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Chapter 1

Introduction

The electronic and optical properties of most of the materials differ from the macroscopic objects to the nanometric ones. Thus, the optical characteristics of particles of nanometric size highly depend on their shapes and dimensions. Indeed, the confinement of the electrons and the existence of localized surface plasmons resonances (collective excitations of electrons in the conduction band of metallic nanoparticles) make such nanoparticles having an optical response significantly different from the bulk materials. A Typical example is the wide set of colors range obtained with solutions of nanoparticles made of a given material but with different dimensions and shapes. The underlying processes at the origin of these observations are the optical absorption and scattering properties of the nanoparticles that are highly dependent on geometrical considerations.

Over the wide application range of the optical properties of nanoparticles, one can cite i.e. biosensors [1], single molecule detection by surface enhanced raman scattering (SERS) [2], solar cells engineering [3], invisibility cloaks [4], etc.

Among all these applications, the surface plasmon amplification by stimulated emission of radiation (SPASER) a coherent hybrid nanosource of light suggested by Bergman and Stockman in 2003 [5], based on the transposition of the LASER principle for plasmonics, is the one that has inspired this thesis. Providing a nanosource of intense and coherent electromagnetic radiation, this device promises a revolution for nano-optics comparable to the laser for optics, as it would help in investigating new horizons such as non-linear nano-optics or quantum nano-optics.

However, while the optical properties of these materials undergo drastic changes in the NIR-Vis-UV domain for sizes varying over a few tens of nm, the standard optical techniques are unable to connect the structural properties with spectral information because of a spatial resolution $\geq 100$ nm in the best cases. Thus the optical studies of such materials have been for a long time limited to ensemble of nanoparticles in solution providing statistical information measured on
several objects. However, it is important to study the individual response of these nanoparticles as their potential applications are numerous and the scientific interest on their fundamental properties is important. Thus, other optical techniques have been used to probe individual nanoobjects like the confocal microscopy [6] or the scanning near-field optical microscopy (SNOM) [7], but the spatial resolution is still limited for the former and the interpretation of the signal is sometimes difficult for the latter. So, to overcome these limitations, alternative techniques based on electron microscopy have been suggested: cathodoluminescence (CL) [8] and electron energy-loss spectroscopy (EELS) [9]. These two techniques are based on the electromagnetic properties of swift electrons that can be considered as a broadband nanosource of light in the NIR-Vis-UV [10]. For the study of plasmonic structures, their interpretation in term of a typical optical quantity, the ElectroMagnetic Local Density Of States (EMLDOS), has been demonstrated [11, 8]. These two techniques allow to correlate the structural and spectral properties of the nanoparticles with a spatial resolution of about 1 \( \text{nm} \).

In this context, the framework of this thesis lies in the ANR project HYNNA that aims at the development of a hybrid plasmon/quantum emitter nanosources of light, ideally a spaser. For that, the Laboratoire de Nanotechnologie et d’Instrumentation Optique (LNIO) of the University of Technology of Troyes and the Stem group of the Laboratoire de Physique des Solides (LPS) at Orsay have worked in the fabrication and characterization of such hybrid systems. Thus, I have been recruited to fabricate such specimens and to conduct nanooptical studies with a Scanning Transmission Electron Microscope (STEM). As mentioned above, this tool has already proven to be interesting for nanooptical studies on plasmonic systems [9, 12, 13, 14] and the Stem group has contributed much to the opening of this new field of study that is the spatially resolved EELS of plasmonic nanoparticles [9, 15, 16, 17, 18]. Recently the implementation of a system to collect and study the cathodoluminescence in the STEM has significantly increased the energy resolution achievable for the study of optical phenomena in an electron microscope together with a consequent spatial resolution [19]. Thus, my thesis has consisted in using this now well established system to study optical specimens much closer to real optical devices than those studied so far. I have studied separately the two basic building bricks of the spaser,
namely the plasmonic cavities and the quantum emitters. As a prospective study I present in conclusion an attempt to couple such objects. Thus I have made an extensive use of the electron lithography to prepare samples that are much closer to those used for standard optical techniques than the specimens typically encountered in electron microscopy studies. However, the lithographed objects are far from ideal, in particular physical vapor deposition of metal causes polycrystalline nanostructures.

In the chapter 3, I present EELS and CL results of experiments made on chemical and lithographed nanorods. Wanting to prepare abacus connecting the localized surface plasmon resonances (LSPR) of nanorods with their dimensions, I noticed that the irregularities of the shape reveal interesting phenomena that makes lithographed objects being different from monocrystalline nanoparticles. In particular, the observation of locally modulated intensity of the EELS and CL signals of the surface plasmon modes due to the presence of roughness.

In the chapter 4, I make a study on dimers of lithographed nanorods that present structural symmetry breaking that makes their coupling slightly different from the ideal symmetric case. In particular, the mapping of the hybridized modes reveals a localization effect over the constituting monomers.

In the chapter 5, I present a study on colloidal core-shell CdSe-CdS quantum dots by cathodoluminescence spectroscopy. The investigation has involved cathodoluminescence and photoluminescence measurements of the same individual quantum dots. Comparing the two techniques on the same object has proven that for this kind of material the cathodoluminescence is an equivalent of the photoluminescence.

Eventually, in the prospectives I present an attempt to observe in a STEM a coupling between plasmonic cavities and quantum emitters.
CHAPTER 2

Experimental techniques

Microscope: instrument that produces enlarged images of small objects, allowing the observer an exceedingly close view of minute structures at a scale convenient for examination and analysis. (Encyclopaedia Britannica)

To offer the promised "exceeding close view of minute structures at a scale convenient" a microscope needs a spatial resolution better than the dimensions of the structures observed. The limit of the resolution is the diffraction and is of the order of the wavelength of the radiation that is used. For an optical microscope working in the visible range [400nm, 700nm], equipped with an oil objective the best resolution expected is close to 200nm. Using electrons instead of photons offers the opportunity to perform imaging with a spatial resolution many times higher. Following the theoretical works of Louis De Broglie (1923), electrons can be seen as waves with a wavelength that decreases when the electrons move faster. Typically for an electron with a kinetic energy of a few tens of kilo-Volts the wavelength is far less than a nanometre. In the work presented here I use a Scanning Transmission Microscope (STEM), such a microscope has the advantage to efficiently combine the possibility to make images of a specimen but also to perform a wide set of spectroscopies at the same time.

2.1 The Scanning Transmission Electron Microscope (STEM)

A scanning transmission electron microscope (STEM) use a focused swift electron beam that is scanned over a specimen (like a Scanning Electron Microscope (SEM) works) and collected after being transmitted through it (like a Transmission Electron Microscope (TEM)). The beam is focused as a probe usually smaller
than 1 nm and is transmitted through the specimen, see figure (2.1). Of course, the specimens need to be thin enough (thickness < 100nm) to allow the electron beam to pass through it. The electron beam is accelerated under a high voltage, generally between 20keV and 200keV. Such a swift electron beam passing through or close to a specimen could interact by several different processes as schematized on figure (2.2). Collecting and measuring the electrons elastically scattered at high angles, gives access to chemical and/or thickness information over the specimen through dark-field imaging. While the direct transmitted electron beam informs on the crystallinity of the specimen through bright-field imaging. Spectroscopic information can be collected by measuring the variation of energy of the inelastically scattered electrons by EELS or through the light emitted by the specimen after being excited by the electron beam with the Cathodoluminescence spectroscopy (CL).

**STEM details**

All the STEM results presented in this thesis has been performed inside the STEM VG HB-501 of the STEM group at the Laboratoire de Physique des Solides. This dedicated STEM can works at 40 kV, 60 kV, 80 kV and 100 kV acceleration voltage. The electron source is a cold field-emission gun (FEG), at 100 keV the FWHM of the electron beam is ~300 meV, the electron probe size is ~1 nm and the current of the probe for a lens aperture half-angle of 15 mrad is 220 pA (single condenser) or 880 pA (double condensers).

**2.2 Imaging with a STEM**

All the images made in a STEM are performed by scanning the swift electron probe point by point over the specimen. Different information could be imaged depending on how the transmitted electrons are collected and measured.

**2.2.1 Bright Field Image (BF)**

The BF image is produced by collecting the direct transmitted beam in the diffraction plane of the microscope with a low aperture detector, see figure (2.3).
Figure 2.1: Simplified representation of a STEM VG HB-510. The microscope is equipped with an EEL spectrometer and an optical output coupled to an optical spectrometer to achieve cathodoluminescence spectroscopy measurements.
Figure 2.2: A swift electron beam passing through a thin specimen (thickness<100nm) interacts with the matter via Coulomb interaction, resulting in several process that could occur, here is listed a few part of them.

Figure 2.3: Detection of the scattered electron with a centered circular detector for the Bright-Field signal and an annular detector to collect at high-angle the HAADF signal.
2.2. Imaging with a STEM

The direct transmitted beam is constituted of electrons that have passed far from the specimen nuclei resulting in a reduced Coulomb interaction, so that the electrons are unscattered or scattered at low angles, figure (2.4). The contrast of a BF image comes from the overlaps of the diffraction pattern spots within the camera spanned area and depends on the camera length. The process leading to diffraction is coherent, the spatial resolution is then not only given by the electron probe size and also depends on the crystalline nature of the object. Figure (2.5.a)

![Figure 2.4: A classical (particle) view of electron scattering by a single atom (carbon). a) Elastic scattering is caused by Coulomb attraction by the nucleus. Inelastic scattering results from Coulomb repulsion by b)inner-, or c) outer-shell electrons, which are excited to a higher energy state. The reverse transitions (de-excitation) are shown by broken arrows. From [20].](image)

2.2.2 High Angle Annular Dark Field Image (HAADF)

A significant part of the transmitted electrons passes close enough to the atomic nuclei of the specimen to be scattered at high angles due to electrostatic Coulomb interaction, also known as Rutherford scattering, figure (2.4.a). To measure these electrons, the detector must collect over a wide aperture angle excepting the low solid angles that correspond to the unscattered and to the diffracted beam. An annular detector allows such detection, figure (2.3). Following the Rutherford scattering process with a screened Yukawa potential, the intensity of the HAADF
signal depends on \( Z \) the atomic mass of a scattering center \(^1\). The intensity being proportional to \( Z \), distinction between chemical components in the specimen can be performed by HAADF imaging \(^2\). The thickness of the specimen also contributes to the intensity of the signal, this contrast is also called mass-thickness contrast. The high-angle elastic scattering being incoherent, the resolution of a HAADF image is given by the size of the probe, figure (2.5.b).

### 2.3 Spectral Studies

It is possible to quantify the energy exchanges that occur when an electron passes through a specimen. The spectral studies may be performed either by measuring the loss of energy that have suffered the transmitted electrons by EELS or by measuring the energy radiated by the specimen via the emission of photons with cathodoluminescence spectroscopy (CL). Moreover as a STEM works point by point, it is possible to collect a local spectroscopic information, giving access to

\(^1\)In our STEM VG HB501 we have collect the HAADF signal through a detector centered at \( \Theta = 112.5 \ mrad \) with an angular aperture \( \delta \Theta = 175 \ mrad \)

\(^2\)Actually only a relative contrast, knowledge of the compounds of the specimen may avoid ambiguities.
spatially resolved spectroscopies.

2.3.1 Electron Energy-Loss Spectroscopy (EELS)

Basic Principle

Inelastically scattered electrons have exchanged energy with the specimen. Their energy is \( E_f = E_i - \Delta E \) where \( E_i \) is the energy before interaction, here 40keV to 100keV \(^3\) provided by the acceleration voltage of the microscope, and \( \Delta E \) the energy exchanged with the specimen. Electron energy gain ( \( \Delta E > 0 \) ) needs a specimen already excited when probed, this situation is almost never accomplished. Electron energy loss ( \( \Delta E < 0 \) ) occurs when the electron probe excites individual or collective electronic states of the specimen. The amount of energy exchanged can be measured by applying an external magnetic field \( \vec{B} \) perpendicular to the electron trajectory. An electron energy-loss spectrum is acquired with a CCD camera coupled to a scintillator film positioned at the focal image plane of the EEL spectrometer, figure (2.6).

The Electron Energy-Loss Spectrum

An EEL spectrum typically exhibits three main regions. The first is a sharp and intense peak centered at 0 eV which principally corresponds to the signal of the unscattered electrons called zero-loss peak (ZLP), figure (2.7). The width of the peak is firstly limited by the physics of electron emission, in addition the Boersch effect, the instabilities of the voltage of the microscope and spectrometer and the aberrations of the optics accentuate the spectral broadening of the probe. The width can be reduced by the use of a monochromated electron source or by deconvolution post-processing (see below). Due to a full width at half-maximum of 300 meV of the ZLP in our microscope, the interactions occurring at energies below typically 300 meV cannot be measured properly. Just after this zero-loss peak is the low-loss region extending from typically 500 meV to a few tens of eV where

\[^3\text{note that electron microscopes are not monochromatic, their spectral width is usually a few hundreds of meV}\]

\[^4\vec{F} = -e\vec{v} \wedge \vec{B} \text{, with } e \text{ the elementary charge } 1.60217665(35) \times 10^{-19} \text{C, } \vec{v} \text{ the velocity of the electron and } \vec{B} \text{ the applied static magnetic field.}\]
Figure 2.6: Schematic representation of the EEL spectrometer. The scattered beam outgoing from the specimen enters the dispersive area (black box) where a static magnetic field \( \vec{B} \) is applied. Electrons that have lost energy (green) are more deflected by the Laplace force\(^4\) than electrons suffering zero energy loss (orange), electrons are detected at different energies indexed by positions on a multichannel detector.
2.3. Spectral Studies

in particular we will find interesting optical phenomena in the [0.5, 6.0 eV] energy range. The higher energy range is the core loss region that contains information on the transitions of core electrons and which is not detailed after.

![EELS Spectrum](image)

*Figure 2.7: EELS spectrum for a carbon nanotube filled with Manganese. Note the different magnifications between the ZLP, the low loss region and the core-loss region.*

**Low Loss**

In the low loss region, the EEL spectrum is related to individual (interband transitions, probing the joint electronic density of states [21]) and collective (plasmons) excitations of the valence electrons of the specimen. It is a measure of the loss function of the specimen: $\Im(-\frac{1}{\varepsilon(\omega)})$ giving information on the bulk response of the materials. The response of the surface is a bit more complex, details for surface plasmon resonances are given below. The energy dependence of an EEL spectrum is then imposed by $\varepsilon$, the complex dielectric function of the specimen. As the optical wavelength considered here are longer than the characteristic dimensions of the noble metals (e.g. size of the unit cell and mean free pat of the electrons), the dielectric function can be considered through the simplification of a spatially local response: $\varepsilon(\mathbf{k}, \omega) = \varepsilon(\omega)$. The Drude-Sommerfeld model for the metals offers an interpretations for $\varepsilon$, considering their conduction electrons as a nearly-free electron gas.
**The Drude-Sommerfeld model**  In this model the nearly free electron gas under an external electric field $\vec{E}(t) = E_0 e^{-i\omega t}$ (with $|E_0|$ and $\omega$ the amplitude and the frequency of the external field respectively) moves around a fixed template of heavy ions following this motion equation:

$$m \frac{\partial^2}{\partial t^2} \vec{x} + m \Gamma \frac{\partial}{\partial t} \vec{x} = -e E_0 e^{-i\omega t}$$  \hspace{1cm} (2.1)

with $\vec{x}$ the deviation from equilibrium position, $m$ the effective mass of a near-free electron and $\Gamma$ the damping factor of the oscillator. Expected solutions are $\vec{x}(t) = \vec{x}_0(\omega) e^{-i\omega t}$ ($\vec{x}_0(\omega)$ is the amplitude of the oscillation at $\omega$) and we find $\vec{x}_0(\omega) = -\frac{e E_0}{m\omega (\omega + i\Gamma)}$. The polarization $\vec{P}(t) = ne \vec{x}(t)$ ($n$ is the density of nearly-free electrons) follows the same motion equation:

$$m \frac{\partial^2}{\partial t^2} \vec{P} + m \Gamma \frac{\partial}{\partial t} \vec{P} = -e \vec{E}$$  \hspace{1cm} (2.2)

which solution is:

$$\vec{P}(t) = \frac{-ne^2}{m\omega (\omega + i\Gamma)} \vec{E}$$  \hspace{1cm} (2.3)

allowing to determine the dielectric displacement $\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$:

$$\vec{D} = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega (\omega + i\Gamma)} \right) \vec{E} \hspace{1cm} \text{or} \hspace{1cm} \vec{D} = \varepsilon_0 \varepsilon \vec{E}$$  \hspace{1cm} (2.4)

where $\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}}$ is the bulk plasmon frequency with $n$ the density of near-free electrons and $\varepsilon$ the complex dielectric function of the Drude-Sommerfeld theory:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}$$  \hspace{1cm} (2.5)

The real and imaginary parts of $\varepsilon$ are found equal to:

$$\begin{cases} 
\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2}, \\
\varepsilon_2(\omega) = \frac{\omega_p^2 \Gamma}{\omega (\omega^2 + \Gamma^2)}
\end{cases}$$  \hspace{1cm} (2.6a-b)
2.3. Spectral Studies

Figure 2.8: (Blue) Real part ($\varepsilon_1$) of the Drude-Lorentz dielectric function $\varepsilon$ of Gold (dotted line = calculation, solid line = Palik’s experimental measurements [22]). (Red) Imaginary part $\varepsilon_2$ with the same convention. Calculations have been performed with $\hbar\omega_p = 5.6\text{eV}$ and $\hbar\Gamma = 0.1\text{eV}$.
Calculated components of the dielectric function $\varepsilon(\omega)$ for gold (with $\hbar \omega_p = 5.6eV$ and $\hbar \Gamma = 0.1eV$) are plotted on figure (2.8) (dotted curves) together with experimental measurements of $\varepsilon_1$ and $\varepsilon_2$ from Palik [22] (solid lines). The calculations are in good agreement with the experimental data for energies below $2eV$, at higher energies the imaginary part shows some intense features that are not reproduced by the calculations. Indeed these features come from the interband transitions contribution to the imaginary part of the dielectric function, that are not considered by the near-free electron model, while gold has interband transitions occurring at energies $>2.4 \text{ eV}$, figure (2.9). A better approximation for the dielectric function must consider the bound electrons instead of the near-free electrons, such bound electrons follow a motion equation close to the former one with a restoring force term:

$$m^* \frac{\partial^2}{\partial t^2} \vec{x} + m^* \gamma \frac{\partial}{\partial t} \vec{x} + \alpha \vec{x} = -e \vec{E}$$  \hspace{1cm} (2.7)

with $m^*$ the effective mass of the bound electrons and $\alpha$ the spring constant of the restoring force. The dielectric function solution of this equation is:

$$\varepsilon_{ib}(\omega) = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2) - i\gamma \omega}$$  \hspace{1cm} (2.8)

where the bulk plasmon frequency $\omega_p^* = \sqrt{\frac{n^*e^2}{m^*\varepsilon_0}}$ with $n^*$ the density of bound electrons and $\omega_0 = \sqrt{\frac{\alpha}{m^*}}$. And the real and imaginary parts:

$$\begin{align*}
\varepsilon_1(\omega) &= 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}, \hspace{1cm} (2.9a) \\
\varepsilon_2(\omega) &= \frac{\omega_p^2 \gamma \omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \hspace{1cm} (2.9b)
\end{align*}$$

This corrected dielectric function shows a better agreement with the experimental measurements as plotted on figure (2.10)

As plotted on figure (2.10), this corrected dielectric function has an imaginary part which takes into account the bound electrons, the resulting peak can be adjusted to correspond to the interband contributions of the material. The real part
2.3. Spectral Studies

Figure 2.9: Calculated band structure of gold, the shaded areas correspond to the points L and X where interband transitions occur. (From [23]).

Figure 2.10: (Blue) Real part ($\varepsilon_1$) of the bound electrons dielectric function with one interband transition $\varepsilon_{ib}$ of Gold (dotted line = calculation, solid line = Palik’s experimental measurements). (Red) Imaginary part $\varepsilon_2$ with the same convention. Calculations have been performed with $\hbar\omega_0^* = 3$eV, $\hbar\gamma = 0.6$eV and $\hbar\omega_0 = 2.5$eV. (Green) Calculated loss function.
of the dielectric function is however in less agreement.

From the dielectric function $\varepsilon$ it is possible to retrieve the conductivity $\sigma$ of the material:

$$\varepsilon(\omega) = 1 + \frac{i\sigma(\omega)}{\varepsilon_0 \omega}$$

(2.10)

which is then used to obtain the internal charge $\rho_{int}$ and current $\vec{J}_{int}$ densities:

$$\begin{cases}
\rho_{int} = -\vec{\nabla} \cdot \vec{P} \\
\vec{J}_{int} = \frac{\partial}{\partial t} \vec{P}
\end{cases}$$

(2.11a, 2.11b)

with $\vec{P}$ the polarization of the medium. And the internal current density $\vec{J}_{int}$ depends on the conductivity of the material $\sigma$ via the electric field $\vec{E}$ as:

$$\vec{J}_{int} = \sigma \vec{E}$$

(2.12)

**Calculation of EELS** What follows is based on the work of Javier Garcia de Abajo published in [24]

In the case of an excitation by a swift electron beam of speed $\vec{v}$, the electric field $\vec{E}$ that accompanies the electrons is principally polarized normally to the beam trajectory and is given by:

$$\vec{E}(\vec{r}, \omega) = \frac{ie}{\pi} \int d^3 \vec{q} \frac{\vec{q} - \frac{k \vec{v}}{q}}{q^2 - k^2} e^{i\vec{q} \cdot \vec{r}} \delta(\omega - \vec{q} \cdot \vec{v})$$

(2.13)

with $\vec{q}$ the electron momentum ($q = \frac{\omega}{v}$) and $k = \frac{\omega}{c}$ the light wave number in free space.

The incoming electron beam interacts with the electric field induced on the specimen $\vec{E}_{ind}$, this interaction gives rise to an energy-loss $\Delta E$ of the swift electrons given by:

$$\Delta E = -e \int dt \vec{v} \cdot \vec{E}_{ind}(r_e(t), t) = \int h\omega \, d\omega \, P_{EELS}(\omega)$$

(2.14)
2.3. Spectral Studies

where \( \vec{r}_e(t) \) is the coordinates of the swift electron and \( P_{EELS}(\omega) \) is the probability for the electron to lose an energy \( \hbar \omega \):

\[
P_{EELS}(\omega) = -\frac{e}{\pi \hbar \omega} \int_0^\infty dt \Re (e^{-i\omega t} \vec{v} \cdot E_{ind}(\vec{r}_e(t), \omega))
\] (2.15)

However, \( P_{EELS}(\omega) \) must be a local information, its spatial dependence is well explained through the correspondence of EELS with the formalism of the Electromagnetic Local Density Of States (EMLDOS), an equivalent for the electromagnetic fields to the electronic local density of states. The EMLDOS, noted \( \rho \), like the electromagnetic fields is a vectorial quantity which projection along a unit vector \( \hat{n} \) is written:

\[
\rho_{\hat{n}}(\vec{r}, \omega) = -\frac{2\omega}{\pi} \Im \hat{n} \cdot G(\vec{r}, \vec{r}, \omega) \cdot \hat{n}
\] (2.16)

where \( G \) is the electric Green tensor of Maxwell’s equation satisfying:

\[
\vec{\nabla} \land \vec{\nabla} \land G(\vec{r}, \vec{r}', \omega) - k^2 \varepsilon(\vec{r}, \omega)G(\vec{r}, \vec{r}', \omega) = \frac{-1}{c^2} \delta(\vec{r} - \vec{r}')
\] (2.17)

Assuming, \( \vec{J}_{ext} \) the external current density associated to the moving electron:

\[
\vec{J}_{ext}(\vec{r}, \omega) = -e \vec{v} \int dt' e^{i\omega t'} \delta(\vec{r} - \vec{r}_e(t))
\] (2.18)

which becomes by considering the \( z^+ \) axis colinear to the electron trajectory (\( z_e(t) = vt \)):

\[
\vec{J}_{ext}(\vec{r}, \omega) = -e \delta(\vec{R} - \vec{R}_e)e^{i\omega \hat{z}} \hat{z}
\] (2.19)

where \( \vec{r} = (\vec{R}, z) \), \( \vec{R} = (x, y) \) and \( \vec{R}_e \) the coordinates of the electrons in the \((x, y)\) plane. And the relation between \( \vec{J}_{ext} \) and the induced electric field \( \vec{E}_{ind} \) of the equation (2.13):

\[
E_{ind} = -4\pi i\omega \int d^3 \vec{r}' G(\vec{r}, \vec{r}', \omega) \vec{J}_{ext}(\vec{r}', \omega)
\] (2.20)

The dependence of \( P_{EELS} \) on the impact parameter of the electron \( R_e \) is obtained by inserting (2.19) into (2.13) and the result into (2.15), then we have:

\[
P_{EELS}(\vec{R}_e, \omega) = -\frac{4e^2 v^2}{\hbar} \int dt dt' \Im (e^{i\omega(t' - t)} \hat{z} \cdot G_{ind}(r_e(t), r_e(t'), \omega) \cdot \hat{z})
\] (2.21)
with $G_{\text{ind}}$ the induced Green tensor obtained by subtracting the free space Green tensor from $G$. The integration of (2.21) gives:

$$P_{\text{EELS}}(\vec{R}_e, \omega) = -\frac{4e^2}{\hbar} \Im(\hat{\mathbf{z}} \cdot G_{\text{ind}}(\vec{R}_e, \vec{R}_e, q, -q, \omega) \cdot \hat{\mathbf{z}}) = \frac{2\pi e^2}{\hbar \omega} \rho_{\mathbf{z}}(\vec{R}_e, q, \omega) \quad (2.22)$$

with $\rho_{\mathbf{z}}(\vec{R}_e, q, \omega)$ a quantity close to the zEMLDOS (the EMLDOS along the z axis) defined in (2.16), local in the $(x,y)$ plane of the real space and in the reciprocal space along the electron trajectory axis z. The link between EELS and zEMLDOS makes possible to understand EELS as a tool to map spectrally and spatially the plasmon modes. However, as EELS and zEMLDOS are not exactly equivalent, care must be taken in the interpretation of EELS maps and spectra [25]. The spatially resolved EELS experiments has to be carried with an accurate spatial resolution, ideally measuring a spectrum for each point of an image with a step size between two pixels equals to the dimensions of the electron probe.

### 2.3.2 Spectra acquisition and Data processing

#### The Spectral Image acquisition mode

All the EELS results (and cathodoluminescence, see below) presented in this thesis have been carried by acquiring the spectra as spectral images. Assuming a standard image as being a 2D matrix of pixels labelled $(x,y)$, a spectral image is a 3D matrix with an additional dimension that contains spectral information $(x,y,E)$, figure (2.11). To do so, all the detectors involved in the process (the BF and/or HAADF detectors for the images, and the camera coupled to the spectrometer for the spectral information) must be synchronized with the deflectors that scans the electron beam over the specimen, figure (2.1). This technique allows to get exact information on the structure at the point where each spectrum is measured.

#### Data processing

**Alignment of the spectra** While performing low-loss EELS to map the surface plasmons resonances, the spectra contain the zero-loss peak that is generally three order of magnitude more intense than the plasmon peaks. Working in high energy dispersion mode ($\Delta E_{\text{CCD}} = 20 \text{ mev}$ to $50 \text{ mev}$ ), the ZLP moves on the CCD
2.3. Spectral Studies

Figure 2.11: a) 2D image, b) 3D spectral image

camera because of the scanning of the probe over the sample that changes the entrance point in the EEL spectrometer and because of the high-voltage instabilities of the electron gun and the spectrometer. These instabilities and potential CCD saturations force to use a very short dwell time. This generally implies a weak signal-to-noise ratio for the plasmon peaks that can be increased by collecting several EEL spectra for a single \((x_i, y_i)\) point of the image (typically 20 to 50 spectra), resulting in a 4D image \((x, y, E(t))\)\(^5\). The time dimension must be binned in order to retrieve a 3D spectral image. However as the ZLP of the different spectra are not at the same position on the CCD channels, an alignment of the spectra must be done before the binning. The alignment is a critical step that needs to be performed carefully at risk of covering the plasmon signal with a misaligned ZLP, figure (2.12).

**Deconvolution of the spectra** As mentioned above, the electron beam is not monochromatic and has a FWHM of ~300 meV. Thus, the signals measured by EELS are a convolution of the energy loss probability \(P_{EELS}\) with the point spread function \(PSF\) of the system microscope + spectrometer. So the measured signal \(S\) is:

\[
S(\omega) = P_{EELS}(\omega) \ast PSF(\omega)
\]

Assuming that a spectra acquired in the vacuum is a good approximation for the \(PSF\), it is possible to perform a deconvolution of the measured signal \(S\) in order

\(^5\)The dwell time generally used are of the order of a few milliseconds, too much to expect plasmon dynamics information (typically a few fs)
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Figure 2.12: EELS spectra a) before alignment, b) the distance on the CCD camera between the spectra does not allow to bin them without preventing the low loss plasmonic signal to be overwritten, c) aligned spectra.

to obtain a spectra with a reduced effect of the polychromaticity of the microscope. The main effect of this deconvolution process is to reduce the elastic background of the ZLP and then to obtain a better signal-to-noise ratio for the physical peaks lying at low energy, figure(2.13). A special care must be given to the number of iterations, an insufficient number limits the advantage of the deconvolution process while a too many iterations may give rises to nonphysical artifacts. A good criterion to limit the number of iteration is the rise of peaks on the left side of the ZLP, or a shift of the EELS peaks as the number of iteration increases.

2.3.3 Cathodoluminescence Spectroscopy (CL)

Geometry of a CL spectrum acquisition The cathodoluminescence emitted by the specimen is collected through an aluminium parabolic mirror which focal point is aligned in the vacuum with the focused electron beam. The radiation collected by the mirror is then reflected as a plane wave to a lens coupled to a bundle of optical fibers [26]. The light is guided to a SP2300A spectrometer (Princeton Instrument) equipped with a PIXIS CCD camera (1024 x 100 pixels) (Princeton Instrument). The spectrometer is equipped with three diffraction gratings, a "near infra-red" grating blazed at 1.2eV and covering a range from 1.1eV to 1.45eV, a "visible" grating blazed at 2.5eV and covering a range from 1.5eV to 4.2eV and an "ultra-violet" grating blazed at 4.1eV and covering a range from 3eV to 6eV.

physically such peaks may come from Electron Energy Gain (EEG), but the condition to measure such a phenomenon are not filled in our setup.
2.3. Spectral Studies

![Graph showing intensity vs. energy loss for different iterations of the Richardson-Lucy deconvolution method.]

**Figure 2.13**: Effects of the number of iterations of the Richardson-Lucy deconvolution method.

**Origins of the CL**  The cathodoluminescence signal can be incoherent or coherent depending on the material and/or the excitation involved. The incoherent signal is related to photoluminescence as emission is due to an inelastic decay of the excited specimen, typically what is observed for electron hole recombination processes occurring in semi-conductors and metals, when excitation and de-excitation are localized. The coherent emission is the one expected when exciting plasmon modes, it is the induced electromagnetic far field, such that:

\[
E^{\text{scat.}} = \frac{e^{ikr}}{r} f(\Omega) \quad (2.24)
\]

with \( \Omega \) the orientation of the radiation \( \vec{r} \) and \( f = \vec{f} - (\vec{f} \cdot \hat{r}) \hat{r} \) the scattered electric field amplitude:

\[
\vec{f}(\Omega) = ik \int_{S_1} ds e^{-ik \hat{r} \cdot \hat{s}} \vec{j}_{\text{int}}(s) \quad (2.25)
\]

with \( \vec{j}_{\text{int}} \) the current induced at the specimen boundary, so the energy emitted by radiation per incoming electron is:

\[
\Delta E = \frac{c}{4\pi} \int dt r^2 \int d\Omega \hat{\vec{r}} \cdot (\vec{E}^{\text{scat.}}(\vec{r}, t) \wedge \vec{H}^{\text{scat.}}(\vec{r}, t)) \quad (2.26)
\]
where $\vec{E}^\text{scat.}$ and $\vec{H}^\text{scat.}$ are the scattered electric and magnetic fields respectively.

### 2.4 Simulation tool

I have used the MNPBEM simulation toolbox [27] that uses the Boundary Element Method (BEM) to compute the surface charge $\sigma$ and current $\hat{h}$ densities knowing the boundary conditions for the scalar $\phi$ and vectorial $\vec{A}$ potentials. More details on the theory can be found in [28, 29, 30].

### 2.5 Sample Preparation

One of the aims of this work is to study photonic specimens inside a STEM, under conditions as close as possible to those of standard optical experiments. However transmission electron microscopy requires thin specimens ($< 100\text{nm}$) while optical experiments are usually made on thick substrates (generally glass $> 100\mu\text{m}$). Widely used as substrate for TEM, amorphous carbon films are not recommended for low-loss EELS experiment because of their high level background signal. However, recently suspended graphene films have been available, promising mono-atomic layer substrate but they are still expensive and offer only small effective surfaces. A compromise for both approaches may be $Si$ and $Si_3N_4$ membranes for TEM, recently proposed to bridge the gap between the requirements of the transmission electron microscopy and conventional optics. With thickness starting from 5nm they offer smooth and homogeneous surfaces and an optical response already characterized (figure 2.14). Above all, they allow for electron beam lithography and metal deposition the same way as it is for conventional substrates, figure (2.15).

Guillaume Boudarham in his work [16] has used such samples, but the samples were prepared by foreign collaborators. Since then the expertise has come to the LNIO where Anne-Laure Baudrion-Beal taught me the know-how, and I prepared all the plasmonic samples and the reference patterns for the combined cathodoluminescence and photoluminescence experiments.
Figure 2.14: Si TEM grid, at the center 9 suspended thin (15 nm thick) Si membranes on a thicker (100 µm) Si wafer. The surrounding thicker area allows the manipulation of the grid with standard tweezers. (image 2spi.com)
Figure 2.15: Simple views of the steps of the electron beam lithography process. 1) A pure Si membrane is used as a substrate, 2) 100-200nm of PMMA are spin-coated on the surface, 3) the PMMA is insolated with the electron beam following a predefined pattern, 4) the insolated PMMA is removed by dissolution in a solution of isopropanol (IPA) and Methyl Isobutyl Ketone (MIBK, C₆H₁₂O), 5) sputtering of 3 nm of Cr as adhesion layer, 6) sputtering of 20 to 100 nm of metal (Au or Ag), 7) the remaining PMMA is removed by dissolution with acetone.)
CHAPTER 3

Effects of the roughness on the properties response of single metallic nanorods

The aim of the work made for the HYNNA project was to make and study a hybrid nano-source of light made up of a plasmonic cavity coupled to a gain medium. As suggested in the pioneering papers announcing the SPASER [31], a core-shell hybrid design may be of great interest. However, the fabrication of such a spherically symmetric system implies strong skills in wet chemical nanoparticles synthesis. Fortunately, such knowledge is available at the Laboratory of Nanotechnology, Instrumentation and Optics but its practical use requires an important time investment, so that the use of this nanofabrication technique has been a substantial part of the PhD thesis of Thomas Lerond at the LNIO, made in parallel to the work presented here. Actually a large variety of geometries are available for these hybrid systems and indeed some are easier to fabricate, in particular by using the electron beam lithography as a key tool for the fabrication of the plasmonic resonators. This technique is not appropriate for spherical materials but is excellent for the design of 2D objects, among which are the nanodiscs [32], the nanotriangles [12] and the nanorods. For my PhD work, the decision has been taken to use a metallic nanorod geometry for the plasmonic cavity. Indeed, such a geometry yields nanorods that act as basic dipole antennas [33], with spectral properties tunable by the dimensions of the nanoparticles (aspect ratio and overall length) and remain easy to study with an unpolarized electron beam. Furthermore, metallic nanorods can also be prepared by wet chemical processes, providing perfectly monocrystalline nanorods with faceted edges but with dimensions not totally controlled and some hardness to pattern the nanoparticles on a substrate.

The optical response of a lithographed nanorod must be altered by the presence of structural defects due to its polycrystallinity. Indeed, previous studies have
shown that compared to perfect nanorods of equivalent dimensions, a shift of the low order multipolar surface plasmon resonances and broadening of their peaks occur for lithographed nanorods [34, 35, 36, 37]. In this chapter, I present a detailed comparative nano-optical study on chemical grown and lithographed metallic nanorods. First, I present a comparative EELS study between individual monocrystalline and polycrystalline nanorods to determine if the latter can be considered as good plasmonic resonators. In particular, I show that the polycrystalline nanorods follow an aspect ratio to wavelength linear dependancy expected for plasmonic resonators (see [38]). Then, I compare EELS and CL measurements made on both types of nanorods for a fine study of the effects of the polycrystallinity on the optical response of lithographed nanorods. The main results of this chapter can be summarized as follows:

- confirmation that the aspect ratio of the nanorods dictates the wavelength dispersion of the three lowest order multipolar surface plasmon modes, the same way for both types of nanorods,

- the nanometric local study on single lithographed nanorods reveals a spatial asymmetry of the measured response of the surface plasmon modes on lithographed nanorods,

- evidence of a coupling of the roughness with the high order surface plasmon modes of the nanorod

- the existence of two types of coupling with the roughness: a bright coupling and a dark coupling, differing by their scattering properties

### 3.1 Effects on the low order multipolar surface plasmon modes

Optical studies and mapping of individual metallic nanorods have already been performed by several techniques, two-photon luminescence microspectroscopy [39], scanning near-field optical microscopy [40, 41], EELS [13, 14] and cathodoluminescence spectroscopy [8, 42]. Since the first surface plasmon mapping performed by spatially resolved EELS on silver nanoprisms [9], a large set of geometries
3.1. Effects on the low order multipolar surface plasmon modes

(e.g. nanorods [13], nanodiscs [32], bow-ties [12] and nanostars [43]) have been investigated made either of gold [44, 12] or silver [16, 17, 13, 14, 32]. Indeed the energies and the localizations of the surface plasmon modes are ruled by the symmetries, dimensions and boundary conditions of metallic nanoparticles. Looking at the surface plasmon dispersion curve \( \omega(k) \) for an infinite metallic cylinder in the air (given for illustration for the case of the Drude model, figure (3.1)) and imposing the longitudinal boundary conditions of a nanorod (wave vector \( k = \frac{m \pi}{L} \) with \( m \) (integer) the multipolar surface plasmon order and \( L \) the length of the rod), reveals that only discretized energies are allowed corresponding to the surface plasmon modes supported by the particle.

At low \( k \), where the curve is highly dispersive, two consecutive surface plasmon modes (\( m \) and \( m+1 \)) are spectrally well separated (e.g. see \( \omega_1 \) and \( \omega_2 \) figure (3.1)). Inversely, at high \( k \), the dispersion of the high order surface plasmon modes is limited by the asymptotical limit \( \omega_{sp} \) \( (\omega_{sp} = \frac{\omega_p}{\sqrt{2}} \) for Drude model or the energy of the interband transition for some real metals), resulting in a high density of modes within a small energy range (e.g. \( \omega_3 \), \( \omega_4 \) and \( \omega_5 \)).

![Figure 3.1: Surface plasmon dispersion curve for a planar interface air/Drude metal (red). The longitudinal boundary conditions of a nanorod impose \( k = \frac{m \pi}{L} \) (vertical dotted lines). At low \( k \) the curve shows a high dispersion and is close to the light line (blue), at high \( k \) the curve has an asymptote for \( \omega = \omega_{sp} = \frac{\omega_p}{\sqrt{2}} \) in this region energies have little dispersion and all the high order surface plasmon modes appear close to the energy \( \omega_{sp} \).](image-url)
Chapter 3. Effects of the roughness on the properties response of single metallic nanorods

Single nanorod surface plasmon dispersion

The use of metallic nanorods made by e-beam lithography and physical vapor deposition processes for the fabrication of a hybrid nanosource of light needs a study on the plasmonic properties of such polycrystalline nanoparticles, in particular for an evaluation of the effects of the roughness on the dispersion of the multipolar surface plasmon modes. The plasmonic response of a metallic nanorod is dictated by its dimensions. Indeed a linear dependency links the aspect ratio of a nanorod to the wavelengths of its longitudinal multipolar surface plasmon modes \( \lambda(AR) \) [38, 45].

To assess the reliability of this law, I have performed a systematic EELS study on tens of monocrystalline silver nanorods from which I have extracted the energies of the first three longitudinal surface plasmon modes \( m = 1, 2 \) and 3. The figure (3.2) shows an illustration of the identification for the mode \( m = 1 \) of a silver nanorod. The result of these measurements are displayed on figure (3.3.a), revealing a clear dependency of the wavelengths of the three modes \( m = 1, 2 \) and 3 related to their aspect ratio as announced. Then, I made another set of measurement on polycrystalline nanorods (figure (3.3.b)) also showing a linear trend, despite the presence of roughness on these nanorods. However, one may note the different ranges in aspect ratio for the two sets of measurements while the spectral ranges are the same. The different aspect ratio ranges comes from technical limits in nanorods fabrication. Indeed, the fabrication of long monocrystalline silver nanorods by wet chemical techniques is still a challenge, those used here are less than 200 nm long with radii close to 15 nm. For the lithographed nanorods, the aspect ratio is difficult to determine because of their imprecise edges, but this problem is solved for nanorods longer than 180 nm (with a width of 45 nm). The different slopes of \( \lambda(AR) \) measured for both types of nanorods show a limit of the model of linear dependency. Indeed, it must be applied to homogeneous sets of nanorods for which only one dimension act as a parameter for the variation of the aspect ratio, the length or the radius, while here the comparison of mono and polycrystalline nanorods as fabricated for this study implies the variation of both parameters (see [38]).

From these measurements, one may conclude that the different fabrication processes that give nanorods of different crystallinity have obviously no consequences on the \( \lambda(AR) \) dispersion diagram, as a linear trend is found for both types of particles. However, the following closer study by compared EELS and CL of individual nanorods reveals that local alterations of the multipolar response occur on
3.1. Effects on the low order multipolar surface plasmon modes

Figure 3.2: EELS mapping of the $m = 1$ multipolar surface plasmon mode of a silver nanorod. a) HAADF image, b) intensity map, c) energy loss map and d) FWHM map.

Figure 3.3: EELS measurement of the three first multipolar modes sustained by silver nanorods (red: $m = 1$, blue: $m = 2$, green: $m = 3$). The linear dependency of the wavelength regarding to the aspect ratio is clear for chemically grown (left) and lithographed (right) nanoparticles. The radii of the nanorods being of comparable size inside each sample: 10nm for chemicals, 45nm for lithographed.
Chapter 3. Effects of the roughness on the properties response of single metallic nanorods

3.2 Monocrystalline nanorods

In this part, I present the first comparative EELS vs. CL study on individuals metallic nanorods. Such comparison can be made only on a restricted spectral range, mainly limited by the CL spectrometer used for this work which uses two different diffraction gratings. The first, a near infra-red grating ranging from 1 eV to 1.4 eV and the second, a near infra-red to visible grating ranging from 1.6 eV to 4.5 eV. The EELS measurement are limited to energies ranging down to 0.5 eV by the presence of the elastic scattering peak.

As a starting point, I present a typical example of the combined EELS and CL measurement made on a single monocrystalline gold nanorod. The figure (3.4.a) shows the HAADF image of a 150 nm long nanorod. For such a size of nanorod, the complete cathodoluminescent spectral features can be measured; for longer nanorods the lowest order surface plasmon resonances generally lie at energies less than 1 eV making them unmeasurable by the CL spectrometer. The figure (3.5) shows both EELS (blue) and CL (red) measured over the nanorod of figure (3.4.a). Peaks are measured on both spectra. To identify their origin it is useful to use spectral dispersion maps such as those displayed on figure (3.4.b, .c and .d). This representation displays the local spectral feature measured along the nanorod for EELS (3.4.b) and CL (3.4.c and .d) with the vertical axis as the position along the nanorod and the horizontal axis containing the spectral information.

These dispersion maps reveal two distincts spectral domains probed by EELS and CL for the nanorods made of gold. For energies below the interband transition occurring at 2.4 eV, the first domain contains information related to multipolar surface plasmons modes. These modes can be identified following their intensity variations along the nanorod. Thus the EELS dispersion map (figure (3.4.b)) shows at 1.3 eV the longitudinal $m = 1$ mode with its typical two lobes signature at the extremities of the nanorod and at 1.81 eV a peak at the center of the nanoparticle may be the signature of either the longitudinal $m = 2$ mode or the transverse $m = 1$

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1 A third diffraction grating, not utilized for this study, covering the [3 eV; 6 eV] spectral range is implemented in the spectrometer.
3.2. Monocrystalline nanorods

Figure 3.4: a) HAADF image of a gold nanorod. Scale bar is 20nm. b) EELS dispersion map, c) CL dispersion map in the near-IR range and d) CL dispersion map in the near-IR/Vis/UV range. The vertical axis of the maps correspond to the position along the nanorod while the dispersion axis is horizontal.

Figure 3.5: EELS (Blue) and CL (Red) spectra extracted from the dispersion map of figure (3.4). CL has been measured with a 300 grids.mm$^{-1}$ grating blazed at 1µm, covering the range from 1 eV to 1.4 eV and with a 150 grids.mm$^{-1}$ grating blazed at 500 nm covering the range from 1.6 eV to 4.5 eV.
Chapter 3. Effects of the roughness on the properties response of single metallic nanorods

mode as both are expected to be measured preferentially at this position. Note that no higher order longitudinal surface plasmon mode \((m > 2)\) is observed because of the high wave-vector \(k\) values of such a small nanorod and because of the low energy threshold of interband transitions of gold at 2.4 eV\(^2\). The CL signal displays a peak at 1.24 eV with the same spectral shape as the mode \(m = 1\) measured by EELS (see figure (3.5)) and the same spatial feature made of two lobes of intensity (figure (3.4,c)). The shift in energy observed between these two peaks is explained by the quantity measured by each technique, the EELS gives the optical extinction of the surface plasmon modes (ie absorption plus scattering) while the CL spectroscopy gives the scattering only. For small metallic nanorods, such as the one studied here, the absorption provides the main contribution to the optical extinction, thus comparing EELS and CL is almost equivalent to comparing absorption and scattering, two different phenomena with proper spectral features. Comparing BEM calculations of extinction and scattering reveals the evolution of this energy shift as a function of the length of a gold nanorod, see figure (3.6). The peak measured by EELS at 1.81 eV is not found by CL, many reasons could explain that. Firstly, the spectral windows covered by the diffraction gratings used for the CL measurements are missing the range between 1.4 eV and 1.6 eV and the efficiency of the near-IR to visible grating is low \((<50\%)\) for energies below 1.8 eV. And secondly, considering that this peak corresponds to the \(m = 2\) longitudinal surface plasmon mode, a weak coupling to the far-field (CL) is expected, even more for a monocrystalline nanorod with no defects which could act as scatterers. Just below the 2.4 eV limit, a high density of surface plasmon modes exists but gives a poor contribution to the measured signal, this observation is explained by the decreasing interaction of the electron beam with the increasing surface plasmon order \(m\). Indeed the electron beam interacts with the electric field lines of the surface plasmon modes which are more confined close to the air/metal interface for the high orders, see [14].

The second spectral domain, starting at 2.4 eV contains information on the Joint Density Of States (JDOS) of gold. The peaks measured in this domain are reminiscent of the interband transitions of gold and by comparing the energies with data found in the literature \([46, 47, 48]\) we can attribute a sp-d interband transitions

\(^2\)As a comparison, the silver case is a bit advantageous with the presence of a surface plasmon resonance as the asymptotic limit at 3.55 eV
3.2. Monocrystalline nanorods

![Graph showing the evolution of the energy shift of the m = 1 mode (E_{ext} - E_{sca}) supported by a gold nanorod as a function of its length, from BEM calculations.](image)

Figure 3.6: Evolution of the energy shift of the m = 1 mode (E_{ext} - E_{sca}) supported by a gold nanorod as a function of its length, from BEM calculations.

to each of the peaks (here labelled by the letters A, B and C). Resonances arising at the same energies in EELS and CL spectra are thus assigned to the same interband transitions. As previously observed for carbon nanostructures [49], even e-beam with aloof trajectory measures these interband transitions, this effect is assigned to the lateral extent of the evanescent field of the traveling charges.

The JDOS measured by EELS depends on the crystallographic plane of the material facing the e-beam trajectory and the radiative part of the JDOS, measured by CL, also depends on the angular matching of the emission coming from a nanorod and the collection angles covered by the parabolic mirror of the CL setup. For these reasons, the whole JDOS is not measured for a given nanorod either by EELS or by CL, and the intensity of the signal coming from an interband transition may vary from a nanorod to an other due to their orientation on the substrate.

At first glance, it may seem surprising to measure CL coming from electron-hole recombinations in a metallic nanoparticle as all the previous observations reported on silver [8, 42] or gold [50] nanostructures show only surface plasmon signal. However several reports of photoluminescence argue that electron-hole recombination luminescence can be measured in noble metals films [46] or individuals nanorods [47], even if these pairs are expected to recombine preferentially by non radiative ways specially via the excitation of surface plasmons [51, 52].
Furthermore, one may note that the signal of interband transitions has no shift between EELS and CL (figures (3.8 and 3.5)), in contrast with the case of surface plasmon resonances (first peak of figure (3.5)).

Figure 3.7: a) HAADF image of a 275 nm long chemical gold nanorod, scale bar is 50 nm. b) near-IR EELS dispersion map, three resonances are observed at 0.92 eV (m = 1, red), 1.35 eV (m = 2, blue) and 1.81 eV (m = 3, green). c) Vis/UV EELS dispersion map and d) Vis/UV CL dispersion map.

Figure (3.7.b) shows the EELS and CL dispersion maps measured over a gold nanorod with an aspect ratio of 7 and 275nm long. Here again, the signal pattern associated to the localized surface plasmon modes allows to identify the modes $m = 1$ at 0.95 eV, $m = 2$ at 1.3 eV and $m = 3$ at 1.65 eV. And from 2.4 eV to 5 eV (figure (3.7.c)), we observe a serie of peaks attributed to the interband transition of gold, see also the figure (3.8). This longer nanorod offers a smaller spectral window measured by CL but has a length comparable to the polycristalline nanorod made by electron beam lithography to which it will be compared.
3.3 Polycrystalline nanorods

3.3.1 Multipolar surface plasmon dispersion

As seen above (see 3.1), the dispersion law of the multipolar surface plasmon modes is not modified by the crystallinity of a nanorod. Using spatially resolved EELS and CL spectroscopy it is possible to find a correlation between the presence of a roughness on a nanorod and a spectral feature with a spatial resolution of about 1 nm. The figure (3.9.a) shows how much the polycrystallinity affects the edges of a lithographed nanorod 3 but the aspect ratio still can be determined (AR=9). Using spatial dispersion mapping over this nanorod reveals how much the roughness locally affects the spectral responses. Indeed, the figure (3.9.b) shows the EELS dispersion along a lithographed gold nanorod in the near-IR range where the multipolar surface plasmon modes resonances occur. As for the monocrystalline

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3Here the contrast of the HAADF image comes only from local variations of the thickness, i.e. protrusions of gold over the surface of the nanorod. The rod is made of a grip layer 3nm of Cr (atomic number Z = 24) and 80nm of Au (Z = 79) sputtered on a flat 15nm Si membrane, no chemical contrast on the nanorod is expected here. Furthermore, SEM images performed on lithographed nanorods shows that the protrusions on the surface could be long as dozens of nm
Chapter 3. Effects of the roughness on the properties response of single metallic nanorods

nanorod, the spatial signatures of the multipolar surface plasmon modes allow to identify two of them, the $m = 1$ mode at 0.8 eV and the $m = 2$ mode at 1.17 eV. Because of the energy range involved for these resonances no CL signal has been measured for comparison. However, unlike the previous case, one may note the lack of signal from the $m = 3$ mode and more important, the asymmetry of the multipolar surface plasmon intensity pattern. In particular, the $m = 1$ mode (0.8 eV) is found with a signal at the upper extremity of the nanorod with a maximum more intense, wider (440 meV vs. 380 meV) and slightly red shifted (0.850 eV vs. 0.824 eV) as compared to the lower extremity. This asymmetry of the signal is assumed to be a reminiscence of the structural asymmetry of the nanorod [53]. In particular, a modification of the electromagnetic local density of states (EMLDOS) or an increase of the interaction of the electron beam with the nanorod due to a local variation of the thickness may cause such an asymmetry.

![Figure 3.9](image)

**Figure 3.9:** a) HAADF image of a 450nm x 50nm lithographed gold nanorod, scale bar is 50 nm. b) near-IR EELS dispersion map, two resonances are observed at 0.8 eV ($m = 1$, red) and 1.27 eV ($m = 2$, blue). c) Vis/UV EELS dispersion map. d) Vis/UV CL dispersion map, range.

To calculate by the BEM the effect of an asymmetric shape on the local plasmonic response, three nanorods with typical shapes are simulated, see figure (3.11), a nanorod with a regular shape (50x450nm), the same nanorod with a 50nm long protrusion at 30nm from the edge and a more realistic shape generated from the
3.3. Polycrystalline nanorods

Figure 3.10: EELS (blue) and CL (red) spectra extracted from the position labelled by the second green arrow (from the top) of figure (3.9). CL has been measured with a 150 grids.mm$^{-1}$ grating blazed at 500nm.

projected outline of the HAADF image of figure (3.9.a), which exhibits a flat surface facing the e-beam but rough side walls. The first nanorod acts as a reference, the second may evidence a local increase of the interaction length of the electron beam with the nanorod due to a protrusion parallel to its trajectory and the last nanorod may help to estimate the effect of an overall asymmetric shape without protrusion.

Figure 3.11: Shapes of the nanorods used for BEM calculations: a) regular shape (50x450nm), b) the same nanorod with a 50nm long protrusion at 30nm from the edge of the rod and c) a realistic shape extruded from the HAADF image of figure (3.9.a).
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Figures 3.12: Calculated EELS spectra for: a) the nanorod with a regular shape, b) the nanorod with a 50 nm long protrusion at an edge (green curve) vs the spectra calculated at the opposite edge (orange curve) and c) the nanorod with a realistic shape.

Comparing the EELS spectra calculated at the edges of these nanorods reveals an asymmetric response intensity for both types of irregularly shaped nanorods for the surface plasmon mode \( m = 1 \), see figure (3.12). Then, a planewave excitation is used to compute the surface charge densities at energies calculated by EELS for the modes \( m = 1 \) and \( m = 3 \) \(^4\). The surface charge density oscillations along the nanorods for a given mode are the same for the three simulated nanorods figure (3.13), although the densities calculated at the extremities are found inhomogeneous for the irregular nanorods. However, the electric near-field associated with these surface charge densities, that gives a closer representation of the EMLDOS, is highly perturbed, see figure (3.14). Both irregular structures may cause an asymmetry in EELS signal, due to the protrusion on the nanorod of figure (3.11) or the sharper edges of the more realistically shaped nanorod. This effect may also be seen as an increase of the EMLDOS, because of the locally reduced volume containing the same number of electromagnetic states. However, the effect is more pronounced in the case of a protrusion. And we thus conclude that the asymmetry is mainly related to the presence of a relatively long excrescence. In the following such excrescences are added over the most realistic shape.

\(^4\)As a consequence, the mode \( m = 2 \) is not studied because of its inability to be excited by a planewave.
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Figure 3.13: Surface charge density maps (blue: min, red: Max) of the modes $m = 1$ and $m = 3$ for the nanorods of figure (3.11).

3.3.2 Energy dispersion close to the interband transition

At energies close to the first interband transition of gold (2.4 eV) and above, the EELS dispersion map of figure (3.9.c) bears no resemblance with the JDOS signal measured over the monocrystalline nanorod, figure (3.7.c). Instead of a constant signal all over the nanorod at these energies, here are found randomly distributed localized maxima of the signal (green arrows on figure (3.9)). A signal with comparable distribution is measured by CL (figure (3.9.d)), revealing the scattering part of these spots, yet no contribution from the interband transition is clearly discernible. These maxima occur at the same positions as the noticeable material protrusions visible in the HAADF image, as indicated by the arrows on figure (3.9.a). One may note the singular spectral feature occurring at the position marked with the red arrow on figure (3.9). A peak, which is not related to the multipolar surface plasmon dispersion intensity pattern, is measured by EELS at 1.6 eV, an energy slightly below those of the peaks marked by the green arrows. And, interestingly, this EELS spot has no CL counterpart (figure (3.9.d)). However, the CL peaks measured at the green arrows locations are energetically
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Figure 3.14: Electric near-field of the modes $m = 1$ and $m = 3$ associated to the surface charge densities displayed on figure (3.13).

red-shifted with respect to the peaks measured by EELS figure (3.10). Contrasting with the interband response of the monocrystalline nanorods for which no shift between EELS and CL is measured. As discussed previously, a red-shift between EELS and CL measurements may be related to the plasmonic signature of small metallic nanoparticles, figure (3.6). A Scanning Electron Microscope (SEM) image of a gold polycrystalline nanorod figure (3.15) helps in estimating the size of the protrusions which are found to be as long as several tens of nm.

We have made BEM simulations of a gold nanorod with excrescences on the top surface, using the in-plane shape extracted from the HAADF image of figure (3.9.a) and locating the protrusions at the proper locations following the contrast of the image, see figure (3.16). Such numerically implemented protrusion has been suggested by Andreas Trugler (Institut fur Physik, Karl-Franzens Universitat Graz), and the particles modeling realized with his kind help.

The figure (3.17) shows the comparison between BEM EELS calculation and experiments. Most of the features experimentally found are retrieved through the
3.3. Polycrystalline nanorods

Figure 3.15: Scanning Electron Microscope image of a lithographed nanorod.

Figure 3.16: Structure of the realistic nanorod with two 50nm long protrusions on the surface used for calculations.

simulation. Among which the asymmetry of the intensity of the $m = 1$ mode signal due to the rough walls of the nanorod and the excrescence at one edge of the nanorod. Also intense localized peaks are calculated at the position of the protruberances for energies below the first interband transition. The calculation are performed without considering the Si substrate, resulting in the red-shift of the cal-
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Figures 3.17: EELS dispersion maps, a) from BEM calculation and b) from experimental measurements.
culated plasmonic responses compared to the experimental results (excepted for the $m = 1$ surface plasmon mode). The CL calculations are also in good agreement with the experimental results, see figure (3.18). However, if the expected shift in energy of CL as compared to EELS is found, the calculated shift is much smaller, only a few $meV$. Interestingly, the intensity ratio of the localized spots measured by EELS and CL is found to depend on the size of the protrusion. For longer protrusions the EELS signal is found much higher than the CL one. Eventually, the experimental observation of an EELS signal measured without a CL counterpart (red arrow on figure (3.9) is obtained for excrescences larger than 50 nm, see figure (3.19).

3.4 Conclusion

In this chapter I have compared the optical responses of chemical and lithographed nanorods. I have shown that if their low order multipolar localized surface plasmon resonances follow the same trend as a function of their dimensions, it appears that the presence of roughness on the lithographed nanorods could locally modify the spectral properties of the particles in two different manners. Firstly, rugosities locally modify the signal of the multipolar plasmon resonances that exhibit a maximum close to them, typically giving rise to asymmetry in the intensity dispersion maps. Secondly, at higher energies, while the monocrystalline nanorods exhibit interband transitions, the polycrystalline nanorods display complex intensity signal, by both EELS and CL, that are modulated by the asperities on the surface. Combining EELS and CL measurements has permitted to give some hint in explaining the mechanism behind these observations. Indeed, the absence of energy shift between the results of the two spectroscopies for the monocrystalline nanorods is a signature of the measurement of interband transitions, while the red shift between EELS and CL found for lithographed nanorods is an evidence of the plasmonic character of the localized intense signals. Interestingly, the localized signals associated with the rugosities can be bright i.e. having EELS and CL signals or dark with only EELS signal. The BEM simulations has provided results in good agreement with experiment as it has retrieved the occurrence of local modulation of the signal at the protrusions location and the intensity dependence of EELS and CL following the size of the excrescences. The conclusion is that, far from the main multipolar
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Figure 3.18: Cathodoluminescence dispersion maps, a) from BEM calculation and b) from experimental measurements.
surface plasmon resonances, a protusion acts essentially as an independent nanoantenna, even when protruded from another (larger) nanoantenna.

This study has shown that the roughness may locally modify the plasmonic response of lithographed nanorods but keeps their optical resonator properties. As such they can be used as elemental components of nanooptical systems. In the following is presented a study on a basic system composed of nanorods, a dimer nanoantenna made of two aligned nanorods separated by a gap of a few tens of nm. I show that for such a device, the polycrystallinity of lithographed nanorods causes a structural asymmetry of the dimer which is the source of the localization of the hybridized coupled modes over the monomers.

**Figure 3.19:** EELS (Blue) and Cathodoluminescence (Red) spectra calculated on the roughness located in the middle of the nanorod (250nm on the vertical axis) of figure (3.16).
As studied in the previous chapter, metallic nanorods act as plasmonic resonators regardless to their crystallinity. Thus, we assume we can use them as elemental bricks for the development of nanooptical sources of light. A practical way to efficiently use metallic nanorods is to couple them in dimers aligned along their long axis. Indeed, such a geometry allows to benefit from the intense electric near-field which concentrate inside the dielectric gap that separate the monomers [54]. A simple idea is to place a quantum emitter inside this gap to easily couple with this electric near-field. Actually, this approach is already used for surface-enhanced Raman scattering (SERS) of single molecules [2, 55], nonlinear optics [45, 56, 57] or tuning the emission of fluorescent molecules [58]. Moreover, dimers of nanorods have the peculiarity to offer a high tunability of the localized surface plasmon resonances properties through the aspect ratio of the rods and the size of the gap [54, 59]. Several EELS studies of dimers of metallic nanoparticles have already been performed. For example, silver nanospheres [60] and silver/gold nanorods alloys [61, 62], have been studied with gap size ranging from several nm down to the point-contact conductivity limit. For practical reasons, we would like to use colloidal CdSe/CdS quantum dots (see the chapter 5) as quantum emitter of to couple to metallic dimers. However, due to the dimensions of such nanocrystals (a few tens of nm), I present a study on lithographed silver nanorods dimers with gap sizes > 20nm. This large gap size regime differs from the conditions involved in the last two cited references, only a weak coupling of the monomers is expected.

Like the case of monomer nanorods and despite the local modulation of the EELS signal observed on the polycrystalline ones due to the roughness (see chapter 3), I could map the intensities, energies and FWHM of the multipolar
surface plasmon modes of polycrystalline dimers, revealing their hybridized modes. It should be noted that the polycrystallinity, inherent to the physical vapour deposition of metal used here, makes these lithographed dimers structurally asymmetric. For such heterodimers (same material but different dimensions), the bonding and antibonding modes of the coupled system are found localized on different arms instead of being homogeneously delocalized all over the dimer. This localization effect is also observed on monocrystalline gold heterodimers of different monomer lengths. These observations are predicted by a model based on the plasmon hybridization model developed by Nordlander et al. [63], which I have specially adapted to the present case. Furthermore, by taking into account the non-monochromaticity of the electron beam, the experimental observations and our interpretations are confirmed by BEM calculations.

Because of the energy range where lies the resonance involved here and the difficulty to collect such a signal through our CL system, no CL measurement has been performed for this study.

### 4.1 Classification of modes in coupled nanoantennas

The classification of individual nanoantennas modes has already been reviewed in the rest of the present manuscript. Basically, plasmons modes in individual nanoantennas are classified through the number of eigencharge density oscillations: the dipolar mode corresponds to an oscillation of half a wavelength (one maximum and one minimum), the quadrupolar to a wavelength (one maximum and two minima, or vice versa), etc... see figure (4.1). In the following, we assign a number \( m \) to the mode of individual nanorods, \( m \) being the number of semi-oscillations of the eigencharge through the nanorod. In the case of perfectly similar nanorods arranged along their long axis with a small gap separation, neglecting intermodes coupling, simple symmetry arguments show that one expects two modes per \( m \) values: a low energy mode which is antisymmetric in charge with respect to the mid plane between both antennas, and a high energy one which is symmetric in charge, see figure (4.2). The antisymmetric mode is at lower energy due to charge attraction through the separation gap, and thus called bonding by analogy to molecular orbital theory. Inversely, the symmetric mode is
at higher energy due to charge repulsion and is called antibonding. We also note that given the symmetry of the charge distribution one can deduce the symmetry of the electrical field. Concerning EELS experiments, it is striking to note that the antibonding modes (symmetric) will have an eigenfield with a component along the electron beam path in the symmetry midplane (inside the gap), when the bonding modes (antisymmetric) won’t. EELS intensity maps, that will be interpreted in details in the following, are thus not expected to show any signal in the middle of the gap at the bonding mode energy.

\[ m = 1 \quad m = 2 \quad m = 3 \]

*Figure 4.1: BEM simulations of the eigencharges spatial distribution for the first three modes of a nanoantenna (red:Max, blue:min)*
Chapter 4. Dimers of metallic nanorods: symmetry breaking and localization of the hybridized modes

4.2 Plasmon hybridization

The plasmonic near-field coupling of two nanorods through a dielectric gap results in the hybridization of the modes supported by each arm of the dimer. This hybridization causes a splitting of the initial modes into bonding and antibonding modes with, respectively, antisymmetric and symmetric charges densities through...
4.2. Plasmon hybridization

the gap. For dimers with a gap larger than 1 nm, the system can be analysed through a classical description [64]. However, in the following, we will develop a model for coupling which is simply solved with a quantum notation, although the problem is strictly classical. In this model, the eigenstates of the monomer are given by the set of \( (E_m, |\phi_m\rangle) \), with \( E_m \) being the plasmon energy and \( |\phi_m(\vec{r})\rangle \) the eigencharge of mode \( m \) such that \( H|\phi_m\rangle = E_m|\phi_m\rangle \). In the absence of coupling, the effective Hamiltonian is that of the sum of both monomers. The coupling is then introduced heuristically. For simplicity, we will restrict ourselves to the case where only two modes of same symmetry (dipole/dipole for example) can couple, which is the case in our experiments. We will then omit for the next calculations the underscript \( m \).

The dimer can be described as a linear combination of the wave function of the isolated monomers:

\[
|\Psi\rangle = R |\phi_R\rangle + L |\phi_L\rangle \tag{4.1}
\]

with \(|\Psi\rangle\) the wave function of the dimer, \(|\phi_R\rangle\) and \(|\phi_L\rangle\) \footnote{the labels R and L stand for right and left, as the position of the monomers in the dimer.} the eigenstate wave function of the isolated monomers with eigenvalues \( \varepsilon_R \) and \( \varepsilon_L \) respectively (equation (4.3)), \( R \) and \( L \) two normalizing factors that ensure \( \langle \Psi | \Psi \rangle = 1 \). The Hamiltonian of the system \( H \) is a linear combination of the Hamiltonian of the isolated nanorods (\( H_R \) and \( H_L \)) and a coupling term \( \hat{C} \):

\[
\hat{H} = \hat{H}_R + \hat{H}_L + \hat{C} \tag{4.2}
\]

with:

\[
\hat{H}_R |\phi_R\rangle = \varepsilon_R |\phi_R\rangle \quad \text{and} \quad \hat{H}_L |\phi_L\rangle = \varepsilon_L |\phi_L\rangle \tag{4.3}
\]

and the coupling term:

\[
\hat{C} = \begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix} \tag{4.4}
\]
with \( c = c(\text{gap size}) \) a coupling parameter that depends on the gap size. Then for the dimer we have:

\[
\begin{align*}
\hat{H} |\Psi\rangle &= E |\Psi\rangle \quad (4.5a) \\
R \hat{H} |\phi_R\rangle + L \hat{H} |\phi_L\rangle &= E (R |\phi_R\rangle + L |\phi_L\rangle) \quad (4.5b)
\end{align*}
\]

Inserting (4.3) into (4.5b) we obtain:

\[
R (\varepsilon_R - E) |\phi_R\rangle + R \hat{C} |\phi_R\rangle + L (\varepsilon_L - E) |\phi_L\rangle + \hat{C} |\phi_L\rangle = 0 \quad (4.6)
\]

A projection on the initial states \( \langle \phi_R | \) and \( \langle \phi_L | \) gives:

\[
\begin{align*}
\begin{cases}
R (\varepsilon_R - E) + R \langle \phi_R | \hat{C} |\phi_R\rangle + L (\varepsilon_L - E) \langle \phi_R | \phi_L\rangle + L \langle \phi_R | \hat{C} |\phi_L\rangle = 0 & (4.7a) \\
R (\varepsilon_R - E) \langle \phi_L | \phi_R\rangle + R \langle \phi_L | \hat{C} |\phi_R\rangle + L (\varepsilon_L - E) + L \langle \phi_L | \hat{C} |\phi_L\rangle = 0 & (4.7b)
\end{cases}
\end{align*}
\]

From equation (4.4) we found:

\[
\begin{align*}
\begin{cases}
\langle \phi_R | \hat{C} |\phi_R\rangle = \langle \phi_L | \hat{C} |\phi_L\rangle = 0 & (4.8a) \\
\langle \phi_R | \hat{C} |\phi_L\rangle = \langle \phi_L | \hat{C} |\phi_R\rangle = c & (4.8b)
\end{cases}
\end{align*}
\]

Noting \( S \) the overlap matrix:

\[
S = \langle \phi_R | \phi_L \rangle = \langle \phi_L | \phi_R \rangle \quad (4.9)
\]

we have:

\[
\begin{align*}
\begin{cases}
R (\varepsilon_R - E) + L (\varepsilon_L - E) S + L c = 0 & (4.10a) \\
R (\varepsilon_R - E) S + R c + L (\varepsilon_L - E) = 0 & (4.10b)
\end{cases}
\end{align*}
\]

or:

\[
\begin{pmatrix}
\varepsilon_R - E & c + (\varepsilon_L - E) S \\
c + (\varepsilon_R - E) S & \varepsilon_L - E
\end{pmatrix} \quad (4.11)
\]
4.2. Plasmon hybridization

with the characteristic polynomial:

\[
(\varepsilon_R - E)(\varepsilon_L - E) - [c + (\varepsilon_L - E)S][c + (\varepsilon_R - E)S] = 0 \quad (4.12)
\]

\[
E^2(1 - S^2) - E[(\varepsilon_R + \varepsilon_L)(1 - S^2) + 2cS] + \varepsilon_R\varepsilon_L(1 - S^2) - c^2 = 0 \quad (4.13)
\]

and determinant:

\[
\Delta = [(\varepsilon_R - \varepsilon_L)(1 - S^2)]^2 + 4cS((\varepsilon_R + \varepsilon_L)(1 - S^2) + 4c^2) \quad (4.14)
\]

thus the eigenenergies of the system are:

\[
\begin{cases}
E_+ = \frac{1}{2}(\varepsilon_R + \varepsilon_L + \sqrt{\Delta}) \\
E_- = \frac{1}{2}(\varepsilon_R + \varepsilon_L - \sqrt{\Delta})
\end{cases} \quad (4.15)
\]

Two eigenenergies are found, with an energy difference \(E_+ - E_- = \sqrt{\Delta}\) \(4.16\).

To determine to which mode they correspond (bonding or antibonding) we need to calculate the normalizing factors \(R\) and \(L\) for each mode. To do so we insert the expression of \(E_-\) and \(E_+\) into the system \(4.11\).

For the eigenenergy \(E_-\):

\[
\begin{cases}
R_- (\varepsilon_R - E_-) + L_- c = 0 \\
R_- c + L_- (\varepsilon_L - E_-) = 0
\end{cases} \quad (4.17)
\]

where \(R_-\) and \(L_-\) stand for the factors of the eigenstate \(|\Psi_-\rangle = R_- |\phi_R\rangle + L_- |\phi_L\rangle\) associated with the eigenvalue \(E_-\).

\[
\begin{cases}
\frac{R_-}{2}(\varepsilon_R - \varepsilon_L + \sqrt{\Delta}) + L_- c = 0 \\
R_- c + \frac{L_-}{2}(\varepsilon_L - \varepsilon_R + \sqrt{\Delta}) = 0
\end{cases} \quad (4.18)
\]
Chapter 4. Dimers of metallic nanorods: symmetry breaking and localization of the hybridized modes

Solving this system we have:

\[ R_- = \frac{(\varepsilon_R - \varepsilon_L) - \sqrt{\Delta}}{2c} L_- \]  \hspace{1cm} (4.19)

And the eigenstate becomes:

\[ |\Psi_-\rangle = \left( \frac{(\varepsilon_R - \varepsilon_L) - \sqrt{\Delta}}{2c} |\phi_R\rangle + |\phi_L\rangle \right) L_- \]  \hspace{1cm} (4.20)

The same manner we have for the eigenenergy \( E_+ \):

\[ R_+ = \frac{(\varepsilon_R - \varepsilon_L) + \sqrt{\Delta}}{2c} L_+ \]  \hspace{1cm} (4.21)

And the associated eigenstate is:

\[ |\Psi_+\rangle = \left( \frac{(\varepsilon_R - \varepsilon_L) + \sqrt{\Delta}}{2c} |\phi_R\rangle + |\phi_L\rangle \right) L_+ \]  \hspace{1cm} (4.22)

From the values of \( \frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} \) depends the symmetry of the wavefunctions \( |\Psi_\pm\rangle \). Thus, for \( \frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} = 1 \) the wavefunction is symmetric while for \( \frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} = -1 \) it is antisymmetric. Symmetric and antisymmetric cases come together when \( \varepsilon_R = \varepsilon_L \), this is typically the case of a perfectly symmetric system, a homodimer that will be discussed below. Non-symmetric cases occur when \( \frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} \neq \pm 1 \), then the wavefunction is much more located over one of the monomers for a hybridized state and over the other monomer for the other hybridized state, see figure (4.3).
4.2. Plasmon hybridization

For the simple case of a homodimer consisting of two identical monomers forming the dimer, we have $\epsilon_R = \epsilon_L = \epsilon_0$. Then, it comes:

$$
\begin{align*}
E_- &= \epsilon_0 - c \\
E_+ &= \epsilon_0 + c
\end{align*}
$$

4.2.1 A simple case: the homodimer

For the simple case of a homodimer consisting of two identical monomers forming the dimer, we have $\epsilon_R = \epsilon_L = \epsilon_0$. Then, it comes:

$$
\begin{align*}
E_- &= \epsilon_0 - c \\
E_+ &= \epsilon_0 + c
\end{align*}
$$

Figure 4.3: BEM simulations of the eigencharges spatial distribution for the first four modes of a nanoantenna heterodimer (red:Max, blue:min).
With an energy splitting of the modes: $E_+ - E_- = \sqrt{\Delta} = 2\varepsilon$.

\[
\begin{aligned}
R_- &= -L_- \\
R_+ &= L_+
\end{aligned}
\]  
(4.24a)  
(4.24b)

and

\[
\begin{aligned}
|\Psi_-\rangle &= (-|\phi_R\rangle + |\phi_L\rangle)L_- \\
|\Psi_+\rangle &= (|\phi_R\rangle + |\phi_L\rangle)L_+
\end{aligned}
\]  
(4.25a)  
(4.25b)

The antisymmetric state $|\Psi_-\rangle$ corresponds to the bonding mode with charge densities of different signs on either sides of the gap, the symmetric state $|\Psi_-\rangle$ is the antibonding mode with charge repulsion through the gap.

For this case the normalization gives:

\[
\begin{aligned}
\langle \Psi_- | \Psi_- \rangle &= (\langle \Psi_R | \Psi_R \rangle + \langle \Psi_L | \Psi_L \rangle - \langle \Psi_L | \Psi_R \rangle - \langle \Psi_R | \Psi_L \rangle)L_-^2 \\
\langle \Psi_+ | \Psi_+ \rangle &= (\langle \Psi_R | \Psi_R \rangle + \langle \Psi_L | \Psi_L \rangle + \langle \Psi_L | \Psi_R \rangle + \langle \Psi_R | \Psi_L \rangle)L_+^2
\end{aligned}
\]  
(4.26a)  
(4.26b)

\[
\begin{aligned}
\langle \Psi_- | \Psi_- \rangle &= (2 - 2S)L_-^2 = 1 \\
\langle \Psi_+ | \Psi_+ \rangle &= (2 + 2S)L_+^2 = 1
\end{aligned}
\]  
(4.27a)  
(4.27b)

\[
\begin{aligned}
L_- &= \frac{1}{\sqrt{(2 - 2S)}} \\
L_+ &= \frac{1}{\sqrt{(2 + 2S)}}
\end{aligned}
\]  
(4.28a)  
(4.28b)

And finally we obtain:

\[
\begin{aligned}
|\Psi_-\rangle &= \frac{1}{\sqrt{(2 - 2S)}}(-|\phi_R\rangle + |\phi_L\rangle) \\
|\Psi_+\rangle &= \frac{1}{\sqrt{(2 + 2S)}}(|\phi_R\rangle + |\phi_L\rangle)
\end{aligned}
\]  
(4.29a)  
(4.29b)
4.3 Lithographed Nanorods

Below are presented some EELS experiments on dimer nanoantennas, the expectations from such experiments may be summarized as follow:

- for a coupled system, the modes are spatially segregated depending on their symmetry. Thus, inside the gap, only the antibonding modes are measured.

- At the external extremities of the monomers (i.e. their edge opposed to the gap), bonding and antibonding modes are measured.

- The bonding modes are expected at lower energies than their corresponding antibonding modes.

I have prepared silver dimer nanoantennas by electron beam lithography, as this technique seems ideal to design devices for which the control of the dimensions is critical [65]. Two nanorods separated by a gap of about $20 - 40 \text{ nm}$ are prepared on a $30\text{nm}$ thick $\text{Si}_3\text{N}_4$ membrane coated with a $5 \text{ nm}$ conductive Indium Tin Oxyde (ITO) layer, the nanorods are made of a $3 \text{ nm}$ Cr adhesion layer and $40 \text{ nm}$ of Ag. The range of sizes used for the gap authorizes a classical description of the system but still allows coupling between the two nanorods as demonstrated in the following.
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Figure 4.4: a) EELS spectra measured along a lithographed silver dimer nanoantenna. The colors of the plot correspond to the marker position on the inset HAADF image, scalebar is 100 nm. b) Intensity map of the peaks fitted in the range [1.2, 1.45 eV], c) energy map and d) FWHM map. e) Intensity map of the peaks fitted in the range [1.5, 2.4 eV], f) energy map and g) FWHM map.

The figure (4.4) displays the results of an EELS experiment performed on a silver dimer antenna with mean dimensions: 34x215 nm + 36 nm(gap) + 38x215 nm. Despite a 36 nm wide gap the coupling of the two nanorods occurs in this dimer. Indeed and as expected for a coupled system, there is an energy shift between the
spectral signatures measured inside the gap and at the external edges of the dimer. Inside the gap a first peak is measured at 1.38 eV (green spectrum of figure (4.4)) while outside the dimer the spectra collected at each monomer end display their first peak close to 1.25 eV (red and blue spectra). To identify the modes of this dimer, I have performed EELS multispectral imaging to measure a spectrum for each pixel of an image over the nanoantenna. Then, the measured peaks are fitted with a lorentzian shape to establish maps of their intensity, energy and full width at half maximum (FWHM). The resulting maps are displayed on figure (4.4 b, c and d) for the peaks at energies ranging in [1.2, 1.45 eV]. The intensity map of figure (4.4. b) shows three maxima of intensity over the nanoantenna, one inside the gap and one at each edges. This clearly identifies the modes mapped as being the bonding and antibonding rising from the dipolar modes of each nanorod. However, two peaks are expected to be probed at the external edges of the dimer, one for the bonding mode and one for the antibonding while only one is measured. This observation is due to the non-monochromatic electron beam used here (FWHM = 300 meV). The probed resonances are broadened, sufficiently enough to make two close resonances measured as a single broad peak. A closer observation of the energy map of figure (4.4.c) reveals that the three local maxima are measured at three different energies and the peak inside the gaps appears at the higher energy (1.4 eV vs. 1.25 eV on the left edge), the mean energy on the right being hard to determine. In addition, the FWHM map of figure (4.4.d) indicates that the peak inside the gap is the narrowest, in line with the presence of the antibonding mode only. Regrettably, the FWHM on the right side is high enough (180 meV) to explain the difficulty to determine a mean energy. Surprisingly, this behavior with three local different energies over the nanoantenna does not correspond to any expected charge distribution. Furthermore, the peak measured in the gap shows no spatial variation of its energy (and FWHM) through the gap, meaning that the corresponding mode is delocalized over the two nanoantenna. The delocalization of this signal is a strong signature of the coupling of the monomers. Following the study of the roughness on single nanorods, it has been

---

2 The same behavior is found for the second peak of each spectrum follows the same trend, inside the gap the peak is measured at 2.1 eV while they are measured close to 1.9 eV at the edges (the corresponding resonances are well probed in the middle of the monomers, see the orange and the light-blue spectra).

3 and on figure (4.4 e, f and g) for the peaks ranging in [1.5, 2.4 eV]
seen that locally the signal provided by a given multipolar surface plasmon mode may be altered in intensity and width, such effect could explain the differences found between the signal measured at each edge.

The intensity map measured for the second energy range, figure (4.4.e), shows intense signal in the center of each nanorod. For isolated monomers, such a dis-

**Figure 4.5:** a) EELS spectra measured along a lithographed silver dimer nanoantenna. The colors of the plot correspond to the marker position on the inset HAADF image, scalebar is 100 nm. b) Intensity map of the peaks fitted in the range [0.80, 0.92 eV], c) energy map and d) FWHM map. e) Intensity map of the peaks fitted in the range [1.2, 1.5 eV], f) energy map and g) FWHM map.
tribution corresponds to the $m = 2$ mode. However, the energy and FWHM maps (figure 4.4 f) and g)) show different values measured over each nanorod while the signal in the gap is too low to be mapped (but still exists as observed on the green spectra). Putting aside the lack of signal in the gap, three reasons may explain the different energies measured:

- a too weak coupling of the nanorods at given energies, turning the measured peaks into those of the uncoupled monomers,

- a localization of the bonding and antibonding modes over the monomers as it is expected for such a heterodimer,

- a local variation of the signal due to the roughness.

The same general behavior is observed over others lithographed dimer nanorods. The figure (4.5) shows another silver dimer antenna with mean dimensions: $41 \times 441 \text{nm} + 32 \text{nm (gap)} + 49 \times 441 \text{nm}$. The observations are the same as for the previous dimer excepting the complete mapping of the peak for the $m = 2$ hybridized modes where the peak is also mapped inside the gap with no spatial variation of its energy. This observation excludes a too weak coupling of the monomeres and favors the assumptions of a coupled heterodimer with localized signal of the modes or an effect of the roughness. A third lithographed dimer is displayed on figure (4.6). This nanoantenna is shorter than the previous ones ($33 \times 111 \text{nm} + 20 \text{nm (gap)} + 37 \times 111 \text{nm}$), so only one mode is mapped but still three energies are measured along the dimer ($1.5 \text{eV}, 1.7 \text{eV}$ and $1.9 \text{eV}$). In the following a study of dimers made of monocrystalline nanorods is presented, such systems are ideal to neglect the local modulation effects of the roughness.
4.4 Monocrystalline Nanorods

To elucidate the effect of roughness, I used monocrystalline chemical colloidal gold nanorods (fabricated by Thomas Lerond and Silvere Schuermans at the LNIO). The preparation of colloidal solutions of gold nanorods with homogeneous size distributions close to several hundreds of nm is still a challenge, thus only a few dimers with monomers of comparable sizes has been accessible. Moreover, as they are made in solution, the nanorods stand randomly on the Si TEM grids. Fortunately I could find some pairs aligned along their long axis like the
lithographed dimers.
The figure (4.7. a) (inset)) shows such a chemical dimer with dimensions $50 \times 273 \text{ nm} + 23 \text{ nm (gap)} + 65 \times 347 \text{ nm}$. Despite the angle between the two nanorods, the mapping of the peaks lying in the energy range $[0.80, 1.20 \text{ eV}]$, reveals an effective coupling through the non-dispersity of the energies fitted inside the gap. Furthermore, the energy map shows a clear signature of a coupled heterodimer with two hybridized modes each localized over one nanorod. Here a peak at $0.90 \text{ eV}$ is localized on the right nanorod while a higher energy peak at $1.0 \text{ eV}$ is localized on the left nanorod and over the gap too. As only the charge symmetric mode can be probed in the gap, this mode can be attributed to the peak measured on the left nanorod and consequently the antisymmetric mode is localized on the right nanorod. In a second energy range $[1.20, 1.45 \text{ eV}]$, a case similar to the lithographed nanorods of figure (4.5) is found with two peaks located at the center of each nanorod at different energies and FWHM.

A second couple is presented on figure (4.8) for which the energy map also exhibits three different energies spatially localized for the first set of peak fitted. This observation, however must take into consideration the width of the peaks measured, that hinders the interpretation.
Figure 4.7: a) EELS spectra measured along a monocrystalline silver dimer nanoantenna. The colors of the plot correspond to the marker position on the inset HAADF image, scalebar is 200 nm. b) Intensity map of the peaks fitted in the range [0.80, 1.20 eV], c) energy map and d) FWHM map. e) Intensity map of the peaks fitted in the range [1.2, 1.45 eV], f) energy map and g) FWHM map.
These observations clearly differ from the behavior expected from a quasi-perfect case, which assume end to end aligned chemical nanorods \[62, 61\]. Indeed we have:

- only one peak measured for each mode \( m \)
- this peak has a different energy at each local intensity maximum
- the \( m = 1 \) modes that seems to be localized while the \( m = 2 \) modes clearly localize on different nanorods

Figure 4.8: EELS spectra measured along a monocrystalline silver dimer nanoantenna. The colors of the plot correspond to the marker position on the inset HAADF image, scalebar is 40 nm. b) Intensity map of the peaks fitted in the range \([1.15, 1.6 \text{ eV}]\), c) energy map and d) FWHM map.
Chapter 4. Dimers of metallic nanorods: symmetry breaking and localization of the hybridized modes

To interpret these experiments, we need to extend the regular interpretation (such as developed in [61]) to take into account that:

- The monomers are far from being identical
- The distance between two rods is large
- The monomers have imperfect geometry
- The spectral resolution is no better than an hundred of meV

Regarding the heuristic model developed above, the most obvious possibility to explain the departure of our observations with respect to the expectations is the imperfect coupling between two nonidentical monomers. To prove this point, I have performed extensive BEM calculations as shown in the following.

4.5 BEM Simulations

I performed BEM calculations of EELS spectra to retrieve the observations via simulations of the dimers. First, I used the nanoantenna of figure (4.4) as an example to study the effect of asymmetry on the energies of the system. As we have seen that the rugosity is not the main cause of the observed deviations, I have assumed that the monomers are perfectly axisymmetric in the following. The table (4.1) shows a comparison of the calculated energy loss diagram of the $m = 1$ and $m = 2$ modes of two dimers, a homodimer ($34 \times 215$ nm $+ 36$ nm(gap)$+34 \times 215$ nm) and a heterodimer ($34 \times 215$ nm $+ 36$ nm(gap)$+38 \times 215$ nm). The energies of the modes are summarized in the table (4.2). Interestingly, as the nanorods of the heterodimer are close in dimensions, only hybridization of modes of the same order $(m)$ is observed.

For both dimers, an energy splitting occurs from the initial modes and the energy differences between the bonding and antibonding modes is more important in the heterodimer, in accordance with the expectation (see equation: (4.16)). Comparing the final and initial energies for both dimers reveals that the differences are larger for the homodimer. Indeed, for the heterodimer the final states are closer to the initial states of its monomers: (equations (4.20) and (4.22)). Thus, the
4.5. BEM Simulations

Table 4.1: a) Calculated energy diagram for a homodimer (in the center) \((34 \times 215 \text{ nm} + 36 \text{ nm(gap)} + 34 \times 215 \text{ nm})\) and its monomers (at both sides). b) for a heterodimer (in the center) and its monomers \((34 \times 215 \text{ nm} + 36 \text{ nm})(\text{left})\) and \((+38 \times 215 \text{ nm})(\text{right})\)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Homodimer</th>
<th>Heterodimer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>left</td>
<td>dimer</td>
</tr>
<tr>
<td>m=1</td>
<td>1.03</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>1.0825</td>
<td></td>
</tr>
<tr>
<td>m=2</td>
<td>1.8625</td>
<td>1.8275</td>
</tr>
<tr>
<td></td>
<td>1.9075</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: table of the energies calculated for the isolated monomers and the coupled homo- and heterodimers shown in the energy diagrams.
bonding modes energies are close to the energies of the isolated monomers with the lower energies (right) and the energies of the antibonding modes are close to the energies of the isolated monomer with the higher energies (left). A study that shows the evolution of the hybridization of the modes (even for different orders \( m \)) with the structural asymmetry of the dimers has been made by Abb et. al. in [56]. Opposite to the present case, Abb et. al. didn’t perform near-field measurements.

After this comparison of the energies of a homodimer and a heterodimer, I have calculated the spatially resolved EELS dispersion over dimer nanoantennas. Figure (4.9) shows the dispersion calculated for a dimer with dimensions comparable with those of the nanoantenna of figure (4.4) ca. (34x215 nm + 36 nm (gap) + 38x215 nm). The lift of degeneracy of the modes is obvious since we observe paired modes. A comparison with the corresponding experimental dispersion map (figure (4.10. bottom) confirms the assumption on the broadening of the measured peaks due to the non-monochromaticity of the e-beam. The localization of the modes in this heterodimer is also observed, the signal of the bonding mode at 0.975 eV is more intense over the left nanorod while the antibonding mode at 1.108 eV is mainly delocalized over the dimer. The same behavior is observed for the upper hybridized modes exhibits a bonding state at 1.848 eV and an antibonding state at 1.973, both localized as above and so one for the higher order \( m \) modes. However, for the modes of higher energy, the localization is increased and the system seems less coupled. Simulations for the nanoantenna of figure (4.11) show the same behavior.
Figure 4.9: Calculated EELS dispersion map for the modelized lithographed heterodimer of figure (4.4).
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Figure 4.10: Top: Calculated EELS dispersion map for the modelized lithographed heterodimer of figure (4.4) convolved along the energy axis with a gaussian shaped peak with 300 meV of FWHM. Bottom: experimental EELS dispersion map.
Figure 4.11: Top: Calculated EELS dispersion map for the modelized lithographed heterodimer of figure (4.5). Bottom: experimental EELS dispersion map.

The study of the evolution of the localization of the modes has been done
by following their EELS intensity profile on a nanoantenna as a function of the size of the gap. The figure (4.12) displays for a nanoantenna with dimensions (15x150 nm (gap) 10x100 nm) the intensity profiles of two hybridized modes for gap size ranging from 2 nm to 32 nm. The monomers have the same aspect ratio, so their modes are energetically close and coupling occurs only for modes of same order. We observe a shift of the maxima that follows the gap opening, but as the gap increases, the profile turns higher over the left nanorod for the lower energy peaks, and on the right nanorod for the higher energy peaks. For large gaps (i.e for less coupled nanorods), the ratio of intensities between the two nanorods is higher for the higher order modes. This can be explained by the lower spatial extent of the near-field for these modes the consequence of which is a lower overlap of the modes.
To retrieve the experimental observation of three energies found over the dimer nanoantennas, one may take into account the energy broadening due to the non-monochromaticity of the electron beam. The experimental EELS spectra are a convolution of the optical response of the sample with a peak of which width is due to the energy distribution of the electron beam, 300 meV FWHM in our case. The latter can be roughly modelized by a 300 meV FWHM gaussian shape. The convolution of such a broad peak with the previous calculation is displayed on figure (4.9. Top) and compared with the experimental results. Applying the effect of the e-beam smooths out the adjacent degenerated peaks. The resulting peaks are then broadened with a maximum at the barycenter of the previous peaks, the
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Figure (4.13) displays three spectra calculated at different positions along the dimer (left and right extremities, and gap) for which three different energies are found like the experimental results. Actually a slight energy shift is found in the gap (30 meV), lower than the shift between the two extremities. Such a shift cannot be measured experimentally as it is lower than the experimental spectral dispersion (50 meV). Finally, the observations have been retrieved by the simulations and are explained by the coupling of the nanorods for the lift of degeneracy of the modes and by the convolution of the signal with the non-monochromatic electron beam for the particular maps established in our microscope that show three different energies for a given mode of a heterodimer.

![Graph showing spectra](image)

*Figure 4.13: Comparison of the spectra calculated at the edges of the dimer and inside the gap before (solid lines) and after (dashed lines) convolution with a gaussian shape. In red: left edge, green: inside the gap and blue: right edge*

### 4.6 Conclusions

In this chapter, I have shown the first EELS mapping of the localization of hybridized modes over dimer nanoantennas. The combination of deconvolution of the spectra and spatial mapping of physical quantities (intensity, energy and FWHM) via fitting of the peaks has allowed to overcome the low energy resolution of our microscope. Performing this experiments in a monochromated electron microscope
may allow to establish EELS dispersion map with an energy resolution comparable with the one of figure (4.9). Moreover this work has shown that the limits inherent to the lithography process for the fabrication of coupled nanorods, \textit{i.e.} limited spatial resolution for the gap and polycrystallinity of the rods, do not prevent the monomers to couple. The bonding modes have intense electric-near field inside the gap, but this signal cannot be probed by EELS (only the electric near-field component parallel to the e-beam is measured). However, coupling effects have been measured otherwise, so these results confirms this dimer structure as a potential good candidate for coupling with quantum emitters through the gap. Still, calculations of electric near-field intensity in the gap need to be performed. Future experiments may be performed by EELS and CL measurements (provided that the CL available energy range contains the coupled resonances) to obtain a more complete description of these systems. Recently, heterodimers made of monomers of different materials have been proposed for new optical applications \cite{66} and coupled EELS-CL experiments as a good tools for studying such structures \cite{67}. As a prospective (chapter 6) a preliminary study on such plasmonic dimer antenna in proximity to quantum emitters is presented.
In this chapter, we present a nano-optical study on colloidal core-shell CdSe/CdS semi-conductors quantum-dots (QDots). Such nano-crystals have already been observed many times at the individual scale by several optical techniques like dark-field optical microscopy, scanning near-field optical microscopy (SNOM) [68], stimulated-emission-depletion microscopy (STED) [69], scanning tunneling luminescence (STL) [70], electron energy-loss spectroscopy (EELS) [71], etc. but there is still a high technological interest for tools able to perform nanoscale optical studies on a wide variety of materials. We propose the STEM-CL as such a suitable tool. Up to now SEM-CL has already been used to study CdSe quantum dots, but has been unable to probe individual objects due to heating of the sample under the e-beam and the generation of secondary electron (SE) causing low spatial resolution. But STEM-CL is a reconsidered approach of the CL, trying to avoid the heating and SE of the specimen and increasing the spatial resolution. Here, after introducing the concepts specific to quantum-dots, we take advantage of their simple spectral feature to perform a comparison of cathodoluminescence and photoluminescence (PL) on the same individual nano-object. Then we use the higher spatial resolution of the STEM-CL to make experiments on small clusters of quantum dots spatially indistinguishable with standard optical resolution. Furthermore, due to their high quantum efficiency these quantum dots seemed to be good objects for a hybrid metal/semiconductor nanosource of light.
5.1 Confined nanocrystals

Bulk semiconductor materials have a band gap over which an electron in the valence band $B_v$ is promoted to the conduction band $B_c$ if excited by a photon with energy higher than the energy of the gap $E_g$. The excited electron in the conduction band leaves a hole in the valence band, this electron-hole pair may interact via Coulomb interaction and can be interpreted as a neutral quasi-particle known as exciton. This exciton has a spatial extent defined as its radius $a_{B_{exc}}$:

$$a_{B_{exc}} = \frac{\varepsilon}{m_{exc}} a_0$$

(5.1)

where $\varepsilon$ is the dielectric constant of the material, $m_{exc} = \frac{m_e m_h}{m_e + m_h}$ is the mass of the exciton (the reduced mass of the electron-hole pair), $m_e$ and $m_h$ the mass of the electron and the hole respectively and $a_0 = 0.053 \text{nm}$ the Bohr radius for the hydrogen atom.

Interesting quantum mechanical phenomena occur when a semiconductor is confined in space to a size comparable to the radius of the exciton (5.4nm for CdSe [72]), figure (5.1). In particular for a nanocrystal smaller than $a_{B_{exc}}$, the system is in high confinement regime where the potential of the confined crystal is much higher than the Coulomb potential of the electron-hole pair, then the energy levels in the conduction band become discretized. From the analogy with atomic spectra these objects have been called artificial atoms. Controlling the size of nanocrystals during the fabrication process allows one to tune the energy of the transition between the ground state and the excited state (which is in a first approximation inversely proportionnal to the size of the particle).

Besides the dimensions of the confining region, the continuity of the band diagram at an heterojunction plays a major role on the confinement of the exciton. Type I heterojunction confines the electron and the hole together, keeping the pair in close proximity it facilitates radiative recombinations (figure 5.2). Type II configuration isolates the carriers, one is confined in the core while the other is delocalised in the shell. This configuration is the less advantageous for radiation emission as one of the carriers can interact at the surface, enhancing the non-radiative deexcitation channels. Also the spatial separation of the pair reduce the Coulomb interaction between the carriers. Quasi-type II is an intermediate
Figure 5.1: Different geometries to confine semiconductors (in blue, the confined region). a) 1D confinement: the carriers are free in the orthogonal plan (ex: disk, platelet), b) 2D confinement: carriers free along the long axis (ex: rod, wire, nanotube) and c) 3D confinement: the carriers have zero degree of liberty (ex: Quantum dots: non-dimensional object). The line drawings below each geometries shows the corresponding band structure with the indicated $B_c$ and $B_v$, for type I heterojunctions.
case where one carrier is confined in the core while the other is delocalised in the whole core-shell structure.

5.2 Optical properties

Quantum dots emit light by the radiative recombination of an electron-hole pair, however other deexcitation channels are competing with photon emission. Three deexcitation ways are mainly considered: the excitation of phonons, the Auger process and the emission of a photon. The latter is the only process we can measure by CL. However, it can be favored by reducing the phonon excitation channel. Thus, the phonons excitations can be reduced by protecting the Qdot with a shell that keeps the exciton far from the surface of the crystal. Indeed, phonons are efficiently excited when a carrier of the exciton is trapped in a non-radiative recombination center, e.g. a crystalline defect that often are located at the surface of the nanocrystals. Auger process happens when more than one exciton is excited (multiexciton), the recombination energy is transferred to an electron or a hole of another pair possibly unbinding the second exciton and putting the particle in an ionised state. The Auger process tend to let the system in a "grey state" [73]
where subsequent excitons will preferably decay via Auger process, drastically reducing the luminescence, see figure (5.3). However the grey state is unstable, the Qdot returns to bright state as soon as the carrier in excess recombines. The switching between bright and grey states makes the qdot blinking when observed. Unfortunately, the blinking process follows complex statistic laws, making the bright and grey periods of a Qdot unpredictable. Combinations of Auger and phonons emission may also occur multiplying the deexcitation channels.

![Diagram of Qdot recombination](image)

*Figure 5.3: Scheme representing the recombinations occurring for a neutral qdot (top) and an ionised qdot (bottom). Non-radiative recombination processes have shorter lifetimes for the ionised qdot ($\tau_A < \tau_{rad}$), which appears darker or "grey".*

### 5.3 Fragile specimens and electron microscopy

Some precautions must be taken when performing STEM-CL in a STEM, particularly for fragile specimens like colloidal II-VI semiconductors. Indeed, focusing a high energy electron beam through a nanocrystal may cause several drawbacks. As reported in a previous SEM-CL work on CdSe/ZnS colloidal core-shell quantum-dots films [74], such a beam may induce irreversible structural damages to the sample, provokes an overheating and produces secondary electrons. As seen in the
previous section, structural defaults on a nanocrystal must reduce the luminescence yield of the Qdot by opening phonon deexcitation channels. As seen on figure (5.4), the electron beam of a STEM could provoke severe damages to the crystalline structure of a dot but not systematically. Furthermore, the high vacuum inside the chamber of a STEM may also alterate the surface of the specimen. The overheating and generation of secondary electron phenomena associated to the interaction of an electron beam with a specimen are strongly reduced in a STEM setup. Indeed, the transmission of the electron beam through the specimen requires thin samples, thereby reducing the interaction. Figure (5.5) shows compared simulations\(^1\) of an electron beam of different energies impinging on a bulky sample (related to SEM) and a 100 keV electron beam passing through a 25 nm nanocrystal and 15 nm of silicium (related to STEM). The interaction volume obviously depends on the setup and the results that follow confirm that STEM-CL is a suitable tool for such studies.

\[\text{Figure 5.4: Structural damages induced by a high energy (100 keV) electron beam on individual Qdots. a) High resolution TEM image of a CdSe/CdS Qdot after PL and STEM-CL measurements, image by Arjen Dijksman (ESPCI). b) and }\] \(c\) shows an exceptional case of a structurally destroyed Qdot (not the same as in a)). The image b) has been performed after several beam exposition as revealed by the exposition pattern visible in the image. c) shows the Qdot after destruction and d) the CL spectrum acquired on this single quantum dot.

\[\text{Preliminary results}\]

We did a first measurement on commercial colloidal core-shell CdSe/ZnS type I quantum-dots\(^2\). The results were not compelling even if performed with a setup

\(^1\)Using the Casino program: [http://www.gel.usherbrooke.ca/casino](http://www.gel.usherbrooke.ca/casino)

\(^2\)from Evident Technology
Figure 5.5: Simulations of the electron-beam/specimen interactions calculated with the software Casino.v3 (Sherbrooke Univ.). The grey region is made of Si while the yellow spot is a 25nm CdSe/CdS nanocrystal. From top-left to bottom-right (excluding the red framed box) a thick (1µm) specimen is probed by an electron beam of increasing energies (10 – 500keV). The interaction volume grows from 10keV to 40keV and decreases for higher energies due to lower duration of interaction. The lower right (red) simulates the STEM-CL setup working conditions: 15nm Si substrate and 100keV e-beam. The scale bar on the top-left is 1µm.
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optimised for such a study. Individual particle study was not possible due to low and unstable signal, spectra were acquired only from aggregates of particles. Indeed, the blinking phenomenon is strong for CdSe/ZnS Qdots. Because of high mismatch between the lattice parameters of CdSe and ZnS, only few ZnS atomic layers (generally 1 or 2) can grow on the CdSe core. Fabrication of thick shell of ZnS to reduce non-radiative recombinations through the surface is then impossible. However, thicker shell can grow on CdSe cores either by adapting the ZnS via a lattice parameter gradient [75] or by using an other material with a good lattice parameter. The latter solution can be achieved with a thick CdS shell on a CdSe core giving quantum dots with reduced blinking. We have found such thick-shell CdSe/CdS quantum dots synthesized by Arjen Dijksman, Clémentine Javaux and Michel Nasilowski from the group of Benoît Dubertret at ESPCI-ParisTech. These nanocrystals are covered by a CdS shell with thickness up to 10nm, following the synthesis process developed by Mahler et al. [76]. With this configuration, the exciton despite being less confined in the core because of the quasi-type II configuration of CdSe/CdS figure (5.2), is much more isolated from the external surface of the crystal, reducing the probability of non radiative decay.

5.4 Cathodoluminescence

Photoluminescence experimental setup

All the PL experiments (spectroscopy and lifetime measurements) have been performed by Arjen Dijksman at ESPCI-ParisTech, using the following setup. An excitation laser (PicoQuant) at \( \lambda = 402 \text{nm} \) (pulsed or cw) focused through an inverted microscope Olympus IX71 equipped with an air objective \((\times 100, \text{NA} = 0.9)\) positioned on a piezoelectric scanner stage. Spectra are acquired through a Shamrock 750 spectrometer with 150g/mm grating and an Andor Technology CCD camera. A photoluminescence spectrum acquired with this setup is displayed on figure (5.7.b (blue)). A Hanbury-Brown and Twiss (HBT) setup for correlation measurements equipped with two single photon avalanche detectors (SPADs) from Micro Photon Devices and a HydraHarp (PicoQuant) acquisition.

\(^3\) (STEM-CL at 150K ; e-beam at 40 – 100keV) Vs. (SEM-CL at room temperature ; e-beam at x10keV) in the work by Rodriguez-Viejo et al. [74]
card that synchronizes the detection with the pulsed laser pulses.

**Localisation pattern and Sample preparation**

I used e-beam lithography to pattern a TEM Si substrate with metallic crosses labelled with alphabetical coordinates, figure (5.6). This reference frame eases the localisation of the nanocrystal by BF/HAADF in the STEM and by fluorescence imaging in the PL setup. A drop of the solution containing the colloidal quantum dots is deposited on the substrate. To prevent the case of non-unique quantum dot under the laser beam, the solution is prepared with a concentration that keeps two neighbouring Qdots separated by at least $5\mu m$. In addition, a polymer sample holder designed under SolidWorks and printed in 3D has been fabricated. It allows to easily manipulate the TEM grids and their fragile 15 nm thick Si membrane.

![Figure 5.6: SEM images of a Si membrane (size 100µm x 100µm) covered by a pattern of metallic crosses for the localisation of the nanocrystals. The letters at the edges are for the alphabetical coordinates (A; a)/ i.e. (Uppercase; lowercase).](image)

**5.4.1 Cathodoluminescence and Photoluminescence of the same individual Quantum-dot**

Cathodoluminescence and photoluminescence spectroscopies have been performed on several individual Qdots. The measured spectra for a given Qdot are displayed
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on figure (5.7) together with HAADF image of the particle.

Figure 5.7: Comparison of STEM-CL and PL measured on the same qdot. a) HAADF image captured after the CL, b) PL (blue) and STEM-CL (red) spectra acquired on the qdot. The shift in wavelength is explained by the temperature difference for the two measures (CL: 150K and PL: 300K). Integration time is 1 min for PL and 50 ms for CL.

Each spectrum shows only one single emission peak, at 637 nm (width 20 nm) for PL and 626 nm (width 14 nm) for CL, both in agreement with the related 3nm core diameter. The spectral shift is explained by the temperatures of each setup, PL is performed at room temperature (300 K) while STEM-CL is performed at (150 K), the temperature of the liquid nitrogen cooled sample holder. Such shift and broadening are predicted following the formulas (5.2a) and (5.2b) given by AlSalman et al. [77] which describe the temperature dependancies of the wavelength and the width of the peak as represented on figure (5.8). This model takes into account the coupling of the exciton with the optical and acoustic phonons of the nanocrystal. The coupling of the exciton with these phonons depends on their Bose-Einstein distributions, which are temperature dependent.

\[
\begin{align*}
E_g(T) &= E_g(0) - \frac{\alpha T^2}{T + \Theta} \\
\Gamma(T) &= \sigma T + \frac{\Gamma_{LO}}{e^{\frac{E_{LO}}{kT}} - 1}
\end{align*}
\]

(5.2a)  
(5.2b)
where $E_g(T)$ is the energy of the gap at the temperature $T$, $E_g(0) (= 2.04 \text{eV})$ the gap energy at 0 K, $\alpha (= 3.2 \pm 0.5 \times 10^{-4} \text{eV.K}^{-1})$ the temperature coefficient and $\Theta (= 78 \pm 35 \text{K})$ a parameter related to the Debye temperature of the crystal. $\Gamma(T)$ is the total linewidth at the temperature $T$, $\sigma (= 21 \pm 8 \mu\text{eV.K}^{-1})$ the exciton-acoustic phonon coupling coefficient $\Gamma_{LO} (= 30 \pm 5 \text{meV})$ the strength of exciton-optical LO phonon coupling, $E_{LO} (= 25 \text{meV})$ the LO-phonon energy and $k_B$ the Boltzmann constant.

The model fits well the wavelength dependency for both STEM-CL and PL, however the experimental linewidth is broader than expected by the model, this is most probably related to the spectral diffusion as the measured FWHM are much larger than the temperatures. The integration time of the PL measurement is 1 min compared to that of the STEM-CL experiments (50 ms), which could explain a larger broadening for the former spectroscopy.

---

**Figure 5.8:** Temperature evolutions of the emission wavelength a) and width of the peak b) according to the formula (5.2a) and (5.2b) respectively. The markers show the experimental STEM-CL and PL measurements. The red-shaded areas correspond to the amplitude of availability of the model, limited by the uncertainties on the parameters values ($\alpha$, $\Theta$, $\sigma$ and $\Gamma_{LO}$).

The cross correlation function of the quantum dot of figure (5.7) is measured before and after the STEM-CL measurement \(^4\) figure (5.9.a). The functions show a zero delay peak smaller than 0.5 for both measurements, ensuring that the single

\(^4\)The quantum dots on substrate quickly photobleach at the contact of the air. The successive measurements have to be performed in a relatively short period of time, typically less than one week.
Cathodoluminescence properties of the Qdot is kept even after the e-beam exposition. However, the emission lifetime is reduced (figure (5.9.b)) but this is not necessarily attributed to electron beam radiation damages, as several days have passed between the measurements and the quantum dots are unstable when exposed to air. This clearly shows that excepting the temperature and pressure conditions, the Qdot was in the same state during the PL and STEM-CL measurements, legitimating the interpretation suggested above for the spectral shift.

![Figure 5.9: a) Intensity auto-correlation measurement made on the Qdot of figure (5.7), before and after CL measurement. b) Photoluminescence decay of the same Qdot.](image)

After this characterisation of the STEM-CL measured on singles Qdot and the comparison with PL, we tried to go further by using STEM-CL to reach configurations where PL is inefficient: the true nanometric spatial resolution for optical spectroscopy. A comparison of the STEM-CL signals with STEM-EELS over the same individual QDot was not conclusive, the main drawback has come from the incapacity to measure the bandgaps of the Qdots due to the background signal of the Si membrane. Carbon films can be used instead of Si membranes for EELS measurements but it reduces the luminescence of the Qdots, finally no direct comparison of EELS and CL signals has been made.
5.5 Cathodoluminescence of small aggregates: STEM-CL and nanometre spatial resolution

5.5.0.1 Spatial resolution defined on a small aggregate

The initial drop of the solution of colloidal Qdots dries on the TEM Si substrates by dividing in several nano-droplets that contain a few number of particles. When the substrate is dry, we observe small aggregates of quantum dots. Figure (5.10.a) shows the HAADF image of such a small cluster containing 6 quantum dots. The scale bar (20nm) reveals that PL best spatial resolution (100nm) cannot distinguish between the components of this cluster. We can perform spatially resolved STEM-CL spectroscopy on the corresponding field of view through the spectrum imaging technique. Figure (5.10.b) is the HAADF image acquired simultaneously to the acquisition of the spectra. The corresponding STEM-CL intensity map after fitting each of the spectra is displayed on figure (5.10.d), obviously only 3 of 6 Qdots are emitting light. Also, no correlation between morphological specific features of the Qdots (orientation, presence of defects...) is observed here or in any other STEM-CL experiment to explain the presence or absence of emission. Spectra extracted from the mentioned areas in b) are shown on figure (5.10.c), the peaks are quite similar and no spectral variation is observed inside a single Qdot. Typically there is no special feature at the center of the particle neither elsewhere revealing the localisation of the core. Above all, this example allows to set a limit in the spatial resolution. Usually, four main parameters affect the spatial resolution of a STEM-CL experiment. First, the size of the electron probe, which is here less than one nanometre and thus not relevant. Second, the emission of secondary electron emission, able to trigger photon emission from the neighbourhood of the impact area. This effect is here clearly ruled out by the absence of detected STEM-CL signal when the beam is hitting the dark Qdots. Third, the broadening of the emission location due to multiple detections and interactions of the incident electron before being absorbed. This broadening known as the "excitation pear" (see figure (5.5)) is shown to be negligible, as a variation of the emitted intensity within individual Qdots can be detected (figure (5.10.d). This rules out the existence of a broad excitation pear, as expected for a 30 nm (Qdot) + 15 nm (substrate) thick sample at 60 keV. Fourth, the charge carriers created by the incoming electron at a given point may diffuse...
in the sample and optionally recombine far away from the point where they have
been created. This effect, known as charge carrier diffusion might again degrade
the spatial resolution, as the emitted light might come from a place far from the
excitation point. As mentioned above, the signal intensity within a dot seems to
scale with its thickness. No wavelength or FWHM changes can be detected within
an individual Qdot. From the point of view of the electron/matter interaction, this
means that either the diffusion length is larger than the dot size, or that the dot
responses as a whole to the electronic excitation. In any case, pragmatically, the
absence of measurable spectroscopic change within an individual dot means that
the effective spatial resolution is set by the Qdot size itself.

![Figure 5.10: High spatial resolution STEM-CL mapping of the Qdots. a) HAADF image of
a set of 6 Qdots. b) HAADF of the same set taken in parallel to a SI. c) Spectra extracted
from the spectral image on areas indicated by circles on b. d) STEM-CL intensity map.
Only 3 Qdots are emitting.](image)

Chapter 5. Cathodoluminescence of colloidal core-shell CdSe-CdS quantum
dots
5.5. Cathodoluminescence of small aggregates: STEM-CL and nanometre spatial resolution

As the STEM-CL has shown its ability to offer a spectral information comparable to PL combined with a true nanometric spatial resolution, we aim at looking at larger clusters containing several hundreds of particles in the following section.

5.5.1 Large aggregates

While no proximity effects have been evidenced for small aggregates, larger aggregates with stacked quantum dots can be thick enough to be sensitive to the heating coming from the e-beam. Figure (5.11) summarises the results obtained on a big aggregate where the spatial sampling of the STEM-CL has been set approximatively the size of a single Qdot. The time to acquire the entire dataset (4096 spectra) is around 10 minutes. As in the previous case, comparing the HAADF image figure (5.11.a) and the emission intensity map figure (5.11.d), we observe that some of the Qdots do not emit light. The intensity variations follow the thickness variations (as measured from the HAADF). The emission wavelength from Qdot to Qdot is of the order of 40 nm (figure (5.11.b and .e) and no correlation could be found between the wavelength changes and the thickness. The FWHM figure (5.11.f), however, do not follow any clear trend. From the fact that neither the wavelength nor the FWHM follows the thickness we can deduce that no obvious heating effect are seen in STEM-CL, even when several Qdots may be stacked along the electron beam direction. The number of pixels containing at least a Qdot is larger than 2000 (over 4096 pixels), with approximately 600 that are emitting. This shows how quickly information on the optical properties of dense ensemble of Qdots can be obtained. The graphs of figure (5.12) display the correlation between the quantities extracted from the gaussian fitting results. From such representations, it is easy to identify singular behaviors.
Figure 5.11: Batch measurement on a large set of QDs. a. HAADF image of the set of QDs. Individual QDs can be seen. b. Selected spectra extracted from areas circled on a. c. HAADF image acquired during an SI on the set. d. Intensity; e. Wavelength; f. FWHM maps extracted from the SI. Scale bars in c, d, e, f are 200 nm.
5.6 Conclusions and perspectives

We have shown that STEM-CL spectroscopy can be applied to study individual II-VI Qdots optical properties. By comparing with PL spectroscopy on the same individual Qdot, we have shown that both spectroscopies offer essentially the same spectral information. Common sources of heating and non-linearities previously attributed to electronic excitation are here shown to be irrelevant in a STEM. While PL is limited by the diffraction limit, and regular (low voltage) SEM on thick samples by the excitation pear and secondary electron reemission, STEM-CL is only limited by the object size, which itself defines the necessary spatial resolution. We have shown how this gain in resolution can be used to rapidly characterise the emission properties of a given set of individual Qdots. This works paves the way towards the systematic study of II-VI or III-V Qdots at the single Qdot scale. Also, it offers the possibility of studying plasmons/II-VI QD coupling at the nanometre scale (see chapter 6), much in the same way as it has been done for III-V systems. We focused in this work on the spectral information which requires relatively long acquisition times. It might be interesting to upgrade the set-up with fast, high sensitivity, low losses serial detection. This would allow to address with the improved spatial resolution other issues like QDs blinking. Figure (5.13.a) shows an acquisition of a cathodoluminescence image detected with a single photon avalanche diode (SPAD). The integration time per pixel is 2µs comparable to the time used for the acquisition of a Bright field image figure (5.13.b).

Figure 5.12: Correlation between the quantities obtained from the fitting. a) Wavelength vs. FWHM, b) Wavelength vs. intensity and c) FWHM vs. intensity
Chapter 5. Cathodoluminescence of colloidal core-shell CdSe-CdS quantum dots

Figure 5.13: a) Cathodoluminescence signal detected with a single photon avalanche diode, the acquisition time (2µs per pixel) is of the same order as for Bright field or HAADF imaging. b) the Bright field image acquired in parallel to a) (same integration time).

The results of this study have been published in [78]
Conclusions and Prospectives

Conclusions  In this thesis I have presented an EELS and CL study in a STEM of the basic components of what could be a hybrid nanosource of light, ideally a SPASER. Up to now EELS and CL have mainly been used on simple and perfect objects to establish proof of principles. The present work is a first step towards their use for the characterization of more mature devices. For this reason, I have made an extensive use of electron beam lithography to prepare the samples as this fabrication process is the closest to a large-scale use.

A study on single gold nanorods has highlighted the differences that exist between lithographed objects and chemical ones in the near-field. Both types of nanorods display a linear wavelength dispersion of their low order surface plasmon modes as a function of the aspect ratio. However, the intensity of the near-field is modified by the local occurrence of asperities on the nanorod surface. These rugosities are responsible for the onset of intense and highly localized signals at energies below the interband transition of gold. EELS and CL experiments have shown that these localized signals due to the roughness may be bright, having EELS and CL signatures or dark, having EELS signature only. The BEM simulations have provided hints on the perturbations of surface charge densities and associated electric near-field by the presence of asperities. While the interpretation on the bright or dark nature of the localized signals deserve further investigations, the appearance of both highly delocalized excitations (multipolar plasmons) and localized excitations on the same nanoantennas due to rugosities has been unveiled.

The EELS study of metallic dimer nanorods by the use of spectral imaging techniques coupled to gaussian fit of the peaks has revealed a localization of the hybridized modes over the monomers due to the structural asymmetry of the dimer. This structural asymmetry is inherent to the electron beam lithography process, as the polycrystallinity of the object cannot be controlled. The same observation
is made for monocrystalline dimers, for which there is no roughness but couples of nanorods with different dimensions. Thus, the involuntary appearance of symmetry breaking in dimers will take place as long as the fabrication process will not be fully mastered.

The cathodoluminescence investigation of colloidal core-shell CdSe-CdS quantum dots has shown that, contrary to a previous study performed in a SEM, the use of a STEM together with thick shell nanocrystals allows for single particle signal mapping. Moreover, a comparison with the photoluminescence on the same single quantum dot has revealed that the CL provides an equivalent signal. Then, the gain in spatial resolution of the CL has been used to study single particles inside clusters of several nanocrystals, thereby taking a certain advantage over the photoluminescence.

The results of this study have been published in [78]

Thus, future studies involving the STEM will be performed with the certainty that EELS and CL are adequate tools to locally probe basics element of complex and realistic nanodevices.

**Prospectives** The upcoming experiments must involve the coupling of the plasmonic systems with the quantum emitters. During my thesis, I have made several attempts to study coupled plasmonic/excitonic systems, either based on a bottom up approach (in collaboration with Thomas Lerond at LNIO) or a top down approach. None could give robust results, but are clearly pointing to the feasibility of such studies. As a preliminary experiment, I have prepared a simple hybrid system, consisting of dimers of gold nanorods over which a drop of a solution of colloidal CdSe-CdS quantum dots has been deposited. The emission of the quantum dots occurs close to 640 nm, while as seen before the roughness signal on such gold lithographed nanorods is between 550 nm and 700 nm. The results are displayed on figure (6.1).

Interestingly no CL signal coming specifically from the quantum dots close to the nanorods has been measured while a narrow signal centered at 648 nm is measured all over the dimer. This emission is slightly red-shifted in comparison to the emission of isolated quantum dots, and broader. It is thus tempting to
attributed it to a coupled quantum dots/plasmon signature. However, no signal is measured for electrons travelling close to the nanorods edges while, as seen before, an aloof trajectory of the electrons may excite the plasmon modes and the gold interband transitions. Thus the signal could also be due to the emission of secondary electrons by the gold nanorods. However such an effect has not been seen inside the clusters of quantum dots.

Further investigations are needed for a complete understanding of these observations. The study of such coupling is the subject of a thesis in progress at the LABORATOIRE DE PHYSIQUE DES SOLIDES, involving an improved version of the CL system able to perform fast measurements and measuring correlation effects with an implemented Hanbury Brown and Twiss setup. The next arrival of a monochromated electron beam STEM in the laboratory and the close development of the electron energy-gain spectroscopy (EEGS) may contribute to make scanning transmission electron microscopy an essential tool for the study of nanometric optical devices.

Figure 6.1: a) HAADF image of a dimer of gold nanorods and colloidal core-shell CdSe-CdS quantum dots. Scale bar is 100 nm. b) Cathodoluminescence dispersion map. c) Spectra extracted from a spectral image at the position specified with the arrows on a).
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L'objet de cette thèse est l'étude par microscopie électronique en trasmission à balayage (en anglais Scanning Transmission Electron Microscope, STEM) des propriétés optiques des composants de bases d'une nanosource hybride de lumière. Le cadre de cette thèse se situe dans le projet ANR HYNNA ayant pour ambition la mise au point de nanosources de lumières hybrides plasmonique/émetteur quantique. Dans cette optique le Laboratoire de Nanotechnologie et d’Instrumentation Optique (LNIO) de l’Université de Technologie de Troyes et le Laboratoire de Physique des Solides (LPS) à Orsay ont collaboré dans la fabrication et la caractérisation de telles systèmes hybrides. Le STEM a déjà fait ses preuves en termes de nanooptiques sur des systèmes plasmoniques et l’équipe STEM du LPS à Orsay a pour beaucoup contribué à l’ouverture de ce nouveau domaine d’études par spectroscopie de perte d’énergie des électrons (en anglais Electron Energy Loss Spectroscopy, EELS). Récemment l’implémentation d’un système de collection de la lumière émise dans un STEM (Cathodoluminescence) couplée a un spectromètre optique a permis d’atteindre des résolutions à la fois spatiale et spectrale de l’ordre du nanomètre. Cette thèse a pour but l’étude de composants pour la nanooptique plus proches de dispositifs optiques que ceux étudiés jusqu’à présent par les techniques de microcopies électroniques. Ainsi l’utilisation de la lithographie électronique pour la fabrication de particules plasmoniques, bien que déjà utilisée lors des travaux de thèse de Guillaume Boudarham a ici été généralisée avec l’acquisition du savoir faire qui était jusque la sous traité.

Mes travaux ont donc porté d’une part sur l’étude de cavités plasmoniques en forme de bâtonnet et des conséquences du procédé de fabrication sur leur propriétés optiques et d’autre part sur des boites quantiques émettrices de lumières sur lesquelles la nature de la cathodoluminescence a pu être caractérisée.
Dans ce chapitre j’étudie les propriétés optiques de nanobâtonnets métalliques individuels et en particuliers les effets relatifs à la cristallinité de ces nanoparticules. Il existe en effet deux procédés majeurs pour leur fabrication qui produisent des nanoparticules à la cristallinité différente. La première, par voie chimique, nécessite une bonne connaissance de la chimie colloïdale à pour avantage de produire des bâtonnets monocristallins mais sa maîtrise est ardue et les nanoparticules produites sont difficiles à organiser sur un substrat. La seconde, par lithographie électronique associée à un dépôt physique en phase vapeur de métal, est aisément mise en pratique et donne des nanoparticules aux dimensions et géométries prédéfinies toutefois celles-ci sont polycristallines. Les résultats présentés dans la suite mettent en évidence l’effet non négligeable de la rugosité sur la réponse locale des bâtonnets lithographiés.

**Dispersion des modes plasmons de surface**

La facilité d’utilisation de la technique de fabrication par lithographie électronique nous a incité à la privilégier pour la fabrication et l’étude de nos cavités plasmoniques devant à terme être couplées à un milieu à gain. Dans un premier temps, nous avons voulu nous assurer que des nanobâtonnets polycristallins répondent bien à la définition de résonateurs plasmoniques. Pour le vérifier, j’ai procédé à une mesure des longueurs d’ondes des modes plasmons de surface supportés par des nanobâtonnets ayant des rapports d’aspects \( \frac{\text{Longueur}}{\text{Largeur}} \) variables. En effet,
la dispersion des modes plasmons de surface doit suivre une tendance linéaire en fonction de ce rapport [1]. Cette tendance a déjà été confirmée sur des ensembles de bâtonnets chimiques observés en solution. Mais il s’agit ici de mesures sur des objets individuels par le biais de l’EELS, cette technique ayant l’intérêt de pouvoir sonder des modes d’ordre \( m \) impairs qui se couplent faiblement à la lumière et qui par conséquent sont rarement étudiés par voies optiques traditionnelles. La figure (1.1.a) confirme la tendance linéaire liant la longueur d’onde d’un mode plasmon de surface au rapport d’aspect d’un bâtonnet d’argent monocrystallin le supportant. Le même comportement est observé pour des nanobâtonnets d’argent polycristallins, voir figure (1.1.b).

\[\text{Figure 1.1: Mesures EELS des trois premiers modes plasmons de surface, } m=1 \text{ (rouge), 2 (bleu) et 3 (vert) pour des bâtonnets chimiques (gauche) et lithographiés (gauche).}\]

Ainsi, puisque la dispersion des modes plasmons de surface multipolaires est comparable sur les deux types de nanobâtonnets, l’utilisation en tant que composant de base d’un système hybride de bâtonnets fabriqués par lithographie électronique est envisagé et l’étude de deux résonateurs couplés est d’ailleurs présentées dans le prochain chapitre. L’étude suivante couple des mesures EELS et CL sur des nanobâtonnets d’or, cette étude plus fine du champ proche de ces nanoparticles révèle une modification de la réponse locale des objets polycristallins dus à la présence de rugosités.
1.1 Nanobâtonnets monocristallin

L’étude comparative par EELS et CL présentée dans la suite de ce chapitre n’est possible que dans une plage restreinte d’énergies. En effet, le spectromètre optique du montage de cathodoluminescence est équipé de trois réseaux de diffractions. Le premier couvre une fenêtre allant de 1 eV à 4 eV, le deuxième réseau va de 1.6 eV à 4.5 eV, quant aux troisième, non utilisé dans cette étude, il couvre la plage du proche ultra-violet de 3 eV à 6 eV. Il existe ainsi une gamme allant de 0.5 eV à 1 eV couverte par l’EELS où la comparaison avec la CL ne sera pas disponible. A noter également une moindre sensibilité (< 30%) de la CCD du spectromètre optique pour les énergies hors de la gamme s’étendant de 1.1 eV à 5 eV.

La figure (1.3.a) représente l’image HAADF d’un nanobâtonnet d’or monocristallin long de 150 nm. Pour un nanobâtonnet de cette taille, les modes plasmons de surface se trouvent à des énergies où il est possible de comparer l’EELS et la CL. Pour des nanobâtonnets de tailles supérieures, les modes d’ordre $m$ peu élevés se trouvent en général à des énergies trop basses pour être mesurés par CL. Sur la figure (1.2) sont présentés les spectre EELS (bleu) et CL (rouge) mesurés sur l’ensemble du nanobâtonnet. L’identification des pics présents sur ces spectres nécessite de connaître la signature spatiale associée à chacun d’eux, on utilise pour cela une représentation qui permet de localiser la réponse spectrale, pour l’EELS (1.3.b) et la CL (1.3.c et .d).
Chapter 1. Effets de la rugosité sur les propriétés optiques de nanobâtonnets métalliques individuels

Figure 1.2: Spectres EELS (bleu) et CL (rouge) sommés sur les cartes de dispersions de la figure (1.3). La CL a été collectée en deux mesures, la première avec un réseau de diffraction à 300 traits.mm$^{-1}$, blisé à 1µm pour la partie du spectre allant de 1 eV à 1.4 eV et un réseau à à 150 grids.mm$^{-1}$, blisé à 500 nm pour la partie allant de 1.6 eV à 4.5 eV.

Figure 1.3: a) image HAADF d’un nanobâtonnet d’or. Barre d’échelle : 20nm. b) Carte de dispersion EELS, c) carte de dispersion CL dans le proche infra-rouge et d) carte de dispersion CL allant du très proche infra-rouge aux UV proche. L’axe vertical de ces cartes correspond à la position le long de nanobâtonnet et l’axe horizontal est l’axe de dispersion en énergie / longueur d’onde.
1.1. Nanobâtonnets monocristallin

Ces cartes de dispersions spectrales révèlent la présence de deux domaines d’énergies distincts auxquels sont liés des phénomènes optiques différents pour des nanobâtonnets d’or. Le premier domaine correspond à la gamme d’énergies inférieure à 2.4 eV, elle contient la réponse plasmonique du nanobâtonnet, on y trouve le mode de plasmon de surface \( m = 1 \) à 1.3 eV reconnaissable à ces deux maxima d’intensités aux extrémités du nanobâtonnet et le mode \( m = 2 \) à 1.81 eV (par EELS uniquement du fait du moment dipolaire nul associé à ce mode). Le second domaine, pour les énergies supérieures à 2.4 eV contient des informations sur la mesure de la Densité Jointe d’états électroniques (Joint Density of States: JDOS en anglais) de l’or. Bien que la JDOS soit une grandeur couramment mesurée par EELS, une telle mesure n’a jusqu’à présent jamais été rapportée pour des nanoparticules d’or, en particulier il est intéressant de noter la présence de la mesure de cette JDOS associée à celle de la zEMLDOS apportée par les plasmons. Les pics correspondants mesurés en CL correspondent à la partie radiative de la JDOS. Les pics observés correspondent aux transitions interbandes de l’or et les énergies mesurées sont celles que l’on peut trouver dans la littérature [2, 3, 4].

La comparaison des spectres EELS et CL dans ces deux gammes d’énergies révèlent deux comportements différents. La réponse plasmonique mesurée par CL est décalée vers le rouge par rapport à la mesure faite par EELS, en revanche les pics mesuré pour les transitions interbandes sont aux mêmes énergies en CL comme en EELS. Le décalage en énergie de la réponse plasmonique s’explique par les grandeurs mesurée par chaque technique, la CL mesure la diffusion optique du nanobâtonnet quand l’EELS mesure son extinction optique (absorption + diffusion optique). Pour des nanoparticules d’or suffisamment petite, l’absorption domine le signal d’extinction optique, ainsi la différence mesuré entre les deux spectre provient de la contribution prépondérante de l’absorption dans la réponse EELS qui intervient à une énergie légèrement supérieure à l’extinction. La figure (1.4) montre un calcul par la méthode des éléments finis de frontières (Boundary Element Method: BEM en anglais) du décalage vers le rouge en fonction de la longueur de nanobâtonnets ayant le même rayon (25nm). On peut noter que ces calculs donnent un décalage vers le rouge seulement pour les petites nanoparticules, pour les plus grandes structures un décalage vers le bleu plus faible est calculé.
Chapter 1. Effets de la rugosité sur les propriétés optiques de nanobâtonnets métalliques individuels

Un second exemple de mesures couplés EELS et CL est donné pour un nanobâtonnet plus long (275nm) figure (1.6 et 1.5). L’EELS permet à nouveau de mesurer les modes de plasmons de surface \( m = 1, m = 2 \) et \( m = 3 \) à 0.95 eV, 1.3 eV et 1.65 eV respectivement et la CL n’a pu être collectée dans cette gamme d’énergie, seule les mesures de la JDOS peuvent être comparées. La comparaison montre un plus grand nombre de pics mesuré par EELS, la CL ne mesurant que la partie radiative de la JDOS quand l’EELS en fournit une mesure plus complète. On peut noter que les pics présent sur les deux spectres (notés A et D) sont aux mêmes énergies. La mesure de la JDOS dépend de l’orientation cristallographique du nanobâtonnets par rapport au faisceau d’électrons, il en découle que les transitions interbandes mesurées peuvent varier d’un bâtonnet à l’autre, à l’exemple des transitions mesurées en figure (1.2) et figure (1.5).
1.1. Nanobâtonnets monocristallin

Figure 1.5: Spectres EELS (bleu) et CL (rouge) extraits des cartes de dispersions de la figure (1.6). La CL a été mesurée avec le réseau de diffraction blisé à 500 nm avec 150 traits.mm$^{-1}$.

Figure 1.6: a) image HAADF d’un nanobâtonnet monocristallin de 275 nm de long, barre d’échelle = 50 nm. b) Carte de dispersion EELS dans le proche infra-rouge, trois résonances sont identifiables à 0.92 eV (m = 1, rouge), 1.35 eV (m = 2, bleu) et 1.81 eV (m = 3, vert). c) carte de dispersion EELS dans le visible et proche ultra-violet, d) carte de dispersion CL dans la même gamme d’énergie.
1.2 Nanobâtonnets polycristallins

De la même manière, les mesures par EELS et CL sur des nanobâtonnets lithographiés, figures (1.7) peuvent être divisées en deux gammes d’Énergies séparées à 2.4 eV. Avec la réponse plasmonique aux basses Énergies, on peut à nouveau identifier les modes de plasmons de surface $m = 1$ et $m = 2$ à 0.8 eV et 1.27 eV respectivement par EELS, avec un mode $m = 1$ à l’intensité asymétrique sur le nanobâtonnet. On constate aux Énergies supérieures à 2.4 eV l’absence de mesures de transitions interbandes par EELS et CL avec la présence de signaux intenses très localisés sur les deux réponses (flèches vertes sur la figure (1.7)). À la différence de la mesure de la JDOS précédemment mesuré sur les nanobâtonnets monocristallins, les pics ici mesurés présentent un décalage vers le rouge sur les mesures CL en les comparant à l’EELS, voir spectres figure (1.8). Ce décalage vers le rouge est une signature typique de résonance de mode plasmon de surface. Un comportement singulier est à noter sur le signal mesuré en EELS et indiqué par une flèche rouge sur la figure (1.7), puisqu’il n’a pas été mesuré par CL, ce signal est donc exclusivement absorbant et non diffusant, il s’agit d’un "point sombre". En comparant la position spatiale de ces pics d’intensité EELS et CL à l’image HAADF du nanobâtonnet, figure (1.7.a) on constate la présence de rugosités à ces mêmes positions, et également qu’un de ces signaux apparaît à la position ou le mode $m = 1$ est mesuré plus intensément.
1.2. Nanobâtonnets polycristallins

Figure 1.7: a) image HAADF d’un nanobâtonnet lithographié polycristallin de 450 x 50 nm, barre d’échelle = 50 nm. b) Carte de dispersion EELS dans le proche infra-rouge, c) carte de dispersion EELS dans le visible et proche ultra-violet, d) carte de dispersion CL dans la même gamme d’énergie.

Figure 1.8: Spectres EELS (bleu) et CL (rouge) extraits des cartes de dispersions de la figure (1.7) à la position de la seconde flèche verte en partant du haut. La CL a été mesurée avec le réseau de diffraction blasé à 500 nm avec 150 traits.mm\(^{-1}\).

Il apparaît évident que ces signaux proviennent de la présence d’aspérités à
la surface du nanobâtonnet, afin d’estimer l’effet qu’elles produisent j’ai effectué avec l’aide d’Andreas Trügler (Université de Graz, Autriche) des simulations BEM sur des nanobâtonnets rugueux. Le premier effet recherché est l’obtention par ces calculs d’une asymétrie du signal du mode $m=1$, pour cela je compare à un nanobâtonnet parfait figure (1.9.a) un bâtonnet avec une extrusion proche d’une extrémité figure (1.9.b) et un bâtonnet dont le contour irrégulier provient de l’image HAADF de la figure (1.7.a), figure (1.9.c). Les spectres mesurés aux deux extrémités de ces nanobâtonnets se trouvent figure (1.10). On constate une intensité asymétrique sur les deux nanobâtonnets irréguliers, avec toutefois un effet plus marqué sur le bâtonnet ayant une extrusion (figure (1.10.b)). Les résultats de ces calculs signifient bien qu’un signal asymétrique provient d’une asymétrie de la structure du nanobâtonnet.

Figure 1.9: Structures des nanobâtonnets simulés pour les calculs BEM: a) structure parfaitement régulière (50x450nm), b) même structure qu’en a) avec l’ajout d’une extrusion longue de 50 nm a 30nm de l’extrémité du nanobâtonnet et c) structure extraite du contour de l’image HAADF de la figure (1.7.a).
1.2. Nanobâtonnets polycristallins

Figure 1.10: Spectres EELS calculés aux deux extrémités des structures de la figure (1.9) 
a) nanobâtonnet régulier, b) nanobâtonnet avec une extrusion (courbe verte, la courbe 
orange est calculée à l’extrémité opposée) et c) nanobâtonnet extrait de l’image HAADF.

Les signaux intenses mesurés à plus hautes énergies peuvent être obtenus 
en simulant un nanobâtonnet ayant une structure plus réaliste. Ceci est possible 
en ajoutant des rugosité sur la structure construite à partir du profil de l’image 
HAADF, voir figure (1.9).

Figure 1.11: Structure extraite de l’image HAADF de la figure (1.7.a) avec l’adjonction de 
deux excroissances (50 nm de long) parallèles au faisceau d’éléctrons simulé.

Les calculs EELS peuvent ainsi être comparés aux mesures expérimentales 
figure (1.12) et constater les correspondances avec à la fois une asymétrie du signal 
à faible énergie et la présence de signaux localisés au niveau des extrusions à plus
hautes énergies. En dehors du modes \( m = 1 \), les énergies calculées diffèrent des énergies mesurées expérimentalement, ceci s’explique par la non prise en compte dans les simulation du substrat de \( Si_3N_4 \) sur lequel repose le nanobâtonnet. La CL est également calculée et comparée à l’expérience figure (1.13), avec un bon accord à nouveau. Un décalage vers le rouge des pics localisés aux hautes énergies est obtenu mais est très faible (quelque \( meV \) et sans communes mesures avec les observations expérimentales.

Le rapport d’intensité des pics calculés par EELS et CL varie selon la longueur des extrusions, avec un signal CL qui diminue lorsque la longueur augmente. Pour des longueurs d’extrusion supérieures à 50 nm le pic de CL disparaît et seul un signal EELS est calculé, figure (1.14), ce qui permet de relier le "point sombre" mesuré expérimentalement à une rugosité plus marquée.

1.3 Conclusion

Dans ce chapitre j’ai pu mettre en évidence l’effet de la présence de rugosités sur des bâtonnets plasmoniques. Ainsi si elle affecte peu la dispersion énergétique des modes plasmons de basses énergies elle modifie toutefois localement leur champs proche électrique si bien que la dispersion spatiale observée devient asymétrique. Plus remarquable, à haute énergie les rugosités donnent naissance à des pics d’intensité très localisés sans équivalences dans les bâtonnets monocristallins. Les simulations BEM ont confirmées ces observations et permis d’en affirmer l’origine.
Figure 1.12: Cartes de dispersion EELS ; a) issue des calculs par BEM et b) issue des mesures experimentales.
Calculated CL dispersion

Experimental CL dispersion

Figure 1.13: Cartes de dispersion CL ; a) issue des calculs par BEM et b) issue des mesures experimentales.
1.3. Conclusion

Figure 1.14: Spectres EELS (bleu) et CL (rouge) calculés au niveau de l’excroissance située au milieu du nanobâtonnet. Un pic à 1.8 eV est obtenu pour l’EELS seulement.
Les dimères de nanoparticules métalliques sont souvent utilisés comme cavité plasmoniques du fait de la concentration d’un champ proche électrique intense dans leur gap\(^5\). Ainsi, celui-ci est mis à contribution pour la détection par diffusion Raman amplifiée (SERS) de molécules uniques \(6, 7\), pour l’optique non linéaire \(1, 8, 9\) ou pour l’ajustement de l’émission de molécules fluorescentes \(10\). Surtout, les propriétés optiques de ces dimères sont facilement paramétrables par la taille du gap séparant les monomères ainsi que par les dimensions des monomères en particulier lorsque ceux-ci sont des nanobâtonnets \(5, 11\). Dans la suite sont présentées des expériences EELS menées sur ces dimères de nanobâtonnets d’argent, nous avons retenu cette géométrie dans l’espoir de pouvoir coupler de telles cavités plasmoniques avec des émetteurs quantiques, si possible positionnés dans le gap. Des dimères de particules plasmoniques ont déjà fait l’objet d’études par EELS, que ce soit des nanosphères d’argent \(12\) ou des nanobâtonnets en alliage or-argent \(13, 14\), sur des systèmes ayant des gaps allant de quelques nm jusqu’au régime de couplage conductif. Cependant dans ce chapitre je présente une étude sur des objets moins fortement couplés car fabriqués par lithographie électronique avec des gaps de taille > 20nm. Bien que la polycristallinité des particules lithographiées modifie localement les propriétés spectrales des nanobâtonnets, nous avons vu au chapitre précédent que ceux-ci étaient malgré cela de bon résonateur plasmonique. Sur ces systèmes couplés j’ai pu réaliser des cartes d’intensité, d’énergie et de largeur à mi-hauteur des modes plasmon de surface hybridé. A nouveau, la polycristallinité des nanobâtonnets lithographiés conduit à des systèmes dimériques asymétriques. Ici, se sont les modes couplés liants et antiliants qui se trouvent affectés avec en particulier un effet de localisation de ces
modes sur les monomères au lieu d’une délocalisation sur le dimère entier comme prévu dans le cas des dimères symétriques. La même constatation est faite sur des dimères asymétriques de nanobâtonnets monocristallins. Ces observations sont finalement mises en regard d’un modèle s’inspirant du modèle d’hybridation des orbitales atomiques développé par Nordlander et et.al. [15] avec la prise en compte de la localisation spatiale des modes hybridés. Les observations expérimentales sont finalement obtenues par des simulations BEM associées à une convolution du signal avec une gaussienne qui imite le faisceau électronique du microscope.

2.1 Classification des modes de nanoantennes couplées

La classification des modes de nanoantennes individuelles a déjà été abordée dans le chapitre précédent. Basiquement pour des systèmes couplés, les densités de charges surfaciques des deux monomères vont être en accord de phase si bien que les oscillations de charges positives et négatives s’étendent sur toute la particule. Pour des raison de symétries deux cas de figures se présentent pour chaque mode avec des densités de signes identiques ou opposés de chaque côté du gap. La dégénérescence est levée pour des systèmes couplés, avec l’apparition de modes antisymétriques en charge (dits modes liants) ou symétriques en charge (dits modes antiliants), voir les figures (2.1) et (2.2).

![Figure 2.1: Simulation BEM de la distribution spatiale des charges propres des trois premiers modes d’une antenne unique (rouge:Max, bleu:min)](null)
2.1. Classification des modes de nanoantennes couplees

Figure 2.2: Simulation BEM de la distribution spatiale des charges propres des trois premiers modes d’un homodimer (rouge:Max, bleu:min)
2.2 Hybridation de modes plasmons

A l’aide d’une notation bra - ket nous allons décrire le système classique fait de deux nanobâtonnets. Dans ce modèle les modes sont décrits par \((E_m, |\phi_m\rangle)\), avec \(E_m\) l’énergie du plasmon et \(|\phi_m(\vec{r})\rangle\) la charge propre du mode \(m\) tels que \(H|\phi_m\rangle = E_m|\phi_m\rangle\). En l’absence de couplage l’hamiltonien est la somme des hamiltoniens des monomères isolés.

Le dimère peut ainsi être décrit par une combinaison linéaire des fonctions d’onde de ces monomères isolés :

\[
|\Psi\rangle = R|\phi_R\rangle + L|\phi_L\rangle 
\]  
(2.1)

avec \(|\Psi\rangle\) la fonction d’onde du dimère, \(|\phi_R\rangle\) et \(|\phi_L\rangle\) les états propres des monomères d’énergies \(\varepsilon_R\) et \(\varepsilon_L\) respectivement (équation (2.3)), R et L deux facteurs de normalisation tels que \(\langle\Psi|\Psi\rangle = 1\). L’hamiltonien du système \(H\) est une combinaison linéaire des hamiltoniens des monomères isolés \((H_R\) et \(H_L)\) et d’un terme de couplage \(\hat{C}\):

\[
\hat{H} = \hat{H}_R + \hat{H}_L + \hat{C} 
\]  
(2.2)

avec:

\[
\hat{H}_R |\phi_R\rangle = \varepsilon_R |\phi_R\rangle \text{ et } \hat{H}_L |\phi_L\rangle = \varepsilon_L |\phi_L\rangle 
\]  
(2.3)

et

\[
\hat{C} = \begin{pmatrix}
0 & c \\
c & 0
\end{pmatrix} 
\]  
(2.4)

Alors pour le dimère :

\[
\begin{cases}
\hat{H} |\Psi\rangle = E |\Psi\rangle \\
R \hat{H} |\phi_R\rangle + L \hat{H} |\phi_L\rangle = E (R |\phi_R\rangle + L |\phi_L\rangle)
\end{cases} 
\]  
(2.5a,b)
2.2. Hybridation de modes plasmons

En insérant (2.3) dans (2.5b), on a:
\[ R (\varepsilon_R - E) |\phi_R\rangle + R \hat{C} |\phi_R\rangle + L (\varepsilon_L - E) |\phi_L\rangle + \hat{C} |\phi_L\rangle = 0 \] (2.6)

après projection sur les états propres initiaux \( \langle \phi_R | \) et \( \langle \phi_L | \):

\[
\begin{cases}
R (\varepsilon_R - E) + R \langle \phi_R | \hat{C} |\phi_R\rangle + L (\varepsilon_L - E) \langle \phi_R | \phi_L\rangle + L \langle \phi_R | \hat{C} |\phi_L\rangle = 0 \quad (2.7a) \\
R (\varepsilon_R - E) \langle \phi_L | \phi_R\rangle + R \langle \phi_L | \hat{C} |\phi_R\rangle + L (\varepsilon_L - E) + L \langle \phi_L | \hat{C} |\phi_L\rangle = 0 \quad (2.7b)
\end{cases}
\]

De (2.4) nous avons:

\[
\begin{cases}
\langle \phi_R | \hat{C} |\phi_R\rangle = \langle \phi_L | \hat{C} |\phi_L\rangle = 0 \quad (2.8a) \\
\langle \phi_R | \hat{C} |\phi_L\rangle = \langle \phi_L | \hat{C} |\phi_R\rangle = c \quad (2.8b)
\end{cases}
\]

avec S la matrice de recouvrement:

\[ S = \langle \phi_R | \phi_L\rangle = \langle \phi_L | \phi_R\rangle \] (2.9)

alors:

\[
\begin{cases}
R (\varepsilon_R - E) + L (\varepsilon_L - E) S + L c = 0 \quad (2.10a) \\
R (\varepsilon_R - E) S + R c + L (\varepsilon_L - E) = 0 \quad (2.10b)
\end{cases}
\]

et donc:

\[ \Delta = [(\varepsilon_R - \varepsilon_L)(1 - S^2)]^2 + 4cS((\varepsilon_R + \varepsilon_L)(1 - S^2) + 4c^2 \] (2.11)

finalement:

\[
\begin{cases}
E_+ = \frac{1}{2}(\varepsilon_R + \varepsilon_L + \sqrt{\Delta}) \quad (2.12a) \\
E_- = \frac{1}{2}(\varepsilon_R + \varepsilon_L - \sqrt{\Delta}) \quad (2.12b)
\end{cases}
\]
La différence en énergie des deux modes est $E_+ - E_- = \sqrt{\Delta}$ (2.13). Il faut alors déterminer à quels modes ils correspondent, pour cela nous calculons les états propres pour $E_-:$

\[
\begin{align*}
R_- (\varepsilon_R - E_-) + L_- c &= 0 \\
R_- c + L_- (\varepsilon_L - E_-) &= 0
\end{align*}
\] (2.14a, 2.14b)

\[
\begin{align*}
\frac{R_-}{2} (\varepsilon_R - \varepsilon_L + \sqrt{\Delta}) + L_- c &= 0 \\
R_- c + \frac{L_-}{2} (\varepsilon_L - \varepsilon_R + \sqrt{\Delta}) &= 0
\end{align*}
\] (2.15a, 2.15b)

nous obtenons:

\[
R_- = \frac{(\varepsilon_R - \varepsilon_L) - \sqrt{\Delta}}{2c} L_-
\] (2.16)

avec les états propres:

\[
|\Psi_-\rangle = \left( \frac{(\varepsilon_R - \varepsilon_L) - \sqrt{\Delta}}{2c} |\phi_R\rangle + |\phi_L\rangle \right) L_-
\] (2.17)

et pour $E_+:

\[
R_+ = \frac{(\varepsilon_R - \varepsilon_L) + \sqrt{\Delta}}{2c} L_+
\] (2.18)

\[
|\Psi_+\rangle = \left( \frac{(\varepsilon_R - \varepsilon_L) + \sqrt{\Delta}}{2c} |\phi_R\rangle + |\phi_L\rangle \right) L_+
\] (2.19)

A partir de $\frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c}$ on peut déterminer la symétrie de la fonction propre $|\Psi_\pm\rangle.$ Pour $\frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} = 1$ la fonction d’onde est symétrique alors que pour $\frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} = -1$ elle est antisymétrique. La non-symétrie intervient lorsque $\frac{(\varepsilon_R - \varepsilon_L) \pm \sqrt{\Delta}}{2c} \neq \pm 1,$ alors la fonction d’onde est localisée sur un monomère pour un mode hybride et sur l’autre monomère pour l’autre mode de couplage, figure (2.3).
Figure 2.3: Simulation BEM de la distribution spatiale des charges propres des trois premiers modes d’un heterodimère (red:Max, blue:min).
Nous avons préparé des dimères de nanobâtonnets d’argent par lithographie électronique, cette technique semble idéal pour concevoir des dispositifs pour lesquels le contrôle des dimensions est critique [16]. Deux nanobâtonnets séparés par un gap d’environ 20 – 40 nm sont fabriqués sur une membrane de Si₃N₄ de 30 nm d’épaisseur, recouverte d’une couche d’ITO conductrice de 5 nm. Les nanobâtonnets sont faits d’une couche d’adhésion de Cr de 3 nm d’épaisseur avec 40 nm d’Ag la recouvrant. Bein que relativement grande pour ce genre de systèmes couplés, la gamme de tailles utilisée pour le gap permet un couplage entre les deux nanobâtonnets et autorise une description classique du système. En outre, les tailles des gaps sont bien adaptées pour l’insertion éventuelle de boîtes quantiques colloïdales de type coeur-coquille telles que celles étudiées au chapitre suivant.
2.3. Dimères de nanobâtonnets lithographiés

Figure 2.4: a) Spectres EELS locaux, image du dimère en insert, barre d'échelle 100 nm. 
b) Carte d'intensité, c) carte d'énergie d) carte des largeurs à mi-hauteur du mode \( m = 1 \). 
e) Carte d'intensité, f) carte d'énergie g) carte des largeurs à mi-hauteur du mode \( m = 2 \). 

Des mesures EELS effectuées sur un dimère d’argent (avec des dimensions moyennes: 34 \( \text{nm} \times 215 \text{nm} \) (gap) 38 \( \text{nm} \times 215 \text{nm} \), voir encadré de l’image HAADF de la figure (2.4. a) sont présentés sur la figure (2.4. a). Les spectres bleu et rouge, mesurés aux deux extrémités présentent des pics proches de 1,25 \( eV \) et 1,9 \( eV \). Le spectre vert mesuré dans le gap montre deux pics à 1,38 \( eV \) et 2,1 \( eV \). Ces écarts en énergies vont dans le sens d’un couplage entre
les monomères, en effet les énergies mesurés dans le gap, où seul le mode antiliant est sondable par EELS, sont supérieures à celles mesurées en dehors, où le mode liant est également mesuré.

Figure 2.5: Spectres EELS locaux, image du dimère en insert, barre d’échelle 100 nm. b) Carte d’intensité, c) carte d’énergie d) carte des largeurs a mi-hauteur du mode \( m = 1 \). e) Carte d’intensité, f) carte d’énergie g) carte des largeurs a mi-hauteur du mode \( m = 2 \).

2.4 Dimères de nanobâtonnets monocristallins

Les mêmes observations sont faites sur des nanobâtonnets monocristallins. Pour ces dimères l’asymétrie du système est due aux dimensions différentes des
2.4. Dimères de nanobâtonnets monocristallins

monomères et non à la présence locale de protrusions sur celles-ci.

Figure 2.6: Spectres EELS locaux, image du dimère en insert, barre d’échelle 100 nm. b) Carte d’intensité, c) carte d’énergie d) carte des largeurs a mi-hauteur du mode $m = 1$. e) Carte d’intensité, f) carte d’énergie g) carte des largeurs a mi-hauteur du mode $m = 2$. 
Chapter 2. Dimères de nanobâtonnets : asymétrie et localisation des modes hybridés

Figure 2.7: Spectres EELS locaux, image du dimère en insert, barre d’échelle 100 nm. b) Carte d’intensité, c) carte d’énergie d) carte des largeurs a mi-hauteur du mode $m = 1$. e) Carte d’intensité, f) carte d’énergie g) carte des largeurs a mi-hauteur du mode $m = 2$.

2.5 Simulations BEM

Les calculs de simulations BEM suivants ont été réalisés afin d’être comparés aux observations expérimentales:

Les cartes de dispersions spatiales de l’EELS suivantes permettent d’observer la nette localisation des modes sur les monomères.
Table 2.1: a) Diagramme d’énergies calculées pour un homodimère (colonne centrale) (34x215 nm + 36 nm(gap)+34x215 nm) et ses monomères isolés (colonnes latérales). b) pour un hétérodimère (colonne centrale) et ses monomères (34x215 nm + 36 nm)(colonne de gauche) et (+38x215 nm)(colonne de droite)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Homodimer</th>
<th>Heterodimer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>left</td>
<td>dimer</td>
</tr>
<tr>
<td>m=1</td>
<td>1.03</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>1.0825</td>
<td></td>
</tr>
<tr>
<td>m=2</td>
<td>1.8625</td>
<td>1.8275</td>
</tr>
<tr>
<td></td>
<td>1.9075</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Table des énergies calculées pour les monomères isolés et les couples d’homodimères et d’heterodimères.
Figure 2.8: Carte de dispersion EELS calculées pour un dimère de dimension comparable à celui de la figure (2.4).
Figure 2.9: Haut: carte de dispersion EELS calculée pour l’hétérodimère modélisé à partir des dimensions extraites de la figure (2.4), les spectres sont convolus avec une gaussienne de largeur à mi-hauteur de 300 meV. Bas: carte de dispersion EELS expérimentale.
Figure 2.10: Haut: carte de dispersion EELS calculée pour l’hétérodimère modélisé à partir des dimensions extraites de la figure (2.5), les spectres sont covolus avec une gaussiennne de largeur à mi-hauter de 300 meV. Bas: carte de dispersion EELS expérimentale.
L’évolution des profils d’intensités des modes hybridés sur le dimères (pour les modes \( m = 1 \) et \( m = 2 \)) en fonction de la taille du gaps permet de constater que le phénomène de localisation des modes est d’autant plus prononcé que les monomères sont éloignés et donc moins couplés, figure (2.11).
**Chapter 2. Dimères de nanobâtonnets : asymétrie et localisation des modes hybridés**

**Figure 2.12:** Comparaison des spectres avant et après convolution avec une gaussienne simulant le faisceau électronique d’excitation, large de 300 meV. Courbe rouge : spectre calculé à l’extrémité gauche du dimère, courbe verte dans le gap et courbe bleue à droite.

### 2.6 Conclusions

Dans ce chapitre, l’observation de la localisation des modes hybridés sur un dimère asymétrique a été présentée. Cette observation n’a été rendue possible que par une étude du champ proche accessible par EELS. Toutefois il a fallu une déconvolution des spectres expérimentaux couplée à une régression gaussienne des pics pour observer le phénomène malgré la faible résolution en énergie de l’EELS. La confirmation de la validité du modèle d’hybridation des modes plasmons a finalement été atteinte par des simulations BEM associées à une simulation de la largeur naturelle du faisceau d’électrons.
Étude par CL de boites quantiques semi-conductrices

Dans ce chapitre je présente une étude de cathodoluminescence réalisée sur des nanocristaux semi-conducteur de CdSe/CdS. Ces objets ont maintes fois été étudiés par diverses techniques optiques et sont ainsi bien caractérisées. Je les soumets ici à la spectroscopie de cathodoluminescence, cette technique offre une résolution spectrale commune aux techniques optiques standards mais avec une résolution spatiale de l’ordre du nm qui peut être fort avantageuse pour l’étude de systèmes dont les tailles varient de 5 nm à 30 nm. Les résultats de ces mesures ont été comparées à des mesures faites par spectroscopie de photoluminescence sur les mêmes objets individuels et ont permis de montrer l’équivalence des deux spectroscopies sur de tels objets.

3.1 Propriétés Optiques

Les boites quantiques de CdSe/CdS présentées dans ce travail sont des systèmes coeur-coquilles de type II dans lesquels l’exciton est confiné dans le coeur, alors que la coquille de CdS est particulièrement épaisse afin de réduire la présence de défauts à proximité de l’exciton. En effet la présence de défaut altère la luminescence de ces nanocristaux, en particulier l’existence d’états dit gris (car peu luminescent) est due à l’ionisation de la boite quantique par la captation d’une charge de l’exciton par des défauts qui sont souvent situés à l’interface avec le milieu extérieur, figure (3.1).
Figure 3.1: Schéma représentant les recombinations ayant lieu dans un qdot électriquement neutre (haut) et ionisé (bas). Les processus de recombinaison non-radiatif ont des temps de vie plus court dans des qdots ionisés ($\tau_A < \tau_{\text{rad}}'$), ils sont alors moins brillants et sont dits "gris".

3.2 Des Objets Fragiles

L’utilisation de faisceau d’électrons hautement énergétique peut détruire les nanocristaux, ainsi des précautions sont nécessaire afin d’envisager des mesures. Des études précédentes faites par microscopie électronique à balayage (MEB) ont conclu sur l’impossibilité de la mesure par CL de boites quantiques isolées telles que celles de CdSe/CdS. Toutefois la configuration du MEB est en partie responsable des leurs observations, en effet leur montage expérimental impliquait une chauffe excessive de l’échantillon ainsi qu’une perte de résolution spatiale due à un substrat trop épais. Ces problèmes sont étudiés ici par l’utilisation de membrane fine comme substrat (15 nm d’épaisseur) et par un choix judicieux de l’énergie du faisceau, qui s’avère moins dommageable lorsque plus énergétique.
3.3. Cathodoluminescence

Figure 3.2: Boîtes quantiques structurellement dégradées par le faisceau d’électrons. a) image TEM haute résolution(image par Arjen Dijksman (ESPCI)), b) et c) cas extrême d’éclatement d’un nanocristal, en d) le spectre d’émission collecté avant la destruction.

Figure 3.3: Images par microscopie électronique à balayage d’une membrane de silicium (dimensions : 100µm x 100µm) recouverte de croix d’alignements métallique afin de faciliter les études croisées par CL et PL. Les lettres sur les bords permettent de localiser un élément sur la grille par des coordonnées de type (Majuscule ; minuscule).

3.3 Cathodoluminescence

3.3.1 Cathodoluminescence et Photoluminescence du même nanocristal individuel

Pour effectuer des mesures comparatives de PL et CL sur le même objet il est nécessaire de réaliser un quadrillage du substrat afin d’identifier clairement les objets, des croix d’alignements faites par lithographie électronique ont ainsi été réalisées voir figure (3.3). Il a ensuite été possible de réaliser successivement la PL puis la CL sur une boîte quantique isolée, figure (3.4). Les spectres montrent
une différence d’énergie mesurées par les deux techniques qui s’explique par l’utilisation d’un support refroidis à l’azote liquide pour les mesures de CL.

Figure 3.4: Comparaison des spectres CL et PL mesurés sur la même boîte quantique. a) Image HAADF, b) Spectres PL (bleu) et CL (rouge)

Figure 3.5: a) Courbes de mesure de l’autocorrélation de l’intensité de photoluminescence du nanocristal de la figure (3.4) et b) courbes de déclin de la photoluminescence, avant (vert) et après (bleu) exposition au faisceau d’électrons.
3.4 Cathodoluminescence de petits agrégats

La correspondance entre PL et CL établie, nous utilisons cette dernière dans des configurations inaccessibles à la PL. La résolution spatiale du nm de la CL permet en effet de venir sonder les particules individuelles constituant un amas quand la PL standard par microscopie confocale est limitée à une résolution de l’ordre de 100 nm au mieux. La figure (3.6) montre les résultats de mesures sur un agrégat de six boîtes quantiques. Seulement trois boîtes sur les six luminescent. Pour des systèmes bons émetteurs de lumière comme les CdSe/CdS les temps d’acquisitions de spectres CL sont de l’ordre de la ms, il est ainsi possible d’effectuer des mesures sur des grands amas avec une résolution spatiale convenable en quelques minutes, figure (3.7)

Figure 3.6: Cartographie de CL haute résolution de Qdots. a) Image HAADF d’un agrégat de 6 Qdots. b) Image HAADF mesurée en parallèle des mesures de CL. c) Spectres extraits de l’image spectrale en b) au positions indiquées par les cercles de couleurs. d) Carte d’intensité de STEM-CL, seules 3 Qdots émettent de la lumière.
Figure 3.7: Mesures sur un grand ensemble de QDots. a. Image HAADF de l’ensemble. Des Qdots isolés sont visibles. b. Spectres extraits des zones encerclées en a. c. Image HAADF acquise en parallèle d’une image spectrale. d. Intensité ; e. Longueur d’onde ; f. et Largeur à mi-hauteurs cartographiées à partir de l’image spectrale. Les barres d’échelles en c,d,e,f font 200 nm.
Nous avons démontrés l’équivalence de la Cathodoluminescence avec la photoluminescence pour les boîtes quantiques de CdSe/CdS. Ensuite nous avons usé de l’avantage de la CL en terme de résolution spatiale pour observer individuellement des boîtes quantiques formant des agrégats et constater que malgré leur proximité elles peuvent être étudiées de manière isolée par le faisceau d’électrons.
Conclusion et perspectives

Les travaux effectués pendant cette thèse ont permis de soumettre des objets imparfaits aux techniques de microscopies électroniques et aux spectroscopies associées. Ils ont permis de mettre à jour les effets de la présence de rugosités sur les propriétés optiques de nanobâtonnets métalliques. Celle-ci affecte peu la dispersion spectrale des modes plasmons de surfaces multipolaires associés à des vecteurs d’ondes de dimensions supérieures aux tailles typique des rugosités (quelques dizaines de nm), en revanche proche des transitions interbandes l’apparition de pics localisés au niveaux des protubérances révèle le couplage de ces aspérités locales avec le bâtonnet. L’étude réalisée par EELS et par CL sur les mêmes objets a permis d’étudier à la fois l’extinction et la diffusion d’un même objet avec une résolution spatiale nanométrique et a permis de mettre à jour l’existence de modes de rugosité de types différents selon qu’ils diffusent ou non le champ électromagnétique. L’étude EELS de dimères de nanobâtonnets par la technique d’imagerie spectrale couplée à une procédure de régression gaussienne des pics a révélée la localisation des modes plasmons hybrides sur les monomères lorsque la particule n’est pas de structure symétrique. Cela se produit lorsque le dimère est réalisé par lithographie électronique où la présence d’aspérités sur les bâtonnets brise la symétrie du dimère ou lorsque fabriqué par voie chimique avec des bâtonnets sans aspérités mais qui sont souvent associés en couples de dimensions différentes. Enfin une étude sur des boîtes quantiques semi-conductrices a permis d’abord de révéler la nature de la cathodoluminescence qui est équivalente à la photoluminescence sur ce genre d’objets. Ensuite l’avantage en terme de résolution spatiale de la CL a été utilisé afin de sonder des particules uniques constituant des agrégats.

En perspectives, le couplage des systèmes plasmoniques avec les émetteurs quantiques font l’objet d’une thèse en cours, avec l’assurance que la microscopie électronique STEM et la spectroscopie associée sont des outils adéquats pour venir sonder localement les propriétés optiques de systèmes dont les dimensions sont souvent inférieures à la longueur d’onde de la lumière avec laquelle ils interagissent. En outre l’amélioration des outils actuels avec notamment l’arrivée prochaine d’un microscope à faisceau d’électron monochromaté ou la mise au point prévue de la spectroscopie de gain d’énergie des électrons (en anglais Electron Energy Gain Spectroscopy, EEGS) en plus d’outils de cathodoluminescence résolue en temps
déjà implémenté (montage de corrélation de type Hanbury-Brown and Twiss, HBT) doit permettre de faire de la microscopie électronique un outil incontournable pour l’étude optique d’objet de taille nanométrique.
Bibliography


Spectroscopies nanométriques de structures plasmoniques et de nanocristaux semi-conducteurs

J’ai réalisé pour cette thèse des travaux expérimentaux à l’aide de la microscopie et de la spectroscopie électronique portant sur l’étude de nanostructures plasmoniques et de nanocristaux semi-conducteurs. Le but étant d’étudier leurs propriétés optiques sur des dimensions spatiales de l’ordre du nm. A cette échelle il est possible d’observer le champs proche électrique associé aux modes de résonances plasmons de surface supportées par des nanostructures métalliques. Ainsi j’ai pu étudier l’effet de la présence de rugosités sur des nano-bâtonnets d’or et constater que leur présence modifiait localement la structure du champs proche électrique. Des mesures combinées par spectroscopie de perte d’énergie des électrons (EELS) et de cathodoluminescence nous ont permis de comparer les réponses mesurées en champs proches à celle effectuées en champs lointain. Une étude faite par EELS portant sur le couplage entre deux nano-bâtonnets métalliques positionnés bout à bout et séparés par une distance de quelques dizaines de nanomètres a permis de cartographier la localisation de modes hybridés séparément sur chaque branche. Enfin des études comparatives de cathodoluminescence et de photoluminescence sur des points quantiques isolés ont permis de constater l’équivalence de l’information collectée par ces deux techniques sur ce type d’émetteurs de lumière.

Mots clés : plasmons - cathodoluminescence - spectroscopie de perte d’énergie des électrons - microscopie électronique à balayage et en transmission - points quantiques.

Nanometric Spectroscopies of Plasmonic Structures and Semiconductors Nanocrystals

For this thesis, I have realised some experimental works using electron microscopy and electron spectroscopies for the study of plasmonic nanostructures and semiconductor nanocrystals. The aim being to study their optical properties with spatial resolutions of the order of a few nm. At this level it is possible to observe the electric near-field associated to the localised surface plasmon resonances supported by metallic nanostructures. So I was able to study the effect due to the presence of roughness on single gold nanorods and I have found that their presence locally alterate the structure of the electric near-field. Combined measurement of electron energy loss spectroscopy (EELS) and cathodoluminescence spectroscopy were used to compare the near-field and far-field responses respectively. A study by EELS on the coupling between two metal nanorods positioned end to end and separated by a distance of tens of nanometers was used to map the localisation of hybridised modes separately on each branch of the dimers. Finally, comparative studies of cathodoluminescence and photoluminescence on single quantum dots have shown the equivalence of the information collected by these two techniques for such light emitters.

Keywords: plasmons (physics) – cathodoluminescence - electron energy loss spectroscopy - scanning transmission electron microscopy – quantum dots.

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