Doctoral Thesis

Shape dependence of Localized Surface Plasmon Resonances and their application in nanoemitters

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Shape dependence of Localized Surface Plasmon Resonances and their application in nanoemitters

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for the degree of
DOCTOR OF SCIENCES

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List of abbreviations

\(a, b\) Principal in-plane axes of the studied NPs.
\(h\) Height of the studied NPs.
\(\epsilon_m\) Dielectric constant of the medium surrounding the NP.
\(\epsilon_p(\lambda)\) Complex dielectric function of NP.
\(\epsilon_1(\lambda)\) Real part of \(\epsilon_p(\lambda)\).
\(\epsilon_2(\lambda)\) Imaginary part of \(\epsilon_p(\lambda)\).
\(\lambda_{\text{Res}}\) Central wavelength of the plasmonic resonance.
\(L\) Depolarization factor (with indexes \(i = a, b, h\) if a specific principal axis discussed).
\(g\) Concavity parameter (with indexes if a specific shape is discussed).
\(R\) Retardation term (with indexes \(i = a, b, h\) if a specific principal axis discussed).
\(d\) Total length of the axis along which a resonance is excited (with indexes \(i = a, b, h\) if a specific principal axis discussed).
\(y\) Shape-term (with indexes \(i = a, b, h\) if a specific principal axis discussed).
\(\lambda_i\) Central wavelength of the plasmonic resonance. \(i = a, b, h\) if a specific principal axis is discussed, \(i = R, D, E\) if a specific footprint of the NP is studied.
\(\lambda_0\) Wavelength in vacuum.
\(\mu\) Eigenvalue of the static boundary integral equation.
\(\vec{E}_i, \vec{H}_i\) Total electric (magnetic) field in the NP.
\(\vec{E}_0, \vec{H}_0\) Applied electric (magnetic) field.
\(\vec{E}_d, \vec{H}_d\) Depolarization (demagnetizing) field.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{P}, \vec{M}$</td>
<td>Particle polarization (magnetization).</td>
</tr>
<tr>
<td>$\vec{L}$</td>
<td>Depolarization (demagnetizing) tensor.</td>
</tr>
<tr>
<td>$\vec{g}$</td>
<td>Concavity tensor.</td>
</tr>
<tr>
<td>$h_{T,B}$</td>
<td>Nanoantenna: height of the top/bottom disk.</td>
</tr>
<tr>
<td>$g$</td>
<td>Nanoantenna: gap size.</td>
</tr>
<tr>
<td>$d$</td>
<td>Nanoantenna: diameter.</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Nanoantenna: diminution angle.</td>
</tr>
<tr>
<td>$r$</td>
<td>Nanoantenna: corner radius.</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index.</td>
</tr>
<tr>
<td>$\lambda_{\text{ex}}$</td>
<td>Excitation wavelength.</td>
</tr>
<tr>
<td>$\lambda_{\text{em}}$</td>
<td>Emission wavelength.</td>
</tr>
<tr>
<td>$I_{\text{ex}}$</td>
<td>Excitation intensity.</td>
</tr>
<tr>
<td>$I_{\text{PL}}$</td>
<td>Photoluminescence intensity.</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Emission intensity at the beginning of the measurement.</td>
</tr>
<tr>
<td>$\alpha_{\text{on/off}}$</td>
<td>Exponent in the on- and off-time probability distributions.</td>
</tr>
<tr>
<td>$\gamma_{\text{ex}}$</td>
<td>Excitation rate.</td>
</tr>
<tr>
<td>$\gamma_{\text{r}}$</td>
<td>Radiative decay rate.</td>
</tr>
<tr>
<td>$\gamma_{\text{nr}}$</td>
<td>Non-radiative decay rate.</td>
</tr>
<tr>
<td>$D1, D2...$</td>
<td>Dipolar antenna modes excited by an electric field parallel to the antenna axis.</td>
</tr>
<tr>
<td>$D_{\text{e}}, D_{\text{m}}$</td>
<td>Dipolar electric and dipolar magnetic antenna mode. Both are excited by an electric field perpendicular to the antenna axis.</td>
</tr>
</tbody>
</table>
Summary

Optical effects based on Localized Surface Plasmon Resonances (LSPRs) in metallic nanoparticles have been used since the Roman epoch, although they were not identified as such until the beginning of the 20th century. In contrast, the engineering of LSPR-based effects is a young technology due to its need for production processes with nm-scale accuracy and computationally intensive numerical simulations. In consequence, the description of dependencies and properties of LSPRs is incomplete. In this study, experiments addressing the optical properties of differently shaped metallic nanoparticles (NPs) with characteristic lengths between 50 nm and 300 nm are performed. Electron-beam lithography is used for the NP production in order to guarantee an independent tuning of the different parameters defining particle shape. An intuitive resonance condition is introduced and the experimental results are interpreted accordingly. The knowledge gained and realized production and measurement methods are then used to pave the way for the realization of an efficient nanoemitter. The studied nanoemitter consists of two stacked gold nanoparticles with Silicon Quantum dots that are incorporated between the two NPs.

After a short introduction, the realized measurement concept for axis-selective excitation of metallic nanoparticles and nanoemitters are presented and the used sample fabrication processes shown. A first set of experiments targets the excitation of different resonances of single metallic NPs. The studied NPs are defined by three principal axes that are tuned in length independently. The observed exclusive excitation of a resonance along each of the three principal axes and the quasi-linear dependence of the resonance wavelengths on the relevant principal axis is in good agreement with the existing picture of LSPRs. Further, it is experimentally confirmed that the overall scattering spectrum of such a NP follows a superposition principle. These first set of measurements also prove the functionality of the realized measurement setup. However, they give indications that additional aspects need to be considered which reduce the validity of quasi-linear, exclusive scaling to a
restricted range of axes lengths and aspect ratios.

The underlying processes leading to the appearance of a LSPR are identified in terms of an intuitive model. The derived resonance condition creates a link between the resonance wavelength of the LSPR and a shape-term which considers quasi-static\(^1\) and dynamic depolarization (retardation) as well as particle concavity. The quasi-static depolarization is described by depolarization factors which can be generalized by the use of a newly introduced concavity parameter. It is discussed why this resonance condition is valid for particles with arbitrary shapes and how information about the different processes can be gathered from experiments. The derived resonance condition differs in these two important points from existing resonance conditions.

Based on a second set of experiments performed on cuboids, characteristic values for the consideration of concavity and retardation are determined and their dependencies on particle shape are highlighted. We show that the dynamic depolarization depends strongly on the relevant particle depolarization factor. This finding contradicts the widely spread opinion of a dominating size contribution to the dynamic depolarization. Even more surprisingly, the decomposition of the shape-term into a quasi-static and dynamic part shows that the dependence of the resonance wavelength on the length of the relevant principal axis is dominated by the corresponding dependence of the depolarization factor in most cases. This statement is confirmed by the observation of a blue-shifting resonance with increasing relevant axis length and by the study of the influence of changing aspect ratios on the resonance measured along an axis that is held constant.

Once the underlying principles that define the wavelengths of the resonances are identified, it becomes possible to discuss the dependencies of a resonance wavelength on particle shape and size in detail. For that purpose, the scattering experiments are extended to particles with elliptical and diamond-like footprints. It is shown that all observations can be reproduced qualitatively by the use of generalized depolarization factors and dynamic depolarization. The result is a detailed picture of the dependence of resonance wavelengths on the the shape and size of metallic NPs.

One of the most remarkable effects of LSPRs is the appearance of strong electromagnetic field enhancement around the NP for fields that

\(^1\)Quasi-static means that the phase of the studied fields is constant over the NP but that their frequency is non-zero.
match one of the particle resonance wavelengths. This can be used to change the excitation and emission properties of an emitter (e.g. a dye) that is placed into the near-field of the NP. The result is an nanoemitter that shows a strongly increased efficiency and emission intensity compared to the emitter alone for specific sets of parameters defining the emitter-antenna hybrid.

In the second part of this thesis, we discuss different aspects for the realization of an efficient nanoemitter using the example of two stacked Au nanodisks with Si-QDs incorporated in the gap between the disks. First, the antenna resonances that appear in the visible wavelength range are identified and their properties are studied. This is done by the use of numerical simulations (Finite Element Method, FEM). Due the chosen antenna design, both the excitation and emission of the Si-QDs need to be coupled to suitable antenna resonances. It is discussed which configurations of antenna modes are most promising for the realization of the nanoemitter.

Two promising configurations are then realized in a first set of nanoemitters. The spectral overlap of appropriate antenna modes with the chosen excitation wavelength and the Si-QD emission is shown by the use of axis-selective scattering experiments. Nevertheless, a photoluminescence signal originating from the Si-QDs placed in the antenna gap cannot be observed. A disturbing signal that originates from the antenna is detected instead. This signal couples to an antenna mode and is therefore strongly enhanced (i.e. by a factor of hundred to thousand). Furthermore, it is expected that the excitation efficiency of the Si-QDs at the chosen excitation wavelength is too low. The modifications of the chosen antenna design needed to realize the nanoemitter in a second development phase are specified and discussed in detail.
Zusammenfassung


Die studierten Nanopartikel haben charakteristische Längen zwischen 50 nm und 300 nm. Sie wurden mittels Elektronenstrahl-Lithographie hergestellt, um eine möglichst hohe Kontrolle über ihre Form zu gewährleisten. In einem zweiten Teil der Arbeit werden dann die gewonnenen Erkenntnisse und realisierten Produktions- und Messmethoden verwendet, um den Weg zur Realisierung eines effizienten Nanoemitters zu ebnen. Dieser besteht aus zwei übereinander angeordneten Goldpartikeln, zwischen welche Silizium Quantum Dots (Si-QDs) eingebaut wurden.

Nach einer kurzen Einführung in das Themengebiet wird der während dieser Arbeit realisierte Messaufbau vorgestellt. Dieser erlaubt es, einzelne Nanopartikel (NPs) und Nanoemitter entlang einer beliebigen Achse anzuregen. Anschliessend werden die verwendeten Herstellungsverfahren kurz zusammengefasst. Eine erste Messreihe ist dann der Anregung von unterschiedlichen Resonanzen in einzelnen NPs gewidmet. Die betrachteten NPs verfügen über drei Hauptachsen, welche unab-

Mit Hilfe eines intuitiven Models werden dann die Prozesse erfasst, welche zum Auftreten einer Plasmonresonanz bei einer bestimmten Wellenlänge führen. Diese Wellenlänge ist über eine Resonanzbedingung mit einem Term (Shape-Term) verknüpft, der seinerseits den quasi-statischen\textsuperscript{2} (Depolarisationsfaktoren) und dynamischen (Retardation) Beitrag zur Depolarisation des NP sowie dessen Konkavität berücksichtigt. Letzteres erlaubt eine Verallgemeinerung der Depolarisationsfaktoren. Es wird dargelegt, weshalb diese Resonanzbedingung für beliebig geformte NPs Gültigkeit hat und wie Aussagen über die verschiedenen Prozesse aus Streuexperimenten gewonnen werden können. In diesen beiden wichtigen Punkten unterscheidet sich die hergeleitete Resonanzbedingung von existierenden, ähnlich gelagerten Ansätzen.


\textsuperscript{2}Quasi-statisch drückt aus, dass die Phase der betrachteten Felder über das Nanopartikel hinweg konstant ist, dass die Felder aber hohe Frequenzen aufweisen.
tung einer blauschiebenden Resonanzwellenlänge bei gleichzeitiger Verlängerung der relevanten Hauptachse, sowie durch die Betrachtung des Einflusses sich ändernder Achsenverhältnisse auf die Resonanz, welche entlang einer konstant gehaltenen Hauptachse angeregt wird.

Nachdem die Grundlagen, welche die Wellenlänge der Resonanzen festlegen, analysiert wurden, kann die Abhängigkeit derselben von der Form und der Größe des NP im Detail diskutiert werden. Dazu wurden die Streuexperimente auf NPs mit elliptischen und rautenförmigen Querschnitten ausgeweitet. Es wird gezeigt, dass alle experimentellen Beobachtungen unter dem Einbezug von allgemeinen Depolarisationssensitiven und dynamischer Depolarisation qualitativ reproduziert werden können. Auf diese Weise entsteht ein detailliertes Bild der Abhängigkeit der Resonanzwellenlängen von der Form und Größe des NP.


1. General introduction

We start this thesis by giving a short introduction to Localized Surface Plasmon Resonances (LSPRs), Metal-enhanced fluorescence (MEF) and to actual and potential applications of these two phenomena. Finally, the aims of the thesis are highlighted and its outline is presented.
Chapter 1. General introduction

1.1. Localized Surface Plasmon Resonance

This thesis concerns Localized Surface Plasmon Resonances (LSPR). In general, a resonance appears when a movable mass is excited by a time-dependent force, affected by a restoring force and damped by energy loss. The physical properties of a system showing these four elements (movable mass, excitation, restoring force, damping) are dominated by the characteristics of the resulting resonances. The most important characteristic values are resonance frequency, amplitude and width. Their absolute values depend on the four elements defining the resonance and they change in value if one of the four elements is changed.

A metallic nanoparticle (NP) embedded in a dielectric environment also shows these four elements. Here, the electrons in the conduction band of the metal are the movable masses and an applied electromagnetic field acts as the excitation. The restoring force is initiated by the particle boundary which restricts the depletion of the electrons from their position in equilibrium. This leads to a non-uniform distribution of the electrons driven by the applied electric field and to a restoring force over Coulomb interaction. Damping is given by the scattering of the electrons on the atomic cores and by radiative damping. From this point of view, it is evident that both the restoring force and damping are influenced by the shape of the particle and the surrounding dielectric material. Additionally, damping depends on the metal the NP is made of. This means that shape, surrounding material and metal influence position, amplitude and width of the possible resonances.

As simple as the basic idea of LSPR is, its mathematical description is very lengthy. The optical properties of metallic NPs are described by Maxwell equations and the resulting wave equations [1]

\[
\nabla \times (\nabla \times E_i) = \omega^2 \epsilon_i E_i \tag{1.1}
\]

\[
\nabla \times (\nabla \times H_i) = \omega^2 \epsilon_i H_i \tag{1.2}
\]

in combination with the corresponding boundary conditions

\[
[E_m(x) - E_p(x)] \times \hat{n} = 0 \tag{1.3}
\]

\[
[H_m(x) - H_p(x)] \times \hat{n} = 0. \tag{1.4}
\]

\(i = p, m\) indicates the particle and the surrounding medium, respectively. \(\epsilon_i\) is the dielectric function of the material, i.e. \(\epsilon_p = \epsilon_1(\lambda) + i \epsilon_2(\lambda)\)
for the particle and $\epsilon_m$ for the surrounding medium. The permeability $\mu$ is assumed to be 1 in both materials. $\hat{n}$ is the outward directed normal to the surface of the particle.

Unfortunately, there is no analytical solution to the problem given by eqn. 1.1-1.4 for an arbitrary particle shape. The only relevant shape that leads to an analytical solution is that of a sphere using Mie theory [1]-[3]. By restricting the discussion to spheres much smaller than the wavelength of the excitation field, i.e. particle diameter $d \ll \lambda_{ex}$, and ignoring the harmonic time dependence of the fields in a first step, the mathematical description can be simplified. This enables an idea of the phenomena appearing due to the excitation of LSPRs. Within these restrictions, the problem is described by the Laplace equation\footnote{The following description is taken from [1] and [4].}

$$\nabla^2 \Phi_i = 0$$

(1.5)

for the potential describing the electric field

$$E_i = -\nabla \Phi_i.$$  

(1.6)

Eqn. 1.6 can be solved using the azimuthal symmetry of the problem. The solution shows that a dipole moment is induced in the sphere by the applied field. This dipole moment can be set in relation to the polarizability of the small sphere,

$$\alpha = 4\pi a^3 \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m},$$

(1.7)

where $a$ is the radius of the sphere. The polarizability shows a resonance if $|\epsilon_p + 2\epsilon_m|$ is a minimum or - in the case of a negligible influence of $\epsilon_2$ - if the Fröhlich condition

$$\text{Re}[\epsilon_p] = -2\epsilon_m.$$  

(1.8)

is fulfilled. This means that the resonance is linked to a polarization state of the nanoparticle. The question if a resonance can be excited or not is therefore equivalent to the question if the excitation is able to generate the related polarization state or not.

Continuing with the electrostatic calculations on a sphere according to [4] shows that the resonance in polarizability leads to a resonant
enhancement of the field within, $E_{\text{in}}$, as well as outside, $E_{\text{out}}$, the sphere

$$E_{\text{in}} = \frac{3\epsilon_m}{\epsilon_p + 2\epsilon_m} E_0$$  \hspace{1cm} (1.9)$$

$$E_{\text{out}} = E_0 + \frac{3\hat{r}(\hat{r} \cdot \mathbf{p}) - \mathbf{p}}{4\pi\epsilon_0\epsilon_m} \frac{1}{r^3}.$$  \hspace{1cm} (1.10)$$

$E_0$ is the uniform excitation field, $\mathbf{p} = \epsilon_0 \epsilon_m \alpha E_0$ is the induced dipole moment, $\hat{r}$ is the unit vector in the direction of the point of interest and $r$ is the distance from this point to the center of the sphere.

Considering the harmonic time-dependence of the fields while keeping the assumption $d = 2a \ll \lambda_{\text{ex}}$, i.e. changing to the so-called quasi-static regime, allows the calculation of the scattering, absorption and extinction cross-section of the small sphere

$$C_{\text{sca}} = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right|^2$$  \hspace{1cm} (1.11)$$

$$C_{\text{abs}} = 4\pi k a^3 \text{Im} \left[ \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right]$$  \hspace{1cm} (1.12)$$

$$C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}$$  \hspace{1cm} (1.13)$$

with $k = 2\pi/\lambda$. Eqn. 1.11 shows that the resonance in polarizability goes hand in hand with a resonance in the cross-sections at the very same frequency. This means that it is possible to determine the resonance frequency from scattering experiments.

Dropping the assumption of a spherical particle makes the situation much more difficult. Only very few highly symmetric shapes, such as ellipsoids and cubes, can be treated under the quasi-static approximation [1][3][4]. For more complex shapes and particle sizes which do not allow discussion based on electrostatics, only a few approaches are available to describe the appearance and dependencies of the LSPR [5]-[7]. A large part of this thesis addresses precisely these two open points in the discussion of optical properties of metallic NP, i.e. the influence of particle shape and particle size. We do this without relying on numerical solutions of eqn. 1.1-1.4.
1.2. Metal-enhanced fluorescence

As for LSPR, the idea behind metal-enhanced fluorescence (MEF) is very intuitive: an emitter in close proximity to a metal changes its properties due to the modified electromagnetic environment. Whether this modification leads to enhanced or quenched fluorescence depends on the exact metal-emitter configuration. The influence of the metal on the emitter is on both the emission and excitation side.

On the emission side, the probability with which an excited fluorophore decays by emitting light can be described by its radiative, $\gamma^0_r$, and non-radiative, $\gamma^0_{nr}$, decay rate in free space and the resulting quantum efficiency

$$\eta^0 = \frac{\gamma^0_r}{\gamma^0_r + \gamma^0_{nr}}. \quad (1.14)$$

The transition of a metallic NP from an (optically) excited state to its equilibrium can be described accordingly. The energy of the excited state is stored in the non-uniform depletion of the conduction electrons. This energy dissipates radiatively over coupling to far-field radiation or non-radiatively by heating up the NP when the NP goes back to its ground state. This means that a metallic NP shows radiative and non-radiative decay channels with wavelength-dependent rates. An emitter in close proximity to the NP can couple to these decay channels. This modifies its quantum efficiency to

$$\eta = \frac{\gamma^0_r + \gamma_r}{\gamma^0_r + \gamma_r + \gamma^0_{nr} + \gamma_{nr}}. \quad (1.15)$$

Eqns. 1.11 and 1.12 indicate that $\eta^0$ is modified most if the emitter couples to the NP at resonance. Therefore, there is a link between metal-enhanced fluorescence (or damping) and LSPRs.

On the excitation side, the presence of a metallic NP changes the applied electric field at the position of the emitter in terms of the field intensity and orientation of the electric field vector. Eqn. 1.10 indicates that the modification of emitter excitation is highest when the wavelength of the excitation, $\lambda_{ex}$, matches the resonance wavelength of the particle, $\lambda_{res}$. Therefore, the link between MEF and LSPRs also holds for the excitation side.

The influence on the excitation of the emitter can be described best by a change in the emitter’s absorption cross-section, $\sigma_{abs}(\lambda_{ex})$ [8]. It
Chapter 1. General introduction

results in a total fluorescence yield for the metal-enhanced fluorescence of

\[
F(\lambda_{\text{ex}}, \lambda_{\text{em}}) = \frac{\lambda_{\text{ex}} I(\lambda_{\text{ex}})}{hc} \sigma_{\text{abs}}(\lambda_{\text{ex}}) \eta(\lambda_{\text{em}}).
\]  

(1.16)

\(\lambda_{\text{em}}\) is the emission wavelength of the emitter, \(\lambda_{\text{ex}}\) is the excitation wavelength and \(I(\lambda_{\text{ex}})\) is the excitation intensity. As mentioned, the absolute value of the fluorescence yield depends on different, linked parameters. The most important ones are \(\lambda_{\text{ex}}\) and \(\lambda_{\text{em}}\) relative to \(\lambda_{\text{Res}}\), the distance between emitter and NP, and the orientation and position of the emitter relative to the NP. Even only slightly different sets of parameters can lead to a completely different value for \(F\), e.g. over a changed coupling efficiency between emitter and NP or a changed weight of the different channels in the overall decay process [8]-[10]. We discuss these issues further at the end of this thesis, based on Si-QD emitters in the gap between two stacked Au disks.

1.3. Application potential

The application potential of LSPRs is based mainly on four effects:

1. The sensitivity of LSPRs on changes at the metal-dielectric boundary.

2. The appearance of significant field enhancement in the near-field of nanoparticles excited at resonance.

3. The influence of the resonance on the extinction cross-section of the NP.

4. The tuning of electric and magnetic properties using structures clearly below the resonant wavelengths.

The first effect is that used in most commercially available applications of surface plasmons. As indicated, the position of the resonance also depends on the dielectric constant of the surrounding medium. This makes metallic NPs and thin metal films promising candidates for sensors measuring changes in refractive indexes. Via proper surface activation, the sensor can be made sensitive to specific materials [11]-[18]. Where the highest sensitivity in combination with information about the detected molecules is needed, Surface Enhanced Raman Scattering
1.3. Application potential

(SERS) has proven its potential. Here, the high field enhancement of both excitation and emission fields near the metallic nanoparticles in combination with a metal-induced increase in the Raman cross-section is used to enhance the Raman signal of a molecule [19]-[26]. Enhancement factors up to $10^{14}$ seem possible.

The potential of metallic NPs for efficiency enhancement in solar cells has recently been studied [27]-[31]. Here, it is mainly the high scattering cross-section of NPs close to their tunable plasmon resonance that is used to enhance the light confinement within the absorber.

Another very interesting field of applications is based on the fact that an electromagnetic wave resonant to the LSPR of an ensemble of nanostructures is not able to resolve the individual nanoparticles but "feels" their presence in terms of changed permittivity $\epsilon$ and permeability $\mu$. By proper tuning of different resonances, artificial materials with negative $\epsilon$ and/or negative $\mu$ can be designed. These so-called metamaterials are currently under extensive study [32]-[40]. Their possible applications are in novel optical devices, such as perfect lenses and optical cloaks, or devices with unique magnetic properties [32][41]-[44].

Thanks to the very local character of most effects related to LSPRs and the subwavelength size of the nanostructures causing these effects, a potentially huge field of application is the miniaturization of existing devices. Straight-forward is the creation of nano-optical elements [45]-[49], which might lead (or at least contribute) to the development of novel miniaturized circuits [50]-[53]. In the same direction goes the realization of nanoemitters and nanoantennas [54]-[57] where an emitter (e.g. a fluorescent molecule or a quantum dot) couples with a metallic nanostructure with a designed radiation pattern and profits from the beneficial influence of the nearby metallic structures in terms of metal-enhanced fluorescence.

A completely different but not less interesting future application is based on the dominant absorption cross-section for small metallic nanoparticles. The related temperature increase of the nanoparticle is used in combination with surface activation as a novel approach for thermal cancer therapy. Thanks to the surface activation, the metallic nanoparticles accumulate around cancer cells. Subsequent radiation with the wavelength to which the particle absorption was tuned heats up the regions with high concentration of metallic NPs. This leads to the destruction of nearby harmful cells [58]-[61].
This overview of realized and possible applications of LSPRs is far from complete. However, we want to point out some fundamental issues that must be overcome before plasmon-based effects can unfold their potential in commercial products. Looking at the costs of such products, the price will be high due to required features in the nm-range which hinder the use of state-of-the-art parallel production processes. Another critical issue is the time stability and reproducibility of the needed nanostructures. Diffusion processes have a measurable effect on the LSPR. Additionally, grains and surface roughness may increase the variation in performance of identically manufactured devices.

Another aspect that must be kept in mind is the not negligible damping of electromagnetic fields coupled to metals, especially when it comes to applications involving propagation and guiding of fields. The dissipative character of surface plasmons will also influence performance. In combination, this might create the need for signal amplification after short distances.

As an overview of possible applications this list is not complete. Time will show which issues can be overcome with acceptable allocation of resources, and which products will make the break-through.

1.4. Aims of the thesis and outline

The first aim of this PhD project was to improve the understanding of the dipolar optical response of metallic nanoparticles in the dynamic scaling and visible wavelength range. This has been approached by the analysis of NPs which are differently shaped in terms of the geometry of the particle footprint, varying the lengths of the principal axes and varying the aspect ratios. An intuitive model was developed in order to extract information on the parameters determining the dipolar optical response from experimental data and to explain the observations in detail. In a second section, a coupled system consisting of two stacked gold nanodisks was studied using both numerical simulation and experiment. These studies aimed to the realization of an efficient nanoemitter realized by the incorporation of silicon quantum dots in the gap between the two nanodisks. Different aspects of the emitter-nanoantenna interaction were addressed using the example of this nanoemitter design.

The thesis starts with the established experimental procedures in
chapter 2. First, the measurement setup realized to generate the needed experimental data is introduced. The setup is able to excite single NPs with a 3D tunable electric field vector of high directional accuracy, and to achieve exact positioning of the NP within the excitation spot. Additional functionalities for the analysis of nanoemitters are introduced in section 2.2. In section 2.3, the production processes for nanoparticle and nanoemitter fabrication as well as the established sample layouts are shown.

The operational reliability of 3D tunable excitation of single NPs is verified at the beginning of the first experimental chapter (chapter 3) by showing axis-selective excitation of different dipolar resonances of a single metallic nanocylinder with an elliptical footprint. The validity of a superposition principle for the overall optical response of a nanocylinder and quasi-static scaling of the different resonances are shown and discussed next, in sections 3.2 and 3.4.

In chapter 4 an intuitive model for the size and shape dependence of the resonance wavelength of the different dipolar modes is established. It generates a resonance condition given by depolarization factors, particle concavity and retardation. These parameters are discussed further in chapter 5 based on experimental data. First, a numerical value describing the concavity of the studied particle shapes is determined in section 5.2. Second, the dependence of the retardation term on the depolarization factor and length of the relevant principal axis is shown (section 5.3). Chapter 5 closes with a description of the contribution of dynamic (retardation) and quasi-static (depolarization factor) depolarization to the position of the plasmon resonance (section 5.4).

Based on the knowledge set out in the previous sections, the overall scaling of the dipolar resonances in metallic NPs with different configurations of principal axis lengths and geometry of the particle footprint is discussed in detail (chapter 6). This chapter brings us full circle with regard to the experimental results discussed in chapter 3 by showing and explaining the limited validity of the observed exclusive, quasi-linear scaling.

While chapters 3-6 discuss the basic properties of non-coupled, non-activated metallic nanoantennas, we turn in chapter 7 to the realization of a nanoemitter consisting of two stacked Au disks with Si-QDs incorporated in the gap between the disks. First, the relevant antenna resonances and their dependencies on antenna design parameters are
discussed based on numerical simulations without Si-QDs (section 7.2). Antennas with promising mode configurations are then realized with and without Si-QDs and their optical properties are studied experimentally (section 7.3). A performing nanoemitter could not be established yet, but the resulting understanding of the system leads to clear suggestions for further improvements 7.4.
2. Experimental procedure

This chapter is the basis for all experimental results shown in the following. It describes in detail the measurement setup that was built and its various functionalities. It also contains a description of the production processes used and the sample layouts for the nanoparticles and nanoantennas studied in the following chapters.


2.1. Introduction

Correlating plasmon resonances of single metallic nanoparticles with particle shapes needs sophisticated measurement methods and analysis routines. Nowadays, dark-field optical microscopy and spectroscopy (DFOMS) correlated with electron microscopy imaging is the technique of choice to isolate the resonance dependencies on size [62]-[65], shape [64]-[68] or substrate [69]-[71] and to deduce, verify or calibrate design rules [6][7][62][64][72]. The use of a dark-field technique is mandatory due to the low scattering cross-section of NPs with dipolar resonances in the visible wavelength range, i.e. NPs in the size range of some tens to a few hundred nanometers. However, the application of DFOMS on arbitrarily shaped nanoparticles to excite and control LSPRs contains a critical point: it leads to a poor definition of the excitation in terms of electric field vector and propagation direction. This prevents a particle excitation along a specific axes and makes it difficult to separate the different resonances. In addition, the definition of the relevant axes and in consequence of their lengths gets difficult in NPs of more complex shapes. Without proper definition of the characteristic lengths and clear identification of the modes dominating the spectra, the direct comparison of different NPs and extracted characteristic values may be misleading. In this chapter, we report a measurement setup that was build up from scratch. It is able to cover different aspects of the optical properties of single metallic NPs based on the detection of far-field signals. The heart of the setup is a modification of DFOMS which is able to excite a single nanoparticle along any direction with high accuracy. The method uses the concept of objective-type total internal reflection fluorescence microscopy in such a flexible way that it also allows an easy exchange of the light sources. This makes it possible to determine the scattering spectra based on axis-selective excitation in a first step and to study the influence of plasmon resonances on the photo-luminescence and Raman activity of nearby molecules and quantum dots by the use of axis-selective, monochromatic excitation in a second step. We also propose and integrate a tool that is able to give information about the radiation pattern of axis-selectively excited NPs and nanoantennas.

Metallic NPs are routinely produced either by chemical synthesis or by electron-beam lithography. Here, we used e-beam lithography and Physical Vapor Deposition (PVD) for the production of
the studied NPs and nanoantennas. For completeness, the established production processes are summarized in this chapter. The used sample layouts for the later study of the shape dependence of the dipolar resonances and for the discussion of nanoantennas consisting of two stacked disks with and without incorporated Si-QDs are also shown.

2.2. Measurement setup realization

2.2.1. Overview and main elements

For the optical characterization of single nanoparticles and nanoantennas in the visible wavelength range a measurement setup was realized (Fig. 2.1). The main elements are:

1. An inverted microscope (Zeiss Axio Observer) equipped with objectives covering an NA-range between 0.25 and 1.46. Two of them are DF-objectives (EC Epiplan Neofluar 50×/0.8 and EC Epiplan Apochromat 100×/0.95); one is an oil-based objective (α Plan- Apochromat 100×/1.46).


3. A sample holder equipped with a 3-axes piezo driver (Thorlabs) for exact positioning of the NPs.

4. Two external broadband light sources: a super-continuum white light source (SuperK Power, NKT Photonics) and a mercury lamp.

5. A He-Ne laser (Thorlabs) and a 405 nm diode laser (PhoxX 405-120, Omicron).

By using standard optical elements (Thorlabs) and an additional camera (C-Cam BCi5-U-40, Lot-Oriel) the following functionalities are realized:

1. Standard dark-field optical microscopy and spectroscopy (DFOMS) in reflection mode of single nanoparticles (section 2.2.2).
Chapter 2. Experimental procedure

Figure 2.1.: Established measurement setup for the optical characterization of single NPs and nanoantennas. The main functionalities are: determination of scattering cross-section of single NPs using 3D tunable excitation; luminescence measurements with 3D tunable and focussed beam excitation; Raman measurements and estimation of radiation pattern.

2. 3D tunable excitation of individual NPs\(^1\) by combining the concepts of DFOMS and objective-type total internal reflection fluorescence microscopy [73][74] (section 2.2.3).

3. Luminescence measurements using focused or axis-selective excitation (section 2.2.4).

4. Raman measurements at 632.8 nm excitation (section 2.2.5).

5. Direction-resolved emitted intensity (radiation pattern) within a cone up to \(\pm 74^\circ\) relative to the substrate’s normal (section 2.2.5).

The setup is optimized for a wavelength range of 550 – 950 nm. For nanoparticle excitation, the collimated and linear polarized emission of the needed external light source is coupled with the microscope using its rear port. Depending on the operation mode, the light is either focused on a well-defined position on the objective’s back focal plane (BFP)

\(^1\)Later, often called axis-selective excitation.
or on the sample, or standard Köhler illumination is used. The light scattered or emitted by the structure under consideration is collected by the same objective used for excitation, guided through the microscope side-port and imaged on the entrance slit of the spectrograph. By narrowing the entrance slit and defining a read-out region on the CCD-array using the spectrograph in imaging mode, the signal of a single NP is isolated [75]. The spectral decomposition of this signal is then analyzed by turning the spectrograph grating into a position where the optimal central wavelength of the measurement coincides with the middle column of the CCD.

The setup contains different conjugate planes: the CCD detector, entrance slit of the spectrograph, external camera in position one, sample and field blind position of the microscope build a first set of conjugate planes. The aperture blind position of the microscope, BFP, external DF-blind, external camera in position two, radiation pattern blinds and external camera in position three build a second set of conjugate planes. Camera position one and two aid proper positioning of the NPs and of the external DF-blind. They differ in the optical elements used rather than the exact position of the C-Cam in the beam path. Position three is used for radiation pattern measurements. A transparent semi-sphere with direction marks is positioned on top of the sample holder. This guarantees a well defined and reproducible propagation direction of the excitation. The sample is aligned by minimizing the defocus of a laser beam focused on the sample surface. The illumination intensity during PL measurements is estimated by the use of a power meter (PM30-S120UV, Thorlabs) for different laser emission intensities (diode laser) and/or filter configurations (He-Ne laser).

In the following, the different functionalities of the setup are discussed in detail.

2.2.2. Extinction cross-section of individual NPs

In order to determine the overall scattering cross-section of single NPs and arrays, standard DFOEMS in reflection is realized. The emission of the mercury lamp (or the extended and collimated emission of the SuperK) is linearly polarized, aligned with the microscope optical axis and coupled to the microscope rear port. For DF excitation and collection of the scattered light either the EC Epiplan Neofluar 50×/0.8NA objective or the EC Epiplan Apochromat 100×/0.95NA objective is
Chapter 2. Experimental procedure

used. The scattered light is guided through the side port of the objective and imaged on the entrance slit of the spectrograph. The eye pieces allows rough positioning of the structure under investigation. Exact positioning proceeds by using the spectrograph in imaging mode and the piezo-controlled stage. The signal of a single NP or any other investigated structure is isolated by narrowing the vertical entrance slit of the spectrograph and defining the CCD rows of interest. Good congruence between the isolated region in imaging mode and the analyzed region in spectroscopy mode was checked routinely. The recorded spectra are background corrected and divided by the reflection spectra of a silver mirror using exactly the same set-up configuration but in bright-field mode. Section 2.2.6 summarizes data acquisition and data handling in detail.

2.2.3. 3D tunable excitation

The most important functionality of the setup is its ability to tune the exciting electric field vector in 3D with high accuracy. This is used to excite single NPs in an axis-selective way, i.e. the electric field vector can be set parallel to any characteristic axis (e.g. principal axis) or in between such axes of an NP. This allows the study of the excitation dependencies and scaling behavior of the plasmon resonances observable in the addressed wavelength range.

Fig. 2.2a shows the concept of realization [73][74]. The emission of the supercontinuum white light source is focused on the objective BFP ($\alpha$ Plan- Apochromat 100×/1.46, oil-based) using the microscope rear port. The angle of incidence on the substrate-air interface can be set by proper positioning of the illumination spot on the BFP. This is done by laterally offsetting the illumination of the external light source from the optical axis of the microscope. Taking into account refraction at the substrate-air interface, a collimated beam with propagation direction tunable between $0^\circ$ and $90^\circ$ (TIR) relative to the sample normal can be realized. In combination with the use of appropriate polarization of the incident light, the electric field vector can be tuned in 3D. In order to excite the NP exclusively along one of the two principal axes parallel to the substrate (in-plane axes), linear-polarized light propagating perpendicular to the substrate can be used. To address the third principal axis (out-of-plane axis), the light propagation needs to be tuned to a direction parallel to the substrate. In this case, TM polarized light
2.2. Measurement setup realization

Figure 2.2.: 3D axis-selective excitation: concept of realization. (a) A light source is focused to an arbitrary point on the objective’s back focal plane (BFP). Moving this point to the edge of the BFP (1) increases the angle of incidence (2) and generates an electric field vector perpendicular to the substrate if an appropriate polarization is chosen (3). Excitation (grey) and collection of the scattered light (red) are done by the same objective. The directly reflected beam (light grey) is blocked by a blind in a plane conjugate to the objective’s BFP. (b) Schematic illustration of axis-selective excitation on the example of a cylinder with elliptical footprint. (c) Generation of a DF signal by positioning a blind in a plane conjugate to the BFP. Images of the BFP visualizing the directly reflected beam (top) and its blocking by a tunable blind (bottom) are shown.
Chapter 2. Experimental procedure

leads to an exclusive excitation along particle height while TE polarization excites along an in-plane axis (Fig. 2.2b). Thanks to the good collimation and precise control of the excitation, a small tunable blind in a plane conjugate to the objective BFP is enough to block out the directly reflected beam and to generate a DFOMS signal. Fig. 2.2c shows an image of the BFP using a $5 \times 5$ NP array (period 1.5 $\mu$m) as sample for better illumination of the whole BFP. The directly reflected beam (top) and its blocking by the small external blind (bottom) can be seen.

The effective illumination cone around a freely adjustable central value at the NP position can be estimated by imaging the BFP and measuring the illumination spot diameter (FWHM) in combination with the derivative of the objective transfer function that describes the relation between a position on BFP, $P_{\text{BFP}}$, and the angle of incidence at the substrate-air interface, $\alpha$,

$$P_{\text{BFP}} = \frac{329n}{2M} \sin \alpha.$$  

(2.1)

$M$ is the magnification of the objective and $n$ is the refractive index of the medium surrounding the objective (index-matching oil). The result is an opening angle better than $10^\circ$ for central angles of incidence as high as $80^\circ$ for the realized setup. A higher $\alpha$ leads to a fast widening of the illumination cone. An $\alpha$ slightly below the critical angle for total internal reflection, $\phi_c$, is also favorable for the excitation along the particle height due to the appearance of electric field components parallel to the substrate in the evanescent field for an angle of incidence higher than $\phi_c$ and TM polarization, [76].

Again, all spectra taken with this measurement method are background corrected and divided by the reflection spectra of a silver mirror using exactly the same set-up configuration but in bright-field mode (section 2.2.6).

2.2.4. Luminescence measurements

In order to study the influence of plasmon resonances on the luminescence of fluorophores close to metallic nanoparticles, two lasers are integrated in the setup. One emits at 632.8 nm and one at 405 nm. Their beam paths are accord with the concept used for 3D tunable excitation. This allows both axis-selective excitation and excitation by
a beam focused on the sample surface. The latter is realized by an additional lens in front of the microscope rear port. In both configurations, the beam spot is kept at a fixed position on the sample plane which coincides with the center axis of the entrance slit of the spectrograph and the middle of the CCD simultaneously. Proper positioning of the NP-fluorophore hybrid is realized by imaging the sample plane on a camera integrated in the beam path using switchable lenses and mirrors. Fig. 2.3 shows the proper positioning of an NP in the spot of an excitation focused on the sample using the piezo-controlled stage. The directly reflected beam is filtered out by a notch filter (Lot-Oriel, 623.8 nm excitation) or an etch filter (Thorlabs FGL550, 405 nm excitation). The excitation intensity, $I_{\text{ex}}$, is tuned by a filter wheel and additional filters (NE2.0, NE3.0) in the case of the He-Ne laser emitting with a power of 35 mW, and by adjusting the emitted power and additional filters (NE2.0, NE3.0) in the case of the 405 nm diode laser. $I_{\text{ex}}$ is determined for the various setup and filter configurations by measuring the power at the sample position and dividing it by the illuminated area (FWHM) estimated from the intensity distribution on the CCD detector. The wavelength dependence of the optical elements passed by the luminescence is considered by multiplying the taken PL spectra with the corresponding quantum efficiency, section 2.2.6.

Section 2.2.3 and 2.2.4 show that the setup allows the determination of the scattering cross-section of a metallic nanostructure, directly followed by the measurement of metal-enhanced luminescence, by

**Figure 2.3.:** Excitation of a nanoantenna by a beam focused on the sample surface. The yellow arrows indicate the position of four NPs. The red arrow indicates the position of the beam spot. (a) Beam spot next to a NP. (b) After moving the NP into the excitation spot.
switching from one beam path (light source) to another. Nevertheless, determining the resonance wavelengths of all structures on a sample in a first step, and studying the luminescence properties in a second, have proved more feasible.

2.2.5. Further functionalities

Raman measurements

The step from the setup used for luminescence measurements (section 2.2.4), to a setup able to take Raman spectra is a small one. A monochromatic excitation focused on the sample and precise positioning of the region of interest by the use of cameras and piezo transducers has already been implemented. The setup is designed for maximum efficiency in the visible wavelength range, and is equipped with a spectrograph and a sensitive CCD-detector and shielded against stray light. The integrated He-Ne laser emits with 35 mW, providing enough power on the sample to generate intense Raman signals. The only element that needs to be changed is the grating used in the spectrograph. With the 1200 g/mm instead of the 100 g/mm grating a resolution of 1.8 cm\(^{-1}\) can be achieved at 633 nm excitation and an entrance slit of 20 µm. With the 600 g/mm grating the resolution is around 4 cm\(^{-1}\).

The operational reliability of the established setup for Raman measurements was verified in the context of a student project which addressed the simulated body fluid assisted formation of oxides in Fe-Mn-Pd alloys [77]. The wavelength-dependent efficiency of the optical elements passed by the Raman signal is considered as described in section 2.2.6.

Radiation pattern

Thanks to the use of a high NA objective (α Plan-Apochromat 100× /1.46) and the realization of planes that are conjugate to the objective’s BFP in the beam path freely propagating between microscope side-port and entrance of the spectrograph, it is possible to gather information about the radiation pattern of the generated luminescence. The angular region that can be addressed is given by the used objective. In our case, radiation emitted up to ±74° relative to the optical axis can be recorded. Two different concepts were developed. The first one is based on putting concentric slits with well-defined but varying inner
2.2. Measurement setup realization

and outer radius \((r_i, r_o)\) in a plane conjugate to the BFP. Combining imaging and magnification of the BFP helps to produce appropriate blinds at the expense of accuracy. The light transmitted through a concentric slit represents luminescence emitted into a certain angular range. Its wavelength-dependent intensity can be analyzed using the spectrograph. The total intensity emitted into a unit angular region compared to another one can be calculated by integration and proper scaling.

The second method is based on direct imaging of the intensity distribution on the BFP using a CCD camera in a conjugate plane. A Matlab routine transforms this intensity distribution to an angular radiation pattern. The routine showed its functionality on real data of a \(5 \times 5\) NP array and on a calculated test pattern. Using this method, a resolution of \(<1.25^\circ\) (\(\sim 0.35^\circ\) in the center) is expected.

At the moment, both methods lack true testing. How they perform on individual NPs (autoluminescence) or metal-fluorophore hybrids is still open. The few publications using similar approaches are very promising [54][78]. Besides the study of mode-dependent radiation pattern, such measurements would help to decouple setup-related changes in PL intensity from true metal-mediated enhancement. This is an important point, comparing the directivity of a dipole [79], of a dipole coupled to an antenna [80][81], and the low enhancement factors observed so far [55][82].

Refractive index sensor testing

A sophisticated and flexible setup as described in the previous sections can easily be adapted to further specific measurement demands. Based on a request by the Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, high aspect-ratio structures were tested according to their sensitivity on a changing refractive index [13]. Thanks to the easy switching between measurement positions, the influence of design parameters which vary over a sample can be analyzed in a straightforward way. The only additional element needed is a small bath for liquids on the sample holder. The measurements are done in bright-field reflection mode using the mercury lamp and a \(10\times/0.25\) objective (Achromplan, Zeiss). The data taken are divided by the reflection spectra of a silver mirror using exactly the same setup configuration (section 2.2.6).
2.2.6. Data acquisition and data handling

**Broad band excitation**

In measurement configurations using broad band excitation (i.e. SuperK or mercury lamp) and operating in reflection mode, all spectra are taken relative to a silver mirror, i.e. the silver mirror measurement is taken as a flat. The silver mirror is measured with exactly the same measurement configuration except in bright-field instead of dark-field mode. The much higher intensity of the signal generated in this way needs to be compensated by a narrowed entrance slit, a reduced number of considered CCD rows and a shortened integration time. The chosen parameters aim at an intensity reaching around 90% of the CCD saturation intensity.

For sample measurements, the entrance slit and the number of rows are determined in a way that a change in sample position on the order of 0.15 µm does not affect the spectra taken. The integration time is optimized for the detected signal intensity. Again, we aimed for a maximal intensity of 90% of the CCD saturation intensity.

From both silver mirror measurement and sample measurement the background signal is subtracted before division. In order to improve the meaning of the measured intensity, the generated output data (sample measurement divided by mirror measurement) is multiplied by the product of slit width, number of read-out rows and integration time during the mirror measurement and divided by the same product of figures used during the sample measurement. In consequence, an intensity given in the scattering spectra corresponds to the average recorded intensity per unit width of the entrance slit, per pixel row and per unit integration time relative to the average recorded intensity of a silver mirror over the same unit width, pixel row and unit integration time. However, this approach fails to account properly for changes in slit width and number of pixel rows due to the position-dependent signal intensity. Therefore, intensities are given in arbitrary units, although comparison of measured intensities using the same slit width and number of pixel rows (i.e. during a cycle of identical measurements on different single nanoparticles) is allowed.

Silver mirror measurements are taken after 15 min light-source burn-in and directly before the first sample measurement. For each setup

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2 0.15 µm on the sample corresponds to one pixel on the CCD if an objective with 100× magnification is used.
configuration (including e.g. changes in polarization or angle of incidence) used during the sample measurements, a mirror measurement is taken. In order to check for instabilities in lamp emission and changing experimental conditions, the initial mirror measurement is repeated for at least one setup configuration at the end of a measurement cycle. A maximum change in intensity of 10% has been observed over all measurement cycles.

The acquired spectra are then fitted with up to three Lorentzian curves using resonance frequency, linewidth, and amplitude as fitting parameters without further manipulation of the original data. The spectra shown in the figures are routinely flattened by applying a floating average over 4 nm (11 measurement points).

**Monochromatic excitation**

All measurements based on an excitation with the He-Ne laser or the 405 nm diode laser are corrected by the wavelength-dependent quantum efficiency of the sum of all setup elements following the place of laser induced signal generation. The corresponding flat file is generated based on a routine of the spectrograph user interface (WinSpec, Princeton Instruments). An Osram 12 W/100 V halogen lamp operated at 10.6 V is used to approximate black body radiation at 3200 K. The calculated Planck spectrum is normalized to the maximum intensity of the measured reference spectra. The correction file (flat file) corresponds to the normalized Planck spectrum divided by the reference measurement. Burn-in of the halogen lamp of 15 min is performed before generating the correction file.

A background spectra which depends on the concrete experimental situation is subtracted before flat correction. PL measurements on Si-QD films are corrected by the signal observed on bare substrate. By doing so, the apparent dark current of the CCD and other offsets not considered by standard background correction are also eliminated. Autoluminescence measurements on nanoparticles are corrected in the same way. In the case of antenna-fluorophore hybrids, uncorrected spectra of the hybrid, of the antenna without fluorophores, of the bare substrate, of the CCD background and, if available, of the corresponding fluorophore film are taken. Quantum efficiency correction and separation of the different signals are undertaken in an additional step after the measurements. Finally, Raman measurements are CCD
background and quantum efficiency corrected, only.

As in the case of broad band excitation, the region of interest (slit width, number of rows) and integration time are chosen to allow a small drift in sample position on the order of 0.15 µm and to generate a maximum signal of 90% of the CCD saturation intensity.

So-called frame measurements are performed if the time dependence of a signal is of interest. An arbitrary number of consecutive measurements are taken automatically without interruption and without changing any parameters. The read-out time between two measurements is 90 ms. This is taken into account during data evaluation. In frame measurements aiming to give a general trend in time-dependent intensity, the taken spectra are flattened by the use of a floating average over 4 nm (11 measurement points) followed by screening for the measurement point showing maximum intensity. If more (e.g. FWHM) or more exact values are needed, the spectra are fitted with up to six characteristic curves (Lorentzian or Gaussian).

2.3. Sample fabrication

2.3.1. Basic production process

Fig. 2.4 shows SEM images of representative examples of the produced nanostructures. In Fig. 2.4a, arrays of NPs with different footprints are shown. Fig. 2.4b gives a more detailed view on two single nanoparticles and a nanoantenna. Standard cover slips (Menzel Nr. 1, 18 × 18 mm) are used as substrate for their production. The substrates are cleaned for 5 min at 40 kHz ultrasonic in an acetone and isopropanol bath, respectively, rinsed with DI water and N2 dried. In order to obtain better resolution during e-beam exposure, an 8 nm thick ITO layer is evaporated on the substrate using Physical Vapor Deposition (PVD). After deposition, the ITO layer is annealed for 30 min at 360°C followed by another acetone/isopropanol cleaning step. For some experiments, a thermally evaporated Au layer on top of the photoresist is used instead of the ITO layer below (see appendix). PMMA 950K diluted in ethyl-lactat (1:1 for low particle height, 2:1 for higher NPs and complete antennas) is used as photoresist. Its thickness is adjusted according to the target height of the nanoparticle by using spin speeds between 1500 and 6000 rpm. Before and after spinning, the sample is baked for 10 min at 180°C. Finally, the thickness of the photoresist layer is de-
2.3. Sample fabrication

Figure 2.4.: Representative examples of studied nanostructures. (a) $5 \times 5$ arrays of NPs with elliptical, rectangular and diamond-like footprints. The height of the shown particles is $h = 20$ nm. (b) SEM pictures of two nanocylinders and a nanoantenna. The white scale bars are 100 nm in length.

determined by the use of a profilometer (Dektak XT Advanced, Bruker).

The footprints of the NPs is written in the resist using a Raith 150 system operating at an acceleration voltage of 30 keV. Details concerning the sample layout can be found in section 2.3.2. Development proceeds by immersing the sample after exposure for 45 s in MIBK:IPA = 1:3 followed by 45 s in isopropanol. The sample is then rinsed in DI-water and dried in $N_2$. With the development time used, a significant undercut of the PMMA used for easier lift-off after NP growth is guaranteed.

After visual inspection of the produced structures and markers using an optical microscope (Nikon Eclipse L200), the nanoparticles are grown within the patterned photoresist using PVD. The gold NPs are grown on top of a 2 nm Ti adhesion layer$^3$ at a rate of 2.5 A/s. During evaporation, the pressure in the vacuum chamber was better than $5 \times 10^{-6}$ mbar. In order to hit the target particle height, calibration runs are performed before sample growth. After growth, the height of the NPs is verified by measuring the Au film thickness using the profilometer. Finally, the remaining PMMA is removed with acetone. Nanoparticles and markers become clearly visible after 3 – 5 min in

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$^3$For some experiments, the NPs are produced without an adhesion layer. The result is a lost of around 15% of the NPs during lift-off.
acetone. The time needed for complete lift-off varies between 30 min and a few hours depending on PMMA and Au thickness, sample layout, and storing time after PVD. In order to avoid NP release, no ultrasonic is applied.

The evaporation process is slightly different for nanoantenna production (two stacked nanoparticles). In the case of an empty nanoantenna, a $SiO_2$ spacer layer is deposited on top of the bottom Au particle after deposition of a 1 nm thick Ti layer. A rate of 2.5 A/s at a base pressure of $5 \times 10^{-6}$ mbar is used. Finally, the top Au particle is deposited on another 1 nm Ti layer. This nanoantenna heterostructure is produced within a single evaporation run. Again, the total height of the antennas is cross-checked by measuring the total thickness of all evaporated films using the profilometer.

In the case of a nanoantenna activated by Si-QDs, the evaporation is interrupted after deposition of the bottom Au particle, a 1 nm Ti adhesion layer, and a 5 nm $SiO_2$ spacer layer. The Si-QDs were then deposited on the substrate at the Institute of Solid State Physics at the Friedrich-Schiller-Universität (FSU) in Jena (Germany) [83][84] (see also Appendix A). In a second in-house evaporation run, the spacer to the top particle of the antenna (5 nm $SiO_2$), an adhesion layer (1 nm Ti), and the top particle itself are evaporated by PVD.

Finally, the produced structures are inspected and the length of the principal axes are determined using a Scanning Electron Microscope (Hitachi SU-70). With low magnification of around 10k and low acceleration voltage of 2 keV the produced structures are checked for defects, missing NPs, and residuals of the production process. The length of the principal axes of the NPs are then determined by analyzing up to ten individual NPs (depending on particle size and accuracy in size determination) for each set of particle design parameters. Magnifications between 150k and 500k at 2 keV and a working distance of 2 mm are used. The average over these measurements is assumed to represent the length of the principal axes of all particles with identical design parameters on the specific sample. As will be shown in the following section, $4 \times 6$ arrays of $5 \times 5$ NPs are produced for each set of design parameters. Length measurements are carried out in an array next to that used for optical characterization in order to avoid e-beam induced changes in NP morphology.

The SEM used is equipped with a stage that can be tilted up to 70°.
2.3. Sample fabrication

This functionality is used to cross-check the particle height using

\[ h_{\text{eff}} = \frac{h}{\sin(\alpha + \beta)}. \]  

(2.2)

\( h \) is the height measured on the screen using the SEM with a stage tilted to \( \alpha \) degrees. The particle diminution of \( \beta = 12^\circ \) is taken into account in determining the effective particle height, \( h_{\text{eff}} \).

2.3.2. Sample layout

The basic element of all layouts used to study the scaling behavior and metal-enhanced luminescence is an assembly containing \( 4 \times 6 \) arrays of \( 5 \times 5 \) NPs (Fig. 2.5a). SEM images of the \( 5 \times 5 \) arrays have been shown in Fig. 2.4a. The period within an array is 1.5 \( \mu \)m in both directions, which allows good signal separation and prevents the appearance of NP coupling effects. The distance between two arrays is 4 \( \mu \)m. Within a basic element, the design parameters of the nanoparticles are unchanged, i.e. for each designed NP footprint, there are 24 arrays or 600 NPs of identical shape. Such elements are arranged in a systematic way over the sample.

Layout for the study of scaling behavior

On the samples used to study the dependence of the plasmon resonance position on the length of the principal axes, the aspect ratio of the two in-plane axes changes in a horizontal direction by (design-) steps of 0.25. In a vertical direction, one of the two in-plane axes changes in steps of 10 nm. In other words, the basic elements are arranged as a grid on the sample. Within a row one of the two in-plane axes is kept constant while the other in-plane axis changes according to the designed aspect ratio. In the following, the axis constant within a row is called the \( b \)-axis and the varying axis is called the \( a \)-axis. From one row to the next, \( b \) changes by 10 nm.

In the concrete realization, all basic elements belonging to the same aspect ratio (i.e. a column of the grid, Fig. 2.5b) are written one after the other before moving to the position of the next column. Two consecutive columns are separated by \( \sim 1 \) mm while the basic elements within a column are separated by 14 \( \mu \)m.\(^4\) For easier identification of

\(^4\)In fact, the given distances are approximate values only. The reason for this
Figure 2.5.: Image of a basic assembly of 4×6 arrays of 5×5 NPs (a) and schemes of their arrangement in units of constant aspect ratio with one in-plane axis varying in steps of 10 nm (b). (c) shows the layout used for studying the overall scaling behavior of dipolar plasmon resonances in dependence of axis configuration and footprint. The aspect ratio between the two in-plane axes increases in steps from 1.0 to 3.0. The footprints of the NPs are Elliptical, Rectangular and Diamond-like. (d) is the corresponding layout for the discussion of nanoantennas with and without incorporated Si-QDs.

a specific set of design parameters on the sample, a marker indicating the designed length of the b-axis is added next to each basic element (Fig. 2.5a,b). Additionally, markers with the designed aspect ratio are written above each column (Fig. 2.5c).

On samples used to study the influence of elliptical, rectangular and diamond-like footprints on plasmon resonance position, basic elements with the corresponding footprint but an identical set of design parameters are written next to each other at the same grid position (Fig. 2.5c). The distance between the last array of one footprint and the

is that the separation of two reference points (e.g. the origin of the writing fields or the origin of the arrays) are separated by round numbers. However, the deviations from the given values are too small by far to have an influence on the measurements.
marker of the neighboring one is on the order of 15 µm.

**Nanoantenna**

The layout used for nanoantenna samples (Fig. 2.5d) is based on exactly the same basic elements of 4×6 arrays of 5×5 NPs. In this case, only columns with $a/b = 1$ are produced. To facilitate finer tuning of the in-plane axes lengths, three basic elements with different dose factors but an otherwise identical set of parameters are written next to each other at the same grid position. This construct is arranged in steps of 2 mm in horizontal and vertical directions over the whole sample in order to compensate for position inaccuracy during the Si-QD deposition. In between, clear fields of $10 \times 10 \mu m^2$ are written.

A mask is used during PVD to make sure that the $10 \times 10 \mu m^2$ fields contain the Si-QDs only. The mask consists of seven 1 mm broad slits separated by 1 mm. By proper positioning, this allows antenna growth in the basic elements but not in the $10 \times 10 \mu m^2$ fields. This is essential for the calculation of enhancement factors. Finally, the sample design contains three $10 \times 10 \mu m^2$ fields that are written in a region not shielded by the mask during PVD. These fields are used to measure the total height of the heterostructure produced. Thanks to a Si-QD deposition restricted to a spot of $\sim 5$ mm in diameter, antennas and $10 \times 10$ fields with and without Si-QDs can be found on the sample.

The samples used for studying the influence of the separation (gap) of two stacked gold nanoparticles as well as tests aiming for the observation of metal-enhanced fluorescence on a monomer consist of the mentioned constructs of three different doses separated by 2 mm around the center of the sample only.
3. **Axis-selectivity, superposition principle and quasi-linear scaling**

This chapter addresses the basics of the optical properties of metallic NPs by discussing scattering experiments on nanocylinders with elliptical footprints. The observed excellent agreement with common models also proves the ability of the measurement setup presented in chapter 2 to excite a single nanoparticle along an arbitrary axis. This ability for 3D axis-selective excitation is then used to study the scaling of the observed resonances with the length of the principal axes.
3.1. Introduction

The basic process that defines the scattering spectrum of a metallic NP is well-known: the particle polarization established by the applied electric field. However, the possible polarization modes depend on the NP shape and their excitation efficiencies depend on the properties of the applied field. If more than one mode is excited, a superposition principle applies. These basics are well described in models such as the electrostatic eigenmode method [85][86] and the spectral representation formalism [87][88] and regularly discussed based on numerical simulations [89]-[93]. In contrast, they are seldom addressed properly by experiments and modes excited with an electric field component perpendicular to the substrate are routinely ignored [94]-[96]. In consequence, the potential of particle shaping along their height or of stacked structures stays unused. Other aspects, such as the dependence of the resonance wavelengths on the absolute and relative lengths of the principal axes, are subject of on-going discussion.

We start this chapter with an explicit separation of three different dipolar resonances of a nanocylinder with elliptical footprint by exciting it along the three principal axes. The existence of a superposition principle is then experimentally confirmed. These experiments also validate the established measurement setup. The individual excitation of the different dipolar resonances is then used to study their dependence on the axis configuration. We show that the dipolar resonances scale exclusively with their relevant principal axis in a linear way, as long as moderate (but not constant) aspect ratios and axis length far from the quasi-static limit are addressed.

The experiments are performed on cylinders with elliptical footprints defined by their principal axes \(a, b, h\). Their in-plane axis lengths are between 100 nm and 200 nm for the \(a\)-axis and between 90 nm and 140 nm for the \(b\)-axis. The realized aspect ratios cover a range between 1 and 1.6. The particle height is between 70 nm and 120 nm, leading to in- to out-of-plane aspect ratios of 1 to 3. The systematic variation of \(a, b, h\) (section 2.3.2) guarantees length configurations with separated dipolar resonances at moderate aspect ratios. The particle height is kept low to avoid cone-like particles resulting from the chosen production process, which leads to particle diminution. The cross-sectional area of the NPs is also kept small to suppress the appearance of possible additional dipolar resonances excited along the particle height.
3.2. Excitation dependence of the scattering spectra

3.2.1. Separation of the dipolar resonances

Fig. 3.1a shows the influence of a particle excitation tuned to the principal axes of a single nanocylinder on its scattering spectra. The cylinder is defined by the length of the principal axes, \((a, b, h) = (132, 95, 110)\) nm. Three different resonances can be identified and exclusively excited at \(\lambda_a = 704\) nm, \(\lambda_b = 632\) nm and \(\lambda_h = 652\) nm. Fig. 3.1b shows more resonances excited along the \(h\)-axis of single nanocylinders. The cylinders differ in height, \(h = 72, 95\) and \(115\) nm, but have comparable lengths of the other two principal axes. The lengths of the two in-plane axes are \((a, b) = (82, 87)\) nm for \(h = 72\) nm, \((81, 82)\) nm for \(h = 95\) nm, and \((77, 78)\) nm for a height of \(115\) nm. The observed resonances show only small signals from other resonances (in-plane resonances or additional out-of-plane resonances) and their positions scale with \(h\), proving a particle polarization along the height of the cylinders. This proofs the ability of the setup to excite single NPs axis-selectively and in 3D and it shows that - in contrast to standard DFOMS - a reduction of the number of excited resonances and a scattering spectrum dominated by a specific resonance can be established. Of course, a complete separation of a resonance from all other resonances is only possible if an excitation can be found (direction of electric field, wavelength range) that couples to exactly one mode.

3.2.2. Superposition principle

Fig. 3.1a shows that there are three dipolar resonances which are excitable by applying an electric field along the principal (i.e. symmetry) axes of the NP. This observation is a manifestation of the underlying superposition principle which is confirmed by experiment in Figs. 3.2 and 3.3. In Fig. 3.2 the direction of the electric field vector is
Figure 3.1.: (a) Experimental observation of three different plasmon resonances of a single nanocylinder with an elliptical footprint by exciting the particle along its principal axes \((a, b, h)\). Effective lengths: \(a = 132\) nm, \(b = 95\) nm, \(h = 110\) nm. (b) Resonances excited along the particle height \(h\) for three nanocylinders that differ in height while \((a, b)\) is of comparable size (see text).

changed in steps of 15° for a wave propagation parallel to the NP height. These measurements are performed on an array of \(5 \times 5\) NPs (period 1.5 \(\mu\)m) in order to reduce the influence of slightly changing measurement conditions during a set of measurements (sample drift, defocus etc.). Fig. 3.2a shows the resulting scattering spectra for a cylinder given by \((a, b, h) = (150, 98, 83)\) nm. Two distinct resonances are observed at 635 nm and 747 nm. There is no evidence of additional resonances in the studied wavelength range. Looking at the evolution of the amplitudes rather than the scattering spectra (Fig. 3.2b) proofs that the optical response is always the superposition of the two reson-
3.2. Excitation dependence of the scattering spectra

Figure 3.2.: (a) Evolution of the scattering spectra of a $5 \times 5$ array of nanocylinders (period $1.5 \, \mu m$) when changing the particle excitation from parallel to $a$-axis ($0^\circ$) to parallel to $b$-axis ($90^\circ$) and back to $a$-axis ($180^\circ$) in steps of $15^\circ$; particle dimension: $(a, b, h) = (150, 98, 83)$ nm. Each scattering spectrum is a superposition of the plasmon resonances observed with an excitation parallel to the $a$ and $b$-axis. (b) Amplitudes from fits using two Lorentzian curves. (c,d) Same as (a,b) but for an array of cuboids with $(a, b, h) = (181, 118, 110)$ nm. The absolute values shown in (b,d) cannot be set in relation due to differences in collection optics.

The observed amplitudes scale with $\sin^2$ and $\cos^2$ respectively, which indicates a weighting with the intensity of the exciting electric field along these axes [94]-[96]. Additionally, the maximum observable amplitude for the two resonances (i.e. electric field vector of the excitation along the two main axes) depends on the axis length.

Exactly the same behavior is observed for cuboids of height $h$ and principal axes $(a, b)$ of the rectangular footprint (Fig. 3.2c,d). The total axis lengths of the studied cuboid are $(a, b, h) = (181, 118, 110)$ nm, leading to in-plane dipole resonances at 669 nm and 795 nm. Again,
there is no evidence of additional resonances besides those excited along the principal axes. An excitation along the diagonals does not lead to additional resonances, either. As in the case of cylinders, the scattering spectrum is the superposition of the resonances excited along the principal axes weighted by the excitation intensity and the size-dependent scattering cross-section. The absolute values shown in Fig. 3.2 for cylinder and cuboid cannot be set in relation due to differences in collection optics.

As an additional feature, Fig. 3.2a,c illustrates so-called isosbestic points [97]. These are wavelengths which show a polarization-independent scattering cross-section.

In order to address possible out-of-plane resonances, the wave vector of the illumination is changed in steps from parallel to the particle height to perpendicular to it for fixed TM polarization. This leads to an electric field vector changing from parallel to an in-plane axis to parallel to \( h \)-axis. Fig. 3.3 shows the corresponding scattering spectra for a nanocylinder with \((a, b, h) = (112, 115, 72)\) nm. A resonance excited along the particle height of around 578 nm appears in addition to the in-plane resonance during this change in excitation direction. Again, the scattering spectra for an electric field vector between the two principal axes is the superposition of the resonances exclusively excited along these two axes.

\[ \begin{align*}
\text{(a)} & \\
\text{(b)} &
\end{align*} \]

**Figure 3.3.** (a) Evolution of the scattering spectra of a single nanocylinder when changing the particle excitation from a parallel to an in-plane axis (0°) to parallel to \( h \)-axis (90°). Particle dimensions: \((a, b, h) = (112, 115, 72)\) nm. The overall optical response is the superposition of the plasmon resonances excited along the principal axes. (b) Amplitudes from fits using two Lorentzian curves.
3.3. Scaling behavior

The scaling of the resonance wavelengths with the length of the principal axes is subject of ongoing discussion. We start the study of the dependence of the three observed resonances on the particle axis configuration by looking at the two in-plane resonances first. \((a, b, h)\) configurations with constant height \((h = 110 \text{ nm})\), three different \(b\)-values and variable \(a\)-axis reveal their scaling behavior with the length of the corresponding axis. For an excitation along the variable \(a\)-axis (Fig. 3.4a), the plasmon resonance scales linearly with axis length. The error bars indicate the standard deviation from the measurement of ten single nanoparticles.\(^1\) A slope on the order of 1.7 corresponding to \(-4.2 \text{ meV/nm}\) is observed. Plasmon resonances for similar \(a\)-values group around the same central wavelength independent of the \(b\)-axis length. Changing the excitation to parallel to \(b\)-axis (Fig. 3.4b) shows similar behavior. The plasmon resonances are independent of significant length changes in the \(a\)-axis, but scale with the length of the \(b\)-axis. The exclusive scaling of the in-plane resonances \(\lambda_a\) and \(\lambda_b\) with their corresponding axis remains true when looking at the influence of particle height on resonance wavelength (Fig. 3.4c). A significant change of particle height from 78 to 115 nm does not lead to a systematic shift of the in-plane plasmon resonances.

In the same way the two in-plane resonances do not depend on the length of the axes perpendicular to the one along which they are excited, the observed out-of-plane resonance is within a narrow wavelength range independent of significant changes in the in-plane axes \(a\) and \(b\) (Fig. 3.5a). Measurement points with constant \(b\)-value and variable \(a\)-values as well as constant \(a\)-value and variable \(b\)-values group around the same resonance wavelength. In consequence, the out-of-plane resonance is nearly independent of the cross-sectional area, at least in the range of \(0.008 \text{ to } 0.019 \mu\text{m}^2\). However, there is a small but observable tendency towards an increasing plasmon resonance position with decreasing cross-sectional area. Analyzing the scaling of \(\lambda_h\) with particle height for two different sets of \((a, b)\) values confirms the indication of limited validity of the linear and exclusive scaling regime (Fig. 3.5b). Linear scaling with a slope depending on the cross-sectional area, \(A = \frac{1}{4}ab\pi\), is observed. For \(A \approx 0.01 \mu\text{m}^2\) the slope is on the order of 1.1 \((-3.6 \text{ meV/nm})\) but it increases to 2.1 \((-6.5 \text{ meV/nm})\) for the

\(^1\)The error is smaller than the marker if no error bar is visible.
Figure 3.4.: Scaling behavior and dependence of the two in-plane resonances $\lambda_a$ and $\lambda_b$ on the principal axes of the nanocylinder. (a) Electric field vector of the excitation parallel to the variable $a$-axis; the position of the plasmon resonance scales linearly with the $a$-axis length. Particle height $h = 110$ nm. (b) Electric field vector parallel to the constant $b$-axis; changes in $a$-axis do not influence the plasmon resonance excited along the $b$-axis, $h = 110$ nm. (c) Influence of particle height on in-plane resonances; a significant change in height ($h = 78/110/115$ nm) does not lead to a systematic shift.
3.3. **Scaling behavior**

![Graph](image)

**Figure 3.5.** Scaling behavior and dependencies of the out-of-plane resonance $\lambda_h$ on the principal axes of the nanocylinder: *(a)* The plasmon resonance observed with an excitation along the $h$-axis is not influenced by length changes of the $a$ and $b$-axes over a wide range of considered $(a,b)$ values. Particle height $h = 110$ nm. *(b)* Electric field vector parallel to the $h$-axis. The position of the plasmon resonance scales linearly with the $h$-axis length. However, a small cross-sectional area generates an increase in the slope of $\lambda_h$.

In the case of $A \approx 0.0056 \, \mu m^2$. Unfortunately, the height determination of nanoparticles using an SEM with a tilted stage is not exact. Therefore, Fig. 3.5b should be seen as revealing only a trend for the dependence of the out-of-plane resonance on $h$.

In sum, Figs. 3.4 and 3.5 show that over a wide range of the considered length configurations the three dipole resonances of a nanocylinder with an elliptical footprint scale only with the axis along which they are excited, but are nearly independent of changes in the other two axes. To what extent this statement is restricted to certain $(a, b, h)$
3.4. Discussion

3.4.1. Dipolar resonances and superposition principle

The experimental observation of a dipolar resonance excited along each of the three principal axes of the studied NPs and the shown validity of a superposition principle is as expected from models. Good descriptions of this behavior are given by the electrostatic eigenmode method [85][86] and the spectral representation formalism [87][88]. The findings are also in full agreement to the routinely studied ellipsoids and rods [62][89][94][95][98][99]. In addition, different literature reports have addressed related topics such as the link between particle symmetry and number of dipolar resonances [1][3][4]. A good summary of this link is given by Sakurai et al. [100]. The fact that the demagnetization of bodies is discussed in [100] does not reduce the validity of the developed picture. It is shown that an individual excitation of three different resonances is possible for an orthorhombic system only. In the case of trigonal, tetragonal and hexagonal systems, two of these three resonances will coincide while in cubic systems all three resonances coincide. In the case of triclinic and monoclinic systems a complete separation of the dipolar resonances will not be possible. The geometries discussed here as well as those used in literature for studying shape dependencies are of orthorhombic, trigonal, tetragonal, hexagonal or cubic symmetry. This reduces the task of finding the axes along which the dipolar resonances can be excited individually to finding the symmetry axes of the NP - something that can be done easily with the established setup.

The amplitude with which a symmetry-allowed mode contributes to the scattering spectra according to the superposition principle is given by the efficiency of its excitation by the applied field and its size- and shape-dependent scattering cross-section [3][4]. Fig. 3.2b,d shows that the former scales with the intensity of the excitation along the corresponding axis. The latter is briefly addressed in section 3.5. A smaller principal axis leads to a smaller scattering cross-section (Fig. 3.6a) while sharper features (e.g. angulated instead of round corners, tips etc.) generate an increased scattering cross-section (Fig. 3.7). In addition, the exact measurement configuration (collection optics, orientation of the induced dipole, substrate, etc.) will influence the weight
of a resonance in a measured scattering spectrum.

The overall optical response of an NP created in this way also explains the appearance of the observed isosbestic points. At the same time, it restricts them to cases in which the exciting electric field contains components along two of the three principal axes only, or in which two dipolar modes coincide in wavelength.

3.4.2. Quasi-linear scaling of dipole resonances

In contrast to this good agreement between experiment and models concerning the scattering spectra of the studied NPs, the observed exclusive and linear scaling may not be generalized to an extended range of axis lengths and aspect ratios. The data shown in Figs. 3.1 and 3.3-3.5 give two indications thereon. First, the dependency of the two in-plane resonances on their corresponding axis, $\lambda_a(a)$ and $\lambda_b(b)$, show different slopes (1.7 and 1.1). Second, there is a trend to a red-shifting out-of-plane resonance for decreasing cross-sectional area. This trend can be seen best in Fig. 3.5 but also by comparing the positions of the out-of-plane resonances shown in Figs. 3.3a and 3.1. These indications of a limited validity of the scaling behavior can be explained by the well-known interpretation of a resonance wavelength as the result of a quasi-static (i.e. scale-invariant) polarization mode and a dynamic (i.e. size-dependent) red-shift [5][6][62][89]. The limited range of aspect ratios around one leads to configurations that do not differ significantly in their quasi-static polarization mode, i.e. the corresponding surface charge distributions and geometrical depolarization factors do not differ much between the various studied axis configurations. The result is an only slightly varying quasi-static contribution to the resonance wavelength. With axis lengths larger than 70 nm, the dipolar modes are influenced by dynamic depolarization (retardation), i.e. linked to the relevant axis length. This explains the observed exclusive dependence of the resonances on the principal axis along which they are excited. Unfortunately, there is no exact analytical formula for the influence of retardation on the quasi-static dipolar resonance wavelength and its dependence on the relevant axis length. However, simulations and experiments showed that the dependence of the dipolar resonance on axis length can be approximated by a second-order polynomial [6][62][65][89][101]. This means that the study of a restricted range of axis length far from the quasi-static limit results in quasi-linear
Chapter 3. Axis-selectivity, superposition principle and scaling as experimentally observed. In addition, shorter axis lengths start addressing the transition from the dynamic to the quasi-static region. This explains the observed smaller slope of $\lambda_b(b)$ ($b$ between 90 and 140 nm) compared to the slope of $\lambda_a(a)$ ($a$ between 100 and 200 nm).

Following this interpretation, the on-setting dependence of $\lambda_h$ on decreasing cross-sectional area at constant particle height can be seen as a manifestation of shape induced changes of the quasi-static polarization modes. Such changes can also explain the differences in the slope of $\lambda_h(h)$ observed in Fig. 3.5b. The increased slope for the particles with reduced cross-sectional area is based on the data points for $(a, b, h) = (86, 89, 110)$ nm and $(a, b, h) = (81, 82, 95)$ nm. These are the only configurations with a particle excitation along the shortest principal axis. In chapter 4, a formalism leading to an intuitive resonance condition will be introduced. With this, the mentioned indications of a limited validity of the observed scaling behavior can be seen as first hints of a bigger picture. For the moment, it is possible to state that the observed linear, exclusive scaling is a direct consequence of axis lengths influenced by retardation and moderate aspect ratios.

3.5. Scaling of linewidth and amplitude

In principle, the generated data allow a detailed discussion of both linewidth and amplitude of the observed resonances. In the case of scattering amplitude, the measurement setup used is not very accurate due to difficult control of the illumination spot diameter and positioning of the NPs therein. In addition, the coupling efficiency of a dipolar mode to the collection optics depends on its orientation relative to the optical axis of the setup. In sum, a straight-forward reconstruction and interpretation of the detected scattering amplitudes for all three modes is not possible. The scaling of linewidth with particle geometry and length of the principal axes is a topic of its own. The interested reader is referred to [102]-[106].

In this work, we restrict the discussion to a short summary of the observed trends for a true cylinder ($a = b$) (Fig. 3.6) and a direct comparison of the two in-plane scattering amplitudes for cylinder and cuboid with identical length on the part of the principal axes (Fig. 3.7).

Fig. 3.6a shows the scaling of the scattering amplitude, $A$, for cyl-
3.5. Scaling of linewidth and amplitude

**Figure 3.6.** Experimentally observed dependence of scattering amplitude, linewidth (FWHM), and resonance wavelength of the in-plane resonance on particle diameter for cylinders \((a \approx b)\); particle height \(h = 72\) nm. (a) Scattering amplitude. (b) Linewidth of the resonance. (c) Corresponding resonance wavelength.
inders of height \( h = 72 \text{ nm} \). For small diameters, \( A \) is very small, which is in agreement with an absorption-dominated extinction cross-section \([3]\). With increasing diameter the scattering cross-section starts to dominate the absorption cross-section. This can be best explained by remembering the \( r^6 \) dependence of the scattering and \( r^3 \) dependence of the absorption cross-section for a small sphere of radius \( r \) shown in eqns. 1.11 and 1.12. The result is a fast increasing scattering amplitude with increasing cylinder diameter.

The linewidth shows a similar dependence on diameter (Fig. 3.6b). Below \( \sim 120 \text{ nm} \) a constant FWHM of around 100 nm is observed. This is as expected from measurements of particles similar to cylinders \([65][107]\). For a larger diameters, the FWHM increases significantly, which is a manifestation of increasing radiative damping.

For completeness, the corresponding position of the in-plane resonance is shown in Fig. 3.6c. A diameter dependence as expected in a length range showing increasing influence of retardation can be seen. The dependence of the resonance positions on length of all principal axes is discussed in section 6.2.

Screening data for nanoparticles that differ only in shape, reveals a shape dependence of the scattering cross-section amplitude (Fig. 3.7). NPs with rectangular footprints and \((a, b, h) = (175, 142, 110) \text{ nm}\) show higher scattering amplitudes than NPs with elliptical footprints of the same size, \((a, b, h) = (173, 140, 110) \text{ nm}\). This can be explained to some extent by a higher effective volume of the particles with rectangular footprints \([1][99]\). The dependence of resonance position on NP footprints is also discussed in detail in section 6.2.

We conclude this section by pointing out two critical details. The usage of axis-selective excitation does only solve half of the problem of separating dipolar resonances of a nanostructure with non-isotropic geometry. Of course, the effect of a not-well-defined excitation, e.g. as a consequence of applying standard DFOMS, disappears. However, if there are different dipolar resonances with identical orientation of the dipole moment, they all may be excited (section 7.2.2). Second, the coupling efficiency of a mode to the detection path needs to be considered when comparing absolute values of intensity. This is of even greater importance when analyzing enhancement effects. An emitter coupled to a nanoantenna will show a different radiation pattern than the one on bare substrate. This may lead to a misinterpretation of experimentally observed enhancement and quenching.
3.5. Scaling of linewidth and amplitude

Figure 3.7.: Scattering spectra of the two in-plane resonances of NPs with rectangular (R) and elliptical (E) footprint of the same size. Rectangular: \((a, b, h) = (175, 142, 110)\) nm. Elliptical: \((a, b, h) = (173, 140, 110)\) nm.
4. Development of an intuitive model

The purpose of this chapter is the derivation of a resonance condition that is able to give insight into the different contributions defining the wavelength of dipolar plasmon resonances and its scaling with particle shape and size. Hence, the NP is assumed to be of arbitrary shape and of a size in which the quasi-static approximation is not valid. Links to the known concepts of depolarization factors and dynamic depolarization are created. Finally, the tools needed for a later determination and discussion of the various parameters are established.
Chapter 4. Development of an intuitive model

4.1. Introduction

Today the optical response of metallic nanoparticles of arbitrary shape is analyzed by using numerical methods such as FEM, MMP or FDTD in order to approximate the solution of the wave equation. Despite their undisputed potential for calculating the dependence of the optical response of NPs on a variety of parameters (shape, material, particle excitation, etc.), these methods are not well suited for delivering a more general picture that includes for example the processes leading to the shape dependence of the plasmon resonance wavelengths. The reasons are the often non-intuitive character of the basic equations and the difficulty of integrating parameters which describe shape variations. In addition, most shapes can not be parameterized properly and even if this is possible, the resulting integrals can not be solved analytically for most cases. In consequence, the approaches at hand to describe the scaling of the resonance wavelengths with particle shape are closer to rules of thumb than to adequate models.

The few existing non-numerical models that help to understand the link between resonance wavelength and shape are restricted to ellipsoidal bodies. This is because an exact analytical solution of the scattering problem is available for spheres [2] and revealing approximate expressions can be found for spheres and ellipsoids in the quasi-static limit [1][3][4]. A generalization to other bodies is not possible. Besides the mentioned difficult parametrization of most bodies, one reason for this is that (small) ellipsoids are the only bodies that polarize uniformly in a uniform external field. The consideration of a non-uniform polarization complicates the description and calculations further. The situation gets even more complex if the particle size is such that the quasi-static approximation is not valid and dynamic depolarization needs to be considered. Based on Mie theory, there are approaches that invoke dynamic depolarization in the quasi-static expressions for ellipsoids [5]. However, attempts to generalize the resulting terms to bodies of arbitrary shapes are rare [6][72].

A consequence of the availability of expressions describing the scattering properties of ellipsoids but not for other shapes is that most studies addressing the scaling of resonance wavelengths with the length of the principal axes have been performed on spheroids and very similar bodies (e.g. rods) [62][63][98][99][101]. In addition, the chemical synthesis of such NPs is now done routinely. The aspect ratio
4.2. Depolarization factors

is a suitable parameter to describe the shape of spheroids and it has been used often to discuss the scaling of resonances with particle size. However, studying spheroids of different sizes but identical aspect ratio reveals the size-dependence of the resonance wavelengths for the chosen aspect ratio only, but it gives no information about the influence of shape on the particle depolarization. The result is a picture that is not able to distinguish between the effects of size and shape on the depolarization and that overestimates the effect of size by ignoring possible influences of shape. Such a picture is not adequate for NPs production methods that do not lead to constant aspect ratios.

In this chapter, we derive a resonance condition that is neither restricted to a specific shape of the NP nor to the quasi-static limit but that allows to get insight in the way the dipolar resonance wavelengths scale with particle size and shape. A promising starting point for such an intuitive resonance condition is the electrostatic eigenmode method [85][86][70]. We link the resulting expression for the permittivity at which a resonance occurs to the concept of depolarization factors extended by an additional parameter that accounts for the surface charge distribution. The result is a resonance condition that is then extended to the dynamic size range by adding a term for dynamic depolarization. This term is assumed to depend on the length of the relevant principal axis and the overall particle shape. However, these dependencies are not further specified. The different parameters are discussed in detail and links are established that allow their later study based on experimentally measured scattering spectra.

4.2. Depolarization factors

4.2.1. Concept of depolarization factors

Depolarization (demagnetizing) factors were introduced in order to describe the electric (magnetic) field induced in ellipsoids due to an applied uniform, static field $\vec{E}_0$ ($\vec{H}_0$). Ellipsoids are the only non-spherical bodies of finite size which show uniform polarization (magnetization), enabling a description of the body’s electromagnetic properties by

$$\vec{E}_i = \vec{E}_0 + \vec{E}_d = \vec{E}_0 - \vec{L} \vec{P}$$

$$\vec{H}_i = \vec{H}_0 + \vec{H}_d = \vec{H}_0 - \vec{L} \vec{M}.$$
\( \vec{E}_i (\vec{H}_i) \) is the field inside the ellipsoid and \( \vec{E}_d (\vec{H}_d) \) is the depolarization (demagnetizing) field given by the product between depolarization (demagnetizing) tensor, \( \vec{L} \), and polarization (magnetization) \( \vec{P} \) (\( \vec{M} \)).\(^1\) If the cartesian coordinates \((x, y, z)\) are chosen along the principal axes of the ellipsoid, \( \vec{L} \) becomes a diagonal tensor with unit trace, \( L_x + L_y + L_z = 1 \), where \( L_i \) \( (i = x, y, z) \) are the depolarization factors (DF) along the principal axes. The unit trace condition leads to a relative character of the depolarization factors along the NP’s principal axes - an important point that needs to be considered in any model which aims to describe the optical properties of particles of arbitrary shape.

The interpretation of a depolarization factor as a measure for particle depolarization along a principal axis relative to the other principal axes gives a preliminary idea of the effect of changing shape on \( L_i \) and on the resonance wavelength of the dipole resonance excited along this axis.\(^2\) The less two complementary surfaces of a NP are separated, i.e. the smaller the corresponding principal axis is, the stronger are the induced depolarization fields. This means that a principal axis which is short compared to the other principal axes has a high depolarization factor and a blue-shifted resonance wavelength while longer principal axes show lower depolarization factors and red-shifted resonances. For example, in-plane resonances for NPs with low height as studied in section 6.2 tend to be based on low \( L \)-values.

An interesting interpretation of the depolarization tensor \( \vec{L} \) that leads to a definition of depolarization factors for arbitrarily shaped NPs is given by Yaghjian. In [108] he discusses the representation of the electric field in terms of the electric dyadic Green’s function, \( \vec{G}_e \), inside and outside the source region of arbitrary shape. In order to account for the excluded volume containing the point source (singularity of \( \vec{G}_e \)) in the volume integral defining the resulting electric field, a term proportional to

\[
\vec{L} \vec{J}(\vec{r})
\]  

needs to be added. \( \vec{J} \) is the enforced current and \( \vec{L} \) is the source

\(^1\) In the following we use the expression depolarization tensor for \( \vec{L} \) only.

\(^2\) In agreement with later experimental results, we focus on the wavelength at which a resonance occurs rather than its frequency or energy.
4.2. Depolarization factors

dyadic defined by

\[ \mathbf{L} = \frac{1}{4\pi} \int_{S_\sigma} \hat{n}' \hat{e}_{R'} \frac{dS'}{R'^2}. \]  

(4.4)

\( \hat{n}' \) is the unit outward surface normal and \( \hat{e}_{R'} \) is the unit vector between the position of the point source, \( \vec{r} \), and a point \( \vec{r}' \) on the surface \( S_\sigma \) of the excluded volume. \( R' \) is given by \( R' = |\vec{r}' - \vec{r}| \). As shown by Yaghjian, \( \mathbf{L} \) can be interpreted as a generalized depolarizing dyadic with diagonal elements that equal the depolarization factors along the principal axes of a particle geometry given by \( S_\sigma \). However, for the study of NPs of arbitrary shapes, a more appropriate definition of the depolarization tensor is needed in order to account for the dependence of \( \mathbf{L} \) on the position within the particle. This issue is solved in the description of the magnetic properties of arbitrarily shaped bodies by the use of a volume averaged demagnetization tensor (magnetometric demagnetization tensor) [109]. Therefore, a volume averaged depolarization dyadic is an evident approach to describe the depolarization properties of arbitrarily shaped NPs. It also allows the use of analytically derived magnetometric demagnetization tensors for particles with susceptibility \( \chi = 0 \) [110]-[113] in order to study the influence of different particle geometries on the plasmon resonance wavelengths. However, depolarization factors that are defined in this way do not consider the established surface charge distribution and they neglect the interaction between surface charges. In other words, they describe only the geometry of the particle and do not account for the non-uniform polarization of the particle in the quasi-static limit. We will come back to this important point in section 4.4.

This generalization of the depolarization tensor to particles of arbitrary shape does not change its properties compared to the case of ellipsoidal bodies [109], i.e. \( \mathbf{L} \) is a symmetric tensor with unit trace, i.e. \( L_x + L_y + L_z = 1 \). Therefore, the relative character of \( L_i \) remains true for particles of arbitrary shape. The volume integral in eqn. 4.4 can be solved analytically for a few particle shapes only. In consequence, this formulation puts the concept of depolarization factors on a solid basis but it does not help to increase the number of particle geometries that can be discussed analytically. However, we show that the few formulas for depolarization factors at hand are already enough to develop an intuitive model and to interpret the experimentally observed resonance wavelengths of differently shaped single NPs.
4.2.2. Discussion of relevant cases

With the experimentally studied geometries in mind (NPs with rectangular, elliptical and diamond-like footprints), in the following we discuss the depolarization factors of the few cases for which non-numerical formulas are at hand, i.e. NPs with rectangular footprints and true cylinders \((a = b)\).\(^3\) Additionally, a diamond with \(a = b\) corresponds to a rectangular with principal in-plane axes of \(\frac{a}{\sqrt{2}}\). As in the experimental chapters, we keep in the following one in-plane principal axis constant, \(b = 125\) nm, while the other in-plane axis \((a\text{-axis})\) is varying between 5 nm and 300 nm. In order to confirm the influence of changing principal axes and particle geometry on the in-plane depolarization factors in the length region of interest, we also consider ellipsoids. Fig. 4.1 shows the calculated depolarization factors in dependence on the variable axis for ellipsoids and cuboids according to [112] and [111] for particle heights of \(h = 13, 20, 50,\) and \(100\) nm. The statements made based on intuitive reasoning are confirmed. Reducing particle height leads to a significant decrease in the in-plane depolarization factors, \(L_{a,b}\), due to an increasing relative depolarization along the particle height. For a decreasing \(a\)-axis (variable axis), the relative depolarization along this axis increased steadily (Fig. 4.1b), leading to a decrease of \(L_b\) (Fig. 4.1a) and \(L_h\) (not shown). The slope of both \(L_a(a)\) and \(L_b(a)\) increases with decreasing \(a\) axis length. Additionally, these slopes are steeper for higher particles.

Please note that a direct comparison between the depolarization factors for cuboids and ellipsoids is not allowed due to their relative character. A change in the basic geometry of the particle (e.g. from an elliptical to a rectangular footprint) will lead to a change in the polarization behavior that cannot be considered by the relative values of the depolarization factors.

The influence of changing particle height on the depolarization factors for the experimentally addressed cases using \(a = b = 125\) nm is shown in Fig. 4.1c. As brought up in section 4.4 and discussed in section 6, configurations with low depolarization factor are in principle good candidates for the experimental observation of shape differences. This makes particles of low height \((h \ll a, b)\) interesting for the further study of the overall scaling behavior. However, many additional aspects need

\(^3\)Again, the NPs are given by the two in-plane principal axes \(a\) and \(b\) and the particle height \(h\).
4.2. Depolarization factors

Figure 4.1: (a,b) Calculated depolarization factors along the in-plane axes after [111] for cuboids (open symbols) and ellipsoids [112] (filled symbols). One in-plane axis is kept constant, \( b = 125 \) nm. Particle height \( h = 13/20/50/100 \) nm. (a) Depolarization factor along constant principal axis in dependence of the variable in-plane axis (\( a \)-axis). (b) Depolarization factor along variable principal axis in dependence on its axis length. (c) Influence of particle height on the in-plane depolarization factor for the footprints studied in section 5 but restricted to \( a = b = 125 \) nm. Square and diamond-like (square) after [111], circular footprint after [110].
to be considered before small changes in shape manifest themselves in a measurable shift in the resonance wavelengths. Among others, an absolute or generalized value for particle depolarization needs to be found.

4.3. Eigenvalue problem

There are different ways to approximate the resonance wavelengths of metallic nanoparticles [1][3][89][114]-[117]. One sort of approach is based on an explicit description of the electric field around or inside the NP followed either by identification of a resonance condition or by calculation of the wavelength-dependent electric field. Another set of approaches uses eigenvalue type equations with eigenfunctions that correspond to the resonance modes. We base our resonance condition on such an eigenvalue problem, namely on the boundary integral technique. The basics of this technique also known as the electrostatic eigenmode method are given by Mayergoyz et al. [85]. Nice summaries thereof can be found in [70][86]. Using their formalism, the eigenvalue problem in the quasi-static approximation reads

\[
\sigma(Q) = \frac{\mu}{2\pi} \int_S \sigma(M) \frac{\vec{r}_{MQ} \cdot \vec{n}_Q}{r_{MQ}^3} dS_M 
\]

\[
\mu = \frac{\epsilon_1(\lambda) - \epsilon_m}{\epsilon_1(\lambda) + \epsilon_m}. 
\]

\(\sigma(Q)\) is the single layer electric charge distribution at position \(Q\) on the particle surface \(S\). \(\mu\) are the eigenvalues which are linked to the real part of the NP permittivity, \(\epsilon_1(\lambda)\), and the permittivity of the surrounding medium, \(\epsilon_m\). \(\vec{r}_{MQ}\) is the vector between two points \(M\) and \(Q\) on \(S\) and \(\vec{n}_Q\) is the outward unit normal to \(S\) at \(Q\). For the following sections it is important to note that the boundary integral equation 4.5 contains the scalar of the kernel of the integral defining the depolarization tensor, eqn. 4.4. We will come back to this point in section 4.5.

Examples of how possible eigenfunctions, i.e. surface charge distributions, look can be found in [91][92][118]. An interesting feature of eqn. 4.5 is that the linear combination of two eigenfunctions \(\sigma_1\) and \(\sigma_2\), \(\sigma_{12} = c_1\sigma_1 + c_2\sigma_2\), is also an eigenfunction only if \(\sigma_{1,2}\) are modes of
the same degenerated state, i.e. $\mu_1 = \mu_2$. In this case, the eigenvalue of $\sigma_{12}$ is $\mu_{12} = \mu_1 = \mu_2$. This allows an additional aspect in the interpretation of the superposition principle observed in section 3.2. For non-equal length of the two in-plane principal axes, $a \neq b$, all linear combinations of the two corresponding dipolar modes are not eigenfunctions of the particle. Therefore, a continuous tuning from $\lambda_a$ to $\lambda_b$ over such modes is not possible. Additionally, other modes that might be efficiently excited by an electric field vector in between the principal axes are symmetry forbidden. In combination, this results in the observed scattering spectra based on the superposition of resonances excited along the principal axes.

In cases with $a = b$, the modes excited along the principal in-plane axes belong to the same degenerated state. Therefore, linear combinations thereof are eigenfunctions of eqn. 4.5. Looking at particles with square footprints, this means that the now symmetry-allowed modes leading to a dipole moment along the diagonals can either be generated by an additional state of surface charge distribution (twice degenerated) or by a linear combination of the modes excited along the principal axes of the square. The former can be resolved by measuring the scattering spectra of the particle if the energy difference between this state and the state leading to dipole moments along the particle’s principal axes is large enough. The latter cannot be resolved due to its equal energy compared to the modes of which it is a linear combination. We will come back to this point in section 5.2.

In the following, we are interested in the interpretation of the eigenvalues of eqn. 4.5 because they allow the calculation of the resonance wavelengths using eqn. 4.6. Generally, a higher eigenvalue $\mu$ means a resonance mode higher in energy (i.e. blue-shifted resonance wavelength). This can be shown by visualizing $E_{\text{Res}}(\mu) = \frac{hc}{\lambda_{\text{Res}}(\mu)}$ in the quasi-static limit.
Chapter 4. Development of an intuitive model

4.4. The resonance condition

In the previous section it was shown that the resonance modes in terms of the surface charge distribution of a NP of arbitrary shape in the quasi-static limit are the eigenfunctions of eqn. 4.5. The resonance wavelengths are obtained from the eigenvalues \( \mu \) according to eqn. 4.6. Rearrangement of the terms leads to

\[
\frac{\varepsilon_m}{\varepsilon_1 - \varepsilon_m} - \frac{1 - \mu}{2\mu} = 0.
\]

(4.7)

Again, \( \varepsilon_1 \) is the wavelength-dependent real part of the dielectric function of the particle, \( \varepsilon = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda) \), and \( \varepsilon_m \) is the constant permittivity of the surrounding medium.

In the case of a spherical particle the eigenfunctions and eigenvalues of eqn. 4.5 can be found analytically [85]. The eigenfunctions are the spherical harmonics \( Y_{lm}(\theta, \varphi) \) and the eigenvalues are given by

\[
\mu_l = 2l + 1,
\]

(4.8)

where \( l \) indicates the mode number. For the 1st order mode, \( l = 1 \), this leads to

\[
\frac{\varepsilon_m}{\varepsilon_1 - \varepsilon_m} + L = 0,
\]

(4.9)

where \( L = \frac{1}{3} \) corresponds to the depolarization factor of a sphere. The resonance condition given by eqn. 4.9 can be generalized to ellipsoidal particles

\[
\frac{\varepsilon_m}{\varepsilon_1 - \varepsilon_m} + L_i = 0,
\]

(4.10)

with \( L_i \) the depolarization factors along the principal axes of the ellipsoid. A further generalization to arbitrary particle shapes based on depolarization factors only is not possible due to the on-setting non-uniformity of the depolarization field and missing consideration of the surface charge distribution and of the interaction between surface charges in the depolarization factor. In order to account for this surface charge distribution based influence, we introduce a correction factor, \( g \), to the depolarization factor. The resonance condition in the quasi-static limit can then be written as

\[
\frac{\varepsilon_m}{\varepsilon_1 - \varepsilon_m} + g_i L_i = 0
\]

(4.11)
4.4. The resonance condition

\[ g_i L_i = -\frac{1 - \mu}{2\mu}. \]  \hspace{1cm} (4.12)

The term \( g_i L_i \) cannot fully represent the complex dependencies between particle shape, surface charge distribution and interaction between surface charges. Nevertheless, it is an intuitive way to describe the effects leading to a plasmonic resonance in a metallic NP. We will come back to this point in section 4.5.

The quasi-static resonance condition, eqn. 4.11, can be directly related to a resonance condition for spheres in the dynamic range via expansion of the first TM mode of Mie theory for particle polarization [5][6],

\[ \alpha_{\text{Mie}} = \frac{V(1 - \frac{1}{10}(\epsilon + \epsilon_m)x^2 + O(x^4))}{\frac{1}{3} + \epsilon_m \epsilon - \epsilon_m - \frac{1}{30}(\epsilon + 10\epsilon_m)x^2 - i\frac{4\pi^2\epsilon_m^{3/2}}{3}\frac{V}{\lambda_0^3} + O(x^4)} \] \hspace{1cm} (4.13)

\[ \frac{\epsilon_m}{\epsilon_1 - \epsilon_m} + \frac{1}{3} - \frac{1}{30}(\epsilon_1 + 10\epsilon_m)x^2 = 0. \] \hspace{1cm} (4.14)

\( V \) is the volume of the sphere, \( \lambda_0 \) is the wavelength in vacuum, and \( x = \pi a/\lambda_0 \) is the size parameter based on the diameter of the sphere \( a \).\(^4\) This means that in our formulation of the quasi-static resonance condition, retardation can be considered by a generalized term \( R \),

\[ \frac{\epsilon_m}{\epsilon_1 - \epsilon_m} + g_i L_i + R_i(g_i, L_i, d_i) = 0. \] \hspace{1cm} (4.15)

The retardation term along a principal axis, \( R_i \), is expected to depend on the correction \( g_i \), the depolarization factor \( L_i \) and the total length of the studied principal axis \( d_i \). Eqn. 4.15 allows the definition of a shape-term \( y_i \),

\[ y_i = g_i L_i + R_i(g_i, L_i, d_i), \] \hspace{1cm} (4.16)

leading to

\[ \frac{\epsilon_m}{\epsilon_1 - \epsilon_m} + y_i = 0. \] \hspace{1cm} (4.17)

In the following, we drop the index \( i \) indicating the principal axis under consideration. Thanks to the incorporation of \( g \) and \( R \), the resonance condition is generalized to particles of arbitrary shapes and

\(^4\)The usage of \( a \) as the diameter of a sphere is exceptional in order to be consistent with [6]. Throughout this thesis, \( a \) is used as the total length of an in-plane principal axis of the studied particles.
Chapter 4. Development of an intuitive model

extended to the dynamic size range. It is the starting point for the
detailed study of the resonance wavelengths of metallic nanoparticles
done in chapter 6.

Encina et al. [72] proposed another resonance condition for nanorods
(nanocylinders) using a geometrical factor \( f \),

\[
\epsilon_1 = -f \epsilon_m. \tag{4.18}
\]

This condition can be derived from eqn. 4.6 as well, leading to \( -f = \frac{1+\mu}{1-\mu} \) and \( y = \frac{1}{f+1} \). In [72], retardation and resonance modes are con-
sidered by introducing surface wave vectors based on the geometrical
condition of standing waves. The resulting resonance condition is there-
fore not directly linked to the depolarization factors and to Mie theory.
This makes a further interpretation of the resonance wavelengths diffi-
cult.

Kuwata et al. [6] derived a resonance condition for particles of arbit-
rary shape from eqn. 4.13 by assuming negligible absorption, \( \epsilon_1 \gg \epsilon_2 \),
and by considering a non-spherical particle shape by direct incorpora-
tion of the depolarization factor \( L \),

\[
L + \frac{\epsilon_m}{\epsilon_1 - \epsilon_m} + A(L)\epsilon_m x^2 + B(L)\epsilon_m^2 x^4 = 0. \tag{4.19}
\]

This formulation is in agreement with the resonance condition eqn. 4.17
using

\[
y_k = L + A(L)\epsilon_m x^2 + B(L)\epsilon_m^2 x^4. \tag{4.20}
\]

With this approach, the influence of the surface charge distribution
on the resonance wavelength in the quasi-static limit is ignored. Addi-
tionally, using a size parameter proportional to the circumference of the
associated sphere is questionable in the case of arbitrary particle shape.
The two parameters \( A(L) \) and \( B(L) \) appearing in the retardation terms
of eqn. 4.19 are determined by fitting eqn. 4.19 to FDTD simulations
on prolate spheroids. The result is two polynomials of 3rd order in \( L \),
\( A(L) = A_A L + B_A L^2 + C_A L^3 \) and \( B(L) = A_B L + B_B L^2 + C_B L^3 \).

In order to find an explicit formula for the resonance wavelength from
resonance condition 4.17, we assume that the real part of the dielectric
function of the metal can be approximated by a Drude-Sommerfeld
function

\[
\epsilon_1(\lambda) = \alpha - \beta^2 \lambda^2. \tag{4.21}
\]

\(^5\) \( A_A = -0.4865, B_A = -1.046, C_A = 0.8481, A_B = 0.01909, B_B = 0.1999, C_B = 0.6077.\)
4.4. The resonance condition

Figure 4.2.: (a) Dependence of the resonance wavelength, $\lambda_{\text{Res}}$, on shape-term $y$ for four different dielectric constants of the surrounding medium, $\epsilon_m = 1, 1.5, 2, 2.5$. (b) Expected influence of a shift of 0.01 in $y$ at the working point indicated by the $y$-value.

and that absorption is negligible, $\epsilon_2 = 0$. Using best fit to experimental gold bulk data [119] in the wavelength range between 600 – 1200 nm leads to $\alpha = 9.84$ and $\beta = 7.1 \, \mu\text{m}^{-1}$. For $\lambda > 600$ nm, the representation of $\epsilon_1(\lambda)$ by eqn. 4.21 is sufficient for our purpose. The influence of finite-size effects on $\epsilon(\lambda)$ are expected to be low in the considered size range of particle sizes [65][120][121]. Therefore, in the range of a valid representation of $\epsilon_1(\lambda)$ by eqn. 4.21, the resonance wavelength is given by

$$\lambda_{\text{Res}} = \mp \sqrt{\frac{\alpha + \epsilon_m/y - \epsilon_m}{\beta}}. \quad (4.22)$$

Fig. 4.2a shows the important dependence of the resonance wavelength $\lambda_{\text{Res}}$ on the shape-term $y$. Derivation of eqn. 4.22 to $y$ leads to an
expression describing the sensitivity of the resonance wavelength on small changes in $y$ (Fig. 4.2b),

$$\frac{\partial \lambda_{\text{Res}}}{\partial y} = \pm \frac{\epsilon_m}{y^2 \sqrt{4\beta^2(\alpha + \epsilon_m/y - \epsilon_m)}}.$$  \hspace{1cm} (4.23)

Dashed lines in Fig. 4.2a,b indicate the range of $y$-values in which $\epsilon_1(\lambda)$ is no longer properly described by eqn. 4.21. A linear relation between $\epsilon_1$ and $\lambda$ fitted to bulk data was used instead. Additionally, in this range the assumption of negligible absorption is not valid. The experimentally realized particle configurations lead to resonances above 600 nm. Thus, their interpretation is not influenced by these concerns.

Fig. 4.2a,b shows that a decreasing shape-term leads to both a red-shift of the resonance wavelength and an increasing sensitivity to changes in shape. The latter becomes apparent by a more pronounced red-shift of $\lambda_{\text{Res}}$ for the same change in $y$ at smaller working points. As we will see in sections 5 and 6, it is not a difficult task to find configurations with low $y$-values, but the potentially complementary contribution of quasi-static and dynamic (retardation) particle depolarization to $y$ needs to be considered in order to observe different $y$-values for changing particle shapes. Additionally, different $y$-values for different geometries can lead to both an increasing or decreasing difference in $y$.

4.5. Concavity parameter

4.5.1. Determination

In order to deduce a resonance condition valid for arbitrary particle shape in the quasi-static limit, a correction to the depolarization factor $L$ was introduced in eqn. 4.11. This factor compensates for the missing information about surface charge distribution and the interaction between surface charges which defines the eigenvalues of eqn. 4.5 and therefore the resonance wavelength. In agreement with the case for ellipsoids in the quasi-static approximation ($g = 1$, eqn. 4.10), we demand for a constant $g$-value within a basic particle geometry in the following. This means that we assume that a change in the eigenvalue $\mu$ due to changing aspect ratios is completely considered by the according changes in the depolarization factors. Although the kernel of the integral of equation 4.5 contains the kernel of the integral defining
the depolarization factor in the source dyadic formalism, eqn. 4.4, the representation of the eigenvalues $\mu$ by

$$\mu = \frac{1}{1 - 2gL},$$

(4.24)

with a constant $g$ within a fixed particle geometry, is an approximation only. We will come back to the consequences of asking for a constant $g$-value later in this section (4.5.2).

Unfortunately there is no satisfactory link via equations between the processes leading to the value of $g$ and the rigid description thereof (eqn. 4.5, 4.6 and 4.12). Berkovitch et al. give an intuitive picture of how the surface charge distribution of a particle influences the resonance wavelength [122][123]. Briefly, the interaction between opposite sign surface charges is exploited by considering the local geometry at particle regions showing highest surface charge density. Based on eqn. 4.5, this is done by comparing the normal to the particle boundary at a point of interaction $Q$, $\hat{n}_Q$, with the vector connecting this point with a point $M$ at the center of the opposite charged surface region, $\vec{r}_{MQ}$. They conclude that the resonance wavelength of a particle red-shifts whenever a significant surface charge distribution is generated on concave edges due to a locally negative value of $\vec{r}_{MQ} \cdot \hat{n}_Q$. Consequently, the concavity or more general the curvature of the particle is identified as a parameter that can be used to tune the resonance wavelength of a particle with otherwise identical lengths of the principal axes. Due to the conceptional analogy between the tuning of plasmon resonances by increasing the concavity of a particle and the introduction of a factor $g$ that accounts for the shape-dependent surface charge distribution and the interaction between surface charges, we call $g$ the concavity parameter in the following.

Interpreting the value of $g$ as the outcome of the interplay between the surface charge density, $\sigma(Q)$, and $\vec{r}_{MQ} \cdot \hat{n}_Q$, the particle shapes analyzed in section 6.2 can be ranked according to their concavity parameter. In the following, we restrict the discussion to particles with identical principal axes and in-plane particle polarization, i.e. we compare ellipse, diamond and rectangular. Obviously, the value of $\vec{r}_{MQ} \cdot \hat{n}_Q$ is larger for an ellipse than for a diamond at a comparable surface charge distribution for the two geometries. This means that particles with diamond-like footprints have a lower concavity parameter. It follows that the consideration of surface charge densities results in a red-shift
of particles with diamond-like footprint compared to particles with elliptical footprint.

A little bit more tricky is the comparison between elliptical and rectangular footprints. This case is also discussed in [122]. Here, $\vec{r}_{MQ} \cdot \hat{n}_Q$ is lower for the ellipse compared to the rectangle as long as $Q$ is on the surface opposite to the position of $M$. However, the region with a relevant surface charge density is widely extended for the rectangle. This means that additional $(M, Q)$ configurations and higher angles between $\vec{r}_{MQ}$ and $\hat{n}_Q$ need to be considered. As a consequence, particles with rectangular footprints are expected to have a lower concavity parameter compared to the particles with elliptical footprints. Again, this results in a red-shift for rectangular footprints upon consideration of $g$. In section 5.2 we confirm this reasoning via experimental results.

An exact determination of $g$ is not possible without numerical methods for most cases. Nevertheless, it can be estimated from experimental data if its value $g_j$ is known for a reference particle geometry. For measured resonance wavelengths along a principal axis of the reference geometry, $\lambda_j$, and the geometry under consideration, $\lambda_i$, the two shape terms $y_{j,i}$ can be calculated using eqn. 4.17. The difference in the shape-terms, $\Delta y$, is then given by

$$\Delta y = y_i - y_j = g_i L_i - g_j L_j + \Delta R. \quad (4.25)$$

$L_{i,j}$ are the depolarization factors of the two geometries and $\Delta R = R_i - R_j$ accounts for the difference in retardation. This leads to a concavity parameter of the particle geometry under discussion of

$$g_i = \frac{1}{L_i} (\Delta y - \Delta R + g_j L_j). \quad (4.26)$$

A good reference geometry is that of an ellipsoid (including sphere) which shows $g = 1$, eqn. 4.10. Thanks to the similarity between a prolate ellipsoid excited along its minor axis and an in-plane excited cylinder with elliptic footprint, $g_j = 1$ can be used as approximation for the concavity parameter of the cylinders.

Eqn. 4.26 can be further simplified by comparing particles of identical lengths of the principal axes, $(a, b, h)_i = (a, b, h)_j$, and the usage of resonances excited along principal axes of equal length. In this case, $\Delta R$ is expected to be small due to a missing contribution of the axis length on the difference in retardation. This leads to an estimation of $g_i$ out
of measured resonance wavelengths of

\[ g_i \approx \frac{1}{L_i} (\Delta y + 1 \cdot L_j). \]  \hspace{1cm} (4.27)

However, the assumption \( R \approx 0 \) ignores the influence of \( gL \) on \( R \) and contributes to the approximative character of the \( g \) values derived from eqn. 4.27. Looking at the values at hand for experimentally determined shape-terms and calculated depolarization factors, we will use true cylinders as reference geometry \((j)\) and cuboids or NPs with diamond-like footprint as geometries with unknown concavity parameter \((i)\). A careful estimation of the error in \( g_i \) caused by the errors in the used values of \( \Delta R, g_j, L_{i,j}, \lambda_{i,j}, \) and \( \epsilon_m \) shows that especially errors in \( L_{i,j} \) and \( \Delta R \) influence the accuracy of the so-determined \( g_i \), while the influence of an error in \( g_j \) is expected to be of minor importance, but still present. We will come back to this point after the experimental determination of \( g \) (section 5.2).

4.5.2. Influence of assumptions

Eqn. 4.27 is based on the assumption that \( \Delta R \) can be neglected within the concept developed for \( g \) determination. Additionally, it is assumed that \( g_j \) is constant for the reference geometry independent of moderately varying aspect ratios. In the same way, the resulting \( g_i \) is seen as constant for the addressed particle geometry. We will briefly discuss the consequences of these assumptions on later data interpretation.

In the case of a non-marginal contribution of \( \Delta R \) to eqn. 4.26 and a fixed value of \( g_j \), the result is a \( \Delta y \) changed from \( \Delta y = g_i L_i - g_j L_j \) to

\[ \Delta y = \tilde{g}_i L_i - g_j L_j \]  \hspace{1cm} (4.28)

with

\[ \tilde{g}_i = g_i + \frac{\Delta R}{L_i}. \]  \hspace{1cm} (4.29)

Using \( \tilde{g}_i \) as it results from eqn. 4.26 by ignoring a non-zero value of \( \Delta R \) in the later data interpretation for particles of fixed geometry leads to

\[ y = \tilde{g}_i L + R, \]  \hspace{1cm} (4.30)

instead of

\[ y = g_i L + R = \tilde{g}_i L - \frac{\Delta R}{L_i} L + R, \]  \hspace{1cm} (4.31)
where the terms with no index correspond to the data point under consideration. This means that the quasi-static part of the shape-term is wrong by $\Delta R_{L_i} L$ on the cost of the dynamic part if $R$ is determined over $R = y - \hat{g}_i L$ (see section 4.6).

Using a constant $g$ for particles of the same geometry but different aspect ratios in combination with eqn. 4.16 has the consequence that differences in $\mu$, due to changing aspect ratios that are not considered by the depolarization factors, will show up in the retardation term. However, the surface charge distribution is expected to vary slowly with changing aspect ratios only. In combination with the part consideration of changing distances between interacting surface charges and changes in $\vec{r}_{MQ} \cdot \hat{n}_Q$ in the depolarization factors, the resulting contribution to $R$ will be small in the considered length range.

Our demand for a constant $g$ defines the relation between $L$ and $R$ to some extent. In principle, it is possible to ask e.g. for retardation that depends on the relevant axis length $d$ (or on $L$) only, instead of a constant $g$. This will change the dependencies and interpretation of the quasi-static and dynamic part contributing to a resonance wavelength. We will not follow this point further.

### 4.6. Retardation

Thanks to the model introduced in the previous sections and the extensive measurements on NPs with differently shaped footprints and aspect ratios of the principal axes, it is possible to gain information about the dependence of the retardation term $R$ on the depolarization factor, $R(L)$, and on the length of the relevant axis $d$, $R(d)$. As pointed out in section 4.5, $g$ is assumed to be constant within a basic particle geometry independent of changing principal axis lengths. A not complete fulfillment of this assumption will result in a small error in $R$. Therefore, it will be considered in the error estimation only.

A prerequisite for determining the $L$ dependence of the retardation term from experimental data is knowing of the depolarization factors for the studied geometry itself. Therefore we will later restrict the detailed discussion of retardation to cuboids for which plenty of data have been generated with widely varying principal axes ($a, b, h$).

The general concept of isolating information regarding retardation from experimental data is as follows: for each resonance wavelength,
4.6. Retardation

\( \lambda_{\text{Res}} \), of a particle given by \((a, b, h)\) the shape-term is calculated,

\[
y = -\frac{\epsilon_m}{\epsilon_1(\lambda_{\text{Res}}) - \epsilon_m}.
\] (4.32)

If \( g \) and \( L \) are known for the axis relevant for this resonance, the corresponding retardation term is given as

\[
R(g, L, d) = y(\lambda_{\text{Res}}) - gL.
\] (4.33)

By calculating \( R(g, L, d) \) for all data points and screening data for varying \( L \) values at constant axis length and vice versa, it is possible to extract the dependence of \( R \) on these two parameters. This is done in section 5.3. There, the influence of the observed dependencies on errors in \( g \) and \( L \) are also discussed.
5. Concavity, retardation and quasi-static depolarization

In the previous chapter, we established the basis we use to gather information on the origin of the shape and size dependence of resonance wavelengths in metallic nanoparticles. In this chapter, we apply the derived links between model and scattering experiments to sets of measurements on cuboids with a varying in-plane axis ($a$-axis), a constant in-plane axis ($b = 123 \pm 6$ nm) and three different particle heights, $h = 13$, 20 and 50 nm. The results are: first, an estimation of the curvature parameter for cuboids excited along the in-plane principal axes and in-plane diagonals. Second, the determination of the dependence of the retardation term on the depolarization factor. Third, the decomposition of the contributions of quasi-static and dynamic depolarization on the resonance wavelength.
5.1. Introduction

The resonance wavelength of a LSPR is determined by the particle depolarization established by the applied field. The overall depolarization can be seen as a combination between a quasi-static part described by depolarization factors and a dynamic part described by retardation. The former depends on particle shape and the latter depends obviously on particle size. But there is also a shape-given contribution to the dynamic depolarization, which can be described by the depolarization factors $L$. Hence, the dependence of retardation on $L$ needs also to be considered when resonance wavelengths are discussed.

In literature, most reports discuss the contributions of quasi-static and dynamic depolarization to the resonance wavelengths by summarizing the corresponding theory for spheroids [62][89][106]. However, a decomposition of experimental or calculated results into these contributions is in general not done. The main reason is the difficult finding of parameters that describe particle size and shape [63][64][124]. Hence, the quasi-static regime is addressed directly [88][125] or valuable general statements concerning the dependence of the resonance wavelengths on the overall particle shape are given [62][65][98][99][101][126]-[128]. The latter contains often studies of NPs with constant shape-contributions (e.g. constant aspect ratios). However, there is no model or formalism that separates size- from shape-effects in a rigid way.

In this chapter, we address the issues of an $L$-dependent dynamic depolarization and the determination of the contribution of quasi-static and dynamic depolarization on the resonance wavelength. Both is done by analyzing the scattering spectra of cuboids and by the use of the findings of chapter 4, i.e. the calculation of the depolarization factors according to [111], the estimation of the concavity parameter after eqn. 4.27,

$$g_i \approx \frac{1}{L_i} (\Delta y + 1 \cdot L_j),$$

and the determination of the shape-term (eqn. 4.17) and the retardation (eqn. 4.33) for each measured resonance wavelength,

$$y = -\frac{\epsilon_m}{\epsilon_1(\lambda_{Res}) - \epsilon_m}$$

$$R(g, L, d) = y(\lambda_{Res}) - gL.$$
5.1. Introduction

The result is the first experimental estimation of the dependence of the retardation term on the depolarization factor. A surprisingly high dependence of the retardation term on the depolarization factor is observed. Further, the contributions of the quasi-static and dynamic depolarization to the scaling behavior of dipolar resonances is shown in a clarity not seen before. It reveals that it is the quasi-static depolarization that dominates the scaling of the resonance wavelengths in most cases. Finally, the estimated concavity parameters for NPs with rectangular, diamond-like and elliptical footprints lead to the generalization of the depolarization factors needed for a direct comparison of differently shaped NPs (chapter 6).

Fig. 5.1 shows examples of the cuboids studied in this chapter and visualizes their excitation. One in-plane principal axis of the cuboids is of constant length, \( b = 123 \pm 6 \) nm while the other in-plane axis varies in steps between 50 and 300 nm. Three different particle heights are considered, \( h = 13, 20 \) and 50 nm. These particle heights lead to resonances excited along the particle height that are blue-shifted out of the wavelength range addressed by the setup. Therefore, standard DFOMS in combination with a properly polarized excitation can be used. Fig. 5.2 shows the resulting resonance wavelengths for a particle excitation along the constant (Fig. 5.2a) and the variable in-plane axis (Fig. 5.2b) as they result from fitting of the measured scattering spectra.
with Lorentzian curves. These data are the basis for the discussions following in this chapter.

5.2. Estimation of the concavity parameter

In order to estimate the concavity parameter $g$ from experimental data according to eqn. 4.27, we need identical measurements on a reference geometry with known $g$-value and depolarization factors, and on the geometry under question with known depolarization factor only. In the case of in-plane particle excitation, the cylinder ($a = b$) can be used as reference geometry. Thanks to its equal cross-section compared to a sphere, its concavity parameter will be close to that of a sphere, i.e
5.2. Estimation of the concavity parameter

\( g_j \approx 1 \). The depolarization factors of a cylinder can be calculated according to Ref. [112].

In principle, this argumentation can be extended to cylinders with elliptical footprints \((a \neq b)\) excited along the in-plane axes, thanks to their similarity to prolate ellipsoids. However, there are no non-numerical formulas for the depolarization factors of cylinders with elliptical footprints at hand. This limits our discussion to cases with \( a = b \).

Thanks to the known depolarization factors for cuboids (section 4.2.2), it is possible to estimate the concavity parameter of particles with cubic footprints from measured resonance wavelengths. We use the measurements shown in Fig. 5.2 for NPs with in-plane axes close to \( a \approx b \approx 123 \text{ nm} \) and \( h = 13/20/50 \text{ nm} \). It results a concavity parameter of \( 0.95\pm 0.11 \) for \( h = 50 \text{ nm} \) and \( 0.94\pm 0.12 \) for \( h = 20 \text{ nm} \). For \( h = 13 \text{ nm} \), the experimental data scatter too much for a determination of \( g \). In the calculations, a permittivity of the surrounding medium of \( \epsilon_m = \frac{1}{2}(\epsilon_{\text{substrate}}+1) = 1.625 \) was assumed. \( \epsilon_1(\lambda) \) was chosen according to eqn. 4.21.

The concavity parameter of particles with diamond-like footprints defined by in-plane axes close to \( a \approx b \approx 123 \text{ nm} \) and \( h = 13/20/50 \text{ nm} \) can also be estimated. Here, \( h \) is a rotational axis of order 4. Therefore \( \vec{\mathbb{L}} \) is invariant under rotation around \( h \) [109] and the required in-plane depolarization factors are the same as for the cuboid defined by \((\frac{b}{\sqrt{2}}, \frac{b}{\sqrt{2}}, h) \text{ nm}\). Using the measurements discussed in section 6.2, the resulting \( g \)-values are \( 0.88\pm 0.07 \) for \( h = 50 \text{ nm} \) and \( 0.86\pm 0.09 \) for \( h = 20 \text{ nm} \).

In total, we see that \( g_D < g_R < g_E^1 \) and the obtained values are nearly independent of particle height. The important question of to which extent the obtained values can be used for other axes lengths and aspect ratios \( \neq 1 \) needs a more detailed analysis based on numerically calculated depolarization factors and further particle shapes.

The different values of \( g \) for the two considered configurations indicate that the excitation along the in-plane diagonal of a cuboid with a square footprint excites a mode of surface charge distribution which is not a linear combination of the modes excited along the principal axes of the footprint. This indication is further confirmed in chapter 6 by showing the appearance and scaling of resonances excited along

\(^1\)Diamond-like, Rectangular, Elliptical
the principal axes of a diamond-like footprint. A square footprint belongs to both rectangular and diamond-like geometry. Therefore, the surface charge distribution excited along its diagonal can be seen as in line with those established in particles with diamond-like footprints, where modes not excited along the principal axes are symmetry forbidden. It follows that the modes excited along the principal diagonal of the square footprint are independent of the modes excited along its principal axes.

We further note that the dependence of $g$ on the induced mode of surface charge distribution breaks the clear link between particle geometry and particle polarization given by $\vec{L}$. While the entries of $\vec{L}$ do not change under rotation around the $h$-axis for a particle with a square footprint, the entries of $\vec{g}$ do. Therefore there is shape anisotropy in directions transverse to $h$, which results in a dependence of the scattering spectra on the exciting electric field vector. Direct experimental proof of this behavior is still pending.

The error in $g$, $\Delta g$, is difficult to estimate due to its manifold dependencies, $g = g(L_i, L_j, g_j, \lambda_i, \lambda_j, \epsilon_m, \Delta R)$. The dependence on $\lambda_i, \lambda_j$ and $\epsilon_m$ comes from the determination of $y_{i,j}$ using eqn. 4.17. $\Delta R$ accounts for an inexact fulfillment of the assumption $\Delta R = 0$ made in section 4.5.1. For the estimation of the error in $L_{i,j}$ the influence of an error in particle height of 10% is calculated. The error in $g_j$ is estimated to 0.035, which is half of the difference of the calculated $g$-values for particles with rectangular and diamond-like footprints and twice the maximum observed difference for a change from $h = 50$ nm to $h = 20$ nm. An error of 10 nm is used for $\lambda_{i,j}$. It accounts for both possible read-out errors and errors based on using the data points closest to $a = b = 123$ nm and their averaging. The error in $\epsilon_m$ is set to 0.325. Finally, we set $\Delta R$ to half of the measured difference in the shape-term, $y_i - y_j$.

Looking at the different contributions to $(\Delta g)^2$ reveals a dominating contribution of the errors in $L_i, L_j$ and $\Delta R$. Their relative values are configuration-dependent but in sum they contribute to more than 70% of the overall error. Of nearly no importance are the errors in $\lambda_{i,j}$ and $\epsilon_m$, while the error in $g_j$ accounts for $9 - 17\%$ of the overall error.

For the discussion of the influence of particle geometry on resonance wavelength, a $g$-value of $\sim 0.87$, $\sim 0.94$ and $\sim 1$ needs to be considered in the resonance condition (eqn. 4.17) for the particles with diamond-like footprints.

\[^2\text{Indices according to section 4.5.}\]
5.3. Retardation term from experimental data

For an NP with a known depolarization factor along the considered principal axis and a known $g$-value, the corresponding retardation term can be calculated from the experimentally observed resonance wavelength according to eqns. 4.32 and 4.33. This was done for all NPs with rectangular footprints and heights of $h = 13/20/50$ nm. Screening the obtained values either for particles with constant $L$ or constant $d$ reveals the general dependence of the retardation term on $L$ and $d$ (Fig. 5.3). A constant concavity parameter of $g = 0.94$ and a permittivity of the surrounding medium of $\epsilon_m = \frac{1}{2}(\epsilon_{\text{substrate}} + 1) = 1.625$ are assumed. $\epsilon_1(\lambda)$ is as in eqn. 4.21. The error bars indicate the effect of an error in $g$, $\lambda_{\text{Res}}$, $L$, and $\epsilon_m$ of 0.12, 5 nm, 0.015, and 0.325, respectively. These values are as in the previous section (error in $g$ and $\epsilon_m$) or slightly adapted to the changed experimental situation (read-out error in $\lambda_{\text{Res}}$ only, maximum observed error in $L$). Using these values, the error in $g$ dominates for the $h = 50$ nm measurements. A reducing particle height increases the contribution of the error in $L$ and to a minor degree in $\epsilon_m$ to the overall error. Possible errors of $\lambda_{\text{Res}}$ in the given range are negligible.

Fig. 5.3a shows that the retardation term of NPs with rectangular footprints and particle excitation along a constant principal axis of length $d = 123 \pm 6$ nm clearly scales with $L$. The lowest order polynomial that leads to a good fit is second order, $R(L) = aL^2 + bL + c$ with $d$-dependent parameters $a(d)$, $b(d)$, and $c = 0$. For $d = 123 \pm 6$ nm these parameters are $a = -1.2316$, $b = -0.2542$, and $c = 0$. A decreasing axis length shifts the polynomial to lower $R$-values, while a longer constant axis leads to a shift of $R(L)$ to higher values. However, in the considered range of axis lengths, $L$ is always larger than the absolute value of $R$. Additionally, for $d = 123 \pm 6$ nm and $L < 0.30$ a change in $L$ of $\Delta L$ causes a shift in $R$ which is always smaller than $\Delta R(\Delta L) < \Delta L$ (i.e. the slope of $R(L)$ is smaller than $-1$). For $L > 0.30$ we enter a region where $\Delta R(\Delta L) \approx \Delta L$ (i.e. slope close
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Figure 5.3.: Dependence of the retardation term $R$ on depolarization factor $L$ and axis length $d$. The legends indicate the average value of the parameter hold constant and the maximum deviation from this value. (a) $R(L)$ for $d = 123 \pm 6$ nm. Some data points for other axis lengths are added (legend). The dashed line represents $R = -L$. (b) $R(d)$ for different $L$-values (legend).

to $-1$). This type of characteristic $L$-value also exists for the other constant axis lengths considered. These findings are important for the interpretation of the dependencies of $\lambda_{\text{Res}}$ in section 6.3.

The overall dependence of the retardation term on axis length is more easily observable by screening data for constant $L$-values. Although the data basis is not sufficient for a clear statement, Fig. 5.3b suggests a linear relation between $R$ and $d$, $R(d) = m(L)d$ in the considered range and for low $L$-values. A linear dependence is also observed if $R$ is plotted against $\frac{d}{\lambda_{\text{Res}}}$, i.e. against the relevant factor in the earlier introduced size parameter $x$ (section 4.4). An extension of the considered range of axes lengths is needed to conclude if a true linear dependence
is observed or if a small part of a non-linear dependence is visualized.

Fig. 5.3 shows that the contribution of retardation to the shape-term $y$ is always negative. In combination with eqn. 4.17 (Fig. 4.2), this motivates the well-known statement that retardation causes a red-shift of the resonance wavelength. In order to get a better feeling for the influence of $R$ and its dependencies on $y$ and therefore on the resonance wavelength, we decompose $y$ into $R$ and $gL$ for all measurements done on cuboids of height $h = 13/20/50$ nm in the following section.

### 5.4. Separation of dynamic and quasi-static depolarization

Thanks to the known depolarization factors for cuboids [111] and the determination of their concavity parameter and retardation term from experimental data using eqn. 4.27 and 4.33, it is possible to decompose the shape-term $y$ for all data points taken on NPs with rectangular footprints in its quasi-static and dynamic part, $gL$ and $R$, respectively. Fig. 5.4 shows the decomposition of the resonance measured along the variable principal in-plane axis in dependence on variable axis length. The $g$-values derived in section 5.2,$^3$ $\epsilon_1(\lambda)$ according to eqn. 4.21, and $\epsilon_m = 1.625$ are used. The error bars are based on the calculated errors in $g$ as well as on errors in $L$, $\epsilon_m$, and $\lambda_{Res}$ of 0.015, 0.325 and 5 nm (see previous sections).

In all configurations of the principal axes $(a, b, h)$, $y$ is dominated by the depolarization factor, and its dependence on axis length follows the trend given by $gL$. This means that a shape-induced change in $L$ is never compensated by the according change in $R$ in such a way that the resulting shift in $y$ does not follow that of $L$.

More generally, four cases can be identified when looking at the interplay between $gL$ (quasi-static part) and $R(d, L)$ (dynamic part) and their dependence on the length of the relevant principal axis:

1. Decreasing $L$ and increasing $|R|$ with increasing axis length.
2. Decreasing $L$ and decreasing $|R|$ with increasing axis length.
3. Increasing $L$ and increasing $|R|$ with increasing axis length.

---

$^3$For a particle height of $h = 13$ nm the $g$-value observed for $h = 20$ nm was used.
Figure 5.4.: Decomposition of the shape-term $y$ in its quasi-static $(gL)$ and dynamic $(R)$ parts for NPs with rectangular footprints. Particle excitation along the variable in-plane axis. $y$, $g$ and $R$ are according to eqn. 4.17, 4.27 and 4.33; depolarization factors are according to [111]; the constant in-plane axis is $b = 123 \pm 6$ nm; particle heights are $h = 50$ nm (a), $h = 20$ nm (b) and $h = 13$ nm (c).
4. Increasing $L$ and decreasing $|R|$ with increasing axis length.

Cases 1 and 2 occur when the relevant axis increases in length and relative to the other principal axes. Additionally, the retardation term $R$ needs to be dominated by $d$ in case 1 and by $L$ in case 2. In both cases, $y$ follows the trend given by $L$, because either $R$ strengthens this trend on $y$ (case 1) or because $\Delta R(\Delta L) < \Delta L$ is valid. According to section 5.3, there may be an upper $L$-limit for the validity of $\Delta R(\Delta L) < \Delta L$. However, in configurations with decreasing $L$ at increasing axis length, this limit will be at higher $L$-values than addressed here. Fig. 5.4a corresponds to case 2 while 5.4b,c tends towards case 1.

Case 3 can be realized when the relevant axis increases and the other principal axes increase in such a way that their relative polarizability decreases. In this configuration, both $L$ and $d$ generate an increase in $|R|$ which makes a $d$-dependence of $y$ against the trend of $L$ in principle possible. As long as such an inversion of the $y$ trend is not present, the remarkable situation of a blue-shifting resonance with increasing axis length can be observed. Screening data for axes configurations with one axis slightly increasing while the other two axes increase significantly, the predicted blue-shift of $\lambda_{\text{Res}}$ and an $y$-value that follows the trend of $L$ in a reduced manner can be only observed (Fig. 5.5). The data points correspond to particles with axes lengths $(a, b, h)$ of $(108, 127, 13), (117, 107, 20), (120, 104, 50), (123, 150, 50)$ and $(124, 173, 50)$ nm. The first number is the length of the axis along which the particle was excited.

In total, case 3 can result in configurations that lead either to a blue-shift on increasing axis length ($L$ dominated $y$) or to a red-shifting resonance with increasing axis length that accompanies an $R$-dominated $y$. The latter is dominant in configurations with a relevant axis high in $L$-value and in length. Its observability can be further increased by measurement points, which are clearly different in $d$.

Finally, we state that case 4 cannot be realized. A decrease in $|R|$ at increasing $L$ and $d$ is not possible according to section 5.3.

Fig. 5.6 shows the decomposition of the resonance excited along the constant in-plane axis of length $b = 123 \pm 6$ nm in dependence on the variable axis. This situation is a special case because the relevant axis is constant. Therefore, retardation is dominated by its $L$ dependence. In agreement with Fig. 5.3a, $R(L)$ shows a decreasing $L$ dependence with decreasing particle height, i.e. when addressing a region of lower
Chapter 5. Concavity, retardation and quasi-static depolarization

$L$-values. Although retardation contributes to $y$ in such a way that it reduces the trend given by $L$, it cannot completely compensate changes in $L$. This is a direct consequence of the $\Delta R(\Delta L) < \Delta L$ statement. However, the higher the $L$-value (long variable axis) the more $\Delta R(\Delta L)$ equals $\Delta L$. This leads to a flattened $y$ with a nearly constant value over a wide range of variable axis lengths.

In total, the decomposition of the shape-term in its quasi-static and dynamic part generates surprising results. So far, the shift of a resonance wavelength triggered by an increasing axis length $d$ is interpreted in terms of $d$ (or volume) -dominated retardation effects. Now, we see strong indications that it is the changing depolarization factor that accounts for the length-dependent shift of $\lambda_{\text{Res}}$ in most cases and that retardation in general in- or decreases the trend given by $L$ only. There is only one kind of axis configuration in which $R$ might dominate $y$. That is when the axis along which the resonance is excited increases in such a way that its aspect ratio decreases relative to the other principal axes.

With these statements on the influence of $gL$ and $R$ on $y$ and the findings of sections 5.2 and 5.3 we created the link between the model presented in section 4 and the experiments. In the next chapter, we use this knowledge to discuss the overall scaling of resonance wavelengths in single metallic NPs in detail.

\textbf{Figure 5.5.} Experimental observation of a blue-shifting resonance (blue curve, right ordinate) at increasing axis length. The contribution of $R$ to the shape-term $y$ is opposite to that of $L$ but it does not dominate $y$. 

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5.4. Separation of dynamic and quasi-static depolarization

Figure 5.6.: Decomposition of the shape-term $y$ in its quasi-static ($gL$) and dynamic ($R$) parts for NPs with rectangular footprints. Particle excitation along the constant in-plane axis, $b = 123 \pm 6$ nm. $y$, $g$ and $R$ are according to eqns. 4.17, 4.27, and 4.33; depolarization factors are according to [111]; particle heights are $h = 50$ nm (a), $h = 20$ nm (b) and $h = 13$ nm (c).
6. Overall scaling behavior

In this chapter, the scattering experiments are extended to NPs with elliptical and diamond-like footprints. The observed dependencies of the in-plane resonances on axis configuration, particle height and shape of the particle footprint are highlighted. The various features are discussed in detail using the findings of chapters 4 and chapter 5. The result is an intuitive understanding of the overall scaling behavior of the plasmon resonance wavelengths in metallic NPs.


## 6.1. Introduction

As mentioned in chapters 4 and 5, the common description of the influence of changing characteristic lengths and changing basic particle shapes (e.g. cuboid vs. cylinder) on resonance wavelengths is incomplete. Analytical formulas and accordingly discussed experiments are only available for ellipsoids and often restricted to the case of constant aspect ratios. Hence, neither the influence of changing particle shape nor the effect of arbitrary changes of the axis configuration are covered in a rigid way. In the chapters 4 and 5, we derived tools needed to bring the description of plasmon resonance wavelengths one step further. In particular, we stated that:

1. In the quasi-static regime, a change in particle shape can be described by generalized depolarization factors.

2. Retardation (dynamic depolarization) depends strongly on the (generalized) depolarization factor.

3. The scaling of the resonance wavelengths is case dependent, but follows in general the trend given by the quasi-static depolarization.

4. Looking at the influence of changing axis configurations on the resonance excited along a principal axis that is hold constant, reveals that the dynamic depolarization tends to compensate the influence of a changing quasi-static depolarization. This statement is especially true for moderate aspect ratios (i.e. a depolarization factor along the constant axis on the order of or higher than 0.2.

In this chapter, we use the gained knowledge to discuss experimentally observed scattering spectra of NPs with rectangular, elliptical and diamond-like footprints and various axis configurations in detail. It arises an intuitive picture of the overall scaling behavior of dipolar resonance wavelengths in dependence of particle shape and size.

Fig. 6.1 shows examples of the studied NPs and the used particle excitation. The scattering experiments are done on NPs with elliptical and diamond-like footprints in addition to the NPs with rectangular footprints (chapter 5). Again, the length of the variable in-plane axis is between 50 and 300 nm while the constant in-plane axis is 123±6 nm in
6.2. Experimental observations

The basic shape of the studied particles of height $h$ is defined by their rectangular (R), elliptical (E) or diamond-like (D) footprints. These footprints are described by the lengths of their principal axes $a$ and $b$.

The optical measurements are restricted to arrays of $5 \times 5$ NPs with comparable $b$-value, $b = 123 \pm 6$ nm. Figs. 6.2 and 6.3 summarize the experimentally observed resonance wavelengths for the different shapes and particle heights. In Fig. 6.2a, SEM images of representative nanoparticles are added for the particles with a height of 20 nm. Fig. 6.2a shows the dependence of the plasmon resonance excited with an electric field vector parallel to the constant $b$-axis on the variable $a$-axis $\lambda_b(a)$. A clear deviation from a nearly constant value as discussed in chapter...
Chapter 6. Overall scaling behavior

Figure 6.2.: Dependence of the resonance wavelengths of nanoparticles with elliptical (E), rectangular (R) and diamond-like (D) footprints on the variable in-plane axis. The second in-plane axis is kept constant, \( b = 123 \pm 6 \) nm. Particle height \( h = 20 \) nm. (a) Excitation along the constant \( b \)-axis. (b) Excitation along the variable \( a \)-axis. The SEM images shown are representatives of the particles in the measured \( 5 \times 5 \) arrays. The white scale bars in the SEM images are 100 nm in length.
3 can be observed for small $a$-values. In Fig. 6.2b, the resonance wavelength of the very same particles but excited along the variable $a$-axis is shown ($\lambda_a(a)$). For small $a$-values, the resonance position no longer depends linearly on $a$. Looking at the influence of a changing footprint, a red-shift of both $\lambda_b(a)$ and $\lambda_a(a)$ is observed for rectangular footprints compared to elliptical and diamond-like footprints. Surprisingly, there is no offset between elliptical and diamond-like footprints.

Fig. 6.3 shows the dependence of the two in-plane resonances for a particle height of 50 nm (Fig. 6.3a and b) and 13 nm (c and d) on the variable $a$-axis. The same overall dependence of the resonance wavelengths as for the $h = 20$ nm case can be observed. Nevertheless, there are some $h$-dependent features. Figs. 6.4b and 6.5b show these dependencies for particles with elliptical footprints in a better way. The $h$ independence observed in chapter 3 for nanoparticles with $h > 75$ nm is no longer valid for particles with $h < 50$ nm. A clear red-shift for decreasing particle height can be observed for both in-plane resonances. In the case of $\lambda_b(a)$, this red-shift is due to an increasing offset for decreasing height from the value for $h > 50$ nm. For $\lambda_a(a)$ it is rather due to an increasing slope than to an offset.

Looking at Figs. 6.2 and 6.3 in detail reveals two additional features. The deviation of a linear $a$-dependence of $\lambda_a(a)$ is better observable for higher NPs, but nearly vanishes for very low particles. Finally, there is a tendency towards an increased slope of $\lambda_a(a)$ for rectangular compared to elliptical and diamond-like footprints. Table 6.1 summarizes all observations on NPs with different footprints, extended length ranges of the variable axis, different (but low) particle heights, and more extreme aspect ratios.

### 6.3. Discussion

The various features of the overall scaling behavior of the resonance wavelengths can be explained with the findings of the previous chapters. One often ignored important aspect is the dependence of the retardation term on the depolarization factor. For a particle excitation along the constant $b$ axis, the according retardation term in dependence on the depolarization factor along the $b$ axis, $R_b(L_b)$ shows two regions with different characters: for $L_b$-values on the order of 0.2 or higher, the slope of $R_b(L_b)$ is close to $-1$. For smaller $L_b$-values, this slope
Figure 6.3.: Dependence of the resonance wavelengths of nanoparticles with rectangular (R), diamond-like (D) and elliptical (E) footprints on the variable in-plane axis. The second in-plane axis is kept constant, $b = 123 \pm 6$ nm. (a),(b) Particle height $h = 50$ nm. (c),(d) Particle height $h = 13$ nm. (a),(c) Excitation along the constant $b$-axis. (b),(d) Excitation along the variable $a$-axis.

goes towards 0. This means that $R_b(L_b)$ compensates for changes in $L_b$ for some axis configurations but not for others. As we will see later, this aspect also helps to explain the observed $h$ dependence. This is because of the equivalence of the situation when $h$ is seen as the variable axis while the particle is excited along an in-plane axis for fixed $(a, b)$ values.
6.3. Discussion

<table>
<thead>
<tr>
<th>Exclusive axis dependence</th>
<th>Constant value of $\lambda_b$ over a wide range of $a, h$-values.</th>
</tr>
</thead>
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<td></td>
<td>Linear dependence of $\lambda_a$ on $a$-axis length over a wide range of $b, h$-values.</td>
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<td>Non-exclusive axis dependence</td>
<td>Deviation from constant value for $\lambda_b(a)$ for small $a$-values.</td>
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<td>Deviation of linear $a$-dependence of $\lambda_a(a)$ for small $a$-values.</td>
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<td></td>
<td>Deviation of linear $a$-dependence of $\lambda_a(a)$ is more pronounced for higher NPs, but almost not observable for very low particles.</td>
</tr>
<tr>
<td>Height influence</td>
<td>Red-shift of $\lambda_b(a)$ and $\lambda_a(a)$ for decreasing $h$.</td>
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<td>Red-shift more pronounced for small particle height.</td>
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<td>Increasing slope of $\lambda_a(a)$ for decreasing $h$.</td>
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<tr>
<td>Influence of footprint</td>
<td>Red-shift of $\lambda_b(a)$ and $\lambda_a(a)$ for rectangular (R) footprint compared to elliptical (E) and diamond-like (D) footprints.</td>
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<td></td>
<td>No offset of $\lambda_b(a)$ and $\lambda_a(a)$ for D compared to E footprints.</td>
</tr>
<tr>
<td></td>
<td>Tendency towards increased slope of $\lambda_a(a)$ for R compared to E/D.</td>
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</tbody>
</table>

Table 6.1.: Summary of the experimentally observed deviations from exclusive axis dependence and quasi-linear scaling as discussed in section 3, due to an extended length range of the variable $a$-axis, different particle heights, and more extreme aspect ratios.

In section 5.4 it was shown that configurations with both changing lengths of the relevant $a$ axis and changing $L_a$ are case-dependent. As long as the scaling of $\lambda_a$ is considered for a fixed particle height, an increase in $a$ goes hand in hand with a decrease in $L_a$ and vice versa. This corresponds to the cases 1 and 2 in section 5.4 and leads to a contribution of the retardation term to $y_a$ that does not change the $a$ dependence given by $L_a$ completely, but might increase the given trend. Therefore, the dependence of the depolarization factor on $a$-axis length is again key to understand the observed scaling behavior.

Once the dependence of the shape-term at resonance on the chosen
Chapter 6. Overall scaling behavior

abscissa (usually the variable $a$-axis) is found and understood, it follows its transformation to the according resonance wavelengths. In fact, the $y(a)$ values for a set of measurements define the $y$-region in $\lambda_{\text{Res}}(y)$ that is read out. Additionally, they contain scaling information for the transition from $a$-abscissa to $y$-abscissa.

6.3.1. Excitation along a constant axis

Fig. 6.4 visualizes the dependencies that are discussed in the following for the example of NPs with elliptical footprints. The shape-term of the resonance excited along the constant in-plane axis ($b$-axis) in dependence on the variable $a$-axis shows a nearly constant value for $a > 100$ nm (Fig. 6.4a). This can be explained by the dependence of the corresponding depolarization factor on $a$, $L_b(a)$ (Fig. 4.1a), and by the discussed onset of compensation of changes in $L$ by $R$ (Fig. 5.3a). For low particle heights, $L_b(a)$ itself is nearly constant while for an increasing particle height $L_b$ increases in both absolute value and in dependence on $a$. The influence of the latter on the shape-term is reduced by the on-setting compensation leading to a nearly constant shape-term. With this, the decreasing $y_b$-value for $a < 100$ nm is also explained. $L_b(a)$ decreases with decreasing $a$ for all particle heights. This reduces the compensation effect and makes the $a$-dependence of $L_b$ visible in $y_b$, including its more pronounced decrease for higher particles.

The decreasing influence of a change in height on the shape-term can be explained accordingly. An increase in height increases $L_b$ and therefore the compensation of the $h$-induced changes in $y_b$ by $R(L_b)$. At a certain particle height, this compensation makes $y_b$ nearly independent of $h$.

The transformation of $y_b$ to the resonance wavelength, $\lambda_{\text{Res}}$, is straightforward. According to Fig. 4.2a, lower $y$-values result in higher resonance wavelengths. Additionally, the slope of $\lambda_{\text{Res}}(y)$ increases for decreasing $y$. This explains why the observed overall red-shift at lower $a$-values is of the same order for all three particle heights although the decrease in $y_b$ is less pronounced for lower particles. In addition, the data points for low particles scatter more, because the resonance wavelengths get more sensitive on changes in $y$, e.g. by production-based shape variations.
Figure 6.4.: Influence of the variable in-plane axis on the shape-term $y$ (a) and on the resonance wavelength (b) for particles with elliptical footprints excited along the constant in-plane axis, $b = 123 \pm 6$ nm. Four different particle heights are shown, $h = 13, 20, 50$ and $110$ nm.

6.3.2. Excitation along a variable axis

Only one argument needs to be added in order to discuss a particle excitation along the variable $a$-axis (Fig. 6.5). It is the additional dependence of the retardation term on $a$. As pointed out in the discussion of Fig. 5.3, this dependence leads to a reduced compensation of the $a$-driven influence of $L_a$ on $y_a$. Therefore, $R_a(L_a, a)$ does not completely compensate changes in $L_a$ and $y_a$ follows the trend given by $L_a(a)$ (Fig. 4.1b) for all addressed $a$-values. In combination with the still valid arguments for the decreasing height influence, the characteristic curves for $y_a(a)$ are obtained (Fig. 6.5a).

The transformation of the shape-term values to the corresponding resonance wavelengths is straightforward again. Particles of lower...
Figure 6.5.: Influence of the variable in-plane axis on the shape-term $y$ (a) and on the resonance wavelength (b) for particles with elliptical footprints excited along the variable in-plane axis, $b = 123 \pm 6$ nm. Four different particle heights are shown, $h = 13, 20, 50$ and $110$ nm.

height cover a range of lower $y_a$-values resulting in the reading-out of red-shifted wavelengths in the steep, nearly linear part of $\lambda_{\text{Res}}(y)$ while higher particles address the rounding towards a constant value (Fig. 4.2a). The result is a seemingly reduced slope and a deviation from linear behavior for higher particles.

Finally, we state that there are no $y_{a,b}$-values larger than 0.2 for the axis configurations chosen. This means that we do not leave the region of correct description of $\epsilon_1(\lambda)$ by eqn. 4.21 and that the assumption of negligible damping is also correct.
6.3.3. Linear and exclusive scaling

As shown in chapter 3, it is possible to find axis configurations that lead to an exclusive linear scaling of the dipolar resonance with the according principal axis. This observation can now be explained in a better way. Exclusive scaling means that $\lambda_{\text{Res}}$ excited along an axis of constant length does not shift due to length changes of the other two principal axes. This is guaranteed if the relevant axis is not significantly smaller than the other two axes. If at least one of the other principal axes is much smaller than the relevant axis, the depolarization factor is in a range where it is insensitive to changes in the axis configuration. If all axes are of the same size, the depolarization factor is around $\frac{1}{3}$ and changes in $L$ are compensated by changes in $R(L)$.

In order to observe a linear scaling of $\lambda_{\text{Res}}$ with the length of the axis along which the resonance is excited, a decrease in $y$ with increasing axis length is needed. This is guaranteed if the relevant axis does not only increase in length but also relative to the other two principal axes. Addressing a restricted range of $y$-values does also help to observe a quasi-linear scaling. Further, it is advantageous if the retardation term is dominated, or at least influenced, by the axis length. This helps to address the favorable region of low $y$-values. The longer the relevant axis is, the more this is the case.

If exclusive and linear scaling should be observed for all three principal axes, moderate aspect ratios and axis lengths that are influenced by retardation are needed. This is in full agreement with the discussion of chapter 3. However, the meaning of retardation has changed. It is now seen as an element that guarantees exclusive scaling by compensating changes in the quasi-static depolarization for a particle excitation along an axis of constant length. It does also not trigger the linear scaling observed for a particle excitation along an axis that changes in length, but does only increase the trend given by the quasi-static depolarization.

6.3.4. Influence of basic particle shape

Finally, we turn to the influence of a change in the basic particle shape. Such changes were realized by producing NPs with different footprints. With respect to the derived model, the estimated values of the concavity parameter (section 5.2) need to be considered now. Based on
experimental data, values for the in-plane resonances of particles with diamond-like and rectangular footprint of 0.87 and 0.94 were estimated and it was reasoned that $g \approx 1$ holds for particles excited along their elliptical footprints. Fig. 6.6 shows the resulting generalized depolarization factors, $gL$, in comparison to the standard depolarization factors for the three studied footprints.\textsuperscript{1} The effect of a changing footprint at constant length of the principal axes is twofold. First, the polarizability along the addressed axis changes relative to the other principal axes. This is expressed by the standard depolarization factors $L$ (empty symbols in Fig. 6.6). Second, the charge distribution and interaction between charges change. The influence of these changes on the resonance wavelength is considered by the concavity parameter $g$ and leads to the generalized depolarization factors $gL$ (filled symbols in Fig. 6.6).

Comparing $L_R$ and $L_E$ shows that the depolarization of a cuboid along its in-plane axes is less pronounced compared to its out-of-plane depolarization as it is the case for a cylinder with elliptical footprints but identical lengths of the principal axes, $L_R < L_E$. Additionally, $g_R$ is smaller than $g_E$, meaning that the in-plane dipolar modes in particles with rectangular footprints are lower in energy compared to those in particles with elliptical footprints. Due to the additive character of the two effects caused by a change from elliptical to rectangular footprints, a well pronounced red-shift of the resonances observed for particles with rectangular footprints results.

The situation is different for particles with diamond-like footprints. For diamond-like footprints, the in-plane depolarization compared to the out-of-plane depolarization is more pronounced as it is the case for particles with elliptical footprints, $L_D > L_E$. Again, $g_D$ is smaller than $g_E$. In combination, a change in footprint from elliptical to diamond-like leads to a decrease in resonance energy caused by the changing surface charge mode which is compensated by the higher relative depolarization of the in-plane resonances caused by this change. Thus, it is possible to observe resonance wavelengths that coincide for certain axis configurations, as it happens for the experimentally addressed configurations.

The explanation of the observed tendency of an increased slope of $\lambda_a(a)$ for R-shaped compared to E/D-shaped particles is once again

\textsuperscript{1}For $h = 10$ and 20 nm the $g$-value determined for $h = 20$ nm is used. For $h = 50$, 100, and 110 nm the value determined for $h = 50$ nm is used.
straightforward. \( \lambda_D = \lambda_E \) indicates identical addressed \( y \) regions in \( \lambda(y) \). Therefore their slopes do not differ. However, \( \lambda_R > \lambda_{D,E} \) means a range of lower \( y \)-values and thus a higher slope.

With the discussion of the experimentally observed scaling behavior of the two in-plane resonances in dependence of axis configuration and particle footprint, we conclude the chapters concerning resonance wavelengths in single NPs. In the next chapter, we turn our attention to a nanoantenna consisting of two stacked nanodisks, i.e. to a coupled plasmonic system.

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**Figure 6.6.** Generalized (filled symbols) and standard (empty symbols) in-plane depolarization factors in dependence of particle height and particle footprint. The length of the in-plane principal axes is \( a = b = 125 \text{ nm} \). (a) Absolute values. (b) Values relative to the case of a circular footprint.
7. Nanoantenna: two stacked Au-disks

The coupling of an emitter to a localized surface plasmon resonance has the potential to influence its photoluminescence in a beneficial way. In this chapter, we study a nanoantenna consisting of two stacked Au disks with the aim to produce an efficient nanoemitter by the incorporation of Si-QDs in the gap between the two disks. FEM-based simulations are performed to characterize the nanoantenna and to identify promising antenna configurations. A first series of produced nanoemitters show antenna resonances at the aimed wavelengths and a strong PL-signal that couples to these resonances - but no Si-QD signal. Reasons for this outcome are discussed and ways to improve the approach chosen are summarized.
7.1. Introduction

In the past decade, much work has been done towards direct observation of metallic nanostructure-mediated PL-intensity enhancement [129]-[134] and the study of PL lifetime modifications [129][132][135]-[139]. Most studies use dyes as the fluorescent material. However, dyes have a limited potential in applications that use an optical excitation due to their poor stability based on non-reversible photo-induced degradation (chemical bleaching). Therefore, Si-QDs have been proposed and used as promising alternatives. Si-QDs show no chemical bleaching up to high excitation intensities and their PL spectra can be tuned over the visible and NIR wavelength range thanks to their size-dependent band gap [140]-[142].

In most applications, an ensemble of Si-QDs is used. Such an ensemble contains three different kinds of QDs in terms of their PL properties. Depending on the production process, 80 − 99% of the QDs are permanently dark while the few bright ones show quantum efficiencies higher than 50% [143]-[148]. In the permanently dark QDs, an excessive concentration of defect states makes non-radiative recombination channels completely dominate the slow, phonon-assisted radiative decay channel. The latter has a decay rate of only $10^3 \text{s}^{-1}$ to $10^5 \text{s}^{-1}$ [143][149]-[151]. The QDs showing PL are either in a neutral (bright) or charged (dark) state. In the charged state, Auger relaxation [152][153] with a decay rate on the order of $10^9$ − $10^{10} \text{s}^{-1}$ is responsible for quenching of the emission [154][155]. The switching of a Si-QD between a neutral and a charged state leads to the well-known phenomena of blinking (emission intermittency) and the resulting physical (i.e. reversible) bleaching.

The existence of three different kinds of Si-QDs in terms of their PL-activity gives rise to three possibilities to increase the PL intensity of a Si-QD ensemble by coupling it to a metallic nanoantenna. First, the radiative decay rate may be increased by the coupling to a faster radiative decay channel over the antenna. Second, physical bleaching may be suppressed if the radiative channel over the antenna can compete with Auger relaxation. Third, otherwise permanently dark QDs may become bright if the decay over the antenna is faster than any defect-assisted recombination. Which of these possibilities can be implemented depends on the emitter-antenna transition rate, the emitter-antenna coupling probability [8][9] and the radiative decay rate of localized surface plas-
7.1. Introduction

Figure 7.1.: Examples of produced nanoantennas. (a) Target height of bottom and top disk of $h_B = h_T = 60$ nm, SiO$_2$-filled gap of $g = 20$ nm. (b,c) Target heights of $h_B = 60$ nm, $h_T = 40$ nm, and $g = 10$ nm. The white scale bars are 500 nm in length.

It is known that the radiative and non-radiative decay of localized surface plasmons is very fast, having rates on the order of $10^{14}$ s$^{-1}$ [104][107][156]. Concerning the transition rate, Shimizu et al. [135] and Ratcford et al. [136] observed the disappearance of blinking in CdSe(ZnS) quantum dots in the vicinity of a rough Au surface and a single Au nanoparticle, respectively. This shows that an energy transfer rate of $\geq 10^{10}$ s$^{-1}$ can be achieved. In consequence, it seems possible to produce Si-QD/metal nanoemitters in which the PL-intensity of the Si-QDs is potentially enhanced by a factor on the order of $10^5$ and not affected by physical bleaching! The latter leads to an emission that is constant in intensity for a constant excitation intensity, a point that is very important for any application. If the decay over the nanoantenna may even be fast enough to turn some of the permanently dark QDs to bright ones cannot be estimated at the moment.

There are different parameters that describe the emitter-antenna coupling probability. The most important parameters that need to be optimized in order to profit from antenna-mediated luminescence are: distance and relative position of the emitter with respect to the metallic structure, orientation of the emitter transition dipole, and absorption and scattering cross-section of the antenna at the excitation and emission wavelength of the emitter, $\lambda_{ex,em}$. The influence of distance [10][129][136][157]-[162] and emitter orientation [129][158][163][164] has been discussed intensively in literature.

In the following, we study the case of a nanoantenna consisting of two stacked Au disks (Fig. 7.1). This antenna design has been chosen due to the expected improved performance of a system consist-
Chapter 7. Nanoantenna: two stacked Au-disks

...ing of coupled metallic NPs (e.g. dimers) [161][165]-[168] compared to monomers, easier positioning of the Si-QDs, and finer tuning of distances and heights thanks to the stacked approach. The latter leads to a better control over the critical parameter of emitter-antenna separation. Such a design makes only sense, if the resonances excited along the antenna axis can also be addressed, i.e. if the antenna can be excited axis-selectively - a task that was already solved during this thesis. The results presented in the following are a first step towards the realization of a nanoemitter that has neither chemical nor physical bleaching, profits from metal-enhanced fluorescence, and has a widely tunable emission wavelength.

FEM-based simulations have been performed first in order to identify the relevant antenna resonances and the dependence of their resonance wavelengths on various antenna design parameters. Focus was laid on the situation within the gap between the disks defining the antenna. The simulations in combination with the mentioned parameters for emitter-antenna coupling led to different promising configurations. Some of them were realized in a first series of nanoemitters containing 1 – 2 monolayer of Si-QDs. However, the optical characterization of the fabricated nanoemitters do not show a signal from the Si-QDs. Possible reasons, such as the appearance of a strong background signal that couples to the antenna resonances and reasons for insufficient antenna performance, are specified and discussed.

7.2. Numerical simulations

The main goals of the following FEM-based numerical simulations [116] [117] on the nanoantenna without incorporated Si-QDs are the identification of the relevant antenna resonances and the visualization of their intensity distributions within the gap. The former is important to guarantee a spectral overlap of the Si-QD excitation and emission with appropriate antenna resonances. The latter allows to estimate the influence of the Si-QD position within the gap on the near- to far-field conversion over the antenna (reciprocity theorem). In addition, the influence of the main antenna parameters (gap, disk height) and of production-based variations (round corners, antenna diminution) are estimated. Other potentially important production-based deviations from perfect geometry, such as surface roughness and adhesion layers,
7.2. Numerical simulations

are ignored.

The experiments on nanoantennas with incorporated Si-QDs (section 7.3) aim for an excitation at $\lambda_{\text{ex}} = 633$ nm. Measurements on Si-QDs on bare substrate (Appendix A) show that they are sufficiently excited at this wavelength and that they emit between 660 and 735 nm. This makes the wavelength range between 600 and 750 nm of special interest in the following simulations.

Fig. 7.2 visualizes the basic antenna design. The main parameters are: gap ($g$) and gap refractive index ($n$, wavelength-independent, no absorption), corner radius ($r$), diminution angle ($\alpha$), and height of the bottom and top disk ($h_{B,T}$). The bottom diameter of the antenna is kept constant at $d = 140$ nm. The discussion is restricted to an antenna excitation parallel to its axis if not otherwise stated. For most simulations, the top and bottom disk are of identical height, $h_T = h_B = 60$ nm. A substrate given by its refractive index of 1.5 is always considered. Table 7.1 on page 121 summarizes the outcome of the made simulations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_2.png}
\caption{(a) Scheme of the calculated antenna design and the used parameters. (b) Example of concrete realization using JCMgeo (part of the computational domain only). The points along the antenna gap at which the field intensity is determined are added.}
\end{figure}
7.2.1. Implementation

The simulations were conducted with JCMsuite (JCMwave GmbH, Berlin) using measured bulk material data taken from [119]. The easy linking of JCMsuite to Matlab routines was used to perform systematic studies of the influence of changing antenna parameters.

The antenna shows a rotational axis along the antenna axis. This allows to use one of the great capabilities of JCMsuite: the computation of a 3D scattering problem with rotational symmetry as a sequence of 2D problems. In consequence, the computational domain contains only half of the antenna cross-section (Fig. 7.2). It is important to note that the incident field is exempt from the symmetry condition. Briefly [169], the 3D to 2D transformation is done by the decomposition of the incident electric field in Fourier modes with respect to the polar angle (i.e. the angle the geometry does not depend on). Using this decomposition in the Maxwell’s equations written in cylinder coordinates leads to independent equations for the different Fourier modes that do not depend on the polar angle. The result is a 2D problem that needs to be computed for each Fourier mode separately until the incoming mode becomes sufficiently small.

In the simulations, the antenna is excited by a plane wave from the air side of the antenna. In the written Matlab routine, 15 points are defined along the center of the antenna gap at which the electric field intensity is read out (Fig. 7.2b). The following statements concerning resonance wavelength, intensity distribution and enhancement factor are based on the calculated intensity at these.

7.2.2. Expected resonances

The studied problem shows full rotational symmetry (i.e. including the incident electric field) if the antenna is excited by a plane wave polarized along the antenna axis. In this case, the surface charge distributions of the excited modes are also rotationally symmetrical with respect to the antenna axis and the resulting dipole moment of both the individual disks and the antenna is parallel to the antenna axis. As it is well-known from the study of cubes [87][92][93] and disks [170], bodies of high symmetry that have two planes with normals parallel to the applied electric field show different modes of dipolar character. These modes differ in the surface charge distribution over these planes, but all of
them have a zero net dipole moment along the planes. The dipolar character of the modes bases on the surface charge distribution along the axis parallel to the excitation.

With respect to the later incorporation of Si-QDs, the intensity distributions of the different modes within the gap are of main interest. Fig. 7.3 visualizes these distributions by showing the intensity enhancement factor\(^1\) at seven points on the gap’s center axis (distances from the rotation axis: 5, 10, 20, 30, 40, 50, 60 and 70 nm, Fig. 7.2b) and eight points on its continuation outside the antenna (distances from the rotation axis: 75, 80, 90, 100, 120, 145 and 170 nm). The simulations are conducted on an antenna given by \(d = 140\) nm, \(h_T = h_B = 60\) nm and gap filling of \(n = 1.5\). It is further assumed that the antenna shows no diminution and that no corner rounding is present (\(\alpha = 0^\circ, r = 0\) nm).

The calculated intensity distributions within the gap follow the simple geometrical condition of standing waves. The relevant boundary is the end of the gap at \(\pm 70\) nm from the rotation axis and the boundary condition demands a maximum in intensity at these points. It follows that the number of minima within the whole gap (i.e. from \(-70\) nm to \(+70\) nm according to Fig. 7.3) starts at one and increases by one from a mode to the next. Therefore we call these resonances \(D1-D4\) in the following. The "\(D\)" indicates the dipolar character of the modes. This notation is in agreement with the one often used for cubes. The insets of Fig. 7.3 visualize roughly the surface charge distribution on the planes defining the gap as they are expected from the calculated intensity distributions. Only the cases where the dipole moment of the top and bottom disk are in phase are shown. An antenna consisting of two disks with dipole moments in opposite directions has no net dipole moment. Hence, it cannot be excited by a plane wave that is polarized parallel to the antenna axis (dark modes). The shown surface charge distributions lead to an electric field in the gap that is dominated by its component along the antenna axis. This is another important aspect in the emitter-antenna coupling because the direction of the electric field defines the average orientation of the dipole moment of the emitters. We will come back to this point in section 7.2.4.

Although an antenna excited along its axis shows a variety of dipolar resonances, it is worth to discuss briefly an antenna excitation perpen-

\(^1\)Field intensity relative to the intensity of the excitation field.
Figure 7.3.: Calculated intensity enhancement factor at resonance along the axis through the center of the gap. Schematics of the expected surface charge distribution on the planes defining the antenna gap are added. The disk separation at which the enhancement factors are calculated is given in the legends. A gap refractive index of $n = 1.5$ is assumed. (a) $D_1$ mode, $g = 5/10/15/20$, and 30 nm. (b) $D_2$ mode, $g = 2/5/10$, and 15 nm. (c) $D_3$ mode, $g = 2$ nm. (d) $D_4$ mode, $g = 2$ nm.

dicular to its axis. This may help to find configurations that guarantee both emission and excitation resonant to an antenna mode. The latter prevents the Si-QDs from being shielded by the disks. Fig. 7.4 shows the calculated enhancement factors of the observed resonances at their resonance wavelengths. The antenna parameters used are: $d = 140$ nm, $h_T = h_B = 60$ nm, $g = 5$ nm, $n = 1.5$, $r = 10$ nm, and $\alpha = 10^\circ$. The antenna is excited from the air side by a plane wave that is polarized perpendicular to the antenna axis. In agreement with [171], two modes of dipolar character are observed: The electric dipolar mode, $D_e$, observed at 630 nm and the magnetic dipolar mode, $D_m$, at 1060 nm. The dipole moment of the disks is along the polarization of the incident wave.

\[\text{The electric and magnetic dipolar modes are also called symmetric and antisymmetric dipolar, respectively.}\]
7.2. Numerical simulations

wave and parallel ($D_e$) or anti-parallel ($D_m$) to each other. The latter can be excited due to the lateral extension of the antenna (i.e. the height of the disks and the gap) and the resulting phase difference in the excitation of the two disks. The insets of Fig. 7.4 visualize roughly the expected surface charge distributions on the planes defining the gap.

For comparison, the corresponding enhancement factors for $D1$ and $D2$ at their resonance wavelengths are added in Fig. 7.4. Surprisingly, $D_m$ shows the same intensity distribution as $D1$ but with around two times higher absolute values. The $D_e$ mode shows an intensity enhancement along the gap that is comparable to the $D2$ mode, except in the region around the center of the antenna.

A detailed study of two stacked Au disks excited perpendicular to their axis can be found in [171]. For the continuation of the antenna realization, three statements are of importance: First, an antenna excitation perpendicular to its axis also leads to field enhancement along the gap. It is expected that this field enhancement moves faster to the value observed for a single disk with increasing gap than in the case of modes excited by an electric field along the antenna axis. Second, the resonance wavelengths can easily be tuned by varying the diameter of the antenna. Third, the $D_m$ and in reduced manner the $D_e$ mode lead to an electric field in the gap that is along the antenna axis.

Due to the chosen sample layout with widely varying antenna diameters, $D_m$ and $D_e$ will appear in the considered wavelength range.

![Figure 7.4](image-url) Intensity enhancement along the gap for an antenna excitation perpendicular to the antenna axis. (a) $D_m$ mode. (b) $D_e$ mode. For comparison, the calculated intensity enhancement for $D1$ and $D2$ are added. Antenna parameters: $d = 140$ nm, $g = 5$ nm, $n = 1.5$, $r = 10$ nm, $\alpha = 10^\circ$. 

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The appearance of the antenna modes excited along the antenna axis depends strongly on the antenna gap. We will have a look at this gap dependence of the $D1-D4$ modes before the most promising mode configurations are discussed in section 7.2.4.

### 7.2.3. Gap dependence of plasmon resonances

As well known from literature [172]-[180], the gap is one of the most important parameters when studying coupled NPs. A series of calculations in which the gap properties are tuned in a systematic way are conducted in order to discuss the dependence of the antenna resonances on the gap. The chosen basic antenna geometry is given by $d = 140$ nm and $h_T = h_B = 60$ nm. The antenna is excited along its axis. It is further assumed that the antenna shows no diminution and that no corner rounding is present ($\alpha = 0^\circ$, $r = 0$ nm). Different gap fillings are considered by using a wavelength-independent material of refractive index $n = 1.25$ and $n = 1.5$.

Fig. 7.5 summarizes the outcome of these simulations. The modes $D1-D4$ are expected in the considered wavelength range between $550-950$ nm. However, only $D1$ and $D2$ appear at gaps that result from the incorporation of emitters. As expected, $D1$ and $D2$ shift blue with increasing disk separation for an antenna excitation along its axis (Fig. 7.5a,b). For the $D1$ mode it is also shown that its resonance wavelength coincide with the resonance wavelength of a single disk for large disk separations (i.e. no coupling). In Fig. 7.5a the resonance position for a single disk without cladding is shown as a single point at the gap $= 60$ nm position.

Red-shifting resonances for increasing gap refractive index at a fixed particle separation is also confirmed. As shown for $D1$, the sensitivity of the resonance wavelength on gap refractive index depends strongly on particle separation (Fig. 7.5c). This behavior is of relevance for antenna realization due to the later incorporation of $1-2$ monolayers of Si-QDs into the spacer material. For a gap of $g = 20$ nm a sensitivity of around $290$ nm/RIU is expected. This value increases to $460$ nm/RIU for $g = 10$ nm and to $630$ nm/RIU for $g = 5$ nm.

In sum, $D1$ and $D2$ are expected for the chosen antenna design in the visible wavelength range besides $D_m$ and $D_e$. The question is now which mode configurations leads to the most promising interaction of emitters (Si-QDs) and antenna.
7.2. Numerical simulations

**Figure 7.5.** Calculated dependencies of antenna resonances on disk separation (gap). (a) Influence of gap and refractive index of spacer material on the resonance wavelength of $D_1$. (b) Calculated resonance wavelengths of $D_2-D_4$. (c) Sensitivity of the resonance wavelength of $D_1$ on gap refractive index in nm/RIU.
7.2.4. Promising antenna configurations

Different aspects are of importance in order to realize an efficient nanoemitter based on the chosen design. Looking on the excitation of the emitters placed in the antenna gap, a good spectral overlap of the chosen excitation wavelength, $\lambda_{ex}$, with an appropriate antenna mode is needed. On emission side, the situation is more complex. Besides a spectral overlap of the wavelength range of emission, $\lambda_{em}$, with an antenna mode, the average orientation of the emitter dipole moments relative to the dipole moment of the antenna is of importance. The more efficient excitation of dipole moments parallel to the direction of the exciting electric field leads to an average orientation that is basically along the exciting field. In the case of emitters with no predefined orientation, their average orientation is exactly according to the excitation field. For the antenna modes at hand, this is mainly along the antenna axis (except for $D_e$). Therefore, an efficient nanoemitter can only be realized if the emission is coupled to $D_1$ or $D_2$. Further, the excited emitters should be at positions that guarantees a good near-to far-field coupling. Such positions can be found by studying the intensity distribution around the nanoantenna. Based on Fig. 7.3, it can be expected that $D_1$ and $D_2$ show good near-to far-field conversion as long as the whole gap is filled with emitters. Finally, the positions promising good near-to far-field coupling should also show good far-to near-field conversion on excitation side in order to guarantee sufficient excitation of the most relevant emitters. This means, that complementary intensity distributions for excitation and emission should be avoided.

Assuming that all four antenna modes ($D_1$, $D_2$, $D_e$ and $D_m$) can be tuned to both $\lambda_{ex}$ and $\lambda_{em}$ over the various design parameters (e.g. diameter, gap and its refractive index, disk heights) leads to the following four very promising mode configurations:

1. Emitter excitation via $D_m$ and emission via $D_1$.

2. Emitter excitation via $D_2$ and emission via $D_1$. Here, the complementary intensity distribution will decrease the antenna performance.\(^3\)

\(^3\)Emitter excitation via $D_1$ and emission via $D_2$ cannot be realized due to $\lambda_{D_1} > \lambda_{D_2}$. 

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3. Emitter excitation and emission via \( D1 \). This is an easy to realize and promising approach if an excitation wavelength close to the emission region of the emitter is chosen (i.e. within FWHM of the antenna mode).

4. Emitter excitation and emission via \( D2 \). The motivation for such a mode configuration is the same as before.

These four mode configurations have in principle the potential to result in an efficient nanoemitter. As mentioned, there are other important parameters that need to be considered, mainly the distance between emitter and Au disks and the exact position of \( \lambda_{\text{ex}} \) and \( \lambda_{\text{em}} \) relative to the resonance wavelength of the chosen antenna modes.

7.2.5. Corner radius and diminution angle

Due to the importance of \( D1 \) and \( D2 \) on the emission of the nanoemitter, we conducted simulations in order to estimate the influence of production-based variations. The most prominent differences between the idealized basic antenna design and the produced antenna are rounded edges and antenna diminution. Rounded edges are taken into account by the introduction of a corner radius \( r \). Antenna diminution is taken into account with a diminution angle \( \alpha \), which is defined by the angle between the substrate normal and the antenna side (Fig. 7.2). The calculations are performed on a nanoantenna with diameter \( d = 140 \) nm, disk heights \( h_T = h_B = 60 \) nm, gap \( g = 5 \) nm, and gap refractive index \( n = 1.5 \). Based on SEM measurements of produced antennas, a diminution angle of \( 10 - 15^\circ \) and a corner radius between \( 10 - 15 \) nm is expected. The calculations aiming for an estimation of the influence of corner radius are performed at \( \alpha = 10^\circ \). The influence of the diminution angle is studied for a corner radius fixed at \( r = 10 \) nm.

The simulations show a significant influence of the corner radius on the resonance wavelength (Fig. 7.6a). In the case of \( D1 \), an increase in the corner radius by 1 nm blue-shifts the resonance by 11 nm. The \( D2 \) mode is less sensitive to the corner radius. A shift of \(-4 \) nm in resonance wavelength per 1 nm increase in corner radius is expected. These statements are true over the whole range of radii considered, \( r \in [2.5, 20] \) nm. The influence of the corner radius on the intensity enhancement and on the intensity distribution is less pronounced (Fig. 7.6b). With increasing corner radius the intensity maxima at the edge
Figure 7.6.: Influence of corner radius on resonance wavelength and intensity enhancement. Antenna parameters: \(d = 140\ \text{nm}, \ h_T = h_B = 60\ \text{nm},\ \ g = 5\ \text{nm},\ \ n = 1.5,\ \ \alpha = 10^\circ.\) (a) The resonance wavelength of both \(D_1\) and \(D_2\) shift linearly with corner radius (slope of \(-11\) and \(-4\)). (b) Dependence of intensity enhancement on position along the gap for \(r = 2.5\ \text{nm}\) and \(r = 20\ \text{nm}.

of the gap shifts towards the center of the antenna while the enhancement factor only changes slightly.

The influence of the diminution angle on the resonance wavelength is even more pronounced (Fig. 7.7a). A linear dependence of the resonance wavelength for \(D_1\) and \(D_2\) is observed in the considered range of \(\alpha \in [0^\circ, 20^\circ]\). The slopes are \(-18\ \frac{\text{nm}}{\text{deg}}\) and \(-7\ \frac{\text{nm}}{\text{deg}}\), respectively. In contrast to the case of corner rounding, there is a significant influence of the antenna diminution on the intensity enhancement factor along the gap (Fig. 7.7b). Besides an overall shift of the maxima towards the center of the antenna, the maximum enhancement factor is reduced by
7.2. Numerical simulations

Figure 7.7.: Influence of antenna diminution on resonance wavelength and intensity enhancement. Antenna parameters: $d = 140$ nm, $h_T = h_B = 60$ nm, $g = 5$ nm, $n = 1.5$, $r = 10$ nm. (a) The resonance wavelength of both $D_1$ and $D_2$ shift linearly with diminution angle (slope of $-18\ \text{nm/deg}$ and $-7\ \text{nm/deg}$). (b) Dependence of intensity enhancement on the position along the gap for $\alpha = 0^\circ$ and $\alpha = 2^\circ$.

10% in the case of $D_1$ and by 35% in the case of $D_2$. Additionally, $D_2$ nearly loses its maximum at the edge of the antenna, while the maximum in the center becomes more localized.

7.2.6. Disk height

A few simulations for a geometry close to the expected experimental situation were performed in order to estimate the influence of varying disk height on the plasmon wavelength. The chosen antenna parameters are $d = 140$ nm, $g = 15$ nm, $n = 1.5$, $r = 10$ nm, and $\alpha = 10^\circ$. Four different disk-height configurations were simulated. In three of them,
Figure 7.8.: Influence of disk height on plasmon resonance position and intensity enhancement. Antenna parameters: \( d = 140 \) nm, \( g = 15 \) nm, \( n = 1.5 \), \( r = 10 \) nm, \( \alpha = 10^\circ \). The plasmon resonance position of \( D1 \) is only slightly influenced by changing disk heights.

...the top and bottom disk are of the same height \( h_T = h_B = 50 \) nm, 55 nm, and 60 nm. In one configuration the height of the top disk was reduced to \( h_T = 40 \) nm while \( h_B = 60 \) nm stayed unchanged. Both resonance wavelength and maximum intensity enhancement within the gap show surprisingly low dependence on disk height for the observed \( D1 \) mode (Fig. 7.8).

7.3. Experimental results

In the following, the experimentally observed optical properties of a first sample containing nanoantennas with and without Si-QDs are discussed. Fig. 7.1 showed examples of how the experimental realization of the chosen antenna design looks like. The studied complete antennas consist of two stacked gold nanodisks and \( 1 - 2 \) monolayers of Si-QDs incorporated in the gap between the disks. There are no other Si-QDs around the antenna. A 5 nm thick \( SiO_2 \) spacer layer is used on both sides of the Si-QDs in order to separate them from the Au disks and to avoid quenching. The antennas are arranged in blocks over the sample (section 2.3.2). Within a block, the antennas are identical while...
7.3. Experimental results

their diameters change in steps from one block to another. The chosen sample layout leads to identical antennas at different positions within the Si-QD deposit (differently sized Si-QDs due to size-selective deposition) and outside the deposit (section 2.3.2). The height of the upper disk was reduced to $h_T = 40 \text{ nm}$ in order to avoid an overfill of the PMMA patterns due to variations in the Si-QD layer thickness. The lower disk was $h_B = 60 \text{ nm}$. No negative impact on intensity distribution and intensity enhancement is expected based on simulations.

We start the discussion of the properties of the nanoemitter by looking at its plasmonic modes in dependence on the antenna diameter $d$ (Fig. 7.9). As expected, two resonances, the $D_m$ and $D_e$ mode, can be observed if the antenna is excited by an electric field perpendicular to its axis (Fig. 7.9a). These two resonances depend strongly on $d$ and they become difficult to separate for low antenna diameters. In the case of an excitation parallel to the antenna axis two additional resonances become observable (Fig. 7.9b). This is as expected from the simulations which predicted the appearance of the $D_1$ and $D_2$ mode in the considered wavelength range. The resonance wavelengths of these modes depend only slightly on $d$ while the amplitude of $D_1$ decreases relative to the one of $D_2$. In sum, the scattering spectra show the expected resonances.

In these first experiments on the complete nanoemitter, we aimed for an excitation of the Si-QDs at $\lambda_{\text{ex}} = 633 \text{ nm}$. The Si-QDs emit between $660 \text{ nm}$ and $735 \text{ nm}$ depending on their diameter (Appendix A). Fig. 7.9c,d shows the position of the antenna resonances relative to $\lambda_{\text{ex}}$ and $\lambda_{\text{em}}$ in a better way. The error bars indicate the FWHM of the resonances as they result from fitting of the scattering spectra with Lorentzian curves. Different configurations that lead to both resonant excitation and emission are observed. Looking at the most promising configurations discussed in section 7.2.4, we state that an excitation via $D_2$ and an emission coupled to $D_1$ is realized for all antenna diameters (Fig. 7.9d). The antenna diameter allows to tune $D_2$ from partly resonant with the excitation to truly resonant. The difference between $\lambda_{\text{ex}}$ and the $D_2$ resonance wavelength decreases from $+31 \text{ nm}$ to $-3 \text{ nm}$ with increasing diameter. The best results in terms of nanoemitter performance can be expected for $d = 190 \text{ nm}$ and Si-QDs that emit around $735 \text{ nm}$. In this case, Fig. 7.9b shows that a good coupling of the $D_1$ mode to the far-field can be expected.

Another promising configuration that is realized is the excitation
and emission coupled to $D_2$. Especially antennas with diameters of $d = 190 \text{ nm}$ and $d = 155 \text{ nm}$ in configuration with Si-QDs emitting around $660 \text{ nm}$ should be studied.

Further, Fig. 7.9c shows that the $D_e$ mode will have a beneficial influence on Si-QD excitation for $d = 110 \text{ nm}$, $125 \text{ nm}$ and $155 \text{ nm}$ as long as the exciting electric field has a non-zero component perpendicular to the antenna axis (e.g. excitation by a beam focused on the antenna). However, an excitation via $D_m$ cannot be established by the realized antennas. In consequence, the configuration with an excitation...
via \( D_m \) and an emission coupled to \( D1 \) is not realized with this first set of nanoantennas. In addition, \( D1 \) is too high in wavelength to observe emission and excitation coupled to it at the same time.

In sum, the four antenna resonances \( D_e, D_m, D1 \) and \( D2 \) are in the region of \( \lambda_{ex} \) and \( \lambda_{em} \). Among the various mode configurations, there are two that are expected to lead to a good excitation of the Si-QDs and a good near- to far-field conversion over an antenna mode according to section 7.2.4. Hence, it is very unlikely that the missing observation of a Si-QD signal discussed in the following originates from unsuitable wavelengths of the antenna resonances.

Two different measurement configurations were probed to generate a Si-QD signal originating from the antenna. Axis-selective excitation using an He-Ne laser did not lead to measurable PL-signals. In order to increase the excitation intensity, a configuration with the antenna in the spot of a focused beam was then performed. Besides a significantly extended range of excitation intensity, a focused beam causes the ex-

\[
\begin{align*}
\text{(a)} & \quad \text{Antenna diameter } d = 110 \text{ nm}, \\
\text{(b)} & \quad d = 125 \text{ nm}, \\
\text{(c)} & \quad d = 155 \text{ nm}, \\
\text{(d)} & \quad d = 190 \text{ nm}.
\end{align*}
\]

**Figure 7.10.**: Coupling of the observed PL-signals to the antenna modes. The antenna is excited at \( \lambda_{ex} = 633 \text{ nm} \). (a) Antenna diameter \( d = 110 \text{ nm} \), (b) \( d = 125 \text{ nm} \), (c) \( d = 155 \text{ nm} \), (d) \( d = 190 \text{ nm} \).
citation of all antenna resonances addressable by the used wavelength due to a widely varying electric field vector. With this measurement configuration strong PL signals could be observed that red-shifts for increasing antenna diameter (Fig. 7.10). This shift in wavelength is due to a coupling of the PL signal to an antenna mode, most probably to the \( D_e \) mode. However, a coupling to \( D_1 \) instead of \( D_e \) cannot be excluded completely due to their similar resonance wavelengths and the difficult estimation of the position of the PL signal when it is close to the excitation. Interestingly, a coupling to \( D_m \) (Fig. 7.10c) and \( D_2 \) (Fig. 7.10d) seems not to happen. If this PL-signal originates from the Si-QDs can be checked by exciting antennas without Si-QDs in the same way. Fig. 7.11 reveals that the empty antennas have the same PL spectra as the Si-QD filled ones. This illustrates that the observed PL signals are not coming from the Si-QDs. Careful correction of the antenna spectra by that taken from the empty antenna and the substrate did not lead to an isolation of a Si-QD PL signal. Possible reasons for this negative result are discussed in section 7.4 in detail. In order to get a better idea of the influence of an Au disk on the properties of the Si-QDs, a sample consisting of single nanodisks with a 5 nm \( SiO_2 \)

![Image](image_url)

**Figure 7.11.** The measured PL spectra for two empty and two filled antennas with diameter \( d = 190 \) nm excited by a focused beam at \( \lambda_{ex} = 633 \) nm. The figure illustrates that the dominating PL signal is not generated by the Si-QDs.
7.3. Experimental results

Spacer layer on top and covered by a few monolayers of Si-QDs was studied. The measured changes in intensity were too small to relate them to a coupling of the Si-QDs with the antenna [181].

In order to study further the origin of the observed PL signal and the influence of the nanoantenna on it, we excited a $10 \times 10 \, \mu m^2$ area in the range without Si-QDs by a focused beam at $\lambda_{ex} = 633 \, nm$ as well. This area contains the same sequence of materials defining the antenna, but it lacks a localized plasmon resonance. A weak PL signal can be observed. Fig. 7.12 shows an example of such a signal (red curve). In contrast to this, there is no detectable PL-signal on bare substrate. This means that the PL signal does not originate from the untreated substrate or any other element in the setup. There are two possible explanations as to the origin of the PL signal. Although seldom reported, it is known that the electron beam used for photoresist patterning can induce color centers in the glass substrate exposed to it. These centers are generated directly below the later grown antenna and therefore profit from plasmon-mediated emission via the lower disk of the antenna. Another possibility is gold luminescence, which is enhanced due to the coupling of Au luminescence bands with the plasmon resonance of the antenna. Such a coupling has already been reported [182]-[186].

The PL spectra taken from nanoantennas with different diameters in comparison to the PL spectra of the $10 \times 10 \, \mu m^2$ area (both without Si-QDs) allow an estimation of the PL enhancement due to coupling with the $D_6$ resonance. For a proper estimation of the enhancement, the cross-sectional area of the exposed structure, i.e. the illuminated part of the $10 \times 10 \, \mu m^2$ area and the nanoantenna, as well as its position within the excitation spot need to be considered. The measured PL intensity is proportional to the integration of the PL intensity at a position $(x, y)$, $I_{PL}(x, y)$, over the exposed cross-sectional area of the structure. In the following, we assume that $I_{PL}(x, y)$ is proportional to the excitation intensity at the considered position, $I_{PL}(x, y) = I^0 I_{ex}(x, y)$, where $I^0$ is the position-independent PL-intensity for unit excitation intensity. The measured intensity is then given by

$$I^M_i = I^0_i \int_{A_i} I_{ex}(x, y) \, dx \, dy. \quad (7.1)$$

$i = 1, 2$ indicates the two different structures and $A_i$ is the corresponding cross-sectional area. In the following, $i = 1$ is used for the
Figure 7.12.: Measured PL spectra for an empty antenna with diameter \( d = 155 \) nm in comparison to the spectra measured on the 10 \( \times \) 10 \( \mu \)m\(^2\) area for identical measurement conditions.

10 \( \times \) 10 \( \mu \)m\(^2\) area and \( i = 2 \) for the antenna. We are interested in the ratio between \( I^0_2 \) and \( I^0_1 \), which is

\[
\frac{I^0_2}{I^0_1} = \frac{I^M_2 \int_{A_1} I_{\text{ex}}(x, y) \, dx \, dy}{I^M_1 \int_{A_2} I_{\text{ex}}(x, y) \, dx \, dy}.
\]  

(7.2)

This means that the ratio of the measured PL-intensity for the antenna and the 10 \( \times \) 10 \( \mu \)m\(^2\) area needs to be corrected by the ratio of the integral of the excitation intensity over the illuminated part of the 10 \( \times \) 10 \( \mu \)m\(^2\) area and the antenna. Imaging the excitation beam spot on the CCD and reading out of the position-dependent intensity\(^4\) leads to an expression for \( I_{\text{ex}}(x, y) \) by fitting a Gaussian curve to the intensity distribution measured. This results in a correction factor on the order of 6 (\( d = 190 \) nm) to 12 (\( d = 125 \) nm) to the measured intensity ratio.

The antenna with \( d = 155 \) nm enhances the luminescence band, dominating the PL spectra of the 10\( \times \)10 \( \mu \)m\(^2\) area. Fig. 7.12 shows two representative PL spectra thereof. In this case, a PL enhancement of 176 is estimated. Taking into account all PL measurements of antennas with \( d = 155 \) nm, a maximum enhancement factor of 300 is observed.

\(^4\)More exact, counts proportional to the intensity.
7.4. Discussion and possibilities for improvement

The $d = 190$ nm antenna enhances luminescence bands not dominating in the PL spectra of the $10 \times 10$ area. Reading out the measured PL intensity of the area at the wavelength of maximum PL signal of the antenna and calculating the corresponding enhancement factor leads to a maximum observed enhancement of 1067 for all realized antenna configurations.

Variations in beam spot diameter and antenna positioning within the spot as well as bleaching of the PL signal reduce the accuracy of the measured intensity values. The maximum observed influence of variations in spot diameter and antenna position results in a change in signal intensity of a factor of two. Possible influences due to bleaching can be deduced by using appropriate measurement procedures (frame measurements: section 2.2.6). No signal decrease below 50% of the initial value was observed with time.

7.4. Discussion and possibilities for improvement

It was shown in the first part of section 7.3 that a photoluminescence signal from the Si-QDs incorporated in the gap between the two Au disks could not be observed although the different antenna resonances tuned to the excitation and emission wavelength of the Si-QDs lead to very promising antenna properties. The most obvious deviation from an ideal situation happens at the Si-QDs excitation. The chosen excitation wavelength of $\lambda_{\text{ex}} = 633$ nm leads to a poor excitation efficiency of the Si-QDs. In consequence, disturbing signals, such as the observed PL, may show higher intensities than the Si-QD PL. In addition, the need for high excitation intensity necessitated the usage of a focused beam instead of the more favorable excitation along the antenna axis. The result is a reduced excitation of the Si-QDs via the $D1$ and $D2$ mode which means a loss in performance for most mode configurations.

The price to pay for improving the issue of Si-QD excitation efficiency is high. A reduction of $\lambda_{\text{ex}}$ makes only sense if the antenna material (and possibly spacer material and substrate) is changed to silver or alumina in order to avoid the on-setting damping of gold below 550 nm. In addition, coupling of the excitation and emission to the same antenna mode will not be possible anymore and the proper tuning of the various antenna modes becomes an even more demanding key task. The
different dependencies of the $D_1$, $D_2$, $D_e$ and $D_m$ mode on the antenna parameters and the appearance of additional dipolar modes ($D_3$ etc.) will help to find a promising configuration of antenna resonances. However, extensive simulations and a measurement setup that allows to determine antenna resonances down to the UV range are needed. Off-resonant excitation is no option because the sub-wavelength cavity defined by the two disks of the antenna, which contains the QDs, shield the QDs from electromagnetic waves not resonant with one of the antenna modes. At the same time, a perfect interaction between Si-QDs and antenna is needed to avoid emission intermittency. As long as a dominating radiative decay channel over the antenna cannot be established, the resulting intensity-dependent physical bleaching remains a critical point towards a well performing Si-QD activated antenna. Appendix A discusses emission intermittency based on measurements on Si-QDs on bare substrate. Recently developed non-blinking QDs [187][188] may be an option, but their successful integration in the chosen antenna design may be problematic.

Looking at the long list of needed modifications in order to improve the issues related to the excitation efficiency of the Si-QDs makes it worth to think about an intermediate step over an alternative emitter. This will help to study the interaction of the emitter with the different antenna modes without significant changes in antenna design and measurement setup. In addition, the alternative emitter can be chosen under the aspect of a simplification of the overall production process. This leads to a much faster sample production and an easier study of the influence of design parameters on antenna performance. There are different organic materials that can be thermally evaporated with good control of layer thickness. In our case, a material with high excitation efficiency around $\lambda_{ex} \approx 633$ nm and emission between 650 nm and 800 nm would help to overcome the issues of low excitation efficiency. Good candidates are DCM2, Pentacene and Cy5. However, the appearance of chemical bleaching will destroy the organic emitter during measurement.

Independent of the emitter used, a characterization of emitter-antenna interaction over the study of PL intensities only has its limitations. Besides bleaching, which leads to a PL-intensity that depends strongly on time, the field intensity of the excitation at the position of the emitter varies in the gap but also from one antenna to another. This results from the dependence of the excitation intensity on the antenna position.
7.4. Discussion and possibilities for improvement

within the beam spot and the unknown situation in the gap (grains, surface roughness etc.). The dependence of the PL intensity on time and the measurement conditions can be compensated by the use of rigid measurement procedures and statistical methods. Nevertheless, the potential of using PL intensity measurements to deduce clear statements concerning antenna-mediated photoluminescence is limited. The use of decay trace measurements would help a lot. Such measurements would verify the existence of coupling directly by measuring changes in the emitter decay rate.

Another approach to increase the observability of the emitter PL is to eliminate the origin of the strong disturbing PL signals and to go for even more promising configurations of antenna modes. The former can be done by the usage of alternative pattern methods in the case that this signal emits from color centers generated in the substrate during e-beam writing. As long as the studies are restricted to antennas with circular cross-sections, colloidal lithography or interference lithography can help. If colloidal lithography is used, the established measurement setup will help to find and analyze good antenna configurations. Thanks to its straightforward, sequential measurement of scattering and PL spectra and the clear link between antenna diameter and in-plane resonances, the antenna characterization will not become more time-consuming. Position markers will help to visualize the analyzed antennas by SEM. It has already been shown that interference lithography can be used to produce sample layouts similar to that produced here [171]. However, the resulting distance between two antennas might become too small for the optical analysis of single antennas.

Another possibility to avoid color centers in the substrate is to change the substrate. Based on chapter 3, there is no need for an antenna excitation perfectly along its axis to get a dominating excitation of out-of-plane resonances. Hence, TIR is not absolutely needed and a non-transparent substrate in combination with face-down mounting of the sample and a high NA objective is sufficient to excite \( D1 \), \( D2 \) etc. The angle of incidence can be increased further if the sample is tilted. In the case of a substrate with high refractive index, the more pronounced substrate effects, such as image charges [69]-[71] or increased back reflection, need to be considered.

Some guidelines showing how the performance of the antenna can be optimized by the choice of appropriate antenna modes are given in section 7.2.4. A better emitter excitation via \( D2 \) than realized in the
produced antennas is not possible. In the same way, emission via $D_1$ and $D_2$ is realized in very good way. Hence, the realization of other mode configurations alone will not lead to an observable Si-QD signal but improve antenna performance if another emitter is chosen. Hence, it would be worth to study the excitation coupled to $D_1$ and/or to $D_m$ and the emission coupled to $D_1$. $D_1$ can be tuned to a lower wavelength by decreasing the gap refractive index and by increasing the gap. The latter will have a direct influence on emitter-antenna coupling. More simulations are needed to estimate better the influence of changing disk height on the position of $D_1$ and $D_2$. The resonance wavelength of $D_m$ can be decreased by decreasing the antenna diameter and by increasing the gap. Additionally, a situation where the top and bottom disks show the same resonance wavelengths when not coupled to each other is also expected to be advantageous. Focusing on the $D_1$ mode, this can be done by using a slightly lower (!) top particle to compensate for particle diminution.

Another critical point concerning antenna performance is the spacer thickness. There are a lot of reports discussing the influence of antenna-emitter separation. However, without measurement series focusing on this point, it will not be possible to find optimal parameters for spacer thickness. Increasing quenching of the emitter and increasing near-to-far-field conversion with decreasing spacer thickness are competitive effects and the best working point needs to be found. Again, optimization of spacer thickness alone will most probably not lead to a working nanoemitter using Si-QDs.

Finally, supporting layers such as adhesion layers and ITO should be avoided. Due to the very local effects associated with antenna-mediated enhancement, their influence on antenna performance is not negligible [189][190] but very difficult to estimate.

With these remarks we end the discussion of metal-enhanced fluorescence on the example of two stacked Au disks. The made observations showed that the usage of a nanoemitter design that relies on the complete embedding of the emitter into the metallic structure results in different critical demands on its concrete realization. The described significant efforts (see also Table 8.1 on page 129) needed to reach the next development stage towards the realization of an efficient, non-blinking and reliable nanoemitter based on the chosen antenna design are beyond the time-frame of this thesis.
Table 7.1: Basic statements concerning the appearance of antenna modes and their dependence on antenna design parameters from own numerical simulations and [171].

<table>
<thead>
<tr>
<th>General statements</th>
<th>Tuning possibilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>The $D_1$ and $D_2$ mode are expected in the wavelength range addressed if an excitation parallel to the antenna axis is used. (Fig. 7.5).</td>
<td>The resonance wavelength of $D_1$ and $D_2$ can be tuned via disk separation (Fig. 7.5a,b).</td>
</tr>
<tr>
<td>Additionally, the $D_e$ (electric dipolar) and $D_m$ (magnetic dipolar) modes are expected if an excitation with non-zero components perpendicular to the antenna axis is used.</td>
<td>Changing the refractive index of the spacer material can also be used for efficient tuning (Fig. 7.5).</td>
</tr>
<tr>
<td>The gap region showing maximum intensity enhancement of $D_1$ is around the edge of the gap. (Fig. 7.3a).</td>
<td>The resonance wavelength can be fine-tuned with the height of the nanodisks (Fig. 7.8).</td>
</tr>
<tr>
<td>The gap region showing maximum intensity enhancement of $D_2$ is around the rotational axis. (Fig. 7.3b).</td>
<td>$D_e$ and $D_m$ can be tuned via the diameter of the antenna.</td>
</tr>
<tr>
<td>$D_e$ is expected to have an intensity distribution within the gap similar to that of $D_2$, but more dependent on disk separation (Fig. 7.4b).</td>
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</tr>
<tr>
<td>$D_m$ is expected to have an intensity distribution within the gap similar to that of $D_1$ except in the center of the gap. An increased dependence of the $D_m$ mode on disk separation is also expected (Fig. 7.4a).</td>
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</tbody>
</table>
### Chapter 7. Nanoantenna: two stacked Au-disks

<table>
<thead>
<tr>
<th>Influence of variations</th>
<th>Increasing corner radius and diminution angle generate a red-shift of $D_1$ and $D_2$ (Figs. 7.6a and 7.7a). However, the production process leads to low variation of these parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The influence of corner radius is of minor importance as regards maximum value and intensity distribution within the gap (Fig. 7.6b).</td>
</tr>
<tr>
<td></td>
<td>An increasing diminution angle shifts the position of maximum intensity enhancement towards the center of the gap, the absolute values decrease (Fig. 7.7b).</td>
</tr>
</tbody>
</table>


8. Summary and Outlook

8.1. General Summary

This doctoral thesis consists of two parts, one addressing the basics of Localized Surface Plasmon Resonances (LSPRs) and the other aiming at the practical application of LSPRs in nanoemitters based on nanoantenna-enhanced luminescence. It begins with the establishment of the experimental procedures required, i.e. the realization of a measurement setup, the definition of the sample designs, and the adaption of the production processes. The measurement setup allows a 3D-tunable excitation of single nanoparticles by both "white" and monochromatic light, followed by a spectral decomposition of the scattered or emitted light. The functionality of 3D axis-selective excitation was validated by the study of nanocylinders with elliptical footprints and lengths of the three principal axes between 90 nm and 200 nm. Three different resonances of a nanocylinder were separated experimentally by exciting it along its three principal axes. By tuning the direction of the excitation in a systematic way, it was confirmed that the overall scattering spectra of nanocylinders follow the expected superposition principle. Finally, the scaling of each resonance wavelength with the lengths of the principal axes was studied. It was found that the resonances scale exclusively with the corresponding axis in a linear way.

Studies of cylinders with elliptical footprints gave various hints that the observed linear, exclusive scaling is limited to a certain range of axis lengths and aspect ratios, and that its explanation via size-dependent retardation only is not sufficient. Therefore we turned to the development of a model that takes additional aspects of the particle shape into account. Its validity for particles of arbitrary shapes bases on the usage of elements from the electrostatic eigenmode method (nonretarded boundary element method). Our reasoning led to a resonance condition that links a shape-term, $y$, with the resonance wavelength in a characteristic way (Fig. 4.2). The shape-term itself depends on the particle depolarization factors, $L$, a retardation term, $R$, and a newly
introduced concavity parameter, \( g \), that accounts for the effects of the established surface charge distributions. The product \( gL \) can be interpreted as a generalized depolarization factor that allows to compare differently shaped NPs directly.

In a next step, we established a link between the terms determining the resonance wavelength and scattering experiments on differently shaped particles. It was reasoned that the concavity parameter of the discussed resonances is \( \approx 1 \) for particles with elliptical footprints. Based on experiments on particles with elliptical (including circular), rectangular and diamond-like (both including square) footprints we estimated the concavity parameter to be \( 0.94 \pm 0.12 \) for particles with rectangular and to be \( 0.87 \pm 0.10 \) for particles with diamond-like footprints.

Next, we determined the dependence of the retardation term on the length of the relevant axis, \( d \), and on the corresponding depolarization factor for particles with rectangular footprints. In the range of the axes configurations considered (particle height \( \leq 50 \) nm, in-plane axes between 60 nm and 300 nm), a strong dependence of \( R \) on \( L \) was observed. It can be described by a 2nd-order polynomial with coefficients leading to a nearly linear relation with a slope close to \(-1\) above a certain \( L \)-value. This finding is of importance for the understanding of the scaling of resonance wavelengths with changing axis configurations. The limited data base for the determination of the dependence of \( R \) on \( d \) suggests a linear relation.

Thanks to the established link between shape-term and experimental measurements, we were able to decompose the contribution of the quasi-static \((gL)\) and dynamic \((R)\) part to the measured resonance wavelengths of particles with rectangular footprints. Surprisingly, under changing axis configurations, the wavelength of the resonance follows the trend given by the quasi-static particle depolarization and not that given by retardation. Based on the model developed, only four cases of interplay between quasi-static and dynamic depolarization are possible for an increasing relevant axis length. Two of them lead to a dominating contribution of \( L \) to the shape-term in the range of \( L \)-values addressed, one cannot be realized and only one may lead to a dominating \( R \)-contribution. However, \( L \) was also for this case dominant in all configurations studied, leading to the remarkable experimental observation of a blue-shifting resonance with increasing axis length. Studying the influence of changing aspect ratios on the resonance measured along an axis that is hold constant confirmed the important contribution of
8.1. General Summary

Thanks to the intuitive model, its link to experimental data and the knowledge gained from linking of model and experiments, we were then able to explain the observed dependence of the in-plane resonance wavelengths, $\lambda_{\text{Res}}$, on principal axis lengths and particle footprint in detail. The lengths of the in-plane axes considered were between 60 nm and 300 nm at particle heights of 13 nm, 20 nm, and 50 nm. With the resulting axis configurations, a range of aspect ratios between 0.5 and 10 was addressed. The particle footprints considered had elliptical, rectangular, and diamond-like shapes. For measurement configurations with one of the two in-plane axes kept constant at $123 \pm 6$ nm, various length-, height- and geometry-dependent features were identified (Table 6.1 on page 87). All these features were explained by the outcome of the previous sections, namely the observation that the shape-term follows the trend given by $L$, the increasing compensation of changes in $L$ by the corresponding change in $R$ at increasing $L$-values, the considered read-out region of $\lambda_{\text{Res}}(y)$, and a depolarization factor generalized by $g$. We also identified axis configurations leading to moderate aspect ratios and axis lengths that are influenced by retardation, in combination with a limited range of $y$ values, as promising prerequisites for the observation of exclusive, quasi-linear scaling.

In the second part of this theses, two coupled gold nanocylinders were studied. The cylinders are arranged in a stacked way with $SiO_2$ as spacer material. These studies aimed towards the realization of an efficient, non-blinking and non-bleaching nanoemitter by the later incorporation of Si-QDs into the gap of the nanoantenna (the two stacked disks). By the use of FEM-based numerical simulations, we identified first the antenna modes that appear in the wavelength range of interest and discussed their most important properties concerning a later integration of Si-QDs. Four very promising configurations of the antenna modes $D_1$, $D_2$ and $D_m$ for a coupling of the Si-QD excitation at 633 nm and of their emission between 660 nm and 735 nm to antenna modes were identified.

Two of these four promising configuration were then realized in a first set of nanoantennas with incorporated Si-QDs. Nevertheless, photoluminescence originating from the Si-QDs could not be observed. This outcome was discussed in detail based on an extensive optical characterization of the realized nanoantennas. The needed modifications on antenna design and next steps for a successful realization of the
nanoemitter are highlighted.

8.2. General outlook and future work

A good part of this doctoral thesis aimed to build up and establish tools for the characterization of nanoantennas, processes and models not yet available at the Laboratory of Metal Physics and Technology. Further capitalization on the various outcomes should have highest priority. 3D axis-selective excitation of single NPs has still not been reported by other groups. Hence, the setup can be used to establish valuable collaborations with groups that produce nanostructures showing interesting effects or high potential for applications. An important contribution to their research can be made if the structures perform best with a well-defined particle excitation not parallel to the substrate. Besides this, the axes relevant for the exclusive excitation of resonances can be determined experimentally and the properties of related effects, e.g. signal enhancement or sensitivity, can be studied. Of course, it is also possible to develop the established production processes further in order to produce and analyze interesting metallic nanostructures in-house.

If structures are analyzed that promise interesting radiation patterns, the setup can also deliver the corresponding information. Thanks to the various light sources, the radiation patterns of both a specific mode and of an emitter coupled to such a mode can be discussed. The number of publications which report such measurements is still very low, but has been increasing since 2010. However, the never before seen determination of radiation patterns in combination with 3D axis-selective excitation makes it possible to study the directional characteristics of different modes of a single NP.

Currently, there is a trend triggered by EELS and simulations towards the identification of different modes of the same polar character. The more the studied NPs differ from ellipsoids, the more relevant such aspects become. Studying the properties of the nanoantenna showed elements of this problem. This trend has not yet fully reached the part of the community that studies the scattering properties of metallic NPs. However, future work on more complex-shaped NPs must include such considerations. In principle, the scattering spectra of a cylinder excited along its axis already contains information on different dipolar modes. Again, it is a question of mode separation, considered wavelength range
and oscillator strength, but also coupling of the mode to far-field radiation which determine whether such a mode can be identified in the scattering spectra or not.

With respect to the derived model and the related experiments conducted, a continuation of the discussion will generate further fruitful information on the basics of resonances in metallic NPs. For example, the dependence of $g$ on the axis configuration at an otherwise fixed particle shape can be studied. Numerical simulations can help to determine the depolarization factors for additional bodies in order to extend the number of particle shapes that can be addressed experimentally. The study of cuboids excited along their in-plane principle axes and diagonals will not only lead to a direct proof of two dipolar resonances for a squared footprint, but also show how the resonance excited along the diagonal emerges.

In section 5.4 it was shown that the often-used statement of a red-shifting resonance for an increasing axis length (or particle volume) is not valid in general. Similarly, one can look for particle shapes for which the statement of a red-shifting resonance for sharper corners is not valid. The experiments performed on particles with elliptical and diamond-like footprints were already close to such a contradictory observation. The key is to play off the relative change in depolarization against the absolute change.

Looking at the use of gold nanostructures in applications, it is worth reconsidering their time-stability with respect to their plasmonic properties. In this thesis, strict production-measurement cycles guarantee that only NPs of the same age after production are compared. However, dipolar resonances that blue-shift with time have been observed. This shift is strongest during the first days after production (up to 80 nm) and seems to stabilize only slowly, i.e. within weeks. SEM imaging of the NPs showed no change in shape that might cause this well-pronounced shift. Hence, the process leading to this time dependence still needs to be found. Its effect on the optical properties of the NPs can be measured easily with the equipment at hand, e.g. in combination with annealing of a newly produced sample.

The experiments on a first set of nanoemitters consisting of two stacked gold disks with Si-QDs incorporated in the gap between the disks revealed various modifications which are needed to successfully realize an efficient nanoemitter. Table 8.1 summarizes the related issues and shows ways to overcome them, but also indicates problems
that may arise. Efforts to produce a nanoemitter based on the design used should initially focus on a higher excitation efficiency of the emitter. A possible approach is a change to an emitter that is excited efficiently above 600 nm, i.e. at wavelengths with low Au damping. If the obvious advantages of the Si-QDs are to be preserved, the excitation wavelength used needs to be shifted towards the blue/UV wavelength range. Both approaches make it possible to reduce the intensity of the excitation and to work with axis-selective excitation. This will help to reduce the prominent disturbing signal observed and to increase the emitter signal relative to it. However, adjusting of $\lambda_{\text{ex}}$ results in a change of the disk material and in modifications of the antenna design. The former is needed to avoid damping of the excitation and the latter aims at an overlap of excitation and emission with appropriate antenna modes.

A second main design adjustment should result in the reduced possibility of complete emitter quenching due to the metallic disks. This can be achieved by a spacer thickness greater than the expected optimal value of around 5 nm. The resulting negative influence on near-to far-field conversion over the antenna must be kept in mind. An increase in spacer thickness leads to a shift of the antenna modes which can be compensated by other parameters, such as antenna diameter, gap refractive index and the height of the disks.

These two significant modifications in antenna design may generate a working nanoemitter. First, the intensity of the disturbing signal decreases absolutely and relative to the PL of the emitter. Second, the emitter emission is surely not quenched by the antenna. In addition, an acceptable level of physical bleaching can be established by tuning of the excitation intensity if an ensemble of Si-QDs are used as emitters. If these modifications do not lead to a detectable emitter signal, using a design based on a complete embedding of the emitter into the metallic structure should be reconsidered. An intermediate step via an emitter that shows a high excitation efficiency at around 633 nm can help to estimate the potential of the chosen antenna design based on the simulations and experiments shown in Chapter 7. Possible candidates are DCM2, Pentacene and Cy5. However, the measurement procedure needs to account for photo-induced degradation if dyes are used as emitters.
### 8.2. General outlook and future work

<table>
<thead>
<tr>
<th>Issue</th>
<th>Approach</th>
<th>Risks</th>
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<tbody>
<tr>
<td>Excitation efficiency of the Si-QDs</td>
<td>Excitation in the blue/UV wavelength range.</td>
<td>Complete design change, including antenna material.</td>
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<td></td>
<td>Usage of alternative emitters.</td>
<td>Photo-induced degradation, need for design changes.</td>
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<tr>
<td>Disturbing PL signal</td>
<td>Reduced excitation intensity.</td>
<td>No Si-QD signal if excitation efficiency is too low.</td>
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<td>Different substrate.</td>
<td>Substrate effects, impact on optical characterization.</td>
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<td></td>
<td>Alternative pattern methods.</td>
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<tr>
<td>Quenching</td>
<td>Increased spacer thickness.</td>
<td>Reduced near- to far-field conversion.</td>
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<tr>
<td>Bleaching</td>
<td>Reduced excitation intensity.</td>
<td>No Si-QD signal if excitation efficiency is too low.</td>
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<tr>
<td></td>
<td>Non-blinking Si-QDs.</td>
<td>Production process, Si-QD possibly too large in diameter.</td>
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<td>Characterization of MEF</td>
<td>Decay trace measurements.</td>
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<td>Statistical data interpretation.</td>
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<tr>
<td>Optimal spacer thickness</td>
<td>Specific series of measurements.</td>
<td>Overload of resources.</td>
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<tr>
<td>Spectral overlap</td>
<td>Finer tuning steps to optimize mode configuration.</td>
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</table>

**Table 8.1:** Summary of issues related to the realization of an efficient, non-blinking and reliable nanoemitter based on two stacked Au-disks with Si-QDs incorporated in the gap between the disks.
Appendices
A. Optical properties of Si-QDs

Emission intermittency ("blinking") is an important phenomena when Si-QDs should be used as light sources or in imaging systems. It was observed first by Nirmal et al. in 1996 [191]. It was interpreted as the result of photoinduced ionization and non-radiative Auger recombination of electron-hole pairs [153]. However, the experiments could not be explained completely by these mechanisms, resulting in an ongoing discussion of the involved processes [192]-[194] and the time-dependent emission of QDs [195]-[198]. The discussion is complicated by the strong influence of the QD production process and the measurement conditions leading to experimental observations that partly contradict and support different models. [193][197][199][200] summarize some of them. Nevertheless, there is a common agreement that emission intermittency is a consequence of charging and discharging of the QD. The QD is charged by electron-hole separation of a photo-generated exciton involving carrier traps. If these traps are at the $Si-SiO_2$ interface or completely outside the $Si$-core, the process by which a carrier becomes localized around a trap, as well as the question of whether electron or hole traps are dominant, are current topics of discussion [193][195]. Concerning the reason for non-radiative electron-hole recombination in charged QDs there is, however, consensus. It is assumed that the PL emission is quenched by fast Auger recombination [152][153] leading to a decay rate of the order of $10^8 - 10^{10}$ s$^{-1}$ [154][155].

This picture reduces the phenomenon of blinking to processes involved in electron-hole separation and trapping of either electron or hole after photoinduced generation of an exciton. A very intuitive description of emission intermittency based on the charged QD model is given by Tang and Marcus based on a diffusion-controlled electron-transfer model [194]. This model leads to on- and off-time probability
Appendix A. Optical properties of Si-QDs

Distributions following a power law [197]

\[ P_{\text{on/off}}(t) \propto t^{\alpha_{\text{on/off}}} \exp(-t/\tau), \quad (A.1) \]

with an exponent \( \alpha_{\text{on/off}} \) of around \(-1.5\) and an exponential damping tail described by a characteristic time \( \tau \). This power law behavior of the statistics of on- and off-time has been confirmed experimentally by several groups. The observed exponents are in a range between \(-1.1\) and \(-2.2\) peaking at around \(-1.5\) [152][194][197][202]. The experimentally observed values for the exponents depend on sample preparation and experimental conditions. It could be shown that blinking is influenced by the surrounding media [197][203][205], by temperature [150][206], and that there are differences between single QD and ensemble measurements [196][201]. However, the exact values of \( \alpha_{\text{off}} \) and \( \alpha_{\text{on}} \) that are responsible for the decreasing PL intensity with illumination time in a system without chemical bleaching.

Again, there are differences in the equation describing the influence of physical bleaching on the time-dependent PL intensity of QDs, which result from different assumptions regarding the exact values of \( \alpha_{\text{on/off}} \). Cichos et al. [152] studied emission intermittency and the resulting bleaching behavior of Si-QDs at room temperature using excitation intensities of 1.8 kW/cm\(^2\) and 6.5 kW/cm\(^2\). For these experimental conditions very close to our own, the time-dependent PL intensity is described by

\[ I(t) = I_0(t + \tau_0)^{-\beta}, \quad (A.2) \]

with \( \beta = 2 - \alpha_{\text{off}} \), and \( \tau_0 \) related to the mean on-time. Increasing physical bleaching with increasing excitation intensity is taken into account in eq. A.2 by showing an intensity dependence of \( \alpha_{\text{off}} \). Starting from a value of \( \alpha_{\text{off}} = 2 \) (no physical bleaching), \( \alpha_{\text{off}} \) decreases with increasing excitation intensity, which results in more and faster bleaching.

We performed different experiments in order to check the optical properties of the Si-QDs produced by the Institute of Solid State Physics at the Friedrich-Schiller-Universität (FSU) in Jena (Germany). The Si-QD production process is described in detail in [83][84]. Briefly, a pulsed \( CO_2 \) laser decomposes silane (\( SiH_4 \)) in a gas flow reactor. After the crystalline \( Si \) nanoparticles are grown to 3–7 nm in diameter, they are extracted through a conical nozzle and transferred into a molecular beam of freely propagating nanoparticles. Within the molecular beam of pulsed character, the particles separate by size due to the slower
Figure A.1.: Tuning of the Si-QD photoluminescence wavelength by changing the observation spot within the deposit. The (normalized) result of a scan over the deposit in steps of 0.5 mm in a horizontal direction is shown. Thanks to the size-selective deposition used, the diameter of the QDs increases continuously from 3 nm to 7 nm during this scan.

velocity of larger particles. This can be used to select a specific size by employing a molecular-beam chopper with proper synchronization to the \( CO_2 \) laser. If the chopper is realized by a rotating slit, the Si-QDs can be deposited size-selectively in horizontal direction over a spot of \( \sim 5 \) mm in diameter.

Sufficient excitation of the Si-QDs produced at 633 nm and 405 nm, as well as the dependence of the PL peak wavelength on the position of the sample due to size-selective deposition, is verified first. The latter needs to be known to guarantee a good overlap between the PL and the plasmon resonance spectra of the nanoantenna. Fig. A.1 shows the normalized PL signals from a horizontal scan over the deposit. The distance between the measurement points is around 0.5 mm. Excitation is conducted at 405 nm. The PL signal peaks at 660 nm for the small QD diameter side of the deposit and at 735 nm at the side where the largest QDs are expected. In the vertical direction, the Si-QD production process leads to only slightly changing diameters (not shown). In total, the peak wavelength scales with Si-QD size as expected from the quantum confinement model [84][141][146].

Although a disadvantage in terms of PL intensity, the high contribution of photophysical bleaching to the overall bleaching behavior of
the Si-QDs gives us the opportunity to identify a PL signal originating from the QDs by their intensity recovery in on/off experiments. Fig. A.2 shows the outcome of such an experiment for Si-QDs on bare substrate. The PL signal from the very same position of the deposit is recorded over 300 s using an integration time of 250 ms for each data point.\footnote{The experimental situation requires the use of such a high integration time. In consequence, the following values for relative intensities and duration for intensity halving are upper limits.} After 10 s of illumination, the laser is blocked with a blind for 110 s followed by laser exposure for the remaining 180 s. Intensities of 240 W/cm\(^2\) and 1620 W/cm\(^2\) were used for excitation at 405 nm and 633 nm, respectively. During the first 10 s of illumination the PL intensity drops from its value \(I_0\) at \(t = 0\) to 0.77\(I_0\) (\(\lambda_{\text{ex}} = 405\) nm) and 0.80\(I_0\) (\(\lambda_{\text{ex}} = 633\) nm). After 110 s without illumination, the PL intensity recovers to 0.90\(I_0\) (\(\lambda_{\text{ex}} = 405\) nm) and 0.94\(I_0\) (\(\lambda_{\text{ex}} = 633\) nm). These findings are in good agreement with literature [152].

Finally, the overall photobleaching of the Si-QDs on bare substrate in dependence on excitation intensity was studied. This is important as long as a complete suppression of the non-radiative decay of charged Si-QDs cannot be realized, due to the expected significant field enhancement at the position of the QDs when the excitation is coupled to a plasmon resonance of the nanoantenna (Fig. 7.3). Excitation intensit-

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{Figure_A.2.png}
\caption{On/off experiment according to [152] with Si-QD excitation at 405 \textit{nm} (\(I_{\text{ex}} = 240\) W/cm\(^2\)) and 633 \textit{nm} (\(I_{\text{ex}} = 1620\) W/cm\(^2\)). The excitation laser is on for 10 s, off for 110 s and on again for 180 s.}
\end{figure}
ies of $I_{\text{ex}} = 240 \text{ W/cm}^2$, $2200 \text{ W/cm}^2$, and $5600 \text{ W/cm}^2$ at 405 nm are used. A surprisingly high excitation intensity dependence on the part of the PL signal is observed (Fig. A.3). The bleaching curves shown are based on fitting a sequence of measured PL spectra (integration time 250 ms) with Gaussian curves. Looking at an excitation intensity of $5600 \text{ W/cm}^2$, the PL signal is reduced to half of its original value after less than 2 s and goes below the detection limit in the following. For an excitation intensity of $2200 \text{ W/cm}^2$, the PL signal is halved after 10 s and finally approximates a value of $0.15I_0$. With $I_{\text{ex}} = 240 \text{ W/cm}^2$ the corresponding value is $0.55I_0$.

As discussed above, photobleaching of a Si-QD ensemble is a manifestation of the emission intermittency of the individual Si-QDs. The dependence of emission intensity on illumination time can be described by a power law, eq. A.2, with an exponent $\beta = 2 - \alpha_{\text{off}}$. Although the integration time used for data generation is, at 250 ms, high for precise fitting, the exponent of the off-time statistic, $\alpha_{\text{off}}$, can be estimated from the experimental data. We find $\alpha_{\text{off}} = 1.92 \pm 0.03$, $1.7 \pm 0.1$, and $1.05 \pm 0.2$ for an excitation intensity of $I_{\text{ex}} = 240 \text{ W/cm}^2$, $2200 \text{ W/cm}^2$, and $5600 \text{ W/cm}^2$, respectively. This is in good agreement with literature, where $\alpha_{\text{off}}$ values of 1.7 and 1.3 are found for excitation intensities of $1800 \text{ W/cm}^2$ and $6500 \text{ W/cm}^2$, respectively [152].

![Figure A.3: Photobleaching of the Si-QDs on bare substrate. Excitation at 405 nm with three different intensities, $I_{\text{ex}} = 240 \text{ W/cm}^2$, $2200 \text{ W/cm}^2$, and $5600 \text{ W/cm}^2$.](image)
Looking at the PL peak position rather than the PL intensity reveals that the peak position does not change with time using a constant excitation intensity (not shown). This is of no surprise, remembering the origin of intermittency. However, a slight dependence of peak position on excitation intensity is observed [150]. Excitation of the same position of the deposit with intensities of $0.24 \text{ kW/cm}^2$, $0.95 \text{ kW/cm}^2$, $2.2 \text{ kW/cm}^2$, $3.4 \text{ kW/cm}^2$, $5.6 \text{ kW/cm}^2$, $8.4 \text{ kW/cm}^2$, and $11.1 \text{ kW/cm}^2$ at 405 nm reveals a nearly linear blue-shift of the peak position with increasing intensity for $I_{ex} > 2 \text{ kW/cm}^2$. The experimentally observed slope is $-0.0009 \frac{\text{nm}}{\text{W/cm}^2}$. Although a stronger dependence of peak position on excitation intensity is observed for intensities below $2 \frac{\text{nm}}{\text{W/cm}^2}$, the overall intensity-induced shift is less than $-25 \text{ nm}$ for a change in excitation intensity from $0.24 \text{ kW/cm}^2$ to $11.1 \text{ W/cm}^2$. This makes a relevant mismatch between PL signal and antenna plasmon resonance due to field enhancement at the Si-QD position in the antenna gap unlikely, especially if one takes the broad linewidth of both plasmon resonance and PL signal into account.

In sum, the experiments on a Si-QD film on bare substrate summarized in appendix A showed the need for a perfectly interacting QD-antenna hybrid. The pronounced appearance of physical bleaching in the Si-QDs and its strong dependence on excitation intensity are crucial for the successful realization of a Si-QD activated antenna from two stacked Au disks, as long as the non-radiative decay channel over Auger processes is not overcome by a radiative antenna decay channel. Achieving a configuration which generates to an optimal relation between excitation wavelength and antenna resonance with respect to reduced intensity-dependent bleaching due to field enhancement in the antenna gap and efficient QD excitation is not trivial. Additionally, direct and reproducible observation of PL enhancement becomes very demanding due to a PL signal which is strongly dependent on illumination time and excitation intensity. The expected time dependence of the antenna signal requires for additional measurement methods. Decay trace measurements reveal changes in the Si-QD decay time due to antenna coupling. This helps a lot to verify emitter-antenna coupling in non-perfect configurations.
## B. Production recipes

### Basic production process

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<table>
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| 1 | Cleaning | 5 min acetone, 30°C, US 3 (40 kHz)  
5 min isopropanol, 30°C, US 3  
1 min DI-bath  
1 min DI-shower  
\(N_2\) dry |
| 2 | 8 nm ITO (PVD) | \(~2\ A/s, 5 \times 10^{-6}\ \text{mbar}\)  
(or coating services) |
| 3 | Annealing | 30 min at 360°C |
| 4 | Cleaning | as step 1 |
| 5 | Photoresist | Pre: 10 min at 180°C  
Height depending on target NP/antenna height:  
PMMA 950K in EL 2:1, 5 s at 500 rpm (Ace 3), 90 s at 1500 – 5000 rpm (Ace 3)  
or  
PMMA 950K in EL 1:1, 5 s at 500 rpm (Ace 3), 90 s at 3000 – 6000 rpm (Ace 3)  
Post: 10 min at 180°C |
| 6 | Exposure | See section 2.3 |
| 7 | Development | MIBK:IPA=1:3, 45 s  
IPA, 45 s  
1 min DI-shower  
\(N_2\) dry |
| 8 | Visual inspection | Microscope |
| 9 | 2 nm Ti (PVD) | \(~2\ A/s, 1 \times 10^{-6}\ \text{mbar}\) |
### Appendix B. Production recipes

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<tbody>
<tr>
<td><strong>10</strong></td>
<td>NP/antenna growth (PVD)</td>
<td>see section 2.3.1</td>
</tr>
<tr>
<td></td>
<td>Au: $\sim 2.5, \text{A/s, } 3 \times 10^{-6}, \text{mbar}$</td>
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<tr>
<td></td>
<td>($SiO_2$: $\sim 2.0, \text{A/s, } 5 \times 10^{-6}, \text{mbar}$)</td>
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<td></td>
<td>(Ti: $\sim 2, \text{A/s, } 1 \times 10^{-6}, \text{mbar}$)</td>
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<td></td>
<td>(Si-QDs: see Refs. [83],[84])</td>
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<td><strong>11</strong></td>
<td>Lift-off</td>
<td>Ace, RT, no US</td>
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<td></td>
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<td>1 min IPA</td>
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<td><strong>12</strong></td>
<td>Visual inspection</td>
<td>Microscope</td>
</tr>
<tr>
<td><strong>13</strong></td>
<td>Visual inspection</td>
<td>SEM</td>
</tr>
</tbody>
</table>

**Table B.1.:** Basic production process. For details and sample layout, see section 2.3.
## Basic production process without ITO

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Details</th>
</tr>
</thead>
</table>
| 1    | Cleaning | 5 min acetone, 30°C, US 3 (40 kHz)  
5 min isopropanol, 30°C, US 3  
1 min DI-bath  
1 min DI-shower  
\(N_2\) dry |
| 2    | Photoresist | Pre: 10 min at 180°C  
Height depending on target NP/antenna height:  
PMMA 950K in EL 2:1, 5 s at 500 rpm (Ace 3), 90 s at 1500 – 5000 rpm (Ace 3)  
or  
PMMA 950K in EL 1:1, 5 s at 500 rpm (Ace 3), 90 s at 3000 – 6000 rpm (Ace 3)  
Post: 10 min at 180°C |
| 3    | 5 nm Au | Thermal evaporation, \(\sim 2.5\) A/s,  
\(< 5 \times 10^{-6}\) mbar |
| 4    | Exposure | See section 2.3 |
| 5    | Au etch | 15 g KI, 5 g \(I_2\), 100 ml DI, 1:10 diluted  
15 s stirring  
1 min DI-bath  
1 min DI-shower  
\(N_2\) dry |
| 6    | Development | MIBK:IPA=1:3, 45 s  
IPA, 45 s  
1 min DI-shower  
\(N_2\) dry |

7-12 | Follow steps 8-13 in Table B.1. |

**Table B.2.:** Basic production process without ITO. For details and sample layout, see section 2.3.
Production process: "Influence of adhesion layers"

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>
| **1** Cleaning | 10 min RCA 1, 70°C  
$(H_2O : H_2O_2 : NH_4OH = 5 : 1 : 1)$  
10 min RCA 2, 70°C  
$(H_2O : H_2O_2 : HCL = 5 : 1 : 1)$  
5 min DI-bath  
1 min DI-shower  
$N_2$ dry |   |
| **2** 5 nm ITO (PVD) | $\sim 2$ A/s, $5 \times 10^{-6}$ mbar  
Mask (section 2.3.2): h orientation |   |
| **3** Annealing | 10 min at 360°C |   |
| **4** Cleaning | 5 min acetone, 30°C, US 3 (40 kHz)  
5 min isopropanol, 30°C, US 3  
1 min DI-bath  
1 min DI-shower  
$N_2$ dry |   |
| **5** Photoresist | Pre: 10 min at 180°C  
Height depending on target NP height:  
PMMA 950K in EL 1:1, 5 s at 500 rpm (Ace 2), 90 s at 3000 – 6000 rpm (Ace 6)  
or  
PMMA 950K in EL 2:1, 5 s at 500 rpm (Ace 2), 90 s at 1500 rpm (Ace 6)  
Post: 10 min at 180°C |   |
| **6** 5 nm Au | Thermal evaporation, $\sim 2$ A/s,  
$< 5 \times 10^{-6}$ mbar |   |
| **7** Exposure | rg120725_x.pls, [190] |   |
| **8** Au etch | 15 g KI, 5 g $I_2$, 100 ml DI, 1:10 diluted  
15 s stirring  
1 min DI-bath  
1 min DI-shower  
$N_2$ dry |   |
| **9** Development | MIBK:IPA=1:3, 45 s  
IPA, 45 s  
1 min DI-shower  
$N_2$ dry |   |
<table>
<thead>
<tr>
<th></th>
<th>Visual inspection</th>
<th>Microscope</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>2 nm Ti (PVD)</td>
<td>∼2 A/s, 2 × 10^{-6} mbar</td>
</tr>
<tr>
<td>12</td>
<td>2 nm Cr (PVD)</td>
<td>∼2 A/s, 2 × 10^{-6} mbar</td>
</tr>
<tr>
<td>13</td>
<td>NP growth (PVD)</td>
<td>Au: ∼2.5 A/s, 3 × 10^{-6} mbar</td>
</tr>
<tr>
<td>14</td>
<td>Lift-off</td>
<td>Ace, RT, no US</td>
</tr>
<tr>
<td>15</td>
<td>Visual inspection</td>
<td>Microscope</td>
</tr>
<tr>
<td>16</td>
<td>(SiO_2)</td>
<td>∼2.5 A/s, 5 × 10^{-6} mbar</td>
</tr>
<tr>
<td>17</td>
<td>Visual inspection</td>
<td>Microscope</td>
</tr>
<tr>
<td>18</td>
<td>Visual inspection</td>
<td>SEM</td>
</tr>
</tbody>
</table>

**Table B.3.:** Production process for studying the influence of adhesion layers. For sample layout see [190].
## Basic production process: "Thin film absorption"

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Details</th>
</tr>
</thead>
</table>
| 1    | Cleaning | 5 min acetone, 30°C, US 3 (40 kHz)  
5 min isopropanol, 30°C, US 3  
1 min DI-bath  
1 min DI-shower  
N\textsubscript{2} dry |
| 2    | TiO\textsubscript{2} (PVD) | \(\sim 3\) A/s, \(1 \times 10^{-5}\) mbar |
| 3    | Annealing | 60 min at 360°C |
| 4    | Au thin film | PVD, \(\sim 2\) A/s, \(3 \times 10^{-6}\) mbar |
| 5    | Photoresist | Pre: 10 min at 180°C  
PMMA 950K in EL 2:1, 3 s at 500 rpm (Ace 2), 90 s at 2000 rpm (Ace 2)  
Post: 10 min at 180°C |
| 6    | Exposure | rg120811\_x.pls |
| 7    | Development | MIBK:IPA=1:3, 45 s  
IPA, 45 s  
1 min DI-shower  
N\textsubscript{2} dry |
| 8    | Visual inspection | Microscope |
| 9    | TiO\textsubscript{2} (PVD) | \(\sim 3\) A/s, \(1 \times 10^{-5}\) mbar  
Half of the sample covered |
| 10   | Lift-off | Ace, RT, no US  
1 min IPA  
1 min DI-shower  
N\textsubscript{2} dry |
| 11   | Visual inspection | Microscope |
| 12   | Visual inspection | SEM |
| 13   | Possibly annealing | 30 min at 360°C |
| 14   | Visual inspection | SEM |

Table B.4.: Basic production process for thin film absorption in combination with TiO\textsubscript{2} grating (Laboratory for Electromagnetic Fields and Microwave Electronics, ETH Zurich).
C. Curriculum vitae

Personal Details

Name: Reto Giannini
Date of birth: 25th July 1978
Place of birth: Chur
Citizenship: Swiss

Education

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>2008-2014</td>
<td>PhD studies at the Laboratory of Metal Physics and Technology, ETH Zurich (Switzerland) in the field of plasmonics.</td>
</tr>
<tr>
<td>1985-1991</td>
<td>Primary school in Ilanz, Switzerland.</td>
</tr>
</tbody>
</table>

Work Experience

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007-2008</td>
<td>Product Engineer at Bookham (Switzerland) AG.</td>
</tr>
<tr>
<td>2006-2007</td>
<td>Research Assistant at the Institute of Microtechnology, University of Neuchâtel and at the Observatoire Cantonal de Neuchâtel.</td>
</tr>
<tr>
<td>2004-2005</td>
<td>Coating Engineer at Unaxis Optics, Low Defect Line.</td>
</tr>
</tbody>
</table>
D. Publications


E. Conference contributions


Bibliography


Bibliography


docles, W.K. Woo, M.G. Bawendi. "Blinking statistics in single
semiconductor nanocrystal quantum dots." Phys. Rev. B 63,
205316 (2001).

[203] A. Issac, C. Borczyskowski, F. Cichos. "Correlation between pho-
toluminescence intermittency of CdSe quantum dots and self-
trapped states in dielectric media." Phys. Rev. B 71,

dependent blinking of single semiconductor nanocrystals and
statistical aging of ensembles." Physica E 26,
19-23 (2005).

C.D. Heyes. "Probing the "dark" fraction of core-shell quantum
dots by ensemble and single particle pH-dependent spectroscopy." 

[206] W.L. Wilson, P.F. Szajowski, L.E. Brus. "Quantum confine-
ment in size-selected surface-oxidized silicon nanocrystals." Sci-