS results in the enhancement of the radiative decay. Replacing Eq.1.39 into Eq.1.35, we obtain the radiative decay of the spontaneous emission in the cavity:

$$\Gamma_{c} = \frac{|\mu_{12} \cdot E|^{2}}{|\mu_{12}|^{2}|E|^{2}} \frac{2\mu_{12}^{2}}{\varepsilon_{0}\hbar} \frac{Q}{V}$$
(1.40)

where $Q = \omega_m / \Delta \omega$ is the quality factor and V is the volume of the cavity. Eq.1.40 demonstrates that the change of the electromagnetic environment of the emitter modifies crucially the decay rate of the spontaneous emission.

The Purcell factor is defined to quantify this modification. It writes as the ratio between the decay rate of an emitter in the cavity (Γ_c) and its decay rate in free space (Γ_0).

$$F_p = \frac{\Gamma_c}{\Gamma_0} = \frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^3 \frac{Q}{V} \tag{1.41}$$

 λ/n is the wavelength in the material with medium index n. This formula is correct only if the dipole orientation is aligned with the electric [75] and if the emitter linewidth is much narrower than the cavity linewidth. For a random orientation of the dipole, one finds that F_p is divided by a factor of 3.

The spontaneous emission of the emitter is enhanced if $F_p > 1$. Since the pioneer work of Haroche [99], there are a wide variety of studies on the lifetime ($\tau = 1/\Gamma$) modification of a single emitter inserted into a cavity. The lifetime reductions give a Purcell factor much more than 10 [53, 54, 100, 101].

1.4.3 Increased quantum yield with Plasmon-Emitter coupling

To end this chapter, we present an application of the Purcell enhancement with plasmonic structures. Even if plasmon modes present losses, we show that it is possible to increase the quantum efficiency of a nano-emitter by its coupling to a metal structure.

From a general point of view, such coupling introduces two decay channels [102, 103]:

- a plasmonic radiative channel corresponding to the radiative emission to the far-field that can be collected (rate Γ_r),
- a plasmonic non-radiative one corresponding to all the other processes including the metal losses (rate Γ_{nr}).

Because the lifetime of plasmon is much shorter than the lifetime of fluorescence of the emitter (about 10 fs) [104], the energy is transferred in only one way from the emitter to the structure. The possibility to increase the quantum yield for a emitter placed near the surface of a plasmonic nanostructure can be qualitatively understood as a consequence of this rapid energy transfer to the plasmon [76]. Additionally, the coupling improves the photostability of the fluorescence because the emitters spend less time in their excited state.

The quantum efficiency is determined by the ratio between the radiative decay rate Γ_r and the total decay rate $\Gamma_r + \Gamma_{nr}$. First, we consider the emitter in free space which is characterized by its quantum efficiency η_0 :

$$\eta_0 = \frac{\Gamma_{r0}}{\Gamma_{r0} + \Gamma_{nr0}} \tag{1.42}$$

where the non-radiative decay rate Γ_{nr0} accounts for intrinsic losses of the emitter such as non radiative surface states for a quantum dot. The lifetime of the emitter is given by:

$$\tau_0 = \frac{1}{\Gamma_{r0} + \Gamma_{nr0}} \tag{1.43}$$

After coupling to the plasmonic nanostructure, the modification of the quantum efficiency η and lifetime τ are expressed as:

$$\eta = \frac{\Gamma_r}{\Gamma_r + \Gamma_{nr} + \Gamma_{nr0}} \tag{1.44}$$

When a dipole emitter is located close to a metallic structure, non-radiative recombinations often dominate leading to the quenching of the fluorescence. Yet, for plasmonic nanoresonators, this is not always the case and the ratio $\frac{\Gamma_r}{\Gamma_r + \Gamma_{nr}} = 0.75$ has been reported [105]. If the radiative Purcell factor $F_p = \frac{\Gamma_r}{\Gamma_{r0}}$ is large, equation 1.44 shows that the contribution of Γ_{nr0} can be neglected in η . The energy transfer is fast enough so the quantum yield is limited by the non radiative plasmons. Such an approach has been implemented efficiently with single-walled carbon nanotubes and bow-tie antennas. The quantum yield for the emitters increases from about 5% to 40% [106].

1.5 Colloidal nanocrystals semiconductor CdSe/CdS

From several years, the "Optics at the Nanoscale group" has studied the coupling between colloidal semiconductor NCs and plasmonic structures. The first aim was to control the NCs emission in the weak coupling regime [107–109] at room or cryogenic temperature. More recently, Rabeb Jazi has also shown during her PhD that a single NC can act as an active probe when glued at the end of a SNOM tip. In this case, before coupling, the characteristics of the probe has first to be well known and we now present the fundamental properties of these nano-emitters.

1.5.1 Properties of colloidal CdSe NCs



Synthesis

Fig. 1.18: Colloidal nucleation and growth processes [110].

There are many ways to fabricate semiconductor NCs. Also referred to quantum dots (QDs), they can be prepared in different media: glasses [61], zeolites [111– 113, ion-exchange membranes [114-116] and inverse micelles [117-120] by various methods [121] such as coprecipitation in aqueous phase, hydrothermal/solvothermal synthesis. The first synthesis methods were elaborated in the 80s. NCs were grown in a transparent dielectric matrix such as a glassy dielectric one [61]. At that time, the microscopic processes were obviously not known, but growth conditions such as duration and temperature were already used to vary the characteristics of the nanoparticles as well as the colors of the resulting glass. Recently, the NCs synthesis is frequently carried out in aqueous or organic solutions or polymer [37–39]. In this part, I just present the synthesis of the NCs in an organic solution which was first developed by Murray *et al* [122]. This technique takes advantage of the organic solvents and of the wide range of the reaction temperature to control the growth kinetics and the size dispersion of QDs, which is crucial for applications. The shape of the NCs can be also tuned. Spherical QDs or nanorods can be obtained. Figure 1.18 describes the fundamental growth process of the NCs by chemistry synthesis in an organic solution. The first step of the growth of NCs is the nucleation which spontaneously gives rise to NCs from an assembly of freely dispersed atoms [123]. Then, ligands on monomers are deposited onto the growing NCs.

The CdSe NCs used during my thesis were synthesized in the group of Benoît Dubertret by the decomposition of organometallic precursors, which allows the type of II-VI semiconductor NCs growth in organic solvent with a very small size dispersion (about 5 %). This method was first reported by P. Alivisatos, M.G. Bawendi and P. Guyot-Sionnest [122,124,125]. Then it has been improved. It is now possible to control the size, the shape and the composition of the QDs. Briefly, dimethylcad-mium and trioctylphosphine (TOP) selenide precursors are used. They are dissolved and injected in a mixture of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) heated to 300°C. CdSe nuclei of 2 nm diameter are formed very rapidly according to the nucleation process (fast nucleation process in 1.18). The nuclei size then increases from 2 nm up to 6 nm. It can be controlled by the amount of injected precursors, the temperature and time synthesis (slow nucleation process in 1.18).

For a bare core, the charge carrier traps on the surface of the QD can capture one of the charges optically excited in the NC. The trap then prevents the fluorescence and the QD exhibits a low radiative quantum yield. During the synthesis, ligands are used to slow the growth and avoid the formation of aggregates. After the synthesis, they passivate the surface. However, they are not sufficient because they only cover 40 % to 50% of the surface, so bare CdSe cores covered by ligands exhibit only a quantum yield about or lower than 10 %. To improve the passivation, a semiconductor shell with a larger forbidden bandgap than the core one can be epitaxially deposited on the NC. Commonly, ZnS, ZnSe or CdS shells are used [126]. The fluorescence quantum yield measured on assemblies of NCs can then reach 85 %. In this manuscript, NCs with thick CdS shell were used since these core-shell exhibit the best photostability and reduced blinking (see section 1.5.3).

Electronic band structure

In order to understand the optical properties of the NCs, one has first to study the energy level of the charge carriers. In a bulk crystalline semiconductor, the occupied band with the highest energy is full filled and is called the valence band (VB). The next band is completely empty and is denoted as the conduction band (CB). The electron in the bulk semiconductor is affected by a periodic potential. Its wave-function then obeys the Bloch theorem and can be identified by the following equation:

$$\psi_{\mu,\vec{k}}(\vec{r}) = e^{ik.\vec{r}} u_{\mu,\vec{k}}(\vec{r}) \tag{1.45}$$

where $u_{\mu,\vec{k}}(\vec{r})$ has the lattice periodicity and shows the variations of the wavefunction at the scale of the unit cell. $e^{i\vec{k}.\vec{r}}$ reflects the variations at higher length scales. The index μ makes it possible to distinguish the different local functions associated with the same wave vector. The corresponding energy is $E_{\mu}(\vec{k})$. For CdSe, $E_{CB}(\vec{k})$ and $E_{VB}(\vec{k})$ present maximum and minimum energies at k = 0 and are given by: $E_{CB} = E_g + \frac{\hbar^2 k^2}{2m_e^*}$ and $E_{VB} = -\frac{\hbar^2 k^2}{2m_h^*}$ respectively, where E_g is the band gap between the CB and VB (figure 1.19). For the CdSe bulk structure, $E_g = 1.8$ eV corresponding to a wavelength emission of 695 nm.

When the semiconductor absorbs a photon, an electron (e) is excited from the

VB into the CB and leaves a positive charge called hole (h). Due to the Coulomb interaction, the electron and the hole attract each other. The e-h pair exhibits hydrogen like bound states also called excitons. For CdSe, the Bohr radius is equal to 5.6 nm.

For a number of atoms between a hundred and few thousands, the size of the material reduces to the nano-scale and can be smaller than the Bohr radius. The confinement energy is then higher than the Coulomb energy. In this case, confinement effects are separately considered for the hole and the electron, the Coulomb interaction being a perturbation. The spherical three-dimensional (3D) confinement potential makes discrete energy levels in each band structure. Under the strong quantum confinement effect, the energy of the fundamental level of the electron (denoted $1S_e$) is:

$$E = \frac{\hbar^2 \pi^2}{2m_e^* r^2}$$
(1.46)



Fig. 1.19: Band structure of the CdSe bulk [127].

where m_e^* is the effective mass of the electron.

For the hole, the complex structure of the valence band of CdSe has to be taken into account. There are two kinds of holes in the VB: the light and heavy holes. After calculation [128], one finds that the energy of the hole in the VB depends on the ratio between the mass of the light hole and the heavy hole one ($\beta = m_{lh}/m_{hh}$).

As for the electron, spherical quantum confinement also results in the possibility to select hydrogen like spectroscopic notations. The energy of the lowest level $1S_{3/2}$ of the hole is given by:

$$E_{3/2}(\beta) = \frac{\hbar^2 \varphi^2(\beta)}{2m_{hh}r^2}$$
(1.47)

where $\varphi(\beta)$ is the first root of the equation $j_0(\varphi)j_2(\sqrt{\beta}\varphi) + j_2(\varphi)j_0(\sqrt{\beta}\varphi) = 0$ $(j_n$ are the first kind of Bessel functions).



Fig. 1.20: (a) Quantization of excitonic energy levels in CdSe NCs with radius of 1.7 nm [127, 129]. (b) Absorption and fluorescence spectrum of a CdSe NC [130].

The quantum energies of the electron and of the hole are ultimately inversely proportional to the square of radius of the NC $(1/r^2)$. The wave function of an exciton is then described by the wave-function of the electron and of the hole. Figure 1.20 (a) shows the structure of the excitonic energy levels in NCs CdSe. The fundamental exciton is determined by the recombination of the electron in the $1S_e$ state and the hole in the $1S_{3/2}$ state.

Figure 1.20 also shows the fine structure of the fundamental exciton level $1S_e$ $1S_{3/2}$ which comes from the states of the electron and the hole (8 levels, 2 levels for the electron and 4 for the hole). The splitting between the different levels is due to:

- the exchange interaction which is strongly enhanced by the confinement of the carriers,
- the wurtzite crystal structure of CdSe,
- the potential ellipticity of the NC.

The good quantum number is the total angular momentum F of the e-h pair [128, 131]. The absolute value of its projection along the wurtzite *c*-axis is equal to 0, 1 or 2. Calculations taking into account all the perturbative terms lead to the result of figure 1.20. Five levels characterized by the value $|F_z| = 0, 1$ or 2 can be distinguished (in the figure, U means upper and L lower). The quantum momentum of a photon being equal to \hbar , the transitions from the fundamental levels ± 2 are forbidden by electric dipole transitions. It is the so-called "dark exciton". Due to destructive interference of the wave functions of two indistinguishable exciton states, the transitions from the level noted 0^L is also optically passive. The degenerate $\pm 1^L$ levels are the fundamental level that are optically active. It corresponds to a 2D-dipole that is orthogonal to the crystal growth *c*-axis.

Optical properties

As shown in the previous section, the nano-size of the NC results in the discrete structure of the energy levels in the electronic band structure. It is then governed
by the size of the NCs (see equations (1.46) and (1.47)). Adjusting the parameters of the organo-metallic precursor decomposition method, it is easy to control the size of the NCs and tune the optical properties of the nano-emitters. As an example, Figure 1.21 presents the absorption and emission spectrum of different sizes from 2 nm to 5 nm of CdSe NCs.



Fig. 1.21: Absorption (a) and emission (b) spectrum of CdSe NCS with a diameter ranging from 2 nm to 6 nm [130].

In the absorption curve, there are different peaks corresponding to the transitions between different excitonic levels (figure 1.20a), broadened by the interaction with the phonon bath. For short wavelengths, the absorption exhibits a quasi continuum spectrum due to the small gap between the hole levels, the non-parabolicity of the band structure, and the large values of the intraband decay rates. Because of the large number of states in the structure of energy levels, the CdSe NCs have then wide range of absorption from 400 nm to more than 685 nm that corresponds to the CdSe bandgap (figure 1.20 (b)). This is one crucial advantage of the NCs for easy optical excitation (1.21a).

In contrast, the fluorescence spectrum shows a narrow line which corresponds to the transition from the lower excitonic level (figure 1.21b). The dependence on the size of the gap between the fundamental levels of the CB and VB of the NC results in the change of the emission wavelength which shifts to the blue when the size decreases. Figure 1.20 also illustrates the so-called Stokes shift [131] corresponding to the redshift of the fluorescence spectrum with respect to the absorption one. It is attributed to the fine structure of the first exciton level. Absorption occurs preferentially from the highest energy levels (the three U levels) that have the highest oscillator strengths. The exciton then thermalizes to the fundamental level ± 2 . At temperature lower than 2K, fluorescence from this level exhibits a very low decay rate since the transition is an electric dipole forbidden one. At higher temperature, emission comes from the $\pm 1^L$ level that is thermally populated [131, 132].

1.5.2 Single photon emission and Auger effect

Single photon emission, that is the possibility to generate photons one by one, is a very promising property of the NCs. It was demonstated at the early 2000's by Michler *et al.* [47, 133]. Fundamentally, this feature comes from the Auger effect. When more than one exciton is created in the NC, the multiexcitonic state decays non-radiatively until only one exciton remains [72]. This non-radiative multicarrier process originates from Coulomb interactions that are enhanced in nano-size structures [69]: figure 1.22 displays the Auger effect for a bi-excitonic state.



Fig. 1.22: Example of a bi-exciton relaxation process induced by the Auger effect [134].

In detail, an e-h pair recombines very fast (typically at a time scale lower than 100 ps) and transfers its energy to a remaining carrier, for example the electron in the CB receives this energy and is excited to the higher energy level (figure 1.22a). Then, this electron relaxes to its ground state and transfers its energy to the hole in the VB (figure 1.22b). After relaxation, the hole comes back to its fundamental energy level and recombines with the electron in the CB (figure 1.22c and d). Finally, a single photon is emitted by this recombination. At the end of process, the Auger effect makes that only one exciton can recombine radiatively and generate a single photon.

However, single photon emission does not always dominate. Auger recombinations can be slowed down by addressing the potential that confines the charge carriers inside the NC. A. Efros has indeed shown that an abrupt potential enhances Auger recombinations [135]. Reducing the bandgap or using a gradient between the core and the shell has recently enabled to observe very efficient biexcitonic emission [136]. Low excitation source also favours single photon emission.

From a general point of view, Auger recombinations play a crucial role in the properties of NCs. Beyond single photon emission, it is at the root of intraband relaxations as shown in 1.22. Blinking of the fluorescence also comes from the efficiency of the Auger recombinations.

1.5.3 Blinking of colloidal NCs

Beyond the very interesting properties of NCs, an important drawback has been identified for a long time: the intermittency of their fluorescence. The blinking of the fluorescence corresponds to the switch between a bright and a dark states [137] (figure 1.23). The origin of blinking is first due of the ionization of the NC (it has been shown that blinking can also come from bandedge carrier trapping or multiple recombination centers, without charging [138–142]).

In the bright state, the NC is neutral and the absorption of one photon gives rise to the emission of one fluorescence photon (the radiative quantum efficiency is then close to 1 [143]). However the NC can be ionized. As an example, if there is more than one e-h pair in the NC, the energy of the recombination of an e-h pair can be transferred to a remaining charge that escapes from the core of the NC. It is then injected into the surrounding matrix or trapped at the surface of the NC. In the ionized state, when a subsequent e-h pair is optically excited, it mainly recombines non-radiatively through an Auger recombination. The NC remains into the dark state until neutralization is recovered.



Fig. 1.23: Blinking phenomenon observed on the PL of an individual CdSe NC(diameter of 3.3 nm) [144].

1.5.4 Contribution of the thick-shell CdS

Because of the defects on the surface of the NC, we have seen that a charge optically excited in the NC can be captured into a trap, that strongly reduces the radiative quantum efficiency (around 10 %). Thus, a shell can be added to passivate the surface. The results following this idea were first obtained with a ZnS shell. However, due to the lattice mismatch between CdSe and ZnS (~ 10 %), only thin shells (1 or 2 atomic layers) can be epitaxially grown. If the quantum efficiency highly increases (around 85 %), blinking is not prevented in this case. From 2008, CdS, which has a lower lattice mismatch with respect to CdSe (~ 4 %), can be used to protect the CdSe core. It is possible to grow a shell up to 10 nm with a very low number of crystalline defects (for very thick shells, few defects are present at the core-shell interface). Using a CdS shell also modifies the confinement properties of the carriers. Figure 1.24 displays the band structure of the CdSe-CdS coreshell structure. Due to the very small barrier between the conduction bands, the

electron is partially delocalized in the whole structure. In contrast, the hole remains confined in the core and its energy levels depends only on the size of the core itself. In contrast, the size of the shell also plays an important role to the energy levels for the electron. As a consequence, the adjustment of the size of the core-shell structure opens a wide range of tunable emission wavelength.



Fig. 1.24: Band structure of a CdSe/CdS core-shell NC

When compared to standard colloidal CdSe NCs, individual core-shell CdSe/CdS NCs with thick shells exhibit strongly reduced blinking [145]. The ionization becomes less likely to occur. Moreover, if very long dark states periods are observed with standard CdSe/ZnS NCs, they do not last more than 100 ms for CdSe/CdS NCs [146].

The nature of the low emitting periods is also modified. For a CdSe/ZnS NCs, low emitting periods are completely dark while only grey states have been identified for CdSe/CdS NCs. In the grey state, the NC is ionized. One carrier of an e-h pair is also ejected from the NC core into the surrounding matrix or trapped at the NC surface. However, due to the partial delocalization of the charges and the resulting reduction of the Auger recombination efficiency of the trion, fluorescence is not quenched. It is possible to have two recombinations processes for an e-h pair (figure 1.25).

The first recombination corresponds to the radiative process while, for the second one, an Auger recombination occurs. The PL of a CdSe/CdS NC is no longer prevented by the Auger effect.

In the bright state, k_{rad} is the decay rate of the radiative emission (the radiative lifetime is equal to $1/k_{rad}$). In the grey state, the two ways of recombination are:

- the radiative recombination of an e-h pair that gives rise to a photon with a rate k'_{rad} .
- due to the Auger process (rate k_A), the e-h pair can transfer its energy to the remaining carrier in the NC.



Fig. 1.25: Bright and grey states recombinations for a CdSe/CdS core-shell NCs [145].

Therefore, the total decay rate is the sum of the two processes rates:

$$k = k'_{rad} + k_A \tag{1.48}$$

The quantum efficiency of the grey state, that is the probability of an e-h pair to recombine radiatively, then writes:

$$Q = \frac{k'_{rad}}{k'_{rad} + k_A} \tag{1.49}$$

Typically it ranges between 20 % and 40 % for the NCs we used. However, recent results showed that Auger recombinations can be completely suppressed with very big gradient CdSe/CdS NCs [147]. Figure 1.26 illustrates the reduction of the blinking when the thick shell CdS is presented. The emission of the grey state is less intense than the neutral state but it is still far above the background noise.



Fig. 1.26: Time dependence of the PL intensity of a single core-shell CdSe/CdS NC [145].

1.6 Conclusion

In this chapter, we first presented the fundamental properties of plasmons and distinguished the delocalized SPP and the LSP. In the weak coupling regime, we showed that metallic structures provide an efficient approach to modify the fluorescence properties of a nano-emitter. Among all the applications that have been implemented, we show that the quantum efficiency can be increased even if optical losses are always observed with plasmons. Reciprocally, the modification of the fluorescence lifetime of a nano-emitter can be used to investigate the plasmon modes of ordered or disordered structures as presented in the following chapters.

Our different experiments will be based on colloidal core-shell CdSe/CdS NCs as relevant active probes. The general properties of CdSe NCs are summarized in the second part. Based on the quantum size effect, the control of the wavelength emission is possible at room temperature. We have also highlighted the role played by the Auger effect for these nano-emitters. It is at the origin of single photon emission but also of the intermittency of the fluorescence. By using a CdS thick shell, a strong reduction of blinking of the NC is obtained, the shell also acting as a spacer avoiding the quenching of the fluorescence when the NCs are deposited directly on plasmonic structures.

2.

PROBING THE "HOT" SPOT PROPERTIES OF SEMI-CONTINUOUS GOLD FILMS THROUGH THE FLUORESCENCE POLARIZATION OF CDSE/CDS COLLOIDAL NCS

The optical properties of nanostructures have been recently studied providing great interests in nanosciences [148–150]. The electromagnetic environment can be controlled by periodic dielectric or metallic materials. They cover a wide range of applications such as quantum information processing, solar cells for photovoltaic or efficient analytical sensing in chemistry and molecular biology [1, 151, 152]. Concerning the metallic nanostructures, surface plasmons play an important role as the modes carrying electromagnetic energy [92]. The energy can be localized in small volumes leading to strong electric field enhancements.

An alternative to ordered nanostructures consists in using random structures without long range spatial correlations in their geometry. Applications that need broadband operations can take advantage of the absence of spatial periodicity. For example, a two-dimensional random pattern can provide promising thin films which enhances the efficiency of solar cell [8, 153]. In the field of quantum optics, the spontaneous emission rate and the emission intensity can be increased following the Purcell approach [154]. The LDOS can be tuned in oder to operate over the a wide range of wavelengths [155]. Disorder can also lead to strong light localization. In semi-continuous films, the localized modes of surface plasmons are enhanced and accurately observed in "hot spots", where the electromagnetic field is much higher than the applied field [156, 157]. When a single nano-emitter is coupled to this kind of structures very high Purcell factors can be achieved. In parallel with the control of the single emitter fluorescence, the study of the coupling of the single emitter with the nanophotonic structure supplies the specific properties of the structure itself with incredible information. The variations of the photoluminescence (PL) decay rate of the nano-emitter depends on the LDOS of the structure. By using the scanning near-field optical microscopy (SNOM), Krachmalnicoff et al. showed that the "hot spots" of a semi-continuous gold film correspond to large LDOS fluctuations that reach their maximum value at the percolation threshold when the film structure is characterized by fractal clusters [157, 158].

In our team, many studies have been devoted to the characteristics of semicontinuous gold films [10, 154, 159–161]. SNOM experiments and coupling with colloidal nanocrystals (NCs) have revealed specific properties of the semi-continuous gold films. Until now, the coupling between the thick shell CdSe/CdS NCs and the semi-continuous films has been characterized by measuring the PL decay dynamic. It has first been shown that the thick shell acts as a spacer preventing the quenching of the fluorescence even when the NCs are directly deposited on the film. The PL dynamic has revealed high Purcell factors (up to 60) and different regimes (single or multiphoton emission) depending on the PL acceleration and on the film morphology. [154]. The amplitudes and fluctuations of the electromagnetic field can be analyzed by this approach but nothing can be deduced about the orientation of the electric field of the plasmon mode. Information about this field orientation can be given by analyzing the polarization of the NC fluorescence. In fact the fluorescence polarization directly carries the information on the field orientation and give insights into the polarization of the plasmon modes on this kind of structures. For this purpose, in parallel to PL lifetime measurements, I performed polarization measurements of the NCs fluorescence [162–165].

In this part, I will describe this method. The "hot spots" of the semi-continuous gold films at the percolation threshold will be studied through the polarization properties encoded in the fluorescence of thick shell CdSe/CdS NCs.

2.1 Semi-continuous film

2.1.1 Fabrication

The semi-continuous gold films are elaborated by thermal evaporation under ultrahigh vacuum conditions (10^{-9} Torr), just below the percolation threshold. Figure 2.1 describes the thermal evaporation method which was used by Julien Laverdant.



Fig. 2.1: Scheme of thermal evaporation [166]

The crucible is heated after the ultrahigh vacuum was obtained. When the melting temperature is reached, the metal evaporates. The amount of evaporated metal is controlled by an oscillating quartz with a free resonance frequency and a removable cover. The mass thickness of the semi-continuous film is considered as the thickness that the sample would have if it was continuous. If we assume that the dimensions of the sample are L_x and L_y and that each point of the sample has the height e(x, y), then the mass thickness is given by the following relationship [166]:

$$\int e(x,y)dxdy = e_{mass}L_xL_y \tag{2.1}$$

where e_{mass} is the thickness of the film. The optical properties of the film are strongly dependent on the thickness and on the distribution of the metal clusters of the granular on the surface.

2.1.2 Far-field optical properties

From 2004 to 2007, a detailed study of the optical properties of nanostructures at the percolation threshold was carried out in our team in the framework of Julien Laverdant thesis [166]. The morphology of the films and the absorption spectra of the disordered gold films are presented in figure 2.2 as an example of the random gold structure. The macroscopic optical properties of semi-continuous metallic films are studied by a spectrophotometer from the near Ultra-Violet (250 nm) to the nearinfrared (2500 nm) that gives us the transmission $T(\lambda)$ and the reflection $R(\lambda)$ of the random gold film as a function of the wavelength. It is possible to determine the absorption $A(\lambda)$ from the $T(\lambda)$ and $R(\lambda)$ of the granular layer by the relationship: $A(\lambda) = 1 - (R(\lambda) + T(\lambda))$. Depending on the concentration of the metal, $A(\lambda)$ can be very different [166]. In the case of the following structure, the minimum absorption is around 500 nm where no plasmons are excited [161]. For higher wavelengths, the absorption starts to increase due to plasmon resonances. This absorption remains high, up to 30% (figure 2.2b) from 600 nm to the far IR. Plasmons resonances exist over this wide range due to the complex shape of the structure. The structure is made of a large distribution of metallic clusters with different shapes and sizes.



Fig. 2.2: (a) AFM topographic image of a semi-continuous gold film. (b) Absorption of the semi-continuous gold film [161].

The plasmon resonances of isolated gold clusters of few tens of nm is shown on figure 2.3 (1.3 nm and 8 nm in thickness). In the first case, the mass thickness is

1.3 nm and we can observe an absorption peak around 530 nm corresponding to the plasmon resonance of the gold cluster. As the gold concentration increases, the peak broadens leading to a continuous absorption in the visible and the infrared part of the spectra for gold films close to the percolation threshold (8 nm mass thickness). The absorption which was around 10 %, reaches 33 %. The behavior of a classical continuous gold film is obtained when a mass thickness of 20 nm is reached.



Fig. 2.3: Apportion of different semi-continuous gold films [166].

2.1.3 Distribution of the "hot spots" in the near-field

The optical properties of the semi-continuous gold films have also been studied in the near-field by using a near-field optical microscope (SNOM). Near-field intensities have been mapped for different wavelengths and statistical analysis such as the autocorrelation function (ACF) and the probability distribution function (PDF) have been used. The PDF is defined as the histogram of the intensity. For a normal distribution, we have:

$$PDF_{\text{Normal}}(I) = \frac{A}{\sigma\sqrt{\frac{\pi}{2}}} \exp\left[-2\frac{(I - \langle I \rangle)^2}{\sigma^2}\right]$$
(2.2)

where I the intensity of the electric field. A is the amplitude of the normal distribution. $\langle I \rangle$ is the average value and σ is the standard deviation. In the case of the electromagnetic field enhancement due to the resonant excitation of surface plasmon, the strong values of the surface intensity tend towards a Log-normal distribution [167]. The PDF is then then given by:

$$PDF_{Log-normal}(I) = \frac{A}{\sigma\sqrt{2\pi}I} \exp\left[-\frac{\left(\ln I - \ln < I >\right)^2}{2\sigma^2}\right]$$
(2.3)



Fig. 2.4: Optical image of a semi-continuous gold film in the near-field [166].

A typical SNOM optical image obtained on a random gold film for a wavelength of 647 nm is presented on figure 2.4. "Hot spots" corresponding to localized field enhancements are observed. To analyze the behavior of these "hot spots", the intensity distribution has been plotted for differents wavelengths. The PDF analysis provides the statistics of the local enhanced intensities in the near-field. Figure 2.5 shows the PDF of a semi-continuous gold film for 3 wavelengths: 514 nm, 568 nm and 647 nm. For 514 nm, no plasmon resonances are excited and this regime corresponds to a purely diffusive regime. All the intensities have been normalyzed to the mean value of the distribution in this regime. The PDF are clearly wavelength dependent [160]. In the diffusive regime, a Gaussian distribution is observed. This distribution becomes asymmetric and tends to a Log-Normal distribution as the plasmonic regime is reached. This behavior is due to the presence of the "hot spots" in this regime. The distribution becomes more and more asymmetric as the wavelength increases, the high fields becoming more and more localized. For these wavelengths, a transition from the diffusive regime to the plasmonic regime is observed. This behavior can also be analyzed by the intensity auto-correlation function (ACF) [161]. The whole data points of the optical image is used. The ACF is defined by [168]:

$$C(\Delta x, \Delta y) = \langle \delta I(x, y) \delta I(x + \Delta x, y + \Delta y) \rangle$$
(2.4)

where

$$\delta I(x,y) = \left[I(x,y) - \langle I(x,y)\rangle\right] / \langle I(x,y)\rangle$$

Figure 2.6 shows that in the plasmonic regime, the localization of light is stronger as the wavelength increases. The shape and the width of the ACF expose properties



Fig. 2.5: Optical images of the semi-continuous gold film for different wavelengths: (a) 514 nm, (b) 568 nm, (c) 647 nm; and their PDF in semilog scales respectively [160].

of different regime of light-gold surface interactions [161]. In the diffusive regime, the ACF is strongly polarization dependent with oscillations appearing prependicularly to the incident polarization [168]. In the plasmonic regime, this function becomes anisotropic and broadens as the wavelength increases.

In order to study further the characteristics of the semi-continuous films, the coupling between NCs and the random gold films have been used. The analysis of the PL dynamics of the NCs on the structure is a very useful tool to get insights in plasmon modes of the structure. The coupling between the thick shell CdSe/CdS NCs with the hot spots of the semi-continuous gold film is cheracterized by measuring simultaneously the PL decay rate and the linear polarization ratio. Previous studies have been performed where NCs hace been deposited directly on the film without any spacer. It was prooved that the thick shell acts as a spacer and very high



Fig. 2.6: ACF of near-field intensity for different wavelengths: (a) 514 nm, (b) 568 nm, (c) 647 nm. The red curve is the ACF in the x direction (perpendicular to the incident polarization direction) and the black curve is the ACF in the y direction (parallel to the incident polarization direction) [161].

Purcell factors that can reach values up to 60 were found [154]. In the experiments I performed, the PL dynamics is analyzed simultaneously with its polarization. In the next part, I will describe the method and the experimental set-up used for these approaches.

2.2 Experimental set-up

2.2.1 Principle of a standard Hanbury-Brown and Twiss set-up

Our detection scheme is based on an Handury-Brown and Twiss (H-B & T) set-up which is commonly used for a fine caracterization of the fluorescence of nanoemitters. This set-up allows to get correlations of the fluorescence intensity. Two detectors are used in order to record the delay between two photons arrived on the two detectors [169]. The set-up is presented in figure 2.7. The necessity to used two detectors comes from the fact that one detector is not able to record two photons separated by a very short delay. In the H-B & T set-up, the fluorescence signal is divided into two equal signals by a 50/50 beam-splitter and detected by two detectors. The "stop" channel is usually delayed by a long cable (100m) in order to visualize negative correlations. The detectors are connected to a counting card. In the experiment, the detection is carried out by two avalanche photodiodes. The autocorrelation of the fluorescence intensity is provided by the histogram of the delays between photons.



Fig. 2.7: Hanbury-Brown and Twiss interferometer set-up for the measurement of the intensity correlation of the fluorescence.

2.2.2 Confocal microscope set-up

The standard H-B & T is installed at the output of a confocal microscope for the study the emission of the NCs. The basic concept of the confocal microscope was developed by Marvin Minsky in 1955. It is an optical imaging technique used to increase the optical resolution and the contrast of a microscope by adding a spatial pinhole placed at the confocal plane of the lens to eliminate out-of-focus light [170].



Fig. 2.8: Principle of the confocal microscopy. A pinhole is used to spatially filter the signal.

The important difference with the conventional microscope is the small pinhole in front of the detector that makes it confocal (figure 2.8). The laser beam (red line) is focused on the sample (in the focal plane) by an objective. The fluorescence (or reflection) from this spot is imaged by the same objective and brought to a pinhole at the focus. In addition, a significant amount of fluorescence emission is still excited outside of the focal plane which is shown in dotted lines. However, only a small fraction of the out-of-focus fluorescence emission is delivered through the pinhole aperture. That means that a bigger detection pinhole reduces the confocal effect. Most of light from the outside focal plane is smeared out over a wide area by the time it reaches the pinhole. Therefore, the confocal image only contains the in-focus information. In biology, by collecting a series of images, changing the focus between each, one can collect a full three-dimensional representation of specimen. The wavelength of the light, the numerical aperture of the objective and the diameter of the diaphragm affect the depth of the focal plane.

The NCs are deposited on glass or on the metallic film by spin coating without any spacer. A low NC concentration is used, so individual emitters can be studied (figure 2.9). The sample is placed on a sample holder which can be moved along two directions at a micro scale resolution. Therefore, we can work in different places of the sample.



Fig. 2.9: Confocal microscope set-up for the study of the coupling between NCs and metallic structures

The optical excitation is provided by a fiber-coupled pulsed laser diode (LDH 405 or 485 Picoquant, pulses of duration ≈ 70 ps or 150 ps) emitting at 405 nm or 485 nm. In both cases, the NCs absorb very well the excitation and emit a fluorescence centered between 630 nm and 660 nm with a linewidth of 30 nm (depending on their size, see following section). When the NCs are coupled to the gold films, besides the fluorescence of the NC, the fluorescence of gold is detected. Since its relative contribution is more important for optical excitation at the shorter wavelengths, the laser diode at 485 nm is preferred. The repetition rate of the excitation is chosen in such a way that the NCs have enough time to relax after one exciting pulse. For the NCs used in these coupling experiments, 5 MHz is a good repetition rate (in the following the maximum value of the lifetime is 60 ns). In order to create only one e-h pair and to avoid as far as possible the contribution of multiexcitonic states, low power excitation is used.

The laser beam is deflected into an inverted confocal microscope (IX 71, Olympus) by a dichroic mirror (560 nm edge BrightLine). It is focused on the sample by an air objective with a numerical aperture (NA) of 0.95 or an oil objective with a NA of 1.4. The beam is scanned across the sample from using a nano-positioning piezoelectric equipment. In order to choose a NC or to characterize the dispersion of the NCs on the structure, the sample can also be illuminated by a continuous UV lamp as in figure 2.9 and observed with a CCD camera (Roper scientific, 512B).

The fluorescence is collected by the same objective. It passes through the dichroic mirror. It is spatially filtered by a pinhole (100 μ m of diameter). A first filter (band-pass 617/73 nm) in front of the detectors provides additional blocking of any

remaining laser light and allows us to be more selective about the wavelength bandpass that we detect and to reduce the remaining contribution of the gold fluorescence. For the detection system, we use two avalanche photodiodes (APDs, SPCM-AQR-13, Perkin-Elmer) configured according to the standard H-B & T scheme. The size of the sensor $(175 \times 175 \ \mu m^2)$ is large enough to collect the entire beam. The temporal resolution of the APDs is 300 ps and the detection efficiency is about 70 % around 620 nm. The dark counts of the photodiodes is less than 200 counts per second.

The electric signal provided by the APDs is sent to a counting card (PicoHarp 300 module, PicoQuant). The time resolution is fixed at 64 ps. From a single set of data, this card provides:

- the delay τ_1 between the sample excitation provided by the diode laser and the arrival time of the emitted photon at the APD. The measurement of this time delay is repeated many times to get the photoluminescence decay and characterize the lifetimes of the emission levels [134, 171].
- the arrival time τ_2 of each photon. For this time, the measuring clock has a time resolution of 100 ns.

Since there is no drift between the laser diode and the internal clock of the PicoHarp300, the two times τ_1 and τ_2 can be added, this data providing the absolute time of arrival of each photon during the overall experiment with a precision limited by the photodiode resolution.

For the polarization analysis of the emission, a rotating polarizer is placed on one arm of the H-B & T set-up. By normalizing the measured intensity on this arm by the intensity detected on the other arm, the polarization can be calculated precisely even when the sample slightly drifts or the collected intensity fluctuates due to the blinking of the NCs.

In conclusion, this set-up also acquires the absolute arrival time of the photons. Then the fluorescence intensity, the PL decay and the polarization of single NC are obtained by the same set of data.

2.3 Experimental results

The NCs CdSe/CdS used in this section are the ones presented in the previous chapter. The emission of these NCs, which is above 600 nm, is within the plasmon resonance of the gold films where as the excitation at 485 nm is out of the plasmon resonances (2.2 b). As already mentionned, previous experiments have demonstrated that the emission of the NCs is not quenched when they are directly deposited by spin-coating on the gold film [10]. Three sizes of CdSe/CdS NCs are used to probe the properties of the near-field modes at different heights. The first NCs (type 1) have a total diameter of 12 nm. Their wavelength emission is around 630 nm with a full width at half maximum (FMWH) of 30 nm. The type 2 NCs exhibits a total diameter of 22 nm and its emission is around 660 nm. The third kind of NCs (type 3) presents a mean diameter of 30 nm and a wavelength also centered at 660 nm. The CdS surface of the NCs is surrounded by organic ligands which are mainly Hexadecylamines and Oleates. Their length is about 2 nm. Since the difference between the emission wavelengths of the different types of NC is of the order of the emission and plasmon linewidth and since the absorption of the semi-continuous film is nearly constant between 600 and 700 nm (Figure 2.2b), we consider that the coupling between the NCs and the gold structures does not depend on the type of NCs.

A continuous gold film is prepared by the same method with 25 nm of thickness and 1 nm of roughness rms. The results on this film will be taken as a reference. They will be compared to the results on the random films and to the numerical simulations for the PL decay and the PL polarization. The gold films used in the experiments have been characterized by spectrophotometric and AFM measurements. We have checked that even if we used different samples, they all had the same characteristics.

Before studying the coupling between the emitter and the gold films, we analyzed their PL decay rate at the single emitter level when deposited on a glass coverslip. In agreement with previous results [154], the mean fluorescence lifetime is around 60 ns and does not change significantly for the three different kinds of NCs. This value will be taken as a reference in the following. Figure 2.10 presents the PL decay of one NC on glass in comparison with NC on semi-continuous gold film. The PL decay is clearly faster on the random film with, in this case, a lifetime of 2.3 ns.



Fig. 2.10: PL decay of a NC deposited on glass or a semi-continuous gold film.

The fluorescence intensity is acquired during the rotation of the polarizer. The linear polarization ratio is determined by:

$$R = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \tag{2.5}$$

where I_{max} is the fluorescence intensity detected along the maximum pass axis of the polarizer, in contrast I_{min} is along the minimum axis. The starting position of the rotating polarizer is the same for every measurements that enables to determine the variation of the maximum pass axis direction θ (figure 2.11). θ ranges between -90° and 90° . If it reaches a minimum first while scanning the polarizer direction, the angle will be negative. Otherwise, we get a positive value for the angle.



Fig. 2.11: Measurement of the maximum pass axis direction θ .

Firstly, the small NCs (type 1) are deposited on a flat gold film (green \diamond of figure 2.12a). The Purcell factors that are defined by the ratio of the PL decay rate measured on gold structures to the one on glass range between 5 and 15. This dispersion on flat gold can be explained not only by the different orientations of the NCs but also by the shell size dispersion of the NCs themselves. Concerning the polarization ratio, it ranges between 10 % and 30 %. This result can be confirmed by the calculation using a Fourier modal method [172]. In that case, the NCs is modeled with two incoherent dipoles perpendicular to the *c*-axis. The NC emits at 630 nm and is placed 10 nm above the surface of the 25 nm thick gold. The calculation predicts a linear polarization ratio ranging from 0 % and 25 %, in agreement with the experimental results.

On the other hand, as a result of the strong spatial localization and enhancements of the field, drastic reductions of the lifetime are observed when the NCs are coupled to the disordered structure (red \Box of figure 2.12a). A wide range of Purcell factors is observed due to strong variations of the LDOS on this structure. As expected, the disorder induces a strong modification of the optical modes, with the generation of "hot" spots close to the percolation threshold [158].

Because the local density modes and the spontaneous emission of the emitter are linked, the modification of the optical modes can be probed by measuring the decay rates on the surface. The CdSe/CdS NCs are characterized by two incoherent dipoles and their orientations are randomly spread over the surface. The decay rate is proportional to the partial LDOS given by:

$$\Gamma = \frac{\Pi \omega^2}{\sin \epsilon_0} \mid \vec{p} \mid^2 \rho_p(\vec{r}, \omega)$$
(2.6)

where ρ_p is the transition dipole between two electronic states and $\rho_p(\vec{r},\omega)$ is the partial LDOS. Equation (2.6) shows that the NCs are more or less coupled to plasmon modes depended on the orientation of 2D dipole. Therefore, the different orientations of the NCs contributes as much as the fluctuations of the LDOS to the lifetime dispersion. Purcell factors on random gold film fluctuate widely from less then 10 to nearly 40 accounting for strong localization modes on the surface, in agreement with previous results [154]. The polarization analysis of the NCs fluorescence reveals a large distribution of polarization degrees on random gold structure. From 20 %, it can exceed 80 % with a standard deviation of 16 %.

In this case, the polarization which is considered as a signature of the complexity of modes on this kind of samples is clearly striking. Strongly polarized modes are



Fig. 2.12: (a) Polarization ratio as a function of the Purcell factor for individual NCs (type 1, 12 nm in diameter) deposited on a flat gold film or a semi-continuous film.
(b) Polarization ratio as a function of the polarization angle for the NCs coupled to the semi-continuous film.

evidenced. This could be explained by highly localized modes induced by a simple geometry corresponding to a dimer configuration. Polarization emission of molecules in a metallic dimer has been demonstrated to be linear and its depolarization has been observed when introducing a third metallic particle [173]. Even though this model is to simple to explain all electromagnetic modes on random gold surface, the polarized emission of some modes can be compared to a dimer mode emission which can also exist on the complex structure surface.

The statistics in the figure (2.12a) includes few NCs which have fast decrease of PL with low polarization level. Otherwise, there are some NCs that have very high polarization degrees with long lifetimes (low Purcell factors) because the dipoles of the NCs do not align with the field or because the plasmon mode is weak. We do not observe any link between Purcell factors and the polarization degree of the emission. Even if the enhancement of the PL decay rate depends on the orientation of the NC, the 2D dipole structure and the large number of NCs suggest that the polarization mode and localization mode are uncorrelated. On the figure (2.12b) the polarization ratio is plotted as a function of the NCs and the semi-continuous film.

Bigger NCs (type 2 and 3 respectively 22 nm and 30 nm in diameter) have been used to probe the modes at a higher position away from the surface. As expected, lifetime reductions are lower on both samples based on the higher distance from the surface. The statistics is presented on figure (2.13).

The Purcell factors are lower than 15 for the two samples. In addition, they are clearly lowest for the biggest NCs (red \Box). Some PL decay rates of these NCs are



Fig. 2.13: Polarization ratio as a function of the Purecell factor for two kinds of individual NCs. The dotted line corresponds to a Purcell factor of 1.

slightly accelerated and represented by the dots close to the dotted line in figure (2.13). This decrease is the result of the very fast decay of the electromagnetic modes with the distance to the surface. The statistics of the polarization ratio is also modified by the increase of the NCs diameter [174].



Fig. 2.14: Histogram of the polarization ratio for two kinds of NCs (type 2 and 3) deposited on a semi-continuous gold film.

The polarization ratio is also influenced by the distance to the structure. The effect of the height is demonstrated in detail by the histogram of the polarization ratio in figure (2.14). The maximum polarization values are 72 % and 60 % for the 22 nm and 30 nm diameter NCs, respectively. Moreover, the standard deviation also decreases from 16 % to 11 %. These results confirm the fast drop of the coupling with the distance between the film and the emitter. They prove that the "hot spots" structure is confined in the near-field at the scale of few nanometers.

When the NC is close to the surface, the fluorescence carries the feature of the plasmonic mode. When the distance to the sample increases, the fluorescence tends to the emission of the NC dipole. This is the interest of the NCs with which the distance to the surface can be controlled from very short distances due to their size.

2.4 Conclusion

In conclusion, the PL of thick-shell NCs directly coupled to random gold films has been investigated in detail. An original approach connecting polarization and lifetime measurements provides new insights concerning the "hot" spots observed in these plasmonic structures. Interestingly, in contrast with the lifetime reduction that depends on the orientation of the NC, the polarization ratio is only determined by the position of the NC and the nature of the mode at this position. The modifications of the statistics of the polarization with the diameter of the NCs show that the near-field distribution is defined at the scale of few nanometers. From a general point of view, our approach could be extended to other plasmonic structures in order to get information about the orientation of the electric field of plasmonic modes [175].

3.

ORDERED HOLE GRATINGS

At the beginning of last century, intensive works have been carried out on the diffraction of light by gratings after first Wood's observations [176–178]. Among all the structures studied, the researchers paid much attention on periodic gratings which exhibit SPPs and Rayleigh anomalies. The century concluded with the very significant discovery of Ebbesen about the extraordinary optical transmission (EOT) through sub-wavelength hole arrays [179]. This observation is in contrast with the prediction of Bethe concerning the cutoff in transmission when the wavelength λ is large in comparison with the hole radius [180]. Following the idea of Ebbesen, many other sub-wavelength nanostructures have been exploited such as triangular aluminum plates on a glass slide [18], rectangular gold and silver absorber [19, 20]. The explanation of EOT is still in debate but, in a first approximation, it results from the coupling between the incident light and the SPPs of the nanohole array [181–185]. Another explanation invokes dynamical light diffraction [186–189].

This extraodinary transmission is observed when nanometric holes are drilled in a thick metallic layer (more than 100 nm). On the other hand, the opposite effect was observed recently in thin metallic films with a thickness close to the skin depth. Braun *et al.* reported that less light is transmitted through perforated structures in very thin gold films with a thickness of 20 nnm [190–192]. The suppressed transmission in a 1D periodically perforated thin film was well explained by Spevak *et al.* [191] by means of analytical and numerical calculations. As for transmission, SP excitation is considered as the origin of the resonance absorption energy. However, on the contrary to the enhanced transmission, an extraordinary absorption up to 50 % can be achieved.

Even if less works have been devoted to thin films compared to EOT, very thin metal films have also been investigated by sevral groups. In this case, the diffraction can be distinguished from the SP coupling effects and the study of a single hole represents a crucial first step. In 2007, Kall *et al.* performed successfully SNOM experiments to analyze in detail the LSP-SPP coupling in a single hole placed in a 20 nm thick gold film [21]. They explained the presence of a dipolar LSP resonance mode in a single hole and the dominance of the SPP mode in the surrounding gold film. Next, it has been demonstrated that the nanohole acts as a nanoparticle [21–24,193,194]. The similarities between the LSPs structures (calculated by FDTD, see next section) of nanoholes and the ones of nanoparticles are presented in the following (figure 3.1). When two holes (or particles) are involved, the coupling field depends on the distance between them. In addition, the electric field distribution of a single hole (figure 3.1c) contains the SPP propagating to the surrounding flat gold film.



Fig. 3.1: Comparison of the electric field distributions for 1 or 2 metallic nanoparticle(s) or nanohole(s), simulated by FDTD with parallel polarization.

One motivation of the work presented in this chapter is the growing interest in this kind of photonic nano-structures where optical properties are related to the coupling between different kinds of plasmons [190, 191, 195–197]. These structures are also a good choice for introducing disorder and studying its influence on the optical properties. This will be made in the last chapter. Before introducing disorder, it is important to understand the behavior of the ordered structure itself. Then, these results will be taken as references for the characterization of the structures with control disordered holes. Simulations have been performed with a FDTD software in order to understand the behavior of the plasmon resonance when different parameters of the hole grating (periodicity, size, thickness of the metal layer) are varied. These studies have been confirmed by experimental analysis using fluorescent nano-emitters to probe the structure. In this case, the grating is probed through its coupling with fluorescent nano-emitters (colloidal NCs). The emission of an individual NC near the surface of the grating will depend crucially on its position and will be directly related to the LDOS. This typical example of light-emitter interaction is at the heart of many studies in nano-photonics [198]. Two strategies have been brought into play. We have studied the modification of the lifetime of the NC coupled to the grating by confocal microscopy and by SNOM using a NC as an active nano-probe.

In the following sections, we will first present the simulation method to predict several optical properties of the grating that will be compared with the experimental results. Then the lifetime distribution of individual NCs deposited on the gratings will be measured by confocal microscopy. The LDOS coupling will be also investigated through the variation of the fluorescence of a NC attached at the end of a SNOM tip with its position on the hole grating.

3.1 Finite Difference Time Domain (FDTD) simulation

Simulation is the first step to design the nanohole structures and predict the optical properties of these hole gratings. A common approach consists in using the FDTD electromagnetic field analysis. FDTD was introduced by Kane Yee in 1966 [199]. It is based on the resolution of the differential and integral forms of Maxwell's equations and gives the solutions for the electric and magnetic fields as a function of time. In three dimensions (3-D) and in a rectangular coordinate system, the vector components of the curl equations in a linear, isotropic, non-dispersive, lossy material are given in ref. [200]. The equations for the magnetic field vector \overrightarrow{H} are:

$$\frac{\partial H_x}{\partial t} = \frac{1}{\mu} \left(\frac{\partial E_y}{\partial z} - \frac{\partial E_z}{\partial y} - (M_{source_x} + \sigma^* H_x) \right)$$
(3.1a)

$$\frac{\partial H_y}{\partial t} = \frac{1}{\mu} \left(\frac{\partial E_z}{\partial x} - \frac{\partial E_x}{\partial z} - \left(M_{source_y} + \sigma^* H_y \right) \right)$$
(3.1b)

$$\frac{\partial H_z}{\partial t} = \frac{1}{\mu} \left(\frac{\partial E_x}{\partial y} - \frac{\partial E_y}{\partial x} - (M_{source_z} + \sigma^* H_z) \right)$$
(3.1c)

where μ is the magnetic permeability, $\overrightarrow{M}_{source}$ is the equivalent magnetic current density and σ^* represents the magnetic loss. For the electric field vector \overrightarrow{E} , we have:

$$\frac{\partial E_x}{\partial t} = \frac{1}{\varepsilon} \left(\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} - (J_{source_x} + \sigma E_x) \right)$$
(3.2a)

$$\frac{\partial E_y}{\partial t} = \frac{1}{\varepsilon} \left(\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} - \left(J_{source_y} + \sigma E_y \right) \right)$$
(3.2b)

$$\frac{\partial E_z}{\partial t} = \frac{1}{\varepsilon} \left(\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} - (J_{source_z} + \sigma E_z) \right)$$
(3.2c)

where ε are electrical permittivity, \vec{J}_{source} is electrical current density and σ is electric conductivity.

The FDTD numerical algorithm for interactions of electromagnetic wave with three dimensional objects is based on the six components in Eq.3.1 and Eq.3.2. Following the Yee algorithm, the \vec{E} and \vec{H} components are centered in the three dimensions space (see figure 3.2). Every \vec{E} component is surrounded by four circulating \vec{H} components, and every \vec{H} component is surrounded by four circulating \vec{E} components [200]. This approach is called the Yee grid. The discretization of the uniform spacial rectangular grid writes:

$$(i, j, k) = (i\Delta x, j\Delta y, k\Delta z)$$
(3.3)

and any function of the space and time will follows [199]:

$$F(i\Delta x, j\Delta y, k\Delta z, n\Delta t) = F^n(i, j, k)$$
(3.4)

where i, j and k represent the discrete spacial point and n is used to quantify the time increment. The 3-D FDTD method calculates the half interval displacement of

the magnetic and electric field vectors in both space $(\Delta x, \Delta y, \Delta z)$ and time (Δt) . By using centered finite-difference expressions for the space and time derivatives, K. Yee presents the first order spatial and time derivatives along the x-direction of a vector field \overrightarrow{F} as:

$$\frac{\partial F}{\partial x}\left(i\Delta x, j\Delta y, k\Delta z, n\Delta t\right) = \frac{F_{i+\frac{1}{2},j,k}^n - F_{i-\frac{1}{2},j,k}^n}{\Delta x} + O\left[\left(\Delta x\right)^2\right]$$
(3.5a)

$$\frac{\partial F}{\partial t} \left(i\Delta x, j\Delta y, k\Delta z, n\Delta t \right) = \frac{F_{i,j,k}^{n+\frac{1}{2}} - F_{i,j,k}^{n-\frac{1}{2}}}{\Delta t} + O\left[\left(\Delta t\right)^2 \right]$$
(3.5b)

where $\pm 1/2$ is the increment of vector field in the *i* and *n* superscript (*x*-coordinate and time coordinate respectively).



Fig. 3.2: Position of the electric and magnetic filed vector components in a cubic unit cell of the Yee space lattice [199, 200].

If we apply the above ideas to the Eq. 3.1 and Eq. 3.2, we achieve the numerical approximation of the Maxwell's curl equations in three dimensions. For example, the E_x field component is expanded as:

$$E_{x} \begin{vmatrix} n+\frac{1}{2} \\ i,j+\frac{1}{2},k+\frac{1}{2} \end{vmatrix} = \left(\frac{1 - \frac{\sigma_{i,j+\frac{1}{2},k+\frac{1}{2}\Delta t}}{2\varepsilon_{i,j+\frac{1}{2},k+\frac{1}{2}}}}{1 + \frac{\sigma_{i,j+\frac{1}{2},k+\frac{1}{2}}}{2\varepsilon_{i,j+\frac{1}{2},k+\frac{1}{2}}}} \right) E_{x} \begin{vmatrix} n-\frac{1}{2} \\ i,j+\frac{1}{2},k+\frac{1}{2} \end{vmatrix}$$

$$+ \left(\frac{\frac{\Delta t}{\varepsilon_{i,j+\frac{1}{2},k+\frac{1}{2}}}{1 + \frac{\sigma_{i,j+\frac{1}{2},k+\frac{1}{2}}}{2\varepsilon_{i,j+\frac{1}{2},k+\frac{1}{2}}}}}{1 + \frac{\sigma_{i,j+\frac{1}{2},k+\frac{1}{2}}}{2\varepsilon_{i,j+\frac{1}{2},k+\frac{1}{2}}}} \right) \left(\frac{\frac{H_{z} \begin{vmatrix} n \\ i,j+1,k+\frac{1}{2} - H_{z} \end{vmatrix} n}{2}}{-\frac{H_{y} \begin{vmatrix} n \\ i,j+\frac{1}{2},k+1 - H_{y} \end{vmatrix} n}{2\varepsilon}}{-\frac{1}{2} - \frac{H_{z} \begin{vmatrix} n \\ i,j+\frac{1}{2},k+1 - H_{y} \end{vmatrix} n}{2\varepsilon}}{-\frac{1}{2} - \frac{1}{2} - \frac{1}{2}$$



Fig. 3.3: A perfect electrical conductor (PEC) is taken into account by reducing the integral contour C to include only the region outside the PEC where the electric field is non-zero (C_1) [201].

The following time stepping expression for the H_z component located at the right corner of the unit cell is:

$$H_{z} \left|_{i,j+1,k+\frac{1}{2}}^{n+\frac{1}{2}} = \left(\frac{1-\frac{\sigma^{*}_{i,j+1,k+\frac{1}{2}}\Delta t}{2\mu_{i,j+1,k+\frac{1}{2}}\Delta t}}{1+\frac{\sigma^{*}_{i,j+1,k+\frac{1}{2}}\Delta t}{2\mu_{i,j+1,k+\frac{1}{2}}}}\right) H_{z} \left|_{i,j+1,k+\frac{1}{2}}^{n} + \left(\frac{1-\frac{\Delta t}{2\mu_{i,j+1,k+\frac{1}{2}}}{1+\frac{\sigma^{*}_{i,j+1,k+\frac{1}{2}}\Delta t}{2\mu_{i,j+1,k+\frac{1}{2}}}}{1+\frac{\sigma^{*}_{i,j+1,k+\frac{1}{2}}\Delta t}{2\mu_{i,j+1,k+\frac{1}{2}}}}\right) \left(\frac{\frac{E_{x}\left|_{i,j+\frac{1}{2},k+\frac{1}{2}}^{n+\frac{1}{2}} - E_{x}\right|_{i,j+\frac{1}{2},k+\frac{1}{2}}^{n+\frac{1}{2}}}{\Delta y}}{-\frac{E_{y}\left|_{i+\frac{1}{2},j+1,k+\frac{1}{2}}^{n+\frac{1}{2}} - E_{y}\right|_{i-\frac{1}{2},j+1,k+\frac{1}{2}}}{\Delta x}}{-M_{source_{z}}\left|_{i,j+1,k+\frac{1}{2}}^{n+\frac{1}{2}} - E_{y}\right|_{i,j+1,k+\frac{1}{2}}^{n+\frac{1}{2}}}\right) \right)$$

$$(3.7)$$

Eq.3.6 and Eq.3.7 show the iteration of the fields which are solved by the FDTD method. The field components at a certain point in time are considered as a function of the fields at a previous time.

The "FDTD Solution" software from Lumerical Solution Inc. is a useful tool to carry out the numerical calculation. It is a commercial software designed for the elaboration, analysis, optimization of nanophotonic devices. FDTD Solution approaches the sophisticated conformal mesh to model complex designs by delivering subcell accuracy. The advanced conformal mesh explains the subcell features by solving Maxwell's integral equations near structure boundaries. Figure 3.3a presents an example of Yu–Mittra method which models curved perfect electrical conductor (PEC) surfaces (see figure 3.3).

The $\oint \vec{E} \cdot d\vec{l}$ contour integral which contributes to *H* field is given by:

$$\oint \vec{E}.d\vec{l} = \int_{\Delta x_0(i)} E_x(i,j,k)dx + \int_{\Delta z_0(k)} E_z(i,j,k)dz + \int_{\Delta x(i,j,k+1)} E_x(i,j,k+1)dx + \int_{\Delta z(i+1,j,k)} E_z(i+1,j,k)dz$$
(3.8)



Fig. 3.4: Example of a simulation for a gold nanohole arrays on a glass substrate using "FDTD Solution" of Lumerical software.



Fig. 3.5: (a) Transmission, Reflection and Absorption in the far-field and (b) near electric field distribution of the hole grating simulated by FDTD Solution.

The "FDTD Solution" program has a user friendly graphical interface to control all the parameters of the simulation. Figure 3.4 presents a screen shot of a simulation of a gold nanohole grating on a glass substrate. A plane wave light source is placed in the far-field (about 2 μ m from the surface of the grating) to optically excite the system. The monitors are used to record the electromagnetic field value at different heights. We can calculate the instantaneous fields at any desired positions by FDTD Simulation. Two "frequency domain field and power" monitors are located in farfield to record the output powers, normalized reflection (R) and transmission (T) of the light through the hole grating as a function of the wavelength or the frequency. Then the absorption (A) of the grating is deduced from R and T by the standard relation A = 1 - R - T (figure 3.5a). A near-field monitor is placed close to the surface to map the distribution of near electric fields (see figure 3.5b). The simulations will be presented together with the eperimental results.

3.2 Fabrication

The hole gratings studied during my thesis are fabricated as part of a collaboration between GEMaC in Versailles and the Institut Lumière Matière (ILM) in Lyon. A flat gold film is first prepared by Bruno Berini in GEMaC by RF sputtering. The thickness is measured by profilometry. Then the holes are etched by Julien Laverdant and Rémy Fulcrand at ILM in Lyon using focused ion beam technology (FIB).



Fig. 3.6: Etching holes arrays in thin gold film using the focused ion beam (FIB) lithography technique [202].



Fig. 3.7: Schematic diagram representing the principle of FIB lithography technique.

The FIB lithography technique is now briefly discribed. It was developed at the beginning of the 1970s [203–209], the most common techniques are summarized in [210]. The ion beam source used in most widespread instruments is a liquid metal ion sources (LMIS), especially gallium ion sources (Ga^+) which has a melting point around 30°C [211]. In addition, LMIS based on gold and iridium are also available. In a gallium LMIS, the gallium is placed in contact with a tungsten needle. A high voltage is applied to create an electric field greater than 10^{10} V.m⁻¹ [202]. When the melting point of gallium is reached, the gallium flows to the tip of the needle. At the end of the tip, the huge electric field causes ionization and field emission of the gallium atoms. Due to the small size of the tip, an extreme current intensity around 10^{6} A.cm⁻² can be focused precisely on the surface. The primary Ga⁺ beam hits the sample surface directly (Figure 3.7). Under the force of the ion beam, a small part of the sample is sputtered and leaves the surface as a secondary ion $(i^+$ and i^{-}), neutral atoms (n^{0}) and electrons (e^{-}) . More precisely, the focal point of the beam depends on the ratio q/M, q is the charge on the particle and M its mass. Using an electrostatic lenses gives us an advantage of FIB technique for the heavy particles, the focal point is then independent of the mass.

After interaction with the surface, the signal from the sputtered ions is collected to form the image of the pattern. The resolution of the images can reach 5 nm with the modern FIB systems under a low beam current [212, 213]. At higher currents, the beam can remove a great deal of material and allows one to increase the precision to a nanometer.



Fig. 3.8: Image of an 15x15 ordered hole arrays with hole diameter of 100 nm and a period of 425 nm made by ion beam etching in ILM. The image is obtained by Scanning electronic microscopy (SEM). Done by Dual-Beam (FIB-SEM) Systems.

3.3 Experimental set-up

Three kinds of experiments will be performed on the ordered gratings. To probe the far-field properties, transmission and reflection spectra will be performed with the confocal microscope in order to get the absorption spectra on one grating and to compare it to the FDTD simulations. To probe the near-field of the structure, the same method as the one described in chapter 2, lifetime measurements on individual NCs at different positions with the confocal microscope, will be used. This method allows us to make a statistical analysis but the lifetime of a NC at a precise position on the grating cannot be deduced. To get a more precise idea of the near-field distribution on the structure, near-field measurements using a near-field active probe will be presented. In this section, we first present the different experimental set-up used for the gratings analysis.

3.3.1 Transmission and Reflection measurements in far-field

During my PhD, I made a development on the confocal microscope presented in the chapter 2 in order to get the absorption spectra of the gratings. To get the spectra in transmission and reflection of the grating in the far-field, I used the set-up represented in figure 3.9 that associates a spectrophotometer, a confocal microscope and a super-continuum source (SuperK EXTREME - white EXW-12 series) which delivers a wide spectra output covering the range of 400-850 nm. The laser is focused on one hole grating through an air objective (NA = 0.4). For the reflection measurements, the light is reflected back and collected by the same objective and for the transmission measurements I used a second air objective (NA=0.4) that is placed in the upside of the sample in front of the first objective. Then the reflection (R)and transmission (T) signals are coupled to a fiber and sent to a spectrophotometer to record the spectra.



Fig. 3.9: Transmission and Reflection measurements in the far-field.

The spectrophotometer (Princeton Instruments - SP2750) is equipped with three diffraction gratings of 300, 600 and 1200 lines and is sent on a CCD camera of 100 x 1340 pixels of 20 x 20 μ m size. The CCD (SPEC-10 100BIXTE) of the spectrophotometer is cooled down to -90 °C by a Peltier module.

Because the spectrum of the laser always remains in the experimental T and R spectra, we have to subtract this irrelevant information before deducing the absorption (A). The simple way to normalize the T and A spectra consists in taking the

spectrum of the laser on the glass as a reference:

$$R_{grating} = \frac{R_{exp} - R_{noise}}{k.R_{ref} - R_{noise}}$$
(3.9a)

$$T_{grating} = \frac{T_{exp} - T_{noise}}{k.T_{ref} - T_{noise}}$$
(3.9b)

The coefficient k is determined from the R and T spectra recorded on the flat gold sample which has the same thickness as the grating. The normalization of flat gold is done with the spectrophotometer in GEMaC by Guillaume Bouchez.

3.3.2 Scanning near-field optical microscopy (SNOM)

The lifetime measurements of NCs deposited on a structure, as presented in the chapter 2, give a relevant information on the LDOS variations on the structure. Nevertheless some parameters as the position on the sample and the dipole orientation of the NC are not known. If we want to learn more about the LDOS, these parameters have to be determined. Controlling the position of a nano-emitter on a surface has become possible with the development of active near-field probes [18]. In this case a nano-emitter is grafted at the end of a near-field probe. This probe is then brought into the near-field of the surface and the position is controlled by the near-field optical microscope feed back. This method has been developed in the group with NCs during the thesis of Rabeb Jazi which was defended in June 2017. Moreover, we have shown that it was possible to know the dipole orientation by measurements performed on a flat gold surface. I participated to this development and applied it to the hole gratings.



Fig. 3.10: Basic principle of near-field optics: light passes through a sub-wavelength diameter aperture and illuminates a sample placed within its near-field, at a distance much less than the wavelength of the light.

In the early 1870s, Ernst Abbe demonstrated that the resolution achievable with light is limited by the diffraction. The well-known limit is $\lambda/2$, that is around 200 nm in the visible range. It means that structures with typical dimensions less than a half of the wavelength cannot be characterized with standard optical microscopy. The development of nanotechnology made it necessary to imagine new experimental

techniques. A new optical method that breaks the far-field resolution limit exploits the properties of evanescent waves (or near-field) located on the surface of the materials (see figure 3.10). It is called Near-field Scanning Optical Microscopy (NSOM or SNOM). The idea of near-field optics was first implemented in 1928 by E.H. Synge who used a small aperture to image a surface with a sub-wavelength resolution [214]. Then the technique was improved [215–217] and the first nanometer-scale spatial-resolution optical experiments with a SNOM were reported in 1984 [218,219]. Now, the SNOM make it possible to obtain lateral resolution of 20 nm and vertical resolution of 25 nm [220, 221].

Basic principle of SNOM



Fig. 3.11: Principle of Scanning Near-Field Optical Microscopy (SNOM) [222]. The scanning can be done along x and y axis at a constant height or with regulated height by using a feedback mechanism.

When an electromagnetic wave illuminates an object, the diffracted field consists in two types of electromagnetic fields:

- First, a propagating wave associated with small spatial frequencies.
- The second one corresponds to evanescent waves associated with high spatial frequencies.

SNOM detects the evanescent wave (or non-propagating fields) existing at the distance very close to the surface of the object. With a device as a thin tip placed very close to the sample in the near-field zone (typically few nanometers for optical wavelengths), we can collect the evanescent near-field which carries the high frequency spatial information about the sample, the intensity of this signal decreasing exponentially with the distance from the surface of the sample. Figure 3.11 shows the principle of a SNOM: the signal is converted by diffraction into a propagating signal and carried out by a small diffractive element called probe. Experimentally, a very sharp tip is approached close to the surface and scans the surface along x and y axis at a constant height or with a regulated height by using shear force feedback mechanism.



Fig. 3.12: Front and back view of a piezoelectric tuning fork with a aluminum coated fiber probe glued along one of its prongs [223].

In the shear fork feedback mode, a tuning fork is mounted along the tip and oscillates at its resonance frequency. The amplitude is proportional to the tip surface distance. The tip scans across the sample with a piezoelectric stage. Figure 3.12 presents a scheme of a piezoelectric tuning fork. The idea was given by K. Karrai and R. D. Grober [223]. They proposed an optical aluminized fiber glued along the side of one of the prongs of a quartz crystal tuning fork. The tuning fork is a mechanical micro-resonator in U form including two prongs. Two electrodes equipe the tuning fork to determine the difference of potential between the two prongs. When the tuning fork is deformed, this difference is then linked to the deformation of the prongs. To excite the mechanical resonance of the fork, it is necessary to expand rigidly a piezoelectric tube serving the purpose of a dither [223]. The tuning fork and the tip vibrate in a plane parallel to the surface of the sample. As a consequence, the probe can approach the surface of the sample.



Fig. 3.13: Comparison of the probe scan on the sample surface at constant height (a) and constant distance (b) [224].

By using a servo-control, the tip can scan the surface by two different modes (see figure 3.13). When the tip scans at a constant height, it is easy to break the tip during the scan because sometimes the roughness of the sample is greater than the tip-sample distance (figure 3.13 a). Therefore, the second scanning method where the tip is at a fixed distance from the surface of the sample is performed (figure 3.13 b).

SNOM tips



Fig. 3.14: Apertured modes of operation: a) Illumination: the excitation comes from the probe and the emitted signal is collected by a micro-objective; b) Collection: the excitation takes place in the far-field in transmission and the probe plays the role of a collector; c) Illumination collection: the fiber both excites and collects the signal of sample; d) Reflection: the excitation is performed through the probe and the collection is obtained by reflection; e) Reflection collection: the excitation takes place in the far-field in reflection and the probe acts as a collector.

Two kinds of tips can be used: aperture and non-aperture (apertureless) ones. For the first ones, an optical fiber is thinned at its end down to tens of nm. The end can be metalized. The light then enters this submicroscopic aperture (see figure 3.14). The spatial resolution reaches 50 nm [225]. Aperture SNOM operation has the advantage of minimizing the noise source which is associated with the scattering from the adjacent areas. However, the heat and the bluntness of the metal-coated tips is the main drawback that makes it impossible to operate with the shear-fork distance lower than 5 nm to 10 nm from a surface [225].



Fig. 3.15: Apertureless tips: a) The excitation is focused in reflection at the end of the tip and the evanescent waves are detected in reflection or transmission. b) The excitation is made in transmission. c) Excitation by evanescent waves using a prism and collection in reflection [226].

In contrast, the probes used in the apertureless systems are very sharp nonmetallic tips (see figure 3.15). The advantage of the apertureless operation is the
high spatial resolution which decreases down to 10-20 nm [227,228]. They are used for many application such as field exaltation, Raman microscopy [229], measurement of photonic state density [230]. The resolution only depends on the apex size of the tip (typically 30-40 nm).

The last and most recent SNOM scheme is known as the "active tip" where the tip is functionalized with a single nanometric light source [18]. By using the nanoemitter source, the resolution does not longer depended on the size of the aperture (aperture tips) or the apex size of the tip (for apertureless systems). It is determined by the size of the emitter. The idea of an "active tip" dates from the 1990s and the first experimental image with an "active tip" was obtained in 2000 by the group of V. Sandoghdar [18]. The crucial point is to operate with a very photostable nano-emitter. Beyond a very good resolution, the "active tip" mode opens the way for new nano-optical studies with the possibility to control the position of a nano-emitter on photonic nanostructures at the nanometer scale.



Fig. 3.16: Principle of an "active tip": a fluorescent nanosource is attached to the apex of the tip. The angular spectrum of this source contains evanescent waves [231].

Experimental set-up of classical SNOM

In this chapter, I will present experiments performed on ordered hole gratings with an active near-field probe and in the last chapter classical SNOM experiments performed on disordered hole gratings. Figure 3.17 describes the classical aperture SNOM that I used to map the near electric field of our plasmonic structures. The commercial head of the SNOM is supplied by the "NTMDT" company and adapted to a inverted microscope (IX 71, Olympus). The tuning fork with a metal coated tip which has an aperture with a diameter of the order of 100 nm is used. The tuning fork is attached to a piezoelectric scanner to perform nanometric displacements in the three directions (x, y, z). In addition, the sample holder is connected to a second piezoelectric scanner with two axes of translation (x-y) which allows us the displacement of the sample in the horizontal plane. It is possible to move the sample or the tip. For this classical aperture SNOM, the collection configuration is used (figure 3.14). The excitation coming from the super-continuum source (SuperK EXTREME-white EXW 12) or from an Argon/Kr laser is focused on the sample



Fig. 3.17: Experimental set-up of the classical SNOM with a metallized tip.

by an air objective (Olympus-LMPLFLN50x) with NA = 0.5. Using the supercontinuum laser, we can excite the sample with a wavelength ranging from 400 to 850 nm, with very a narrow linewidth (FWHM of 1 nm). The evanescent field at the surface of the sample is collected in transmission by a metal coated optical fiber. At the output of the fiber, the signal is detected by an APD (TTi QL355). An analogto-digital converter is necessary between the APD and the SNOM electronics. The integration time of the converter can be adjusted from 200 ps to 1s. Before mapping the electric field, the tip is placed inside the focused spot laser. Then the tip is fixed in the region where the excitation beam is focused while the sample is moving in the (x-y) plane.

Experimental set-up of SNOM "active tip" operation

For the "active tip" configuration, we used a dielectric probe to collect the signal (figure 3.18). CdSe/CdS NC is the nano-emitter attached at the end of a tip functionalized with a polymer containing silanes and thiols to ensure a chemical bond between the tip and the NC. The techniques of fabrication for the tip and the mode operation to catch a single NC at the end of the tip were developed in our team and described in detail in the Rabeb Jazi's PhD manuscript [224]. After catching the NC, the tip is approached to the metallic structure. The "active tip" set-up offers the possibility to investigate the plasmon modes through the changes in the lifetime and intensity of the NC fluorescence at different positions on the structure.

The optical excitation of the NC is provided by a diode laser (LDH 405) emitting at 405 nm. The laser beam comes from an optical fiber and is deflected into the inverted microscope (IX 71, Olympus) by a dichroic mirror (560 nm edge BrightLine). As previously, the tip is centered on the focused point of the laser excitation. Due to the 1.5 refractive index of the fiber, most of the NC fluorescence gets into the



Fig. 3.18: Experimental set-up of a SNOM with a single NC acting as an active tip.

optical fiber and is next focused on the APD. A pass-band filter (center: 629nm, band-pass: 60 nm) in front of the detectors blocks the laser light in order to collect the NC fluorescence. The APD is connected to a counting card (National Instrument PCI-6602) and a photon counting card (TimeHarp 200 module, PicoQuant) that measures the time delay between the sample excitation by the diode laser and the arrival time of the emitted photon. To study the fluorescence of the NC for different positions on the hole grating, we used the mode for which the tip is fixed and the sample is moving in order to keep the tip always inside the spot laser during all the data acquisition.

3.4 Simulation and experimental results

3.4.1 Optical properties of the nanohole arrays in the far-field

The modification of the optical properties of the nanohole arrays with the hole diameter [232] and the periodicities [233] have been reported in many papers. Most of authors pay much attention to the transmission of the light through the hole arrays because of the enhance optical transmission (EOT) [179, 181, 234]. However, this specific mode only appears in very thick layers of metal (more than 100 nm [179]). For nanohole arrays built in thick metal layers, propagating plasmons appear inside the holes and change the transmission properties. Enhancement of the transmission can be observed. However, when the thickness of the metal layer is reduced down to the metal skin depth which is around 35 nm for gold, the LSP created by the holes plays a significant role in the near-field properties. In this case, the LSP resonance modes are associated to modes leading to a greater absorption [197]. Figure 3.19 displays the strong absorption in an ordered hole array (hole dimameter

100 nm and period 425nm) in comparison to a flat gold layer of the same thickness. Two absorption peaks associated to plasmon resonances can be observed with an absorption up to nearly 40 % for one resonance.



Fig. 3.19: Comparison of the absorption between a flat gold film and a ordered hole grating. Simulated by FDTD.

In order to couple efficiently the NCs to the nanohole gratings, we first identified the parameters of the hole grating for which the absorption peaks correspond to the wavelength emission of the NCs (620-630 nm). We performed FDTD simulations to analyze the dependence of the plasmon resonances with the grating parameters (thickness, periodicity and diameter of holes). The FDTD simulations do not give us directly the absorption spectra, but they can be deduced from the far-field transmission and reflection spectra which are described in section 3.1.



Fig. 3.20: Optical absorption spectra of 15x15 nano-hole arrays with circular holes (diameter of 150 nm, in a 58 nm gold film with different periodicities). Simulated by FDTD.

We first consider the influence of the spatial periodicity in figure 3.20. The diameter of the holes is 150 nm and the thickness of the layer is 58 nm, value that corresponds to the first experimental grating we studied. For periods ranging between 400 and 480 nm, two resonance peaks appear around 620 nm and 750 nm (figure 3.20a). This two resonances have the same behavior. When the period is varied, the resonance position tends towards the blue part of the spectrum when the period is decreased. This behavior is the same as the blueshift of the LSP resonance already reported by Kall et al. when increasing the hole density of nanohole arrays [193]. These resonances are due to a mixing between SPP and LSP created by the nanoholes. The evolution of the peak shape with the periodicity is different for the first and second resonance. While the intensity of the second peak remains constant, the height of the first peak decreases for longer periodicities. This peak also broadens. We can note here that in terms of coupling with NCs, the 425 nm periodicity is the best choice as it has a resonance around 620 nm. For a periodicity smaller than 400 nm, the absorption curves are shifted to the blue part and the first peak disappears (figure 3.20b). Only one resonance peak remains in the spectrum, which is the result of the blue-shift of the second peak of figure 3.20a.



Fig. 3.21: Optical absorption spectra of 15x15 nano-hole arrays with circular holes (periodicity of 425 nm). Simulated by FDTD Solution.

To get insight into the resonances observed by the absorption spectra, we analyze the influence of the size of the hole. The figure 3.21a displays the absorption for a grating with a period of 425 nm and a thickness of 58 nm for different sizes of the holes. The position of the first resonance does not change when the size of the hole is changed whereas the second peak shifts towards higher wavelengths when the hole diameter is increased. Only the second peak is influenced by the shape of the hole. As this peak is also influenced by the period of the grating, we can attribute this resonance to a coupling between LSP and SPP. The first peak is then attributed only to a SPP mode as it is not influenced by the shape of the hole.

The influence of the thickness has also been analyzed. The thickness does not seem to influence the absorption peaks for thickness higher than 50 nm. For lower wavelengths, the evolution of the absorption is very fast when the wavelength



Fig. 3.22: Comparison between simulated and experimental absorption spectra of 15x15 nano-hole arrays with circular holes with different diameters (periodicity of 425 nm, 58 nm gold film thickness).

changes. The absorption starts decreasing with the thickness and the peaks, mainly the first one, shift toward higher wavelength. In this behavior, we can see a transition and a value of the thickness close to the skin depth of gold.

To check the validity of the simulations and of the gratings we fabricate, we made reflection and transmission experiments with the set-up described in the previous section. On figure 3.22, we present the simulations of the absorption and the corresponding experiments made on a grating with a period of 425 nm and different sizes of the holes. These numerical simulations are qualitatively in good agreement with the experimental results in figure 3.22 with the same x axis range. The two absorption peaks are clearly observed even if we are limited by the white laser spectrum for the second one. As for the simulations, we observe that the first peak does not change with the size of the holes and that the second one shifts towards higher wavelengths when the hole diameter is increased. To end, the contribution of the hole diameter affects only the shape of the first resonance peaks. However, the experimental resonance absorption shifts 5 nm to the blue part comparing with the simulation. This could be explained by the thickness of the real film and the permittivity of the gold. With these simulations, we can find the good parameter of the grating in order to get the resonance at the same wavelength as the NC fluorescence.

3.4.2 Optical properties of the nanohole arrays in the near-field

It has been demonstrated that the nanohole acts as a nanoparticle [21–24, 193, 194]. The similarities between the LSPs structures (calculated by FDTD, see next section) of nanoholes and the ones of nanoparticles were already presented in figure 3.1. When two holes (or particles) are involved, the coupling field depends on the distance between them. In addition, the electric field distribution of a single hole (figure 3.1c) contains the SPP propagating to the surrounding flat gold film.



Fig. 3.23: Near electric field distribution of 15x15 ordered hole array (58 nm gold film thickness, periodicity of 425 nm and hole diameter of 150 nm). The electric field is mapped under three wavelengths of excitation: (a) 620 nm, (b) 700 nm, (c) 760 nm. Simulated by FDTD Solution.

In the previous section, we discussed the properties of the hole arrays in the far-field and analyzed the resonant peaks in the absorption curve corresponding to plasmon resonances. We now study the near electric field of the nano-structure. Figure 3.23 presents the near electric field of a hole array grating under three wavelengths of excitation: 620 nm, 700 nm and 760 nm. There are two wavelengths corresponding to resonant absorption in far-field ($\lambda = 620$ nm and 760 nm) and one is out of resonance regime ($\lambda = 700$ nm). With an excitation in the resonant regime, we observe a strong electric field located around the edge of the holes. The very weak fields are observed in the case of wavelength out of the resonance (figure 3.23b). The high fields are due to the plasmon excitation and these results are coherent with the far-field properties.

3.4.3 Coupling ordered hole grating with NCs

In the previous part, we highlighted the strong absorption peaks linked to SPP and LSP resonances. The absorption comes with particular near-field properties and strong fluctuations of the LDOS. To get insight into the near-field properties, nearfield simulations have been used. These near-field fluctuations are linked with LDOS variations. Besides, the coupling with NCs has been used. There are two different ways to couple the NCs with the hole gratings: depositing the NCs directly on the structure or using the "active tip" configuration of the SNOM to probe different positions on the grating.

Study the NCs fluorescence deposited on the grating by confocal microscopy

The CdSe/CdS NCs are once again deposited directly on the grating without any spacer by spin coating. The confocal microscope set-up presented in chapter 2 is used to study the fluorescence of the NCs on the ordered grating. Five different gratings have been investigated here. The experimental results are compared to absorption spectra and near-field distributions of the electromagnetic field. The gratings have been chosen in order to present different value of the absorption at 620 nm.

To vary the absorption, we modified the period of the grating. In order to get an absorption peak at 620 nm, the thickness of the layer and the diameter of the holes can be changed. The grating with the best absorption for the NCs has a period of 425 nm and a thickness of 38 nm (experimental thickness) and a hole diameter of 100 nm. To drastically change the absorption, we choose higher periods (620 and 590 nm). In this case, to keep an absorption peak around 620 nm, we can decrease the thickness down to 25 nm. The experiments will be compared to a flat gold film with the same thickness.



Fig. 3.24: Histogram of Purcell factors of single CdSe/CdS NCs coupled to an ordered hole grating (25 nm gold film thickness, periodicity of 590 nm). Two hole diameters are considered (a) 130 nm and (b) 200 nm.

Figure 3.24 first presents the histogram of Purcell factors of single CdSe/CdS NCs on the grating with a 590 nm periodicity for a hole diameter of 130 nm and 200 nm. The absorptions corresponding to these two gratings is presented on figure

3.25a and the near-field on figure 3.25c. We can see that the aborption is very low, a peak at 620 nm is still present for holes with a diameter of 200 nm but very weak and broad. For holes with a diameter of 130 nm, the peak is no more at 620 nm. The near-field image does not show strong near-field variations. Purcell factors are calculated with the neutral state as in the chapter 2 [235], the neutral state which has a lifetime around 60 ns when NCs are deposited on a glass coverslip.



Fig. 3.25: Absorption spectra (a) and near-field optical image (b, c) of an 15x15 ordered hole grating (590 nm periodicity, 25 nm gold film thickness). The polarization of the excitation is along the x axis.

For the smallest holes, for which the emission wavelength is out of the absorption, the same values of Purcell factors as for a flat gold are found. No effects of the grating are observed as we can expect from the absorption. The effect on the bigger holes is slightly stronger and expressed by some high Purcell factors (more than 25). The Purcell factors distribution broadens from 10 to 13 when the size of the hole increases. We can observe a slight influence of the grating but the effect is not very strong as the absorption peak is quite weak (see figure 3.25a). The enhancement of the decay rate depends on the position of the NCs on the grating. If the NCs is located at a position for which the electric field is strong, that is around the edge of the holes (see figure 3.25c), the modification of the lifetime is more pronounced. This explains the few higher Purcell factors we observe. But of course as the absorption is weak, the effect is weak.



Fig. 3.26: Histogram of Purcell factors for single CdSe/CdS NCs coupled with two ordered hole gratings (25 nm gold film thickness, periodicity of 620 nm). Two hole diameters are considered: (a) 130 nm and (b) 250 nm.

The same kind of behavior is observed for the periodicity of 620 nm and two hole diameters, 130 nm and 250 nm. The biggest hole presents the highest Purcell factors which can reach 30 (figure 3.26b). Some NCs exhibit low Purcell factors (around 4) less than the Purcell factors on flat gold (figure 3.26 a and b). As the holes are quite big, this may correspond to NCs inside the hole where there is no effect of the resonance at 620 nm (see figure 3.27c). In the comparison with periodicity of 590 nm, we observe stronger effects based on the higher absorption in figure 3.27a (16%). It leads the Purcell factors of NCs on periodicity of 620 nm reaching 25 and more than 30 for the hole size of 130 nm and 250 nm respectively.

Let us now observe what happens when the absorption is stronger. For this, we tune the periodicity to 425 nm and increase the layer thickness to 38 nm. The high absorption (nearly 40 %) at the wavelength emission of CdSe/CdS NCs is shown in figure 3.29a. On the figure 3.29b, we observe a stronger electric field than previously.



Fig. 3.27: Absorption spectra (a) and near-field optical images (b, c) of two 15x15 ordered hole gratings (periodicity of 620 nm, 25 nm gold film thickness). Two hole diameters are considered: 130 nm or 200 nm.

Figure 3.28 exhibits a obvious effect of the grating on the Purcell factors. The Purcell factors are higher. A mean value of 16 is found for Purcell factors on the grating compared to a mean value of 10 on the flat gold layer. The Purcell factors are in agreement with the absorption spectra and the near-field images.

This comparison between 5 kinds of periodicities and hole diameters shows that the best coupling is achieved for the periodicity of 425 nm and the thickness of 38 nm. Therefore, this grating will be the starting point of the disordered structures studied in the next chapter.

To study more precisely the distribution of the near-field on this grating, we now used the "active tip" mode operation of the SNOM.

Coupling with the NCs at the end of the tip

Confocal microscopy experiments as presented before can only give a statistics of the Purcell factors and then an idea of the LDOS variations. To get more precise



Fig. 3.28: Histogram of Purcell factors for single CdSe/CdS NCs coupled to an ordered hole grating (38 nm gold film thickness, periodicity of 425 nm, hole diameter of 100 nm).



Fig. 3.29: (a)Experiment absorption spectra and (b) near-field optical image (Simulated by FDTD) of an 15x15 ordered hole grating (periodicity of 425 nm, 38 nm gold film thickness, hole diameter of 100 nm).

information the position of the NC on the grating has to be controlled. For this we performed SNOM experiments with the NC at the end of the SNOM tip. These experiments have been performed when the NC fluorescence is at the same wavelength as the resonance peak of the grating. It means that the grating with periodicity of 425 nm in 38 nm of thick gold is a good sample for this coupling.

Figure 3.30 presents the near reflected electric field for the grating at the resonance SP wavelength, considering different distances to the surface. We observe a very fast modification of the electric field with z. The transition is observed around 30 nm above the surface. The strongest intensity locations generated by LSP are also mainly distributed at the edges of the holes for short distances to the surface, whereas they move to the space between holes when z is greater than 40 nm.

Simulations show that we can consider three characteristic positions on the sample: inside the hole, at the edges of the hole and between the holes, and this for



Fig. 3.30: Electric fields reflected by an ordered nanohole array and observed at different distances from the surface (periodicity of 425 nm, hole diameter of 100 nm, etched in a gold film with a 38 nm thickness). The incident wavelength is 630 nm at resonance absorption of the grating. Simulated by FDTD.

different z.

Concerning the measurements, we have caught two NCs at the end of the SNOM tip. As shown below, the first NC has the *c*-axis parallel to the surface, one dipole in the surface plane and the other perpendicular to the surface. For the second one, the angle between the *c*-axis and the vertical is close to 40° .

NC_1 -c-axis parallel to the surface

Due to their respective orientation, the interaction with the surface will be then different for the two NCs and we have then to consider the near-field distribution of the different components of the electric field E_x (or E_y) and E_z .

After catching the CdSe/CdS NC at the end of the SNOM tip, we made lifetime measurements at different z on a flat gold sample to determine the orientation of the dipole of the NC on the surface. These measurents are compared to the theoretical curved obtained by calculater. The determination of the c-axis is done by the procedure developed successfully during the PhD of Rabeb Jazi [224]. The first NC presents the experimental Purcell factors close to the blue curve corresponding to theoretical calculations for the case of a c-axis parallel to the surface (figure 3.31). Therefore, the NC has a dipole parallel to the surface and an other perpendicular to the surface. For this configuration, we plotted on Figure 3.32 the E_x and E_z electric field components which affect the radiative lifetime (Purcell factor) of the NC. We observe that the distribution of these two components is very different. The E_x component of the electric field is stronger inside the hole where as the E_z has its maximum at the edge of the hole.



Fig. 3.31: Theoretical curves for the Purcell factor as a function of the distance z for a c-axis parallel to the surface (blue curve) and perpendicular to the surface (red curve), simulated for a flat gold film of 38 nm thickness. The green curve corresponds to the case of a 35° angle of the c-axis with respect to the vertical.

Figure 3.33 shows the Purcell factor of the NC at three characteristic positions on the hole grating: inside the hole, in between holes and at the edge of the hole. We found that the Purcell factors at the edge of the hole are higher than between holes and inside a hole. In comparison with the FDTD simulation, this behavior is caused by the strong localized electric field around the hole, similar to the E_z component of the electric field in figure 3.32b. The component in the plane has less influence than the component perpendicular to the plane of the surface in this case as illustrated by the map of the total electric field. The Purcell factors are in agreement with the fact that the field is concentrated around the holes. Moreover when the distance to the surface increases the Purcell factors at the three positions get close to a same value which is in agreement with the evolution of the electric field with z deduced from the FDTD simulations.



Fig. 3.32: Square modulus of E_x , E_z components and of the total electric field at 30 nm from the surface, simulated by FDTD.



Fig. 3.33: Purcell factors of the NC1 as a function of z for different position on the hole grating.

NC_2 -c-axis with a 40° angle with respect to the vertical

We performed the same measurements for the second NC. The adjustment of the Purcell factor on the continuous gold is presented in figure 3.34. The experimental data lie in between the curve corresponding to a parallel *c*-axis and a perpendicular



Fig. 3.34: Theoretical curves Purcell factor of NC as a function of distance z for a c-axis parallel to the surface (blue curve) and perpendicular to the surface (red curve), simulated on a flat gold of 38 nm thickness. The green curve corresponds to the case of a 40° angle of the c'-axis with respect to the vertical.

c-axis indicating an angle of 40° of the *c*-axis with respect to the vertical *z* axis. In this case, we expect a lower influence of the *z* component of the electric field. Figure 3.35 presents the near-field distribution for each component and the total field. We expect mixing of E_x and E_z on the NC fluorescence.



Fig. 3.35: Square modulus of E_x , E_z components and of the total electric field at 20 nm from the surface, simulated by FDTD.

Figure 3.36 represents the Purcell factors for the NC_2 in three positions. The Purcell factor close to the edge is still a little bit higher but not as much as in the previous case. This is in agreement with the fact that the NC dipole has a lower component in the z direction than the first NC. FDTD calculates strong electric field both at the edge and inside the hole.

3.5 Conclusion

In this chapter, we focused on designing and characterizing the optical properties of ordered hole gratings. It is the first step to understand the properties of the hole



Fig. 3.36: Purcell factors of the NC_2 as a function of z for different position on the hole grating.

grating and the background for the further study of disordered holes. We described in detail the numerical simulation methods (FDTD) to numerically calculate the optical properties of the plasmonic structures that we used. The simulation pointed out that the thickness of the metal film and the periodicity of the grating play an important role in the absorption resonance wavelength. These resonances are due to a mixing of SPP and LSP. On the other hand, the FDTD simulation allows us to map the total field or field components at different height above the plasmonic structure. Two kinds of experiments were performed in order to get the optical properties of the ordered hole arrays in the far-field (using inverted microscope) or in the near-field (using SNOM). There is a good agreement between the simulations and the experimental results. The coupling of two individual NCs at the end of the SNOM tip with the grating demonstrated that strong electric fields are observed on the ordered grating. In the next chapter, we will investigate the modification of this coupling when a controlled disorder is introduced.

DISORDERED HOLE GRATING

In 1958, P. W. Anderson predicted the unusual transport properties of disordered materials leading to the so-called Anderson localization phenomenon [236]. In a first approach, the origin of this unusual localization is the wave interference between multiple-scattering paths induced by defects in the solid [237–241]. In the field of optics, localization of the electromagnetic field has been investigated in two-dimensional disordered structures by many groups [242–245].

More specifically, we have seen in chapter 2 that metallic semi-continuous films close to the percolation threshold present light localization in sub-wavelength areas ("hot" spots). As reported by several papers, this localization strongly depends on excitation conditions. Different optical regimes can also exist like scattering regimes, or localized and delocalized plasmons resonances. The disorder also leads to the broad spectrum of plasmon resonances.

Recently, it has been also shown that the FDTD approach is an appropriate and powerful tool to study the disordered metal films [246–248]. The hot spots and even the full vectorial structure of the electromagnetic field on a real 3D topography measured by AFM can be determined [249]. The electromagnetic field exhibits a very complex structure depending on many parameters such as the polarization and the wavelength of the incident light. It also changes strongly when moving few nanometers away from the surface. Experimentally, semi-continuous films can be obtained by thermal evaporation or sputtering. The position and shape of the gold nanoparticles is then random. Hence, the amount of disorder is difficult to control and quantify. Additionally, the optical behavior of this sample is hard to predict.

In the previous chapter, we discussed the optical properties of ordered structures. In the case of hole gratings, we could determine the plasmon resonances and the electric field distributions. In contrast with semi-continuous gold films, in this chapter we are going to generate disorder starting from a periodic arrangement of nanoholes in order to control the amount of disorder of the sample which is not possible with semi-continuous gold films.

There are many ways to create the disordered hole grating. A Gaussian distribution for the hole displacement [55,250–254], a random-walk method starting from a perfect periodic arrangement [255] or a radial distribution function [103] can be used.

In this chapter, we present the results we obtained numerically and experimentally about the optical properties of disordered holes gratings with increasing disorder using a Gaussian distribution. The characterizations in the near-field and far-field are provided by complementary approaches (FDTD, SNOM, absorption spectroscopy, statistical analysis of the intensity distribution). The influence of the

4.

disorder but also of the gold layer thickness and starting hole periodicity are demonstrated. Finally, the variation of the plasmon resonances is investigated through their coupling with CdSe/CdS NCs.

4.1 Controlling the disorder by a Gaussian distribution

Starting from an ordered grating, the holes are moved out from their original positions in random directions with random distances following a Gaussian statistics. The disorder level of the hole grating only depends on the standard deviation (σ) of the Gaussian function. Figure 4.1 shows an example of a disordered hole structure generated by this procedure.



Fig. 4.1: Example of a disordered configuration. Starting from an ordered hole arrays (black circles), the disordered grating is represented by red circles.

The original position (X_0, Y_0) becomes:

$$X = X_0 + rand_x \times a \tag{4.1}$$

$$Y = Y_0 + rand_y \times a \tag{4.2}$$

where $rand_x$ and $rand_y$ are normally distributed random number with a zero mean value and a is an unitary standard deviation. a characterizes the magnitude of the displacement of the holes and the amount of disorder for the final structure. To

avoid many overlaps between holes, the displacement of the holes has to be less than the periodicity of the ordered structure. It means that a must be less than a haft of periodicity. The moving distance of the holes is given by:

$$d = \sqrt{\left(X - X_0\right)^2 + \left(Y - Y_0\right)^2} \tag{4.3}$$

It can be shown that the Gaussian distribution of the holes displacement is given by [256]:

$$f(d) = \frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(d-m)}{2\sigma^2}} \tag{4.4}$$

where m is the mean value of the moving distance and σ is the standard deviation of the Gaussian distribution. The disorder level is determined by the parameter δ which is defined by the ratio [55]:

$$\delta = \frac{\sigma}{p} \tag{4.5}$$

where p is the periodicity of the ordered hole grating we start from. In the study concerning the disordered holes, two periodicities (280 nm and 425 nm) were used to define the initial configuration of the disordered structure that consists in a matrix of 15x15 holes. The parameter δ ranges between 1% and 19%.

Figure 4.2 presents some examples of the first kind of disordered hole gratings. The starting ordered hole arrays has a periodicity of 425 nm. Each hole has a diameter of 100 nm and the thickness of the gold film is 38 nm. The disordered level δ takes eleven values in the range [1.5%, 10%]. The statistical distribution of the moving distances from the initial configuration is shown in figure 4.3, where the distance distributions are well fitted by Gaussian profiles. The random holes have been generated for moving distances ranging between 10 nm and 400 nm. For the high disorder levels, some holes overlap occurs. For values of δ larger than 13%, we find that the fraction of nano holes with an overlap is between 1.7 % and 4 %. These value are calculated by counting the overlap holes of real sample from the FIB images.

The second type of disordered hole gratings exhibits a shorter original periodicity of 280 nm, holes diameter of 150 nm etched in a 25 nm thick gold film. Figure 4.4 presents the eight disordered hole gratings generated from this initial ordered configuration. The statistical distributions of the moving distances are shown in figure 4.5. Because of the shorter periodicity, the moving distances of the second type has to be shorter than for the first type but also corresponds to high disorder level δ , up to 19 %. The random holes have been generated for moving distances from 10 nm to 250 nm. The percentage of the holes overlap in this second type is higher (between 2 % and 16 %) since the hole size is larger with respect to the periodicity. These value are calculated by counting the overlap holes of real sample from the SNOM images.



Fig. 4.2: Images of 15x15 disordered hole arrays with a hole diameter of 100 nm fabricated in a 38 nm thick gold film. They are obtained by Scanning electronic microscopy (SEM) and the gratings are made by ion beam etching in ILM. The original ordered hole grating has a periodicity of 425 nm.



Fig. 4.3: Gaussian distribution of the nano-hole moving distances for eleven values of disorder δ .



Fig. 4.4: Images of 15x15 disordered hole gratings obtained by SNOM. The hole diameter is 150 nm an the gold film thickness is 25 nm. The ordered hole grating has a periodicity of 280 nm.



Fig. 4.5: Gaussian distribution of the nano-hole moving distances for eight values of disorder δ .

4.2 Near-field simulation by FDTD Solution

To characterize the optical properties of the disordered hole gratings, FDTD simulations with different monitors at different heights were first carried out to map the near electric field. In this section, the goal is to observe the evolution of the near-field distribution of the electric field with disorder. As for the random gold films, we expect to have near-field localization that depends on the incident wavelength and of course on the amount of disorder. So we will study the influence of δ and λ on the near-field distribution. The effect of the sample thickness will also be taken into account.

4.2.1 Influence of randomness to the near-field distribution

Using the FDTD Solution software, we can explore the field distribution at a given incident wavelength. For the simulation, the excitation plane wave is incident from the bottom of the sample and normal to the surface. The electric field of the incident wave is polarized along the x axis. The monitors are placed at the near-field to record the transmitted signal.

Figure 4.6 shows the distribution of the transmitted near electric field at 30 nm from the film. The disordered gratings are generated from an initial ordered hole array with a thickness of 38 nm, a periodicity of 425 nm and a hole diameter of 100 nm. The incident wavelength excitation is 730 nm and does not correspond to any plasmon resonance of the ordered grating as presented in the previous chapter. On the ordered hole arrays, the electric fields are weak and are confined around the edges of the holes. This resonance has been attributed to the coupling between the LSPs of the nanoholes. There are marginal electric fields in the gold between holes. When the disorder of the hole grating δ increases, "hot" spots appear inside and



Fig. 4.6: Distribution of the near-field intensity with increasing values of the disorder δ for an excitation wavelength of $\lambda = 730 nm$. The transmitted near electric field is plotted at 30 nm of the disordered holes (hole diameter of 100 nm, gold film thickness of 38 nm). The ordered hole grating has a periodicity of 425 nm. Simulated by FDTD Solution.

around the spaces of some local holes (figure 4.6 c-f). Moreover, there are also fields in between holes.

Figure 4.7 describes the evolution of the maximum near-field intensity as a function of the disorder δ . The field intensity has been renormalized by the intensity of the ordered grating. We can observe that this value increases as the disorder increases an compared with the ordered structure, the maximum electric field of the most disordered holes ($\delta = 19\%$) can be up to four times higher.



Fig. 4.7: Maximum near-field intensity of the hole grating as a function of the disorder δ . The incident wavelength is 730 nm. The maximum intensity of disordered hole is normalized by the maximum intensity of ordered hole grating.

To analyze these results, we also determined the intensity statistics from the data of the optical images in the near-field. The PDF which is describes in detail in section 2.1.3 is defined as the histogram of the intensity.

Figure 4.8 shows the PDF distributions for three values of δ : 0 %, 9 % and 16 %. The PDF calculation is in good agreement with Gaussian profiles. For the ordered hole ($\delta = 0$ %), the intensities are centered around a small mean value. When the disorder increases, the intensities reaches high values with a long tail tending to Log-normal fits. The long tail of the distribution curve corresponds to the intensity of the "hot" spots in the optical images [249]. This evolution of the PDF intensity can be compared to the evolution observed on the random structure when starting out of plasmon resonances and entering the plasmonic regime with the apparition of "hot" spots.

The second type of disordered hole gratings exhibits a shorter original periodicity of 280 nm, holes diameter of 150 nm etched in a 25 nm thick gold film. The near-field PDF distribution of this type presents more "hot" spot than the grating generated from periodicity of 425 nm (figure 4.9).



Fig. 4.8: Probability Density Function (PDF) of the near-field intensity under excitation wavelength of 730 nm for three disordered hole gratings etched in a 38 nm gold film (hole diameter of 100 nm). The initial ordered hole grating has a periodicity of 425 nm.



Fig. 4.9: Near-field PDF distribution of two disordered types which are generated from two ordered gratings with periodicity of 425 nm (type1) and 280 nm (type2). The hole is etched in a 25 nm of gold film.

4.2.2 Near electric field distribution with different excitation wavelengths

In this part, we choose the maximum disorder ($\delta = 19\%$) and analyze the influence



Fig. 4.10: Increase of the intensity of the transmitted near-field at 30 nm above the disordered holes ($\delta = 19\%$, hole diameter of 100 nm, 38 nm thick gold film).

of the incident wavelength. The maximum intensity of the near electric field for this grating is plotted versus the wavelength λ on figure 4.10. We observe that this intensity starts drastically increasing from 550 nm to reach a maximum value around 730 nm. This increase with the wavelength has already been observed for the semi-continuous gold films [160, 249].

Figure 4.11 shows the intensity distribution of the transmitted electric field at 30 nm from the film for different wavelengths and a disorder $\delta = 19\%$. In the right column, the PDF of the intensities were plotted. The optical images mapped for short wavelengths of 400 and 500 nm (figure 4.11 a and c) show very weak fields concentrated inside the holes, whereas the ones performed for wavelengths larger than 620 nm present localized areas with strong intensity field enhancements (figure 4.11 e and g). The maximum plasmonic intensities are observed in areas around the holes or in between holes which are very closed together. In the metal areas between holes, the intensity amplitudes are weaker. For a higher wavelength (730 nm), fields are even more localized with higher intensity. As already mentioned, when the excitation wavelength increases, the distribution of the intensities tends to the Log-normal law [167].

4.2.3 Contribution of thickness

In contrast with perforated thick opaque metal films showing extraordinary transmission, three different papers reported that less light is transmitted through very thin semitransparent metallic films that are perforated [190–192]. It means that the thickness of the metallic film always plays a significant role in the absorption of nano-holes arrays. In chapter 3, FDTD simulations already demonstrated the effect of the thickness of the gold film in the far-field. In this section, we discuss about the effect of the thickness in the near-field. As in the discussion in section 4.2.2 about the effect of the incident wavelength, we calculate the structure of the near electric fields for various wavelengths. We map the near-field distribution for two thicknesses (38 nm and 25 nm) for a short wavelength of 400 nm (figure 4.12) and



Fig. 4.11: Distribution of the near-field intensities for different excitation wavelengths (left column) and PDF of the intensities (right column). The transmitted near electric field is calculated at 30 nm from the disordered holes $\delta = 19\%$ (hole diameter of 100 nm, 38 nm gold film).



Fig. 4.12: Comparison of the near-field distribution for 38 nm and 25 nm thicknesses. The transmitted fields are mapped at 30 nm from the film. The excitation wavelength is 400 nm.



Fig. 4.13: Comparison of the near-field distribution for 38 nm and 25 nm thicknesses. The fields are mapped at 30 nm above the holes for an excitation wavelength of 650 nm.

long wavelengths of 650 nm (figure 4.13) and 740 nm (figure 4.14). In the case of the short excitation wavelength, the electric fields are only concentrated inside the holes



Fig. 4.14: Comparison of the near-field distribution for 38 nm and 25 nm thicknesses. The fields are mapped at 30 nm above the holes for an excitation wavelength of 740 nm.

for both thicknesses. The thickness does not play any role on the field localization for short values of λ . For the intermediate wavelength when λ is equal to 650 nm, the fields start to be localized and some differences between two thicknesses start to appear. Nevertheless, some "hot" spots remain stable but they are more pronounced for the thicker layer. The difference becomes more striking for 740 nm. Even if few "hot" spots are visible for the two thicknesses, the other are quite different.

4.2.4 Effect of the number of holes

In this section, we study the effect of the number of holes on the field distribution. The main question is: what is the influence of long range interactions in this kind of disorder?. For a given disorder, the influence of the number of holes considered for the simulation on the near-field structure is studied in this section. Starting from an initial disordered hole grating of 5x5 holes, we add gradually holes around the 5x5 holes area and study the modification of the electric field in the area of the 5x5 holes. We consider four kinds of disordered hole gratings in the comparison: 5x5, 10x10, 20x20 and 30x30 holes structures.



Fig. 4.15: Effect of the holes number on the near-field distribution for an excitation wavelength of 400 nm.



Fig. 4.16: Effect of the holes number on the near-field distribution for an excitation wavelength of 730 nm.

The simulation for the ordered hole grating were carried out for short and long excitation wavelengths (section 4.2.2). Therefore, we investigate the near-field distribution for two excitation wavelengths: short excitation of 400 nm(figure 4.15) nm and long excitation of 730 nm (figure 4.16). While for the short excitation wavelength, no "hot" spots are observed, the longer excitation wavelength results in the generation of some "hot" spots specifically near the boundary of the studied area of the 5x5 holes. In parallel, at 400 nm, the near-field distribution remains unchanged whatever the size of the disordered holes structure. At 730 nm, it is clearly modified between 5x5 holes and 10x10 holes.

In figure 4.17, we represent the ratio of the intensities obtained for the areas of 10x10 and 5x5 hole gratings to quantify the modification of the near-field. With the short wavelength of 400 nm, we get that the ratio lies between 1 and 1.5, that means the intensity remains nearly constant (figure 4.17a). On the contrary, a significant change is observed for the ratio of the intensity at 730 nm. It is up to more than 4 (figure 4.17b). The "hot" spot regions in figure 4.17b display the changes induced by the modification of the region size. We clearly see that some "hot" spots remain stable for the two sizes but the other don't. We could think that the first ones are only due to the resonance coming from the distance between holes whereas the other ones come from longer range interactions. But this influence of longer range interactions is stronger for longer wavelengths. Nevertheless, no difference are observed for a larger number of holes with 740 nm.



Fig. 4.17: Ratio of the near-field intensities obtained for the 10x10 and 5x5 holes structures in the studied area for 400 nm and 730 nm excitation wavelengths.

However, for the hole grating of 20x20 and 30x30 holes, the distribution of the electric field does not change.

4.2.5 Statiscal analysis: autocorrelation function of the intensity

As already mentionned in chapter 2, previous studies in the group have proved that the 2D-autocorrelation function (ACF) of the intensity is a very efficient tool to identify the different regimes of the interaction between the electromagnetic field and a semi-continuous metallic surface [161, 168, 257].



Fig. 4.18: a. $\delta = 0\%, \lambda = 400 nm$, b. $\delta = 0\%, \lambda = 690 nm$, c. $\delta = 16\%, \lambda = 500 nm$, d. $\delta = 16\%, \lambda = 730 nm$

In this section, we calculate the ACF for the gratings with an original periodicity at 425 nm, 150 holes diameter and 25 nm gold thickness. Figure represents the obtained results for different values of δ and excitation wavelengths λ . The incident polarization is along the x axis. In figure 4.18.a ($\lambda = 400nm$, $\delta = 0\%$), the ACF exhibits a high periodicity corresponding to the one of the grating. Its maximum is very close to 1 that illustrates that the field is homogeneous. In this case, the incident light is only scattered by the grating. When a plasmonic resonance of the grating is excited (figure 4.18.b, $\lambda = 690$ nm, $\delta = 0\%$), the ACF reaches higher values (~ 1.15).

In the case of high disorder $\delta = 16\%$, different regimes are also evidenced. For $\lambda = 500$ nm (figure 4.18.c), diffusion by the holes is mostly observed so the correlation keeps very low values (less than 1.01). The ACF decreases due to the disorder and remains anisotropic. When the incident light generates strong "hot" spots ($\lambda = 730$ nm), only a central peak mostly isotropic with a high value (1.16) is observed (figure 4.18.d).

In order to characterize the evolution of regimes with the disorder (δ), and the excitation wavelength, we plotted the maximum value of the ACF for 4 excitation wavelengths ($\lambda = 590$ nm, 640 nm, 690 nm, 730 nm) and 5 disorder levels ($\delta = 0\%$, 3%, 6.5%, 13% and 16%). For small values of δ , the maximum value is reached



Fig. 4.19: Maximum value of the ACF for 4 excitation wavelengths ($\lambda = 590$ nm, 640 nm, 690 nm and 730 nm)

when λ is close to one absorption peak of the grating. In contrast, for higher values of δ , the different curves show the increase of the height of the ACF peak with the excitation wavelength λ . Except for $\lambda = 590$ nm, the increase of δ also results in the increase of the height of the central ACF peak which highlights the growing role played by the "hot" spots with the increase of λ and δ . These results are also in agreement with the ones obtained for semi-continuous films.

4.3 Measurement of the absorption spectra

The first optical measurements concern a global property in the far-field of the structures that is the absorption spectrum. The transmission (T) and refection (R) measurements in far-field are described in detail in section 3.3.1 of chapter 3. The absorption of the hole grating is deduced from: $A(\lambda) = 1 - T(\lambda) - R(\lambda)$. Figure 4.20 displays the absorption of the disordered hole gratings in the far-field for a gold thickness of 38 nm.

In the case of the ordered grating, there are two absorption resonance peaks appearing at 610 nm and 740 nm with significant values up to 40 %. This result is qualitatively in good agreement with the simulations. The 40 % absorption peaks are slightly blue shifted (20 nm). This can be explained by the thickness of the gold layer. It has been measured by a profilometer and the value of 38 nm cannot be taken without a 10 nm incertainly. The real thickness is certainly slightly thicker because the peak shifts very quikly to the blue part as the thickness increases. When the disorder δ increases, the curve is modified. We observe a decrease of the absorption values between 610 nm and 740 nm. The two peaks still exist for the low disordered levels ($\delta < 10\%$ in figure 4.20 b, c and d). The peaks broaden and their amplitude is reduced but remain above 30 %. For the highly disordered gratings ($\delta > 13\%$ in figure 4.20 e, f, g and h), the curves become flat but the absorption reamains arounds 30%. As for the semi-continuous films, the new resonances appear and broaden the absorption curve [160, 174, 258].


Fig. 4.20: Absorption spectra of 15x15 disordered hole gratings with hole diameter of 100 nm, 38 nm gold thickness. The disorder δ ranges between 0 % and 19 %. The ordered grating has a periodicity of 425 nm.

4.4 Experimental optical properties in the near-field

The near-field intensity on the sample is collected by a metallic coated tip with a submicroscopic aperture of 100 nm diameter. The excitation is in the far-field while the SNOM is in transmission mode (the setup is described in detail in section 3.3.2). Using the super-continuum laser as the optical excitation, we can map the near electric field of the hole grating for wavelengths in the whole visible range. The resolution of the experiments varying from an experiment to the other depends on the quality of the SNOM tip. The best resolution we obtained is roughly around 100 nm. In this manuscript, we present only the experimental results with this resolution in order to make the comparison between them.

In this section, we study the structures previously investigated by FDTD, that is the disordered hole gratings which are generated from ordered hole gratings with periodicities of 425 nm. Besides, we compare the results obtained for gold thicknesses of 38 nm and 25 nm and the same disorder. Next, the effect of the number of holes is also considered. Finally, the modification of the ACF with the disorder δ and excitation wavelength λ are analyzed.

4.4.1 Impact of the disorder level

The effect of disorder on the near-field distribution is investigated firstly on disordered gratings generated from an ordered holes array with a 425 nm periodicity, a hole diameter of 150 nm and a gold thickness of 38 nm. Figure 4.21 presents the distribution of the transmitted near-field for an incident wavelength of 647 nm. The absorption spectra of these gratings are presented on figure 4.20. The excitation of 647 nm is out of the plasmon resonance for the ordered grating. The excitation is performed by an Kr/Ar laser source.

In the ordered hole grating (figure 4.21a), the electric field distributes evenly the whole grating with a weak intensity because the excitation source is completely out the resonant peak (see figure 4.20a). It seems that the field only locates inside the hole. When the disorder increases, as expected from simulation, there are some "hot" spots appearing with higher intensities (figure 4.21 b - f). As soon as a slight disorder induced the change of the field distribution. When the disorder increases, the energy gets more localized and the "hot" spots get stronger. Plasmon resonances appearing for this wavelength are expected from the simulations.

The effect of disorder on the near-field distribution is also investigated on the second series of disordered gratings generated from an ordered holes array with a 425 nm periodicity, a hole diameter of 150 nm and a gold thickness of 25 nm. Figure 4.22 presents the distribution of the transmitted near-field for an incident wavelength of 740 nm performed by the super-continuum laser. In the ordered hole arrays, the electric field with a low intensity covers evenly the whole grating (figure 4.22a). The simulation in section 4.2.1 shows that the field distribution is located around the edges of the holes. However, the low resolution of the metallic coated tip (around 100 nm) does not allow us to evidence the precise intensity around the holes in the optical images. When the degree of disorder of the hole grating increases, more and more "hot" spots appear with a higher intensity (figure 4.22 b - f). Figure 4.23 describes the increase of the near electric field intensities versus the parameter



Fig. 4.21: Distribution of the transmitted near-field mapped by the SNOM at $\lambda = 647nm$ for a disorder increasing from 0 % to 14 %. The disordered holes have a diameter of 100 nm and the gold thickness is 38 nm. The initial ordered grating has a periodicity of 425 nm.

 δ . The experimental data (black curve) has the pattern obtained with the FDTD simulations (red curve), demonstrating the good agreement between simulations and experiments.

In addition, the PDF of the measured intensities is well fitted by the profiles deduced from the simulations (figure 4.24). For the ordered hole ($\delta = 0\%$), the intensities are centered around a very low mean value with a Gaussian distribution. When the disorder increases ($\delta = 9\%$ and 16%), the intensities tend towards higher values and the PDF shows a long tail. The Gaussian profile disappears in the case



Fig. 4.22: Distribution of the transmitted near-field mapped by the SNOM at $\lambda = 740nm$ for a disorder increasing from 0 % to 16 %. The disordered holes have a diameter of 150 nm and the gold thickness is 25 nm. The initial ordered grating has a periodicity of 425 nm.

of disordered hole. As expected, the long tail of the distribution curve describes the intensity of the "hot" spots in the optical images and tends to Log-Normal distribution [174].



Fig. 4.23: Normalized near-field intensity of the hole grating as a function of δ . The ordered hole grating has a periodicity of 425 nm. The hole diameter is 150 nm and the gold film thickness is 25 nm. The incident wavelength is 740 nm.



Fig. 4.24: Comparison between experiments and simulations for the Probability Density Function (PDF) of the near-field intensity. The excitation wavelength is 740 nm. The three disordered arrays are built in a 25 nm gold film with holes of 150 nm diameter. The initial periodicity is 425 nm.

4.4.2 Effect of excitation wavelength on the near-field distribution.

Using the super-continuum laser and a laser diode, we can excite the hole grating with wavelengths ranging from 405 nm to 750 nm with a narrow 2 nm bandwidth. Figure 4.25 shows the intensity distribution of the transmitted near-field for different wavelengths and a highly disordered grating ($\delta = 16\%$, initial periodicity of 425 nm, hole size of 150 nm, and gold thickness of 25 nm). The PDF of the intensities is also plotted (right column). The optical image mapped at a short wavelength of 405 nm performed by a diode laser(figure 4.25a) shows very weak intensities with a normalized value around 1.6. In contrast, the images performed at longer wavelength (590 nm, 620 nm and 740 nm) present localized areas with stronger intensity enhancements (figure 4.25 c, e and g). Respectively, normalized intensities of 2.6, 3 and 5.9 are measured.



Fig. 4.25: Distribution of the transmitted near-field mapped by SNOM and PDF of the intensity for different excitation wavelengths. The disorder is $\delta = 16\%$, the hole diameter is 150 nm and the film has a thickness of 25 nm.

The PDF profiles of the experimetal data is in agreement with the simulation profiles. The PDF curve for the short wavelength (405 nm) is well fitted by a Gaussian distribution. When the excitation wavelength increases, the distribution of the intensities broaden and tend to the Log-normal law [167].

The maximum intensity of the near electric field for this grating is then plotted versus the wavelength λ on figure 4.26. The maximum intensities are normalized with the maximum intensity of the ordered grating. We observe the highest intensity when the wavlength increases. This increase with the wavelength is quite in agreement with the simulations and has already been observed for the semi-continuous gold films [160, 249].



Fig. 4.26: Max intensity of near-field as a function of wavelength in disordered hole $\delta = 16\%$, the hole diameter of 150 nm in 25 nm of thick gold film.

As we can see on the previous pictures, the position of the "hot" spots for different wavelengths is presented. To consider more precisely the evolution of the position of these "hot" spots, we made the measurements with the supercontinuum laser every 20 nm. Figure 4.27 presents the optical images of the disordered hole grating with $\delta = 14\%$. There are some "hot" spots that remain stable. However, it exists some "hot" spots appearing or disappearing when the wavelength increases. The *number* 1 lasts for a wide range of wavelength. It exists for 590 nm and only starts disappearing around 750 nm. The same behavior is observed with number2that starts decreasing around 730 nm. These two "hot" spots remain strong for a wide range of wavelengths. Other "hot" spots are less resistant with the wavelength such as *number3* and *number4*. That means that the wavelength bandwidth to excite the "hot" spot is quite broad (around 100 nm). Of course this study has to be done quantitatively and will be done. However, it is not easy because the images are randomly spatially shifted from one wavelength to the another. Additionally, the renormalization of intensity from one wavelength to another one is not obvious neither. Nevertheless, this qualitative study shows a particular behavior of the system. The "hot" spots are more resistant to the wavelength change than for the random structures for which the bandwidth of the "hot" spots is narrow.



Fig. 4.27: Appearance of the "hot" spots due to the wavelength excitation. The disordered hole grating ($\delta = 14\%$) is generated from the ordered hole grating with periodicity of 425 nm and hole size of 150 nm in a 25 nm of gold film.

4.4.3 Effect of the gold film thickness

In the theoretical part, we studied the influence of the thickness on the near-field distribution. We observed that the near-field distribution is more and more different as the wavelength increases. Unfortunately the images mapped with higher wavelengths by the super-continuum laser do not have the same resolution and could not be compared. Therefore, the near electric field is mapped for an excitation wavelength of 647 nm performed by Kr/Ar laser source. This wavelength corresponds to a regime where some "hot" spots remain the same and other have a different intensity. First, like in the simulations, we observe higher near-field variations for the thicker layer. Concerning the near-field localization we first observed that the two brightest spots remain the same for both structures. Other have different intensities, we can for example observe the spots marked 1, 2 and 3 on the pictures. This behavior is in good agreement with the simulations.

8



(a) 38 nm of gold



(b) 25 nm of gold

Fig. 4.28: Comparison of the near-field distribution for 38 nm and 25 nm thicknesses. The transmitted fields are mapped for an excitation wavelength of 647 nm. The disordered structure corresponds to $\delta = 14\%$, starting from an ordered hole grating with a periodicity of 425 nm.

4.4.4 Impact of the number of holes.

Following the approach used for the FDTD simulations, we now study the effect of the number of holes. Gratings have been fabricated with a different number of holes but the same central region. Figure 4.29 compares the optical images of the 5x5 and 10x10 hole gratings (28 nm of gold thickness) for a 730 nm excitation wavelength. The "hot" spots move to the edge of the places when the size region increases. This result is also in good agreement with the simulation predictions.



(a) 5x5 holes



(b) 10x10 holes

Fig. 4.29: Effect of the number of holes on the near-field distribution for an excitation wavelength of 730 nm.



Fig. 4.30: Maximum value of the ACF for 4 excitation wavelengths ($\lambda = 590$ nm, 640 nm, 690 nm and 730 nm).

4.4.5 Autocorrelation function of the intensity.

Figure 4.30 represents the evolution of the maximum of the ACF we measured for the 4 excitation wavelengths considering for the simulations (see section 4.2.5). For $\delta = 0$ %, we note a discrepancy between the simulation and experimental results. Due to the limited resolution of the SNOM, we already mentioned that we are not able to observe the resonance of the ordered gratings. The signal is averaged over 100 nm and no correlation is observed. For higher disorder, the size of the "hot" spots is not resolved but their high intensity make possible their detection. The maximum of the ACF then exhibits the tendency that is expected from the simulations: its maximum value increases with the disorder δ and the excitation wavelength λ . Beyond, the order of magnitude is also in good agreement even if the resolution of the experiment is limited with respect to the meshing of the FDTD simulations.

4.5 Coupling disordered gratings with CdSe/CdS NCs

The "hot" spots in the disordered structures are finally studied though their coupling with nano-emitters randomly deposited on the surface. As we already mentioned the emission rate of the nano-emitter is directly linked to the LDOS of the structure. The nano-emitter is then used to probe the surface, the fluctuations of the emission rate can give an idea the LDOS fluctuations. Of course these fluctuations are linked on some way to the near electric field fluctuations but this link is not easy to quantify. This LDOS fluctuations can then be compared to the near-field measurements. In this section, we use thick shell CdSe/CdS NCs and characterize the modification of the NCs fluorescence lifetimes. The CdSe/CdS NCs having a total diameter of 12 nm are deposited directly on the grating without any spacer by spin coating. To carry out the experiments, we used the confocal microscope set-up presented in chapter 2. The distribution of the fluorescence lifetime will be compared to the absorption spectra and the near-field distribution of the electromagnetic field.



Fig. 4.31: Histogram of the Purcell factor for NCs CdSe/CdS deposited on a flat gold film, an ordered hole grating and a disordered hole grating ($\delta = 16\%$). The hole grating are made from a 38 nm of thick gold film and has an initial periodicity of 425 nm.

In section 4.4.1, we have observed different distributions of the near electric field with different wavelengths for the grating generated from a periodicity of 425 nm, particularly for the resonant wavelengths. More importantly, the absorption at the wavelength emission of the CdSe/CdS NCs for this type of grating is high (around 40 %). Therefore, these gratings have been chosen in order to present the effect of surface plasmon on the NCs. The experiments will be compared to the results obtained for a flat gold film with the same thickness, taken as a reference. The results are presented for gratings with a periodicity of 425 nm with two thicknesses 25 nm and 38 nm.

Figure 4.31 presents the histogram of the Purcell factors measured for single CdSe/CdS NCs desposited on a hole grating with a hole diameter of 100 nm and a gold thickness of 38 nm. Purcell factors are calculated for the neutral state as in the chapter 2 [72]. The neutral state has a lifetime around 60 ns when NCs are deposited on a glass coverslip. We carried out the lifetime measurements for the ordered hole grating and a disordered one ($\delta = 16\%$) to study the effect of the disorder on the coupling between the grating and the NCs.

On the ordered grating, an obvious effect of the structure on the NCs fluorescence is demonstrated. The Purcell factors are higher on the grating than on the flat gold. A mean value of 15.6 is found for the Purcell factors on the ordered grating compared to a mean value of 10 on the flat gold film. We observe the coupling between the NC and the plasmon resonance of the grating in agreement with the absorption spectrum (figure 4.32a) and the near-field image (figure 4.32b). The absorption at the emission wavelength of the NC reaches nearly 35% with a strong near electric field located both around the holes and between holes. Comparing the Purcell factors for ordered and disordered structures etched in a 38 nm gold film, a slight change is observed. The mean value reaches 16.7 for the disordered grating. These results are understood by the flat absorption spectra peak covering a large range of wavelength including the wavelength emission of the NCs (figure 4.32c). Besides, the near-field distribution in figure 4.32d presents some "hot" spots appearing only on disordered structures as highlighted by the PDF distributions ploted in figure 4.33. If a NC is coupled to such a "hot" spot, its fluorescence is strongly enhanced and its PL lifetime highly reduced. These "hot" spots may explain the broadening of the Purcell factor distribution as well as the highest values observed (about 20 % of NCs on the disordered grating exhibits higher Purcell than for the ordered grating). In brief, the ordered grating enhances the NC fluorescence when compared to the flat gold film. For the disordered grating, a supplemental increase is shown. The effect is weak because the nearfield distribution does not exhibit many "hot" spots.

According to the discussion in section 4.2.3 and in section 4.4.3, we can achieve higher electric fields in between holes and more "hot" spots for the same structure etched in a thicker gold film of 38 nm in the transmission. However, when we work on coupling with the NC, we have to consider the near-field in reflection. The simulation proves the better near-field distribution for the thinner gold film of 25 nm. Figure 4.34 plots the histogram of Purcell factors for single CdSe/CdS NCs placed on a hole grating with a 25 nm gold thickness and holes diameter of 150



(c) Absorption spectra of $\delta = 16\%$

(d) Near-field optical image of $\delta = 16\%$

Fig. 4.32: Absorption spectra (a, c) and near-field optical images in the reflection (b, d) of 15x15 ordered hole grating ($\delta = 0\%$) and disordered hole grating ($\delta = 16\%$). The hole grating are fabricated in a 38 nm gold film with an initial periodicity of 425 nm. The polarization of the excitation is along the x axis.

nm. In comparison with a flat gold film having the same thickness, the ordered hole grating induces higher Purcell factors. The mean value is 16.4 while it only reaches 10 for the flat film. Turning to the disordered grating ($\delta = 16\%$), we see that the mean value of the Purcell factors reaches 24. Moreover, 50 % of the NCs exhibits strong Purcell factors more than 26. Some of them even show acceleration characterized by Purcell factors close to 50. The stronger effect on the disordered hole is explained by the presence of many "hot" spots with a high intensity of the near electric field (figure 4.35b). We then get a very clear effect of the disorder in the case of a thin gold film. In detail, in the PDF distribution of the near-field intensity (figure 4.36), the disordered holes display the broader distribution than the ordered one. It explains the broad distribution of the Purcell factor in $\delta = 16\%$. The long tail of the PDF curve displays the "hot" spots in the disordered sample.

To highlight the effect of the thickness, we end by comparing the Purcell factors



Fig. 4.33: PDF distribution of the near-field intensity in reflection of ordered and disordered hole ($\delta = 16\%$). The hole grating are made from a 38 nm of thick gold film and has an initial periodicity of 425 nm.



Fig. 4.34: Histogram of the Purcell factor for NCs CdSe/CdS deposited on a flat gold film, an ordered hole grating and a disordered one ($\delta = 16\%$). The hole grating are fabricated on a 25 nm gold film with an original periodicity of 425 nm.

distribution obtained for the 38 nm and 25 nm film thickness. First, Figure 4.37 presents the histogram of the Purcell factors for the NCs CdSe/CdS deposited on



Fig. 4.35: Near-field optical images in the reflection configuration for a 15x15 ordered hole grating ($\delta = 0\%$) and a disordered hole grating ($\delta = 16\%$). The hole grating are etched in a 25 nm gold film with an initial periodicity of 425 nm. The polarization of the excitation is along the x axis.



Fig. 4.36: PDF distribution of the near-field intensity in reflection of ordered and disordered hole ($\delta = 16\%$). The hole grating are made from a 25 nm of thick gold film and has an initial periodicity of 425 nm.

the ordered hole gratings. Very small effects of the film thickness are observed. The mean value of the Purcell factors is around 16 in both cases. Looking at the near electric fields in figure 4.32b and 4.35a, we see that the intensity and the distribution of the near-fields are nearly the same for the two thicknesses.

In contrast, figure 4.38 displays a significant increase of the coupling effect on the disordered structure with a thinner thickness. For the 38 nm gold film, the Purcell factors distribution has a mean value of 16.4. When the thickness decreases to 25 nm, the mean value of the Purcell factors rises remarkably to 24 and exhibits some very strong accelerations about 50. A broadening of the Purcell factors distribution is then observed due to the strong variations of the LDOS on this structure.



Fig. 4.37: Histogram of the Purcell factor for the NCs CdSe/CdS deposited on an ordered hole grating with a periodicity of 425 nm. The thickness of the gold film is 38 nm or 25 nm.



Fig. 4.38: Histogram of the Purcell factor for the NCs CdSe/CdS deposited on a disordered hole grating ($\delta = 16\%$). The thickness of the gold film is 38 nm or 25 nm. The original ordered hole grating has a periodicity of 425 nm.

4.6 Conclusion

In this chapter, we focused on designing hole gratings with a controled disorder. The disorder is generated by the movement of the holes starting from an ordered hole array. The optical properties in the far-field are first studied by a classical trans-

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mission and reflection setup I developed. The experimental results prove the good absorption reaching to 30 % for the disordered grating. Next, the optical properties of the disordered hole gratings in the near-field were characterized by simulations (FDTD) and experiments (SNOM measurements). The simulation pointed out the effect of the disorder, the wavelength excitation, the thickness of the gold film and the number of holes. We demonstrated a good agreement between the simulations and the experimental results. Finally, the coupling of the disordered hole gratings with CdSe/CdS NCs confirmed that strong electric fields are observed on the grating. The wide range of Purcell factors display strong variations of the LDOS on these disordered structures. We were also able to observe the transition between plasmonic resonances in a periodic structure and a disordered one by several complementary approaches.

5.

CONCLUSION AND PERSPECTIVES

The main thread of my PhD work is the influence of the disorder on the optical properties of plasmonic 2D structures. Two approaches are presented in this manuscript. First, completely random nanostructures, semi-continuous gold films fabricated close to the percolation threshold, are studied through their coupling with NCS. The analysis of the polarization of the NCs fluorescence simultaneously with Purcell factors deepen previous experiments carried out in the group on this structures. A second part of my manuscript is devoted to the controlled disorder induced step by step in an ordered nanostructure, a hole grating in a thin gold layer. In this case a theoretical part is devoted to the optical properties of first the ordered structures and after that of more and more disordered structures. This is made by FDTD simulations. Various experimental approaches such as confocal and near-field microscopies and coupling with CdSe NCs are used to support this approach.

We presented at first the fundamental properties of plasmons and distinguished the delocalized SPPs and localized SP. In the weak coupling regime, we insisted on the possibility to use the Purcell effect to investigate the plasmon modes of metallic nano-structures through their coupling with a single emitter. From this point of view, CdSe/CdS NCs are particularly well suited. They show a very good photostability at room temperature and their thick-shell strongly reduces their blinking and prevents the fluorescence quenching when they are deposited directly on a metallic film. The first chapter ends with a summary of the main properties of these nanoemitters that are needed to interpret the experiments presented in the manuscript where NCs play the role of active probes.

The first experiments were carried out on semi-continuous gold films. These completely random structures exhibit strong enhancements and localization of the electromagnetic field corresponding to the specific "hot" spots generated by the fractal structure of the gold grains. As a tool, we used the modification of the fluorescence of thick-shell NCs coupled to the random gold films. The original approach of this study is the use of polarization and lifetime measurements that provides new insights concerning the "hot" spots observed in these plasmonic structures. The key point is that, in contrast with the Purcell factor that depends on the orientation of the NC on the metallic structure, the polarization ratio is only determined by the plasmon mode existing at the NC position. By changing the size of NCs, we were able to show that the near-field distribution varies at the scale of few nanometers. Moreover, no correlations were found between the polarization ratio and the Purcell factor showing that lifetime measurements are not sufficient to interpret the plasmon mode structures. This general approach can be implemented to other plasmonic structures in order to determine the local orientation of the electric field. Semi-continuous gold films can display high polarization ratios and strong localization of the electromagnetic field induced by the high disorder of the structure. However, the degree of disorder of these samples cannot be controlled through the fabrication process (radio frequency sputtering or thermal evaporation). Following the general motivation of this thesis, the use of a hole grating represents a promising alternative since the position of the holes is determined by lithography so the disorder can be tuned precisely.

In the third chapter, we focused on designing and characterizing the optical properties of ordered hole gratings. It was the first step to understand the properties of the hole gratings and the background for the further studies on disordered holes. The simulations pointed out that the thickness of the metal film and the periodicity of the grating play an important role in the absorption resonance wavelengths. Moreover, the FDTD simulations allowed us to map the field intensity or the field components at different heights above the plasmonic structure. Two kinds of experiments were performed in order to get the optical properties of the ordered hole arrays in the far-field (using inverted microscope) or in the near-field (using SNOM). We got a good agreement between the simulations and the experimental results.

The simulations also enabled to determine the good periodicity for which the grating presents an absorption resonance at the emission wavelength of the NCs. The coupling with the NCs was firstly characterized by confocal microscopy. Gratings with different absorption at the wavelength NC emission were studied. Higher Purcell factors with wider distributions were observed for resonant gratings. The results highlighted the drawback of the spin-coating method, i.e. the position of the NCs is random. Taking advantage of the SNOM, we used a SNOM tip which is functionalized by silanes-thiols to catch a NC at the end of the tip. The active probe tip allowed us to work at three interesting positions of the ordered hole grating (inside, at the edge and between holes). The coupling of two individual NCs with different orientations at the end of the SNOM tip with the grating demonstrated that strong electric fields are observed on the grating. The Purcell factors at these 3 positions are different for the 2 NC orientations. This is linked to the different components of the electric field on the grating.

In the last chapter, we investigated hole gratings with a controlled disorder. The disorder is generated by the movement of the holes starting from an ordered hole array. As the previous one, this chapter presents a theoretical and an experimental part. The optical properties in the far-field are first studied by a classical transmission and reflection setup I developed. Next, the optical properties of the disordered hole gratings in the near-field were characterized by FDTD simulations and SNOM experiments. The simulation showed the effect of the amount of disorder, the wavelength excitation, the thickness of the gold film and the number of holes. We observed the localization of the electric field around some holes as the disorder increases. As for the random films this can be analyzed in terms of PDF and auto-correlation functions. It is also shown that the near-field intensity increases with the wavelength and saturates for higher values. This behavior is comparable with random films. Nevertheless, the "hot" spots seem to last on a wide range of wavelengths at a certain position which is not the case for random gold films. For the same amount of disorder, higher electric fields are observed for shorter periods which is certainly due to the lower distance between holes. The high disordered gratings in the thinnest layer of gold (38 nm) exhibit the strongest "hot" spots. We demonstrated a good agreement between the simulations and the experimental results for several optical properties. Finally, the coupling of the disordered hole gratings with CdSe/CdS NCs confirmed that strong electric fields are observed on the grating. These fields are stronger than on an ordered grating. The wide range of Purcell factors confirms the strong variations of the LDOS on these disordered structures. Introducing disorder in an ordered structure induces broader plasmonic resonances that can reach the whole visible range when the disorder is high. The bandwidth of the plasmonic resonances can be controlled by the amount of disorder. The near-field intensity is also localized and depends on the disorder degree. In the case of the disorder chosen in this thesis the localization seems to depends on the distance between holes that decreases when disorder in increased and on the thickness that allows more or less SPP propagation. Of course a lot of questions remain and open some perspectives.

From this point of view, measurements involving polarization similar to the ones detailed previously could be done.

• Polarization of the NCs fluorescence

First, the strategy implemented to study semi-continuous films could be applied to the disordered structures. After deposition of NCs on the gratings, the measurement of the linear polarization of their fluorescence will provide statistical information about the orientation of the electric field of the plasmonic modes. Moreover, a more accurate measurement of the polarization state of light could be carried out by association a rotating quarter-wave plate to the polarizer. The polarization ratio, represented with a Poincaré sphere, could be measured from a more general point of view. As the FDTD method gives a description of the full 3D-vector of the electromagnetic field, a more precise comparison between simulations and experimental results could be obtained.



Fig. 5.1: Confocal microscope set-up for the study the polarization of the fluorescence of NCs in metallic structures.

• Polarization effects for the disordered gratings

In classical SNOM experiments, the near-field properties of the electromagnetic field can be investigated through the dependence of the near-field distribution with the polarization of the laser source. First, the dependence of the "hot" spots localization and intensity with the incident polarization could be analyzed numerically and experimentally.

More specifically, in the case of a semi-continuous film, it has been reported that the transition between the scattering regime and the plasmon resonances excitation can be highlighted by the ACF. When scattering by the disordered structure dominates, the central peak of the ACF is narrow and anisotropic. Its shape also depends on the polarization of the incident light. In contrast, plasmons resonances and "hot" spots results in an isotropic central peak for the ACF. It becomes wide, with a width being directly linked to the "hot" spots that dominate the ACF (figure 5.2). A systematic study with the supercontinuum laser could be done for the disordered gratings. The results could evidence other similarities but also differences between the disordered gratings and the semi-continuous gold films.



Fig. 5.2: ACF of the "hot" spot in fractal gold for three polarizations, 0 deg (a), 45 deg (b) and 90 deg (c) at $\lambda = 647nm$ [161].

Beyond these first experiments, the most promising perspectives to this work were opened by the results obtained with single NC glued to a SNOM tip and acting as an active probe. Two kinds of experiments can be carried out:

• Optical image of the hole grating corresponding to the fluorescence a single NC or nanoplatelet attached at the end of a SNOM tip

As for the ordered hole gratings, experiments with an active near-field could be performed in order to get Purcell factors at different positions of the grating. This experiment is very reach as it can also be performed with different orientation of the NC to get insights in the field orientation on the structure. Coupled with the NC intensity, radiative and non radiative modes could be identified. First experiments with an active near-field probe have been performed on the disordered gratings and are presented on Figure 5.3. Three gratings with increasing disorder were scanned with an active NC-SNOM tip. In theses images only the NC intensity is recorded. Even if they show very interesting features, without the lifetime measurements, conclusions are difficult to make. We clearly observe the fluorescence intensity inside the holes for the ordered grating with a very good resolution that evolves towards a kind of channels when the disorder increases. Of course we cannot forget the distribution of the pump field itself in this picture which is hard to evaluate. Complementary measurements should be coupled to this kind of experiments in order to determine the radiative and non-radiative channels. Experiments could also be performed with other kinds of nano-emitters. For example NC with another wavelength emission could be used to study the wavelength behavior. The use of nanoplatelets could also be an alternative way to control the orientation of the emitter at the end of the tip. Even is it is possible to determine the orientation of the NC at the end of the tip we don't control it. Indeed, due to the shape their shape, these nanostructures (figure 5.4 [28]) should be glue to the tip in a more deterministic way.



Fig. 5.3: Optical image of the disordered hole grating mapped by the fluorescence of one NC at the end of the SNOM tip.



Fig. 5.4: Core/Shell Colloidal Semiconductor Nanoplatelets [28].

• Time resolved experiment for an active probe SNOM tip

I performed first measurement of Purcell factors on a disorder grating with an active near-field probe. The results are presented on Figure 5.5. The experiment was done for 4 positions and 4 distances. Different Purcell factors could already be observed but in the case of disorder, random positions have to be checked in order to make comparison. A NC stable for a very long time



Fig. 5.5: Purcell factors of a NC as a function of z for different position in the disordered hole grating.

is necessary. I could not go further during my PhD as this experiment need a lot of time but these results show the interest of the method.

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