Controlling light emission of nanoparticles

Lesage, A.

Citation for published version (APA):
Integrating quantum-dots and dielectric Mie resonators: A hierarchical metamaterial inheriting the best of both

Much research concentrates on improving the limited quantum efficiency of Si nanocrystals (NCs) or on exploring their optical and electronic properties, in order to be able to efficiently exploit this material in applications. But if one were to use Si NCs as efficient down converters integrated into an existing photovoltaic device, one would face a fundamental issue; due to lower than unity photoluminescence quantum efficiency (PLQY), any absorption of light will have a parasitic effect, that has to be overcome by efficiency enhancing effects such as space separated quantum cutting. In practice, efficiency enhancing effects are possible to apply only on a small part of the solar spectrum. In this chapter we explore the use of Mie resonances, in order to selectively enhance the absorption in those parts of the spectrum that we wish to utilize efficiently. This work is directly useful for Si-NCs related applications, but the concepts shown here are generally applicable also for other similar nanomaterials.
3.1 Introduction

A number of pioneering works have investigated the interplay between plasmonic resonators and quantum dots, showing that an interaction can yield enhanced absorption and emission rates. [44–46] Unfortunately, plasmonic resonances come with large parasitic losses, heating due to dissipation in the metal, and incompatibility with CMOS fabrication technology. [47–49] This drawback is particularly detrimental for energy-related and -sustainable applications, which require technological solutions excluding lossy metals and expensive/toxic semiconductors.

Alternatively, high-index dielectric nanoparticles (HI-DNP) with size of hundreds of nanometers support Mie resonances without utilizing metal components. [50, 51] Different from plasmonic nanoparticles, whose scattering is dominated by electric modes, HI-DNPs’ resonances are both magnetic and electric in nature, with comparable strengths. [48, 49, 52] For refractive indices \( n > 2 \), available with group-IV and group III-V semiconductors, dipolar and quadrupolar resonant modes are well-defined. [49] Moreover, they guarantee reduced optical losses with respect of their plasmonic counterpart. [47, 49] Interference effects between magnetic and electric dipolar modes have been shown to enable directional light scattering, as well as scattering suppression. [53, 54] Building on the spectrally-selective optical properties of the dielectric scatterers, [52, 55] dielectric metamaterials have been recently investigated for controlling the transmission/reflection ratio in the infrared, [56] for light concentration to an absorbing substrate, [57] for nonlinear optical applications, [58] and for flat optics, [59, 60] and are currently being studied for photovoltaic applications. [61, 62]

Here, we explore the opportunity to combine quantum dots and dielectric resonators as building blocks of a hierarchical metamaterial, which not only inherits the intrinsic optical and electronic properties of its nanoscale constituents, but also features enhanced performance. The building block in question are silicon nanocrystals (Si-NCs) dispersed in SiO\(_2\) films, a widely studied material which was also used in chapters 2, 5, and 7, and is highly compatible with nano-lithography techniques necessary for this work.

3.1.1 The hierarchical metamaterial approach

In this chapter, we integrate quantum-confined luminescent Si-NCs within SiO\(_2\) nanocylinders, arranged in a 2D array as depicted in Fig. 3.1(a-c). We demonstrate that the resulting metamaterial preserves the Si-NC radiative recombination properties, inherits the nanocylinder spectrally-selective absorption, and henceforth features enhanced emission intensity. As a proof of concept, we tackle the spectral requirements of a light down-converter for solar cells, [63] namely: i) total absorption of photons with energy \( E > 2E_{\text{gap}} \) and ii) total transmission of photons with \( E < 2E_{\text{gap}} \).
3.1. Introduction

**Figure 3.1:** Schematic of the hierarchical metamaterial: (a) quantum-confined Si-NCs, (b) SiO$_2$ nanocylinders resonating at the excitation wavelength, and (c) photoluminescent 2D planar array. (d) HRTEM of a Si-NC in a SiO$_2$ matrix, (e) SEM of a SiO$_2$ nanocylinder with a height of 300 nm and diameter of 215 nm, and (f) SEM of the 2D metamaterial. Scale bars for panels (d)-(f) are 1 nm, 100 nm, and 1 µm, respectively.
where $E_{\text{gap}}$ is the cell bandgap (with $E_{\text{gap}} \sim 1.11$ eV for Si).

We address these requirements by designing a hierarchical metamaterial optimized on three levels:

- Si-NCs are quantum dots made of crystalline Si (see HRTEM in Fig. 3.1(d)) with typical diameter $< 10$ nm. The electron wavefunction is broadened in momentum space due to the Heisenberg uncertainty principle, increasing the rate of radiative recombination. Therefore, the constraint of momentum conservation is relaxed (Si is an indirect semiconductor) and Si-NCs show excitonic photoluminescence (PL) in the red/infrared spectrum. Notably, the occurrence of carrier multiplication in ensembles of Si-NCs, due to SSQC, enables the down-conversion of one high-energy photon into two photons with half of the original energy. This has the huge potential to enable sunlight spectral shaping and to truly improve the efficiency of solar cells by down-conversion.

- The dielectric nanocylinders, shown in the SEM image of Fig. 3.1(e), are made of a solid-state dispersion of Si-NCs in a SiO$_2$ matrix (Si-NC:SiO$_2$, in brief) and defined by electron-beam lithography. The size of Si-NCs ($\sim 2.5$ nm) is two orders of magnitude smaller than the wavelength of visible light and, therefore, Si-NC:SiO$_2$ is effectively an optically homogeneous medium. The effective refractive index $n_{\text{eff}}$ is a function of the volume fraction of Si-NCs, and it is $n_{\text{eff}} \sim 1.9$ for the samples produced in this work. The excellent scattering properties of the nanocylinders depend on their size, shape and refractive index $n_{\text{eff}}$, enabling the onset of Mie resonances in the visible spectrum.

- The 2D hexagonal array of scattering nanocylinders forms an optically-thin metamaterial, as shown in Fig. 3.1(f). Superabsorption in a thin 1D dielectric metamaterial has been recently shown to arise from the interference between the scattered and the incident waves, which enables an optimal match of the optical impedances. This results into a maximum absorption of 50% for freestanding dielectric metamaterials like their metal counterpart, and 100% absorption with the support of a back-reflector.

We experimentally demonstrate that the investigated metamaterial supports extinction peaks in correspondence of the nanocylinder Mie resonances and of the grating condition of the array, whose spectral positions are tailored by geometrical design parameters. Our numerical predictions show that the metamaterial absorption can reach up to 50%. The optical losses in SiO$_2$ are negligible in the visible spectrum and, therefore, the main contribution to the absorption comes from optical transitions in the Si-NCs. We experimentally prove that that the increased absorption directly couples to the Si-NCs, resulting in a 3-fold av-
3.2. Experimental details

The investigated metamaterial can find application as an optically-thin down-converter of light on the front surface of commercial solar cells. It is fair to remark that this application necessarily requires PL quantum yield (QY) above 50%, while the maximum value achieved so far for Si-NC:SiO$_2$ is 35%. [6] A florid and growing field of research is tackling the increase of QY to match the requirements for applications. [6,70] Nevertheless, the fundamental goal of this work is to demonstrate that the integration of quantum emitters into dielectric resonators enables spectrally-selective enhancement of photon absorption, obtained without affecting the emitter radiative properties, and resulting in an overall increase of PL intensity. Although we propose and use a specific material platform, the demonstrated principle is general and can be applied to other semiconductor quantum-dots and emitting species, such as rare-earth ions and organic molecules. We envision the application of this principle to applications such as light-conversion and spectral shaping for photovoltaics, but also photocatalysis and artificial photosynthesis.

3.2 Experimental details

3.2.1 Metamaterial fabrication process and sample list

The materials produced in this work, were fabricated by sputter-deposition SiO$_x$ films, high temperature annealing for Si-NC formation and consequent electron-beam lithography to form the array of pillars. Following is the detailed process:

- Substrate cleaning. The fused-silica substrate was sonicated in H$_2$O and immersed in a Base Piranha solution for 15 minutes.

- Sputter deposition. A sub-stoichiometric film of SiO$_2$ (with a 17 ± 4 vol% excess Si) was deposited by magnetron RF co-sputtering system (AJA int.), using high purity Si (99.99%) and SiO$_2$ (99.99%) [6,35,71,72]. The resulting stoichiometry and thickness were determined from the deposition rates, which were calibrated by a quartz crystal microbalance, and validated by Scanning Electron Microscope (SEM) analysis of the film cross-sections.

- Thermal annealing. The sputtered film was annealed for 30min at a temperature of 1100 – 1150 °C in a N$_2$ environment. This resulted in both phase separation of Si and SiO$_2$, and crystallization of the Si clusters. The optical properties of the resulting Si-NC:SiO$_2$ films are strongly dependent on the thickness $H$. 

average PL enhancement per Si-NC. Specifically, our experiments indicate that the PL intensity from the best performing metamaterial is +30% compared to a planar Si-NC:SiO$_2$ film (without the nanocylinder patterning), despite that the number of photoluminescent Si-NCs is reduced to 43%.

The materials produced in this work, were fabricated by sputter-deposition SiO$_x$ films, high temperature annealing for Si-NC formation and consequent electron-beam lithography to form the array of pillars. Following is the detailed process:

- Substrate cleaning. The fused-silica substrate was sonicated in H$_2$O and immersed in a Base Piranha solution for 15 minutes.

- Sputter deposition. A sub-stoichiometric film of SiO$_2$ (with a 17 ± 4 vol% excess Si) was deposited by magnetron RF co-sputtering system (AJA int.), using high purity Si (99.99%) and SiO$_2$ (99.99%) [6,35,71,72]. The resulting stoichiometry and thickness were determined from the deposition rates, which were calibrated by a quartz crystal microbalance, and validated by Scanning Electron Microscope (SEM) analysis of the film cross-sections.

- Thermal annealing. The sputtered film was annealed for 30min at a temperature of 1100 – 1150 °C in a N$_2$ environment. This resulted in both phase separation of Si and SiO$_2$, and crystallization of the Si clusters. The optical properties of the resulting Si-NC:SiO$_2$ films are strongly dependent on the thickness $H$. 

average PL enhancement per Si-NC. Specifically, our experiments indicate that the PL intensity from the best performing metamaterial is +30% compared to a planar Si-NC:SiO$_2$ film (without the nanocylinder patterning), despite that the number of photoluminescent Si-NCs is reduced to 43%.

The materials produced in this work, were fabricated by sputter-deposition SiO$_x$ films, high temperature annealing for Si-NC formation and consequent electron-beam lithography to form the array of pillars. Following is the detailed process:

- Substrate cleaning. The fused-silica substrate was sonicated in H$_2$O and immersed in a Base Piranha solution for 15 minutes.

- Sputter deposition. A sub-stoichiometric film of SiO$_2$ (with a 17 ± 4 vol% excess Si) was deposited by magnetron RF co-sputtering system (AJA int.), using high purity Si (99.99%) and SiO$_2$ (99.99%) [6,35,71,72]. The resulting stoichiometry and thickness were determined from the deposition rates, which were calibrated by a quartz crystal microbalance, and validated by Scanning Electron Microscope (SEM) analysis of the film cross-sections.

- Thermal annealing. The sputtered film was annealed for 30min at a temperature of 1100 – 1150 °C in a N$_2$ environment. This resulted in both phase separation of Si and SiO$_2$, and crystallization of the Si clusters. The optical properties of the resulting Si-NC:SiO$_2$ films are strongly dependent on the thickness $H$. 

average PL enhancement per Si-NC. Specifically, our experiments indicate that the PL intensity from the best performing metamaterial is +30% compared to a planar Si-NC:SiO$_2$ film (without the nanocylinder patterning), despite that the number of photoluminescent Si-NCs is reduced to 43%.
Chapter 3. Si NCs hierarchical metamaterial

Figure 3.2: Schematic of the fabrication steps: a) substrate cleaning, b) sputtering deposition, c) thermal annealing, d) resist spin-coating, e) EBL, f) development, g) etching, h) resist removal and Si-NC passivation.

Therefore, for each produced height, $H$ (100 nm, 300 nm and 450 nm), the sputter rates were tuned ad hoc in order to maintain the PL spectral position and bandwidth approximately the same. This guarantees that the size distribution of the Si-NCs is also similar, as determined by the empirical dependence $E_g = 1.12 + 1.86/d^{1.39}$, with $E_g$ and $d$ being the Si-NC band-gap (in eV) and the NC diameter (in nm), respectively, established for Si-NCs prepared in the same way as done here. [11, 34, 35]

- Resist spin-coating. A layer of HDMS primer, a thin film of MaN-2403 electron-beam resist and a layer of Espacer 300Z were consecutively spin-coated on the sample.
- EBL. The resist is patterned by electron-beam lithography (Raith e-LiNE). The complete list of metamaterial geometries is listed in Table 3.1.
- Development. The un-exposed regions of resist were removed by immersing the samples in the ma-D 525 developer.
- Etching. The nano-pattern was transferred to the underlying Si-NC:SiO$_2$ film by using an Oxford PlasmaPro100 Cobra etcher with a 10 sccm flow of C$_4$F$_8$ and of Ar.
- Resist removal and Si-NC passivation. The remaining resist was removed by immersing the sample in acetone and by O$_2$ descum for 15min. As a final step, the sample was placed in a forming gas environment (5% H$_2$ in N$_2$) for 60 minutes at 500 $^\circ$C. This process is performed to passivate the interface between the Si-NCs and the SiO$_2$ matrix.

Slightly different sputtering and annealing parameters were used in order to produce the three thicknesses ($H = 100 \text{ nm}, 300 \text{ nm} \text{ and} 450 \text{ nm}$) with a Si-NCs size
3.2. Experimental details

<table>
<thead>
<tr>
<th>( H = )</th>
<th>100 nm</th>
<th>300 nm</th>
<th>450 nm</th>
<th>Average</th>
<th>100 nm</th>
<th>300 nm</th>
<th>450 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S(\text{nm}) )</td>
<td>( D(\text{nm}) )</td>
<td></td>
<td></td>
<td>( \Delta AC (\pm %) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>158</td>
<td>168</td>
<td>168</td>
<td>164</td>
<td>-5</td>
<td>-1</td>
<td>+4</td>
</tr>
<tr>
<td>308</td>
<td>208</td>
<td>219</td>
<td>218</td>
<td>215</td>
<td>-5</td>
<td>-2</td>
<td>+2</td>
</tr>
<tr>
<td>388</td>
<td>260</td>
<td>272</td>
<td>261</td>
<td>264</td>
<td>-6</td>
<td>-3</td>
<td>+1</td>
</tr>
<tr>
<td>462</td>
<td>313</td>
<td>322</td>
<td>308</td>
<td>314</td>
<td>-5</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>543</td>
<td>368</td>
<td>374</td>
<td>374</td>
<td>372</td>
<td>-6</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>617</td>
<td>416</td>
<td>425</td>
<td>419</td>
<td>420</td>
<td>-5</td>
<td>-2</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.1: List of the metamaterial geometrical parameters for all the fabricated metamaterial height \( H \), array spacing \( S \), nanocylinder diameter \( D \), and deviation \( \Delta AC \) from the nominal area coverage \( AC=43\% \).

distribution, which was determined to be almost identical (average diameter of \( \sim 2.5 \text{nm} \)). The size was established from the PL spectra (see Fig. 3.3) as done in our past works and established in literature. [34, 35]

The nano-patterning process introduces some deviations between the nominal geometry and the fabricated ones. The nanocylinders center-to-center separation distance, \( S \), is barely affected by fabrication imperfections, and the fabricated values are equal to the nominal ones within a \( \pm 2 \text{nm} \) error, as shown in Table 3.1. On the other hand, the cylinder shape is significantly affected. The upper and lower bases differ in diameter and the sides are not perfectly vertical. Moreover, the nanocylinder surface shows some roughness. The fabricated diameter, as it appear from SEM analysis, is reported in Table 3.1. It shows significant deviation from the nominal values depending on the diameter and size. We take these deviations from the nominal parameters into account by using the mean between the observed lower and upper bases of the nanocylinders as the AC in Eq. 3.4.

3.2.2 Optical characterization

The optical extinction is measured in a Zeiss Axio Observer inverted microscope. The light source is a halogen lamp focused by a condenser with numerical aperture NA=0.35, and the transmitted light is collected through a NA=0.75 100x objective. The spectra are recorded by a Princeton Instruments Acton SpectraPro SP2300 spectrometer equipped with a PyLoN:400 (1340 x 400) cryogenically-cooled charge-coupled device (CCD). For the 0th order extinction, we use a custom system where the light source is a fiber-coupled lamp focused by a NA=0.42 lens. The transmitted and reflected light beams are collected by identical lenses (for the reflection we additionally use a half transparent mirror) and delivered to an OceanOptics USB2000+Vis-NIR Spectrometer. The PL experiments are performed in the same Zeiss Axio Ob-
Chapter 3. Si NCs hierarchical metamaterial

server inverted microscope. The excitation is the 488 nm line of a Spectra-Physics Stabilite 2017 Ar laser, focused onto a fixed spot of 50 µm by a 100x objective with NA=0.75. The excitation power is fixed at 2.5 mW. The PL signal is collected by the same objective by using a dichroic mirror, and measured by the spectrometer and the CCD camera. The values reported in this manuscript are the PL intensities integrated across the emission spectrum. For the PL excitation experiment, we use the 415 – 537.5 nm signal of a SOLAR LP603-I Optical Parametric Oscillator (OPO), pumped by the third harmonic of a Nd:YAG LQ629-10 1064 nm laser with 100 Hz repetition rate and 12 ns pulse duration. The OPO signal is collimated and coupled to the inverted microscope, exciting the samples perpendicularly to their surface. For the PL lifetime measurements, we use the CW output at 445 nm of a Becker and Hickl diode laser, modulated by a square wave with 1 kHz frequency, 100 µs ON-state and 3 µs fall time. [73] The detector is an ID100 Quantique silicon avalanche photodiode with 40 ps timing resolution, connected to a DPC-230 Becker & Hickl timing card. Absolute QY measurements are performed for the planar Si-NC:SiO$_2$ films before nano-patterning. The samples are placed in an integrating sphere (7.5 cm in diameter, Newport) with the PL directed into a Solar LS M266 spectrometer coupled with a Hamamatsu S7031-1108S Vis-CCD camera. For excitation, we used a 150W Hamamatsu L2273 xenon lamp coupled to double grating Solar MSA130 monochromator. The home-built Fourier microscopy setup consists of a 100x objective with NA=0.90, a set of telescope lenses L1 and L2 with equal focal lengths ($f = 20$ mm) and a Fourier lens L3 ($f = 200$ mm). The detector is an Andor Technology silicon CCD. The excitation is a PicoQuant LDH diode laser at 450 nm and a pinhole is used to selectively excite one metamaterial sample per each acquisition.

3.2.3 Nanomaterial geometry considerations

In the deposited Si-NC:SiO$_2$ films, the size of Si-NCs is 2 orders of magnitude smaller than the wavelength of visible light and their volume fraction $f$ is $17 \pm 4\%$. Therefore, Si-NC:SiO$_2$ can be effectively approximated as a homogeneous medium, with intermediate optical properties between Si and SiO$_2$. Detailed studies of the refractive index of Si-NC:SiO$_2$ films can be found in literature, [74, 75] showing that its value approaches 1.9 for the stoichiometry of interest in our work (SiO$_x$ with $x \approx 1.37$), and that there is good agreement with the Maxwell-Garnett formula. [76] Small deviations are due to the fact that the electronic states of Si-NCs are strongly affected by quantum confinement, and therefore the NC refractive index is different from bulk Si. We apply the Maxwell-Garnett homogenization formula to estimate the effective refractive index $n_{eff}$, and we find a good agreement with the measured transmission and reflection data. The volume fraction $f$ affects both the optical and electronic properties of the Si-NC:SiO$_2$ medium. Any change of $f$ modifies the effective refractive index of the Si-NC:SiO$_2$ medium, according to the homogenization
3.2. Experimental details

models: as the concentration of Si increases, the refractive index becomes higher.

Moreover, as $f$ increases, the average distance between the Si-NCs is reduced and the probability of SSQC increases as well. Other work has demonstrated the existence of an optimal distance as far as the probability of SSQC is concerned. \[39\] Furthermore, the Si-NC size has a strong influence on the QY and an optimum size exists. \[6\] Therefore, the interplay between $f$, the deposition parameters and the film thickness determines the resulting PL spectrum, QY and SSQC efficiency. \[21, 77\]

We fabricate three sets of metamaterials with nominal nanocylinder height $H = 100 \text{ nm}$, $300 \text{ nm}$, and $450 \text{ nm}$. For each height, we produce (on the same substrate) 6 arrays with nanocylinder diameter from $D = 164 \text{ nm}$ to $420 \text{ nm}$. A complete list of investigated samples is provided in Table 3.1. In order to have a fair comparison between metamaterials with the same height, we keep the number of Si-NCs equal in all the metamaterial geometries by fixing the nanocylinder area coverage ($AC \sim 43\%$). This choice also determines the array spacing. Moreover, all the samples with the same height, including the planar film used as reference, are made starting from the same deposited Si-NC:SiO$_2$ layer, and therefore the optical and electronic properties are the same. The fabrication process consists of a sequence of eight steps (a-h), as illustrated in Fig. 3.2. First, we deposit a planar layer made of Si-NC:SiO$_2$ with thickness $H = 100 \text{ nm}$, $300 \text{ nm}$ and $450 \text{ nm}$ (on different substrates, steps (a-c)). Then, a nano-lithographic method is used to pattern the metamaterial geometry into the Si-NC:SiO$_2$ layers (steps (d-h)). The fabrication process results in hexagonal 2D arrays of Si-NC:SiO$_2$ nanocylinders. The arrays have a total size of $30 \mu\text{m}$. The resulting pillar height $H$ is equal to the thickness of the original layer deposited in steps (a-c).

3.2.4 Calculations

We use the transition matrix method, also known as null-field, to calculate the scattering cross-section spectra of individual nanocylinders. \[28\] In this method, the expansion coefficients for the scattered field are retrieved by combining the null-field equation with the boundary conditions. We also use the rigorous coupled wave approach, also known as Fourier modal method, to calculate the transmission ($T$), reflection ($R$) and absorption $A = (1 - T - R)$ spectra of the 2D arrays of nanocylinders. \[79\] This method is particularly suitable for simulating light interaction with periodic layered structures which are invariant in the direction normal to the periodicity, due to its Fourier basis representation. For perfectly planar films and periodic arrays in the metamaterial regime (when the incident wavelength is larger than the lattice spacing), one can write $T_0 + R_0 + A = 1$, where $T_0$ is the $0^{th}$ order transmittance, $R_0$ is the $0^{th}$ order reflectance and A is the absorption. In transmission experiments, the extinction is the fraction of incident light that does not reach the detector, defined as $\text{Ext} = 1 - T_0$, and therefore $\text{Ext} = R_0 + A$. For real films and metamaterials with
surface roughness and geometrical imperfections, diffuse (i.e. non directional) scattering is also present, both transmitted towards the side of the transmission ($T_{ds}$) and to the side of the reflection. Therefore, the actual transmittance measured in a transmission experiment is $T = T_0 - T_{ds}$ and $\text{Ext} = 1 - T = 1 - T_0 - T_{ds}$. Given the diffuse character of $T_{ds}$, its contribution strongly varies with the angular aperture of the collection optics, as observed in the experiments of Fig. 3.3.

For periodic metamaterials in the grating regime (the incident wavelength is equal or shorter than the lattice spacing), then highly directional diffraction modes take place both in transmission and in reflection. Our rigorous coupled wave approach (RCWA) calculations, the total transmittance $T$ and reflectance $R$ take into account all the diffraction modes of any order, including the $0^{th}$:

$$T = T_0 + T_{\pm 1} + \ldots + T_{\pm n}$$

and

$$R = R_0 + R_{\pm 1} + \ldots + R_{\pm n},$$

with $n > 0$. In these calculations, the diffuse scattering is zero because a perfect periodic geometry (in terms of periodicity and unit cell shape) is assumed. Therefore, we can calculate the absorption as $A = 1 - T - R$.

### 3.3 Results

#### 3.3.1 Optical properties

The metamaterial transmission, scattering and absorption depend on the nanocylinder size and distance. We quantify this dependence by measuring the extinction spectra in the 350 – 600 nm spectral range, as showed in Fig. 3.3(a-c) for the nanocylinder height $H = 100$ nm, 300 nm and 450 nm. The extinction is defined as $1 - T$, with $T$ being the transmittance collected with an angular aperture $\pm 49^\circ$, which comprises also significant contributions from diffuse scattering (see Methods). The extinction spectra of the three homogeneous Si-NC:SiO$_2$ films are conveniently reported in black, and are used as reference samples throughout the manuscript. For very thin metamaterials ($H = 100$ nm, Fig. 3.3(a)), an extinction band appears with increasing diameter $D$, and the amplitude increases from 5% to only 20% at $\lambda \approx 400$ nm. For metamaterials with $H = 300$ nm (Fig. 3.3(b)), the maximum extinction amplitude is increased up to 70%. In particular, for diameters from 215 nm to 372 nm, we can distinguish the occurrence of broad extinction peaks in the spectra. These spectra confirm that the nanocylinders with height of approximately 300 nm are efficient Mie scatterers, whose modes rely on significant retardation effects along the propagation direction. Eventually, if we further increase the metamaterials height to $H = 450$ nm (Fig. 3.3(c)), we observe a slight increase with respect to the previous height and a shift in the extinction spectral features, in agreement with previous numerical studies. [57]

To shed light on the origin of the observed spectral features, we focus on the metamaterials with $H=300$ nm and measure the $0^{th}$ order transmission by narrowing the collection angular aperture to $\pm 25^\circ$ to reduce the contribution of diffuse scattering.
3.3. Results

Figure 3.3: Extinction spectra (collection aperture ±49°) of metamaterials with nanocylinder height (a) $H = 100$ nm, (b) $300$ nm, and (c) $450$ nm, parametrized for a diameter in the range $164 - 420$ nm. The spectra of the reference planar films are reported in black for each thickness $H$. The insets show representative SEMs of the nanocylinder for each height. (d) 0$^{th}$-order extinction spectra (collection aperture ±25°) of metamaterials with $H = 300$ nm, parametrized for a diameter from $D = 215$ to $372$ nm. The continuous (dashed) part of the spectra indicates that the wavelength is longer (shorter) than the array spacing.
Chapter 3. Si NCs hierarchical metamaterial

The spectra, shown in Fig. 3.3(d), feature neat extinction maxima, whose spectral position spans a wide range from $\lambda = 400 \text{ nm}$ to $700 \text{ nm}$, depending on the nanocylinder diameter. We can easily attribute them to the occurrence of dipolar Mie resonances in the nanocylinders. In fact, according to a simple rule-of-thumb formula, electric and magnetic dipole resonance appear close in the spectrum, approximately at the wavelength:

$$\lambda_{\text{Mie,dipolar}} = n_{\text{eff}} \cdot D,$$

(3.1)

as indicated by the vertical arrows in Fig. 3.3(d). In resonators with similar refractive index, the magnetic resonance has been predicted to have slightly longer wavelength than the electric one. [57] Moreover, the electric mode is expected to red-shift more quickly than the magnetic one, by increasing the nanocylinder size. [56] In our measurements, we observe a pronounced peak asymmetry for all the investigated metamaterials, and even a double peak for the case $D = 264 \text{ nm}$. In addition, we observe extinction maxima occurring at shorter wavelengths than the Mie resonances. Their spectral position approximately coincides with the array spacing, $S$, revealing the fact that they are related to the grating condition:

$$\lambda_{\text{grating}} = S.$$

(3.2)

We conclude that our 2D metamaterial design supports extinction peaks due to the occurrence of Mie resonances of the nanocylinders and due to the grating condition. Their spectral position can be independently tuned by the nanocylinder shape (mainly the diameter) and the array spacing.
3.3. Results

Figure 3.4: (a) Calculated scattering cross-section spectra of isolated nanocylinders parametrized for the diameter $D = 164 \text{ nm}$ (cyan), $215 \text{ nm}$ (blue), $264 \text{ nm}$ (green), $314 \text{ nm}$ (red), $372 \text{ nm}$ (orange), and $420 \text{ nm}$ (magenta). (b) Calculated extinction spectra of a 2D array of nanocylinders parametrized for the diameter $D$ (colors as in panel a). (c) Electric (left) and magnetic (right) field distributions for the metamaterial with $D = 264 \text{ nm}$ excited at $\lambda_{\text{Exc}} = 440 \text{ nm}$ (top) and $485 \text{ nm}$ (bottom). (d) Same as panel (b) for absorption spectra. All the calculations are relative to nanocylinders with height $H = 300 \text{ nm}$. 
3.3.2 Calculations of optical properties

To better interpret the difference between the measured extinction spectra of Fig. 3.3(b) and 3.3(d), we perform rigorous full-wave electromagnetic calculations of individual (i.e., isolated) nanocylinders and 2D arrays. The scattering spectra of individual nanocylinders with \( H = 300 \text{ nm} \) are shown in Fig. 3.4(a), and are characterized by broadband features, with local maxima shifting as the nanocylinder diameter increases. On the other hand, the calculated extinction spectra \((1 - T)\) for 2D arrays of nanocylinders are shown in Fig. 3.4(b), and we can clearly distinguish sharp extinction peaks due to dipolar Mie resonances and grating modes. These calculations indicate that the extinction measurements of Fig. 3.3(b) are dominated by diffuse scattering from the nanocylinders, while the peaks in the spectra of Fig. 3.3(d) are due to collective resonant modes. This difference in the experimental results is simply obtained by reducing the angular aperture of the detection optics. The identification of the resonances modes in the calculations for 2D arrays can be made by calculating the spatial distribution of the electromagnetic field. As an example, in Fig. 3.4(c) we show the electric and magnetic fields for the metamaterial with \( D = 264 \text{ nm} \) excited at \( \lambda_{\text{exc}} = 440 \text{ nm} \) (top) and \( 485 \text{ nm} \) (bottom). The first case corresponds to the Mie electric dipole resonance, while the second case to the magnetic one. The calculated peaks differ from the experimental ones in terms of their higher amplitude and of the wider spectral separation between the electric and magnetic resonances. We attribute this to two main factors. First, the scatterers in the fabricated metamaterials show significant geometrical imperfections, being not ideal cylinders. The top and bottom bases have different diameter, the sides are not perfectly vertical and the surface is not smooth. Second, the substrate is neglected in the calculations (i.e., the 2D array is free-standing). The effects of the substrate have been already investigated, and they are well-known to determine a red-shift of the resonances and a change in the resonance amplitude. Eventually, it is important to remark that the effective refractive index \( n_{\text{eff}} \) used in the calculations is just an approximation of the actual index, since it is derived from a homogenization method.

The calculations in Fig. 3.4(b) also predict the onset of peaks due to the grating condition at shorter wavelengths than the Mie ones. Their spectral position is in good agreement with the experimental spectra of Fig. 3.3(d), due to the excellent definition in terms of array spacing in the fabrication process. We calculate the contribution of the absorption to the extinction peak and show it in Fig. 3.4(d). Both the nanocylinder Mie resonances and the grating condition induce absorption peaks, and a maximum absorption value of \( \sim 50\% \) is predicted. This is in agreement with a recent investigation on superabsorbing free-standing metamaterials, showing that 50% absorption is achieved if the forward-scattered wave is exactly \( \pi \)-delayed with respect of the incident one. The comparison between experiments and calculations conclusively
3.3. Results

confirms the existence of absorption peaks in the investigated 2D Si-NC:SiO$_2$ metamaterials due to both the nanocylinder Mie resonances and the grating condition.

### 3.3.3 Photoluminescence characterization

Enhanced absorption in the Si-NCs is expected to lead to enhancement of their photoluminescence intensity as well. Considering that for many applications photoluminescence is the output product of interest, we have therefore opted to characterize it here and see whether the prediction agrees with reality.

At steady state excitation the PL intensity, $I_{PL}$, expressed as photon flux, is:

$$I_{PL} \propto QY \cdot N_T \cdot \sigma \cdot I_{exc},$$

where $N_T$ is the number of Si-NCs and $I_{exc}$ is the excitation flux. The absorption cross-section is $\sigma \approx 10^{-15}$ cm$^{-2}$ under blue excitation, a value comparable with direct-bandgap semiconductor quantum dots. [80, 81] We measure the PL spectra, shown in Fig. 3.5(a), by exciting the samples with the 488 nm line of an Ar laser. To quantify the effect of the absorption enhancement on the emission, we measure the PL intensity of the metamaterials (for the three heights $H$) and compare it with that of the planar Si-NC:SiO$_2$ film (of thickness equal to $H$) used as reference, under the same excitation conditions. We perform these measurements as function of the nanocylinder size and of the excitation wavelength. The average Si-NC concentration and QY are the same for all the samples with the same height $H$ (including the reference), because they are fabricated starting from the same SiNC:SiO$_2$ layer (see Methods section). However, the total number $N_T$ of emitting Si-NCs in the metamaterials is lower than the reference $N_T,ref/N_T,meta = AC^{-1}$. Therefore, we define the PL enhancement as:

$$\text{PL}_{enh} = \frac{I_{PL,meta}}{I_{PL,ref}} \cdot \frac{N_T,ref}{N_T,meta} \approx \frac{I_{PL,meta}}{I_{PL,ref}} \cdot AC^{-1}.$$

The PL enhancement is shown in Fig. 3.5(b) as function of the pillar parameter, for pillar height $H = 100$ nm (celeste), 300 nm (olive) and 450 nm (honey). For the metamaterial with $H = 100$ nm, the PL enhancement increases with the diameter and then it stays constant at a value of $\approx 1$. This simply means that the average PL intensity per Si-NC is equal to that of the reference planar film. Remarkably, for the sample with $H = 300$ nm, $I_{PL,meta} \approx I_{PL,ref}$ despite the lower amount of Si-NCs, and the maximum PL enhancement exceeds $2 \text{PL}_{enh} \approx AC^{-1}$. Eventually, for the sample with $H = 450$ nm, the PL enhancement slightly decreases from the previous case, confirming again the existence of an optimum nanocylinder height.

In order to confirm the dependence of the absorption enhancement (and therefore of the PL intensity) on the excitation wavelength, we performed photoluminescence excitation (PLE) experiments by scanning the excitation range $\lambda_{exc} = 415 - 530$ nm.
Chapter 3. Si NCs hierarchical metamaterial

Figure 3.5: (a) Representative PL spectra of metamaterials with $H = 100$ nm (cyan), 300 nm (olive-green), and 450 nm (tan) and with $D = 215$ nm excited at $\lambda_{\text{Exc}} = 488$ nm. (b) PL enhancement as a function of nanocylinder diameter of metamaterials with $H = 100$ nm (cyan), 300 nm (olive-green), and 450 nm (tan), for $\lambda_{\text{Exc}} = 488$ nm. (c) PLE enhancement for the metamaterial with $D = 215$ nm (blue), 264 nm (green), 314 nm (red), and 372 nm (orange). Circles are relative to the metamaterials with $H = 300$ nm; triangles are for $H = 450$ nm. (d) CCD image (false color) of the PL intensity from the metamaterial with $H = 300$ nm and $D = 372$ nm (left) and the reference sample (right).
3.4. Discussion

The results are shown in Fig. 3.5(c), where the circles are relative to the metamaterials with $H = 300\,\text{nm}$, triangles are for $H = 450\,\text{nm}$. The metamaterial with $H = 300\,\text{nm}$ and $D = 215\,\text{nm}$ (blue line) shows an increase of PL enhancement towards short wavelengths, in proximity of the Mie extinction peak at $\lambda \approx 420\,\text{nm}$ measured in Fig. 3.3(d). Analogously, the sample with $D = 264\,\text{nm}$ (green line), which features an absorption peak at $\lambda \approx 500\,\text{nm}$, shows increased PL toward longer wavelength up to $\approx 2.6$. The sample with $D = 372\,\text{nm}$ (orange line) deserves a separate mention, because it features a grating condition in the investigated excitation range and, interestingly, it shows the highest enhancement value: the $I_{\text{PL,meta}}/I_{\text{PL,ref}}$ ratio is 130\% (+30\%), and the nominal $AC_{\text{meta}}$ is 43\%, resulting in an enhancement $PL_{\text{enh}} = 3.02$.

This excellent performance is easily explained, since the fabrication method determines a small deviation on the nanocylinders separations ($\pm 2\,\text{nm}$), which controls the grating condition, while a much larger error affects their diameter ($\pm 10\,\text{nm}$) and shape (bases and surface roughness), reducing the amplitude of the Mie absorption peak. The metamaterials with $H = 450\,\text{nm}$ show analogous trends, but with lower absolute PL enhancement, as already observed in Fig. 3.5(b). In order to increase the enhancement factor, we could improve the quality of the nano-patterning, in terms of the nanocylinder diameter, shape and distance, and by accurately match the optical impedance of the substrate, as previously discussed in the text. However, while this effort is needed for real applications, it is not strictly necessary to demonstrate the validity of our concept.

3.4 Discussion

In the following, we consider and systematically address all the possible alternative explanations for the observed increase of PL emission, namely: (i) the PL extraction efficiency and (ii) directionality, (iii) the photonic density of states (PDOS) and (iv) the saturation of the Si-NC absorption/emission states (iv). As a matter of fact, the metamaterial nano-pattern can modify the PL extraction efficiency and directionality by changing the effective Fresnel reflection and transmission coefficients in the emission spectrum. Moreover, it can modify the PDOS and affect the Si-NC radiative lifetime, due to the Purcell effect. [82,83] Eventually, it can lead to the saturation of the absorption/emission of the Si-NCs, resulting in unfair comparison between samples and artefacts in the determination of the PL enhancement. We unambiguously prove that these phenomena do not significantly affect the PL intensity of the investigated metamaterial geometries with respect to the reference planar film, and we conclude that the increased absorption efficiency is indeed the dominant process. A modification of Fresnel coefficients is simply detectable in the reflection and transmission spectra. Figures 3.6(a) and 3.6(b) show the variation of the reflectance
Chapter 3. Si NCs hierarchical metamaterial

Figure 3.6: Variation of the measured reflectance (a) and transmittance (b) of the metamaterials with $H = 300 \text{ nm}$ and $D = 215 \text{ nm}$ (blue), 264 nm (green), 314 nm (red), and 372 nm (orange), with respect to the reference. The PL full width at half-maximum (fwhm) spectral width is indicated by the sea-green-shaded area. Fourier image of the transmitted light (c) and PL (d) for the metamaterial with $H = 300 \text{ nm}$ and $D = 264 \text{ nm}$. (e) PL intensity time dynamics for the planar reference film (black) and stretched-exponential fit (red). The inset shows the PL decays for the sample metamaterial samples as in panel (a), plotted with an artificial vertical offset, for the sake of clarity. (f) Dependence of the PL intensity on the excitation power for the same sample as in panel (c).
3.4. Discussion

\[ \delta R(\lambda) \] and of the transmittance \[ \delta T(\lambda) \], respectively, for the metamaterial samples with respect to the unpatterned film at normal incidence. For all samples, the Mie resonances and the grating conditions are far from the emission spectrum, indicated by the sea-green shaded area. The maximum values of \[ \left| \frac{\delta R(\lambda)}{R(\lambda)} \right| \] and \[ \left| \frac{\delta T(\lambda)}{T(\lambda)} \right| \] are 8% at \( \lambda = 758 \) nm and 22% at \( \lambda = 832 \) nm, respectively, while the average across the emission spectrum is \(< 2\%\) for both. For each wavelength, we quantify the variation of PL intensity due to changes of R and T by using a first-order approximation:

\[ \frac{\delta I_{PL,s}(\lambda)}{I_{PL,s}(\lambda)} = \frac{\delta R(\lambda)}{R(\lambda)} \delta R(\lambda) \quad \text{and} \quad \frac{\delta I_{PL,s}(\lambda)}{I_{PL,s}(\lambda)} = \frac{\delta T(\lambda)}{T(\lambda)} \delta T(\lambda). \]

By considering that the integrated PL intensity is \( I_{PL} = \int I_{PL,s}(\lambda) d\lambda \), we find that the overall change in PL intensity is only \( \left| \frac{\delta I_{PL}(\lambda)}{I_{PL}(\lambda)} \right| R < 2\% \) and \( \left| \frac{\delta I_{PL}(\lambda)}{I_{PL}(\lambda)} \right| T < 3\% \). Therefore, the PL extraction efficiency is approximately the same for the metamaterial and the reference samples.

To directly exclude any change in the PL directionality, we perform Fourier (k-space) microscopy of the PL intensity. This technique is based on capturing the Fourier plane image formed in the back focal plane of a high NA objective, which contains the k-space information of the radiative field. For all the samples, including the reference, the Fourier image is homogeneous, which indicates an isotropic PL emission. Here we focus on one representative metamaterial sample with \( H = 300 \) nm and \( D = 264 \) nm, and we first report in Fig. 3.6(c) the Fourier image of the transmitted light. It only shows the 0th order central spot, which simply confirms that the metamaterial is sub-wavelength at the excitation wavelength. The Fourier image of PL is displayed in Fig. 3.6(d), and it shows isotropic emission. Therefore, we can exclude any effect of the PL angular dependence on the observed PL enhancement.

Ultimately, a change in the PDOS in the metamaterial samples would significantly affect the PL spectrum and lifetime. On the contrary, our measurements indicate that they do not change with the nanocylinder diameter, and most importantly, they are equal to those of the reference sample. Specifically, the average PL lifetime is \( \tau \approx 45 \pm 2 \) µs, as obtained by fitting the decay with a stretched-exponential function. In Fig. 3.6(e), we show the PL time-dynamics of the reference sample (black) and of the metamaterials with the highest PL enhancement (\( H = 300 \) nm and \( D = 215 \) nm, 264 nm and 372 nm). Therefore, we can exclude any effect of the PDOS on the observed PL enhancement. Eventually, Figure 3.6(f) shows the dependence of the PL intensity on the excitation power for the representative sample with \( H = 300 \) nm and \( D = 264 \) nm, which clearly indicates that all the samples were characterized in the linear absorption regime, far from the saturation of the Si-NCs. We can safely attribute the increased PL in the metamaterial samples exclusively to the enhancement of the absorption at the excitation wavelength. This result was remarkably achieved without affecting the transmission/reflection properties in the emission part of the spectrum. Moreover, the emission properties in terms of angular pattern, lifetime and spectral shape are approximately the same as the planar sample without nanocylinders.
Chapter 3. Si NCs hierarchical metamaterial

While it would be most accurate to also measure the PLQY of each metamaterial in an integrating sphere, this is not possible in our case. The samples are microscopic, which does not allow the integrating sphere measurements. Furthermore, the metamaterial, is not expected to affect the PLQY, as the absorption is enhanced, while the PL properties are not influenced dramatically. Nevertheless, the PLQY was determined directly for the reference sample, as that sample is not microscopic. The measured PLQY is \( \sim 2\% \), while the maximum value achieved so far in literature is 35\% \cite{6}. For applications this would require a time-consuming optimization of the material deposition process (the absolute value of QY is not relevant for the concept demonstrated in this work).

Lastly, any potential application as envisioned in the introduction would have to benefit from high PLQY Si-NCs combined with efficiency enhancing effects such as SSQC, and now, as we have shown, an optimized metamaterial geometry. The first two optimizations in the underlying SiNC films, would lead to modifications in the refractive index, and the resulting metamaterial effects. One could wonder whether these optimized SiNC films would also benefit from the metamaterial effects shown here. Nevertheless, the scope of this work encompassing over 50 metamaterial geometries, has shown that it is possible to optimize the structure and obtain selective enhancements in extinction the whole UV/Vis region. Therefore, using the two separate knobs, namely pillar shape and array spacing, it is possible to obtain the desired results also for well optimized Si-NC films.

3.5 Conclusion

In conclusion, we have successfully integrated quantum-confined Si-NCs into SiO\(_2\) nanocylinders, arranged into a 2D metamaterial. This hierarchical metamaterial inherits the optical and electronic properties of its building blocks and shows performance enhanced compared than the individual components. We have experimentally detected the occurrence of extinction peaks related to dipolar Mie resonances in the nanocylinders and to the grating condition, which can be tailored throughout the visible spectrum. Both of them induce spectrally-selective enhancement of the absorption, as predicted by our rigorous calculations. The Si-NCs experience increased excitation and, as a consequence, exhibit a more intense light emission. Remarkably, our experiments show that our best-performing metamaterial shows higher light emission than a planar film without nano-patterning, despite the reduced absolute amount of Si-NCs. The metamaterial design principles described in this work are applicable to any QD semiconductor and to other emitters, such as rare-earth ions and organic molecules. The specific implementation investigated in this work is completely based on Si, it is fully compatible with CMOS technology and it can be integrated with Si solar cells for spectral shaping purposes. We envision the application of this approach to photo-
voltaics, photocatalysis and photosynthesis.