PHOTOCHEMICAL TUNING OF SURFACE PLASMON RESONANCES IN METAL NANOPARTICLES

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Preface

Books on the optical properties of metal nanoparticles (MNPs) often start with a retrospective on particle applications dating back more than two millenia. The use of MNPs for the coloring of decorative objects, church windows and the like was indeed known already in ancient Rome, and the archaeological finds are real masterpieces of art [1].

However, these achievements were certainly based on experience more than on scientific insight into the processes of light-particle interaction. Thus, a much broader range of technical applications of MNPs has been opened up by detailed investigations of metal colloids. First experimental examinations of metal nanoparticles were reported in the 19th century by Faraday [2]. In the early 20th century, the work of Svedberg [3] and Zsigmondy [4] was rewarded with the Nobel prize, which indicates the significance attributed to the research on colloidal materials already in those days. A detailed theory of the electromagnetic effects occurring in the particles was developed by Mie in 1908 [5], and with the work of Ostwald [6] the scientific domain called “Kolloidwissenschaft” (colloidal science) was finally fully established in the 1920s.

Most of the knowledge gained by researchers in this field was directly employed in technical applications and considerably influenced the economic development in those decades. The properties of metal nanoparticles were exploited for the fabrication of long-living lubricants and for more efficient filaments in light bulbs - to name only two examples that had high impact on the growing industry at the turn of the century [6]. Print and copying technology benefited from colloidal science [7], and last but not least MNPs played an important role in the emerging field of photography [8].

Due to its multidisciplinarity, colloidal science somewhat disappeared in the overlapping areas of physics, chemistry and biology in the years to follow. Nowadays, nanotechnology brings these and further research areas together, and thus causes metal nanoparticles to again receive a lot of attention. Such metallic colloids promise important contributions to some of mankind’s most urgent problems: They may foster the production of clean energy by solar and fuel cells [9, 10], provide new approaches to cancer therapy [11] and medical imaging [12], allow the fabrication of new materials with unprecedented physical properties [13], and facilitate the chemical analysis of the smallest sample volumes in biochemistry [14].
In this work, the optical properties of MNPs are of central interest. The collective electron oscillations (so-called localized surface plasmons or LSPs) induced in illuminated particles provide a means to concentrate light-matter interactions on the sub-wavelength scale, to enhance optical signals, and to ease their detection. A successful exploitation of these particle-induced effects requires a precise adjustment of the plasmonic MNP properties according to the demands of the desired application. In this thesis, photochemical metal deposition was pursued to tune the LSP resonances in metal particles. This technique renders manipulable not only the optical properties of MNPs, but also their surface material composition. Thus, the method builds a bridge between nanooptics and other fields of nanotechnology such as catalysis or the nanoscale modification of adhesion coefficients. The presented results show how interwoven the individual fields of nanotechnology are, and the author hopes that this book will contribute to their development.
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Abstract / Kurzfassung

Illuminated metal nanoparticles (MNPs) feature collective electron oscillations (so-called localized surface plasmons or LSPs) which facilitate concentrating light-matter interactions to length scales below the diffraction limit. Part I of this book describes two applications of this confinement effect. Firstly, the use of single particles as optically active probes for scanning near-field optical microscopy is demonstrated. Secondly, fluorescence enhancement in the vicinity of a single MNP is described theoretically. This description focuses on how the particle diameter and the surrounding medium influence the enhancement. It turned out that in these two examples the optical signal levels can be improved by manipulating the spectral LSP resonance position of the particles. This finding triggered the search for a method allowing optical particle tuning.

Part II of this thesis describes an approach which allows such a spectral LSP manipulation on the single-particle level. The method makes use of the optically induced reduction of metal salt complexes in solution, which leads to the deposition of thin layers of elemental metal onto single, intentionally addressed particles. The deposition process is monitored by optical LSP analysis, and thus the tuning of the optical particle properties is controlled in situ.

With this technique, a manipulation of both the size and the shape of single nanoparticles was achieved. Initial experiences were gained by manipulating spherical and ellipsoidal gold particles, for which a red- and a blueshift of the LSP resonance was observed, respectively. The insights obtained from these experiments were then applied to tune the interparticle separation in nanoparticle pairs, i.e., to tune the resonance wavelength of these plasmonic nanoresonators. Subsequently, single resonators were used to reshape the fluorescence emission spectrum of organic molecules.

Besides size and shape, also material parameters such as the surface roughness and the surface material composition influence the optical properties of MNPs. Both aspects are addressed using the example of rough platinum spheres and demonstrating the fabrication of bimetallic core-shell particles. As the material composition of particles not only influences their optical, but for example also their catalytic or magnetic properties, photochemical metal deposition with in-situ optical LSP read-out builds a bridge to other fields of nanoscience. The presented method is a versatile tool for the fabrication and manipulation of nanostructures, and it is not limited to the field of plasmonics.


Mit der beschriebenen Technik können die Größe und die Form einzelner metallischer Partikel beeinflusst werden, was sich in einer Rot- bzw. Blauverschiebung der LOP-Resonanz äußert. Dieses Prinzip konnte zuerst an sphärischen und ellipsoidalen Goldpartikeln gezeigt werden. Die gewonnen Erkenntnisse wurden dann auf die gezielte Einstellung des Teilchenabstandes in Partikelpaaren übertragen, d. h., die Resonanzwellenlänge solcher plasmonischer Nanoresonatoren wurde gezielt manipuliert. Die Resonatoren konnten in einem zweiten Schritt zur Steuerung des Fluoreszenzspektrums organischer Moleküle eingesetzt werden.

Neben Größe und Form spielen auch Materialparameter wie die Oberflächenraugigkeit und das Oberflächenmaterial eine wichtige Rolle für die optischen Eigenschaften der Partikel. Diese Parameter wurden am Beispiel von rauen Platinpartikeln sowie an bimetallischen Kern-Schale-Partikeln untersucht. Da das Oberflächenmaterial nicht nur die optischen, sondern z. B. auch katalytischen und magnetischen Eigenschaften der Partikel beeinflusst, verbindet die vorgestellte Methode die Plasmonik mit vielen anderen Bereichen der Nanotechnologie. Sie stellt eine vielseitige Technik zur Herstellung und Manipulation von Nanostrukturen dar, ohne dabei auf die Nanooptik limitiert zu sein.
Part I

Metal particles in nanooptics
1 Introduction

Most macroscopic objects experience an alteration of their physical and chemical properties if the object dimensions are reduced down to the nanoscale. Especially material properties undergo drastic changes in such a dimensional scaling. During the last decade, nanoscience and nanotechnology have rapidly advanced in understanding many of these size effects. From this research, interesting applications of nanosized objects or nanostructured surfaces arise that are not realizable with the respective macroscopic pendants.

In nanooptics, metal nanoparticles (MNPs) are of special interest. The collective electron oscillations (so-called localized surface plasmons or LSPs) featured by illuminated particles facilitate concentrating light-matter interactions to length scales below the wavelength of light. These LSPs make metal particles versatile nanooptical tools for refractive-index sensing [15], molecular labelling [16], or nanoscale optical field enhancement [17], to name only a few examples. In future, metal nanoparticles may even allow noninvasive, all-optical cancer diagnostics and treatment [18].

For all these applications, a precise control of the optical features of the particles, especially of their LSP resonance wavelength, is necessary. This resonance wavelength depends on the particle size, shape, and material composition, and can therefore be set by a proper choice of the particle(s) in use. However, instead of searching for a suitable particle, it often appears more advantageous to tune the plasmonic properties of a given particle under in-situ conditions.

In this thesis, a method is described which allows such a manipulation of the optical properties of single particles by means of photochemical metal deposition. The method makes use of the optically induced reduction of metal salt complexes in solution, which leads to the deposition of ultrathin layers of elemental metal onto single, intentionally addressed particles. Due to deposition monitoring by optical LSP analysis, the deposition process and the optical properties of the particles are controlled in situ.

Understanding the light-particle interaction helps to manipulate the optical properties of metal nanoparticles in a targeted way. This book therefore starts with a theoretical description of the interaction and continues with a discussion of the equipment necessary to determine the optical properties of single particles experimentally. At the end of Part I, two nanooptical applications of MNPs are described which can benefit from a spectral manipulation of the LSP resonances of the particles. This finding motivated the author
to develop a technique for such spectral tuning, and photochemical metal deposition on
the single-particle level was found to be highly suitable for the purpose. The method and
its application to several particle systems are described in detail in Part II of this book.
2 Theoretical considerations

In the visible spectral range, the interaction of electromagnetic radiation with metals is governed by the behavior of the free electrons in the material. Upon illumination, the charge carriers follow the optical excitation field, i.e., surface charge density oscillations – so-called surface plasmons – are induced.\(^1\) The characteristics of these oscillations, e.g. their amplitude, depends first of all on the dielectric function \(\varepsilon(\omega)\) of the material. This chapter therefore starts with a theoretical description of this function valid for bulk material. However, the discussion is not intended to lead to exact values of \(\varepsilon(\omega)\) (high-quality data have already been provided by experimentalists), but it much more aims at a clear picture of the physics underlying the light-metal interaction. For the sake of this clarity, the description presented on the next pages is condensed and restricted to a classical picture of the processes taking place.\(^2\)

As in metal nanoparticles the electron gas is confined in three dimensions, the net displacement of the electrons with respect to the lattice leads to a restoring force. The latter is responsible for the electron oscillations to exhibit a resonance which depends not only on the material, but additionally on the size and the shape of the particles. Understanding these dependencies paves the way to manipulate the optical particle properties in a targeted way. The discussion of \(\varepsilon(\omega)\) is therefore followed by a section dealing with the solution of MAXWELL’s equations for small particles. Finally the parameters influencing the particle-plasmon resonances will be discussed.

2.1 The dielectric function of metals

2.1.1 Theoretical description

In the visible wavelength range, the dielectric function of a metal consolidates contributions from free conduction electrons and from interband transitions. The latter can occur in a spectral range where the energy of an incident photon exceeds the band gap of the respective material. In contrast, the behavior of the free electrons is important

---

\(^1\)By definition surface plasmons are the quanta of surface charge density oscillations, but the same terminology is commonly used for collective oscillations in the charge density at the surface of a metal.

\(^2\)Comprehensive theoretical descriptions can be found in several textbooks such as [19] - [22].
for the entire spectral window and therefore renders the starting point of the theoretical description.

**Drude-Sommerfeld model**

In the classical picture applied here, the presence of an electric field $E$ leads to a displacement $r$ of an electron, associated with an electric dipole moment. The integral effect of all individual dipole moments in a material can be summarized as the macroscopic polarization $P$. From the constitutive relations [23] it is known that for a linear and isotropic medium $P$ can be expressed as

$$P = \varepsilon_0 \chi_e(\omega)E(\omega)$$

(2.1)

with $\varepsilon_0$ the vacuum permittivity, and $\chi_e = \varepsilon(\omega) - 1$ the electric susceptibility containing the dielectric function $\varepsilon(\omega)$. Obviously, $\varepsilon(\omega)$ can be obtained through determining $r$, i.e., solving the equation of motion of the electrons under the influence of an external field. Within the Drude-Sommerfeld model, only the effects of the free electrons are taken into account. Their equation of motion reads

$$m_e \frac{\partial^2 r}{\partial t^2} + m_e \Gamma \frac{\partial r}{\partial t} = e_0 E_0 e^{-i\omega t},$$

(2.2)

where $e_0$ and $m_e$ denote the elementary charge and the effective mass of the free electrons, respectively, $E = E_0 e^{-i\omega t}$ the excitation field, and $\Gamma$ the damping constant. Assuming an isotropic medium ($P \parallel E$), one obtains an expression for the contribution of free electrons to $\varepsilon(\omega)$:

$$\varepsilon^D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma \omega}.$$  

(2.3)

Here, $\omega_p$ is the plasma frequency of the metal which can be expressed as

$$\omega_p = \sqrt{\frac{n_e e_0^2}{\varepsilon_0 m_e}} = \sqrt{\frac{\sigma}{\varepsilon_0 \tau}}.$$  

(2.4)

Besides the conductivity $\sigma$ of the material, the mean time $\tau$ between two electron-electron scattering events is contained in Eq. 2.4. These scattering events represent the main damping process of free electron motion, which in the case of bulk metal is not influenced by a restoring force. The damping constant $\Gamma$ is related to the mean time $\tau$ by

$$\Gamma = \frac{1}{\tau} = \frac{v_F}{l_m}$$

(2.5)

with $v_F$ the Fermi velocity and $l_m$ the free mean path of the electrons between subsequent scattering events.
2.1 The dielectric function of metals

Interband transitions

The Drude-Sommerfeld model yields a relatively exact result for the dielectric function in the near-infrared spectral range. When setting out to describe the optical properties of metals in the visible regime, the contributions of bound electrons have necessarily to be taken into account. In this wavelength range, incident photons have higher energy and can promote electrons from lower levels into the conduction band. Such high-energetic interband transitions strongly affect $\varepsilon(\omega)$ over a wide spectral range, and the more of these transitions are taken into account, the more precisely theoretical values will approximate experimental data.

The effect of interband transitions is illustrated here using the examples of platinum and the noble metals of the first subgroup. The transitions of these metals occur predominantly between the $3d \rightarrow 4sp$ (Cu), $4d \rightarrow 5sp$ (Ag), and $5d \rightarrow 6sp$ (Pt, Au) levels [19, 24]. Further transitions may occur with lower probability. The absorption edge for copper and gold is situated in the visible range (590 nm and 515 nm, respectively), which manifests itself in the colors of these metals [25, 26]. In the case of silver, the absorption edge is located in the ultraviolet (320 nm, [25]), but it still influences the dielectric function in the visible regime considerably. Platinum shows absorption throughout the entire visible wavelength range due to a very broad absorption peak centered around 320 nm [27, 28]. Generally, the transitions from the conduction band back to the d-band can occur radiatively. In this case they are observable as visible photoluminescence [29] and have to be taken into account if metal structures are illuminated with high light intensities.

In the classical picture interband transitions can be treated as oscillations of bound electrons. Their equation of motion can be written as

$$\mathcal{M} \frac{\partial^2 \mathbf{r}}{\partial t^2} + \mathcal{M} \gamma \frac{\partial \mathbf{r}}{\partial t} + \zeta \mathbf{r} = e \mathbf{E}_0 e^{-i \omega t}.$$  \hspace{1cm} (2.6)

Here, $\mathcal{M}$ stands for the effective mass of bound electrons, which in general is different from the effective mass of a free electron in a periodic potential. The damping constant $\gamma$ describes mainly radiative damping, and $\zeta$ is the spring constant of the potential responsible for the restoring force. The lowest-order contribution of the bound electrons to $\varepsilon(\omega)$ therefore is

$$\varepsilon^{IB}(\omega) = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} + i \frac{\gamma \omega_p^2 \omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}.$$  \hspace{1cm} (2.7)

with $\omega_p = \sqrt{n e/\mathcal{M} \varepsilon_0}$ und $\omega_0 = \sqrt{\zeta / \mathcal{M}}$. For sake of simplicity, higher-order contributions caused by further electronic transitions are neglected here.
2 Theoretical considerations

2.1.2 Properties of the dielectric function

The expressions derived above give an insight into the properties of \( \varepsilon(\omega) \) and, hence, into the optical properties of metals and metal particles. As a summary, the dielectric function of a metal can be written as

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = [\varepsilon_D(\omega) + \varepsilon^{IB}_1(\omega)] + i[\varepsilon_D^I(\omega) + \varepsilon^{IB}_2(\omega)].
\] (2.8)

The real part \( \varepsilon_1(\omega) \) in Eq. 2.8 represents the polarization of the metal as in the case of a purely dielectric material, while the imaginary part \( \varepsilon_2(\omega) \) describes the energy dissipation (absorption) due to electron-electron scattering and interband transitions. A negative \( \varepsilon_1(\omega) \) is typical for metals at optical frequencies, while \( \varepsilon_2(\omega) \) is positive.

Fig. 2.1 shows experimentally determined \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) of Au, Ag, Cu, and Pt within the visible wavelength range. Gold and silver are most commonly used in nanooptics due to their relatively small \( \varepsilon_2(\omega) \). The depicted dielectric data for these two metals have been reported by JOHNSON [30]. For copper and platinum, the data of HAGEMANN [31] and WEAVER [28] are displayed. The depicted functions have been used as material data for the theoretical calculations in this work.

Fig. 2.1: Real (\( \varepsilon_1 \)) and imaginary part (\( \varepsilon_2 \)) of the dielectric function of Au, Ag, Cu, and Pt in the visible wavelength range. Note the different y - scales.
2.1 The dielectric function of metals

Penetration depth

The distance a plane wave travels inside a metal before its amplitude has dropped to $1/e$ of the initial value is called penetration depth and can be expressed as [22]

$$\delta(\omega) = \frac{\lambda}{4\pi} \left( \frac{1}{2} \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \frac{\varepsilon_1(\omega)}{2}} \right)^{-0.5}$$

(2.9)

with $\lambda$ the wavelength of the incident light. In the visible range, $\delta(\omega)$ takes on values of some tens of nanometers only, i.e., it is of the same order of magnitude as the free mean path $l_m$ (see Eq. 2.5). This is a very important point, as the metal structures used in nanooptics typically also have dimensions on the length scale below 100 nm. Therefore, precise figures for both $l_m$ and $\delta(\omega)$ are necessary to correctly interpret the optical response of the nanostructure under investigation. Experimental values for both the penetration depth and the mean free path of Ag, Au, Cu, and Pt are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ag</th>
<th>Au</th>
<th>Cu</th>
<th>Pt</th>
</tr>
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<tbody>
<tr>
<td>$\delta$ @ 620 nm</td>
<td>24</td>
<td>31</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>$\delta$ @ 413 nm</td>
<td>29</td>
<td>37</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td>$\delta$ @ 310 nm</td>
<td>82</td>
<td>27</td>
<td>29</td>
<td>17</td>
</tr>
<tr>
<td>$l_m$</td>
<td>52</td>
<td>42</td>
<td>42</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 2.1: Experimental values for the penetration depth $\delta$ [nm] as a function of incident wavelength and the bulk mean free path $l_m$ [nm] of Ag, Au, Cu, and Pt. Data from [28, 30, 32, 33].

Size effects

The description of nanostructures and particles by means of the bulk dielectric function becomes inadequate as soon as the structure dimensions are smaller than the mean free path of the electrons [34]. For structure sizes below this critical threshold the dielectric function becomes size-dependent. The occurring size effects have several origins: changes of the atomic structure, the influence of the surface (increased localization of the electrons, higher electron scattering at the surface), or higher influence of impurities and inhomogeneities.3

3Different approaches to account for these effects by means of an effective, size-dependent dielectric constant $\varepsilon(\omega, R)$ have been reported, including for example the limitation of the mean free path or the
Such size effects become significant in noble metal structures with dimensions below 10 nm, e.g. metal spheres with a radius smaller than 5 nm. As the nanoparticles investigated in this work is larger than this value, the use of the bulk dielectric function, for example for electrodynamics simulations, is justified. However, size effects are important in context with thin metal shells on particles and will be discussed briefly in chapter 8.

In the next section, $\varepsilon(\omega)$ is applied to describe the optical response of an illuminated metal nanosphere theoretically. This theory describes not only the physics of light-particle interaction. It also renders the basis of calculations performed in order to validate the experimental results presented in this book.

### 2.2 Localized surface plasmons in metal nanoparticles

The illumination of a metallic nanoparticle by means of a plane wave leads to fluctuations of the surface charge density as depicted in Fig. 2.2 a). The charge carriers in the particle collectively follow the external excitation, i.e., they oscillate with optical frequencies. Under these conditions, a small particle acts like an electric dipole and radiates (scatters) light. Furthermore, in regions of high charge densities, e.g. in the vicinity of the poles of a sphere, the near-field is enhanced in comparison to the incident excitation field (see Fig. 2.2 b).

For certain particle materials, the surface charge density oscillations exhibit resonances in the visible wavelength range. Such resonances are especially pronounced in noble metal particles and their optical properties are governed by this effect. The optical response of such small particles to incident electromagnetic radiation has first been calculated by MIE already in 1908 [5]. The MIE theory gives an analytical solution of Maxwell’s equations for a spherical geometry and thus leads to exact scattering and absorption cross sections for spherical particles. However, the price for the exact solution is the rather high mathematical complexity of the description. In order to follow the previous chapter in providing clear physical insight into the optical particle properties, the description is again simplified and condensed. Thus, the so-called quasi-static approximation is employed instead of the exact electrodynamical solution developed by MIE.

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4 “Small” means compared to the wavelength of the incident light, which here includes particles of 10 - 30 nm diameter. For this size, the bulk dielectric function still holds.
2.2 Localized surface plasmons in metal nanoparticles

Fig. 2.2: a) Schematic picture of the surface charge oscillations induced in a metal nanoparticle by an incident plane wave. A small particle (compared to the wavelength of the light) acts like an electric dipole with dipole moment \( \mathbf{p} \). b) Near-field distribution of a 30-nm gold particle in air. Due to the high charge density at the poles of the sphere, the local (non-propagating) field is enhanced in this region.

### 2.2.1 The quasi-static approximation

The key feature of an electrodynamical treatment using the quasi-static approximation is the negligence of retardation. With this approximation it is assumed that all volume elements \( dV \) of a particle respond simultaneously to an electromagnetic excitation field. This is only true if the characteristic size of the particle, i.e., the radius, is much smaller than the wavelength of the light. Consequently, there are no spatial variations of the electric field \( \mathbf{E} \) over the particle, but the field temporally oscillates according to \( e^{i\omega t} \).

Describing the optical response of a particle predominantly means determining the electric field distribution inside and outside of the particle. From this field distribution, several optical properties such as the absorption and scattering cross section can be derived. To this end, even the remaining time dependence \( e^{i\omega t} \) of the electric field is neglected and only the static field is analyzed.

The description starts with an expression for \( \mathbf{E} \) which in the quasi-static approximation can be represented by a potential \( \Phi \) as

\[
\mathbf{E} = -\nabla \Phi. \tag{2.10}
\]

The Helmholtz equation in the quasi-static limit reduces to the Laplace equation which is easier to solve. This means that the potential \( \Phi \) has to satisfy the condition

\[
\nabla^2 \Phi = 0. \tag{2.11}
\]
As spherical particles are considered here, Eq. 2.11 is rewritten in spherical coordinates \( r, \theta, \phi \):

\[
\frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \right] \Phi(r, \theta, \phi) = 0
\]  
(2.12)

with solutions

\[
\Phi(r, \theta, \phi) = \sum_{l,m} a_{l,m} \cdot \Phi_{l,m}(r, \theta, \phi).
\]  
(2.13)

In Eq. 2.13, \( a_{l,m} \) denote constant coefficients, and the \( \Phi_{l,m} \) are of the form

\[
\Phi_{l,m} = \left\{ \begin{array}{c} r^l \left( \frac{r}{r-l-1} \right) \\ P^m_l(\cos \theta) \\ Q^m_l(\cos \theta) \\ e^{im\phi} \end{array} \right\}
\]  
(2.14)

where \( P^m_l \) are the associated Legendre functions and the \( Q^m_l \) the Legendre functions of the second kind. Evaluation of the boundary conditions for \( \Phi(r, \theta, \phi) \) at the surface of the sphere and subsequently solving Eq. 2.10 finally yields the electric fields inside and outside the sphere:

\[
\begin{align*}
E_{\text{in}} &= E_{\text{exc}} \frac{3\varepsilon(\omega)}{\varepsilon(\omega) + 2\varepsilon(\omega)_m} n_{\text{exc}} \\
E_{\text{out}} &= E_{\text{exc}} + E_{\text{sca}} \\
&= E_{\text{exc}} n_{\text{exc}} + E_0 (2 \cos \theta n_r + \sin \theta n_\theta) \frac{R^3 \varepsilon(\omega) - \varepsilon_m}{r^3 \varepsilon(\omega) + 2\varepsilon_m}
\end{align*}
\]  
(2.15)

with \( n_{\text{exc}}, n_r, n_\theta \) the respective unit vectors, \( E_{\text{exc}} \) and \( E_{\text{sca}} \) the excitation and scattered field, respectively, \( R \) the radius of the sphere, and \( \varepsilon_m \) the dielectric constant of the surrounding medium which is assumed to be real.\(^5\) The field inside the sphere is homogeneous, which contradicts Eq. 2.9 describing the exponential decay of an electromagnetic field inside a metal. This homogeneity is a result of the quasi-static approximation, which is only valid for particle diameters smaller than the penetration depth (see Table 2.1). Another important point is that the second term of Eq. 2.15 (the induced scattering field) turns out to be identical to the electric field of a dipole moment

\[
p = \alpha \varepsilon_m E_{\text{exc}}
\]  
(2.16)

located at the center of the sphere and driven by the external field \( E_{\text{exc}} \). A comparison with Eq. 2.15 yields the polarizability \( \alpha \) of the sphere:

\[
\alpha = 4\pi \varepsilon_0 R^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m}
\]  
(2.17)

\(^5\)The dielectric constant is dimensionless here, i.e., the vacuum permittivity \( \varepsilon_0 \) is not contained in \( \varepsilon_m \).
2.2 Localized surface plasmons in metal nanoparticles

Expression 2.17 reveals the parameters which influence the polarizability, and, hence, the plasmonic properties of a MNP. In particular, these parameters are the particle size ($R$), the particle material (via $\varepsilon(\omega)$), and the dielectric constant of the surrounding medium ($\varepsilon_m$). In the case of a sphere, $\alpha$ is isotropic. For other particle shapes, however, different polarizabilities may exist for different spatial directions, which leads to a shape dependence of the optical response of a particle already within the quasi-static approximation. As the scattering and absorption cross section of a nanoparticle can directly be derived from $\alpha$ (see section 2.2.3) these magnitudes also depend on the abovementioned parameters. However, before these dependencies are discussed a closer look at the electric fields induced by a nanoparticle follows.

2.2.2 Electric fields induced by a nanosphere

In this work not only the optical properties of single nanospheres, but also their interactions with other particles as well as with fluorescent molecules are of interest. It is therefore worthwhile to have a closer look at the fields in the vicinity of a metallic nanoparticle.

In this context, the finding that these fields equal the ones induced by a single dipole located at the center of the sphere is used again. The electric field of an oscillating dipole is given by

$$
E = \frac{1}{4\pi\varepsilon_0\varepsilon_m} \left( -\frac{\mathbf{p}(t_0)}{r^3} + \frac{3\mathbf{r} \cdot \mathbf{p}(t_0)}{r^5} + \frac{ik\mathbf{p}(t_0)}{r^2} 
- \frac{3ik\mathbf{r} \cdot \mathbf{p}(t_0)}{r^4} - \frac{k^2}{r^3} \mathbf{r} \times [\mathbf{r} \times \mathbf{p}(t_0)] \right)
$$

(2.18)

with $t_0 = t - kr/\omega$ and $k$ the wave vector in the surrounding medium. The first two terms of Eq. 2.18 are the so-called static field and represent the scattering field discussed in the previous section. The following two terms are called induction field and are induced by the current due to the dipole oscillation, while the last term is the radiation field. These three fields decay as $r^{-3}$, $r^{-2}$, and $r^{-1}$, respectively, and only the radiation field propagates to infinite distances. The other two are fast decaying, so-called evanescent fields, i.e., they constitute the near-field of the sphere. As in nanooptics these evanescent fields are of central interest, for example in the context of near-field particle-particle coupling, the question arises how far these near-fields extend from the particle surface.
into the surrounding medium. To find an answer, one can at first develop Eq. 2.18 to

\[ E = \frac{\mathbf{p} e^{ikr}}{4\pi \varepsilon_0 \varepsilon_m} \left[ \left( \frac{2}{r^3} - \frac{2ik}{r^2} \right) \cos \theta n_r + \left( \frac{1}{r^3} - \frac{ik}{r^2} - \frac{k^2}{r} \right) \sin \theta n_\theta \right]. \quad (2.19) \]

When the origin of the coordinate system is placed at the center of the sphere, field profiles along any sphere diameter do not depend on the sphere radius \( R \), but exclusively on the distance \( r \) from the origin. The size of the sphere influences only the amplitude of the fields. In the region \( r \ll k = 0.16\lambda \), the static field dominates as

\[ |E| \propto \left( \frac{R}{r} \right)^3. \quad (2.20) \]

This feature in retrospect justifies the neglection of the time dependence used in section 2.2.1, and again demonstrates the limitation of the quasi-static approximation to particles smaller than the penetration depth. When the origin of the coordinate system is shifted to the surface of the metal sphere, Eq. 2.20 changes to

\[ |E| \propto \left( \frac{R}{R + d} \right)^3 \quad (2.21) \]

with \( d \) denoting the distance from the sphere surface. Within the region \( 0 \leq d \leq 2R \), Eq. 2.21 can be approximated by an exponential decay function of the form \( e^{-d/d^*} \) with a decay length of \( d^* = 0.63R \) [19]. Thus, as a rule of thumb, the near-field of a metal sphere extends over approximately \( R/2 \) from the particle surface. This means that for observing near-field coupling effects, for example in a particle pair, the interparticle separation has to be in the order of \( 2 \cdot R/2 = R \) or smaller.

### 2.2.3 Scattering and absorption of light by a metal nanosphere

When a single particle is illuminated, for example by a plane wave of intensity \( I_{\text{exc}}(\omega) \), the intensity of the light scattered by the particle depends on the particle scattering cross section \( \sigma_{\text{sca}} \) according to

\[ I_{\text{sca}}(\omega) = \sigma_{\text{sca}}(\omega) \frac{I_{\text{exc}}(\omega)}{A} \quad (2.22) \]

with \( A = \pi R^2 \) the projected area of the particle. In this denotation, \( \sigma_{\text{sca}}(\omega) \) gives an effective particle area and is one of the most important parameters for the optical characterization of particles. Especially in its spectral distribution \( \sigma_{\text{sca}} \) contains ample information, e.g. on the particle geometry, and is at the same time well accessible in experiments.
Expressed in a more general way, the scattering cross section can be calculated from

$$\sigma_{sca}(\omega) = \frac{I_{sca}}{I_{exc}} A = \frac{W_{sca}}{S_{exc}}. \quad (2.23)$$

Here, $W_{sca}$ is the total power of the scattering (radiation) field, i.e., the total power emitted by a dipole again located at the sphere’s center and driven by the external field $E_{exc}$:

$$W_{sca} = \int_0^{2\pi} \int_0^{\pi} |S_{sca}| r^2 \sin \theta d\theta d\phi = \frac{\omega k^3 |p|^2}{12\pi \varepsilon_0 \varepsilon_m} = \frac{\omega k^3 \varepsilon_m}{12\pi \varepsilon_0} |\alpha|^2 E_{exc}^2 \quad (2.24)$$

with $S_{sca}$ the time-averaged energy flow carried by the scattering field into 3D space. The other term in Eq. 2.23, $S_{exc}$, is the time-averaged energy flow of the external excitation field through the projected particle area. It can be expressed by the real part of the Poynting vector:

$$|S_{exc}| = \frac{1}{2} \Re \left( \mathbf{E}_{exc} \times \mathbf{H}_{exc}^* \right) = \frac{\omega \varepsilon_0 \varepsilon_m}{2k} E_{exc}^2. \quad (2.25)$$

Consequently, the scattering cross section is obtained as

$$\sigma_{sca}(\omega) = \frac{k^4}{6\pi \varepsilon_0^2} |\alpha(\omega)|^2 = \frac{8}{3} \pi k^4 R^6 \left| \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \right|^2. \quad (2.26)$$

From a light beam incident on a particle, power is not only removed by scattering but also by absorption. The power dissipated in the particle can be calculated as the power dissipated by the point dipole representing the sphere [23]:

$$W_{abs} = \frac{\omega}{2} \Im [\mathbf{p} \cdot \mathbf{E}_{exc}^*]. \quad (2.27)$$

Inserting relation 2.16 then yields the absorption cross section:

$$\sigma_{abs}(\omega) = \frac{W_{abs}}{S_{exc}} = \frac{k}{\varepsilon_0} \Im [\alpha(\omega)] = k \Im \left[ \frac{4\pi R^3 \varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \right]. \quad (2.28)$$

Both cross sections and the scattering field (see Eq. 2.15 on page 12) exhibit especially high values wherever the denominator of the polarizability goes through a minimum, i.e., if the resonance condition

$$|\varepsilon(\omega) + 2\varepsilon_m| \to min \quad (2.29)$$

is fulfilled. At this point, the properties of the dielectric function of the sphere material come into play again. When $\varepsilon(\omega)$ fulfills condition 2.29 due to the behavior of the electrons in the metal, i.e., a resonance of the surface charge density oscillations occurs,
the resonance is called a localized surface plasmon (LSP) resonance. If \( \varepsilon_2(\omega) \) or its frequency dependence \( \partial \varepsilon_2(\omega) / \partial \omega \) is small as is the case for gold, the spectral resonance position can be established from the relation

\[
\varepsilon_1 = -2\varepsilon_m.
\]  
(2.30)

Thus, the maximum scattering efficiency occurs where \( \varepsilon_1(\omega) = -2 \) if air is the surrounding medium. In a medium with \( n = \sqrt{\varepsilon_m} = 1.52 \) such as BK7 glass, the scattering efficiency is maximized for \( \varepsilon_1 = -4.62 \).

As long as the quasi-static approximation is applied, the spectral position of the LSP resonances is determined by \( \varepsilon(\omega) \) and \( \varepsilon_m \), while the size of the sphere has influence solely on the amplitude of the scattered and absorbed light. However, the quasi-static description does not hold for particle diameters \( >30 \text{ nm} \), as for larger particles the condition \( R \ll \lambda \) is not fulfilled anymore. On such large particles, depolarization of the incident electric field and other size-dependent effects occur, leading to a size dependence of the spectral LSP resonance position. In particular, the LSP resonances of larger particles are clearly red-shifted compared to the spectra obtained from quasi-static calculations. As the dimensions of the particles investigated in this work are typically between 30 and 100 nm, these retardation effects have to be taken into account to obtain reliable theoretical predictions. This can be achieved by using the so-called modified long wavelength approximation (MLWA) - an extension of the quasi-static description, which is discussed in the next section.

### 2.2.4 Modified long wavelength approximation

In the previous section, both advantages and limitations of the quasi-static approximation have been discussed. To develop a more accurate theory it is necessary to correct the quasi-static results for finite wavelength effects. In the modified long wavelength approximation (MLWA), these corrections are introduced by rewriting Eq. 2.16 as [35]

\[
p = \alpha \varepsilon_m [E_{\text{exc}} + E_{\text{rad}}] 
\]  
(2.31)

where the radiative correction field \( E_{\text{rad}} \) is

\[
E_{\text{rad}} = \frac{2}{3} ik^3 p + \frac{k^2}{R} p.
\]  
(2.32)

Inserting Eq. 2.32 into Eq. 2.31 gives a corrected polarizability

\[
\alpha'(\omega) = \alpha(\omega) \left[ 1 - \frac{2}{3} ik^3 \alpha(\omega) - \frac{k^2}{2R} \alpha(\omega) \right]^{-1}
\]  
(2.33)
which leads to corrected scattering and absorption cross sections

\[
\sigma'_{\text{sca}}(\omega) = \frac{k^4}{6\pi\varepsilon_0} |\alpha'(\omega)|^2 \quad \sigma'_{\text{abs}}(\omega) = \frac{k}{\varepsilon_0} \Im\{\alpha'(\omega)\}.
\]  

(2.34)

Briefly, the introduced corrections concern two effects. The first term in Eq. 2.32 describes the radiative damping arising from spontaneous emission of radiation by the induced dipole. This emission grows rapidly with particle size, eventually reducing the size of the induced dipole and increasing the LSP resonance linewidth. The second term comes from depolarization of the radiation across the particle surface due to the finite ratio of particle size to wavelength. This dynamic depolarization term causes a redshift of the LSP resonance position as the particle size is increased.

It has been shown [35] that the MLWA gives an accurate description of the electrodynamic effects induced by the collective dipolar electron oscillations in metal nanoparticles. Both the spectral position of the LSP resonance and its linewidth calculated by means of this method agree very well with experimental data. If not stated otherwise, it is this dipolar LSP mode which is analysed and exploited in the experiments described in this book.

### 2.2.5 Semi-analytical calculations

The MLWA is based on the assumption that the scattered fields can be represented by the (corrected) fields of an oscillating dipole located at the center of the particle. This leads to the negligence of higher-order oscillation modes, e.g. quadrupoles, which are supported by larger particles and experimentally observed for particle diameters \( > 100 \text{ nm} \). For these higher-order modes analytical corrections and extensions have been developed [35]. However, at some point the approach advances to a similar level of complexity as inherent in the correct MIE theory, and it then looses its simplifying character.

On the other hand, although in the MIE theory Maxwell’s equations are solved analytically without approximations, it also has some intrinsic drawbacks besides its rather high degree of complexity. In particular, full analytical solutions only exist for a very limited number of particle geometries [5]. Therefore, a semi-analytical method has been employed in this work to perform electrodynamics simulations, i.e., to verify and understand experimentally obtained optical responses of nanoparticles. The applied method is called multiple-multipole (MMP) method, comprehensively described in [38], and shortly sketched in Appendix A. The advantages of MMP include yielding reliable

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6 A more detailed discussion of the origin of the corrections can be found in [36] and [37].
results in relatively short computation times and not being limited to special geometrical shapes.

2.3 Parameters affecting the optical properties of nanoparticles

Choosing particles with optical properties suitable for the desired application, e.g. for particle-enhanced microscopy, is a critical issue and sometimes not straightforward due to the interplay between the size-, shape-, and material dependencies. In what follows, the influences of these parameters on both the intensity and the spectral distribution of the light scattered from and absorbed by a nanoparticle are discussed.

Particle size

A closer look at the quasi-static scattering and absorption cross sections (Eq.s 2.26 and 2.28)

\[
\sigma_{\text{sca}} = \frac{8}{3} \pi k^4 R^6 \left| \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \right|^2 \\
\sigma_{\text{abs}} = k \Im \left[ 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \right]
\]

reveals that \(\sigma_{\text{sca}}\) and \(\sigma_{\text{abs}}\) have different dependences on the size of the particle. The scattering cross section scales with the 6th power of \(R\), whereas \(\sigma_{\text{abs}}\) goes only with \(R^3\). Consequently, for larger particles scattering dominates the optical behavior, whereas for smaller particles absorption prevails. In the case of gold particles in a surrounding medium with \(n = 1.52\), the cross-over between the two effects takes place at a particle diameter of approximately 20 nm. A particle with a diameter smaller than this threshold value will appear as an absorbing, hence, dark point in a microscope image, whereas larger particles appear as bright scattering centers.

This interplay between scattering and absorption leads to interesting color effects. For example, small gold particles absorb predominantly green light and thus cause a red color. Large particles, on the other hand, scatter green light and therefore render a green color. Without being completely understood back then, this effect has been applied over centuries for the coloring of church windows or decorative objects made of glass containing nanometer-sized gold particles [39].
2.3 Parameters affecting the optical properties of nanoparticles

The size of the particle, i.e., the radius of a sphere, not only influences the intensity of the scattered light. As discussed in section 2.2.4, also the spectral position of the LSP resonance is affected by the particle size. On larger particles retardation and other finite-wavelength effects occur and lead to a redshift of the LSP resonance. The investigation of this spectral shift by means of MMP yielded an empirical relation between the LSP resonance wavelength $\lambda_{\text{res}}$ and the sphere diameter $D$ for gold particles embedded in a medium with $n = 1.5$ [40]:

$$\lambda_{\text{res}}[\text{nm}] = \frac{478 \cdot D[\text{nm}] - 91500}{D[\text{nm}] - 171.35}. \quad (2.35)$$

**Particle shape**

Not only the size, but also the shape of a particle influences the spectral LSP resonance position. In the last decade, the fabrication of nanoparticles with many different complex shapes has been reported (e.g. nanotriangles [41], nanocubes [42], nanostars [43], etc.). Many of them reveal completely new plasmonic modes compared to a sphere. However, a detailed discussion of each of these shapes would be way beyond the scope of these rather general theoretical considerations. Therefore, only a short comment on ellipsoidal particles is made here.

For simple geometries such as a prolate spheroid, the influence of the shape can be described within the quasi-static approximation by considering different polarizabilities $\alpha_i$ for different particle axes. Hence, different LSP oscillation directions exhibit different resonance conditions. In particular, the quasi-static polarizabilities of an ellipsoidal particle with axes lengths $a$, $b$, and $c$ reads [20]

$$\alpha_i = 4\pi\varepsilon_0 abc \frac{\varepsilon(\omega) - \varepsilon_m}{3L_i[\varepsilon(\omega) - \varepsilon_m] + 3\varepsilon_m}. \quad (2.36)$$

For the geometry factors $L_i$ the condition $\sum_i L_i = 1$ applies, and for a cigar-shaped prolate spheroid with equal axes $a$ and $b$ also $L_1$ and $L_2$ are equal. The remaining factor $L_3$ can be obtained from

$$L_3 = \frac{1 - e^2}{e^2} \left( -1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right) \quad (2.37)$$

with $e$ the eccentricity

$$e = \sqrt{1 - \frac{c^2}{a^2}}. \quad (2.38)$$

As a consequence, such elongated particles exhibit several resonance wavelengths when illuminated with non-polarized light [44] (see Fig. 2.3). Ellipsoidal particles are discussed in more detail in chapter 6.
2 Theoretical considerations

Fig. 2.3: Scattering spectrum of a gold nanorod with 50 nm short and 100 nm long axis ($\varepsilon_m = 2.25$). According to the different axis lengths the spectrum exhibits two peaks as response to non-polarized white-light illumination.

**Dielectric constant of the surrounding medium**

The polarizability of a nanoparticle, and thus $\sigma_{abs}$ and $\sigma_{sca}$, depend on the dielectric constant $\varepsilon_m$ of the surrounding. A change of $\varepsilon_m$ alters the resonance condition 2.29, and thus shifts the spectral position of the LSP resonance. At the same time, also the absolute value of the polarizability is influenced. Fig. 2.4 illustrates this effect for a 100 nm gold particle, embedded either in water ($\varepsilon_m = 1.77$) or immersion oil ($\varepsilon_m = 2.25$). A clear redshift as well as an increase of the scattering peak can be observed for increasing $\varepsilon_m$.

It has been shown that the LSP resonance is influenced only by the dielectric constant of the very vicinity of the particle, i.e., the particles “sees” only a few nanometers of its surrounding [46]. Noble metal particles therefore find applications as refractive-index sensors with very high spatial resolution [15, 47].

**Dielectric function of the particle material**

Most obviously, the plasmonic properties of a nanoparticle depend on the dielectric function of the particle material itself. As different metals exhibit different electron densities, lattice structure etc., the frequency at which the resonance condition 2.29 is fulfilled varies dramatically from one material to the other. Especially noble metals show plasmonic resonances in the visible wavelength regime, and each of them does so only for a part of this range. For example, gold sphere embedded in a medium with $n = 1.5$ are
2.3 Parameters affecting the optical properties of nanoparticles

Fig. 2.4: Scattering spectra of a gold particle of 100 nm diameter, supported by a cover glass and embedded in two different dielectrics. An increase in $\varepsilon_m$ leads to a redshift of the LSP resonance wavelength as well as to a higher scattering cross section. Taken from [45] with permission.

resonant at wavelengths $\geq 550$ nm (depending on the other parameters discussed above), whereas under these conditions silver resonances are found below 500 nm only [48].

This resonance range can be broadened by alloy particles consisting of a mixture of several materials. Gold-silver alloys, for example, bridge the gap between 500 nm and 550 nm in terms of resonance wavelength [49]. For such particles, a theoretical description is not straightforward because the dielectric function of the alloy cannot be considered the weighted sum of the combined materials [50]. Instead, a distinctly determined dielectric function has to be used for the alloy.

Another possibility to combine two (or more) different materials are so-called core-shell particles, in which a core of material A is surrounded by a shell of material B. Both materials A and B may either be a metal [51, 52] or a dielectric [53, 54], either directly supporting electron oscillations or acting as surrounding media with distinct values of $\varepsilon_m$. Again, the number of possible material combinations for core-shell particles and the resulting optical properties are enormous - even hollow particles have been reported [55, 56].

Finally, the dielectric function of the particle can not only be altered by combining different materials. Also particles of the same material might exhibit different plasmonic spectra depending on the material structure [57]. Single-crystalline particles, for example, typically have much “better” resonances, i.e., higher scattering cross section and
smaller linewidth, compared to their poly-crystalline pendants [58]. The latter exhibit grain boundaries which lead to additional electron scattering, i.e., higher absorption, lower scattering cross sections and wider resonance curves.

All of the abovementioned parameters can be combined to design particles with optical properties meeting the demands of the desired application. As a result, a huge variety of particles with different plasmonic spectra have been synthesized during the last decade. In order to precisely determine a plasmonic spectrum, single-particle investigations are indispensable. Suitable techniques for such investigations are described in the next chapter.
3 Experimental techniques

This chapter deals with the experimental techniques applied for characterizing the optical properties of metal nanoparticles. After a general description of the sample layout, the principle of confocal microscopy is discussed. This type of scanning far-field optical microscopy was used in a special configuration, the so-called wide-field excitation mode. Finally, near-field optical microscopy is shortly sketched.

3.1 Sample layout

The majority of optical measurements presented in this book were carried out on single nanoparticles or single particle pairs by means of optical microscopy and spectroscopy. Investigating the properties of single particles intrinsically bears the advantage that clear information can be derived from the measured optical signals. No size distributions or unwanted interparticle coupling effects occur, as might be the case in ensemble measurements. Fortunately, metal particles are very forgiving samples for optical microscopy as they withstand high excitation intensities, do not bleach, and exhibit a rather strong scattering signal. Furthermore, the latter reveals many structural and geometrical properties of the particle under investigation (see section 2.3).

The typical sample layout is depicted in Fig. 3.1. Metal nanoparticles are spread on a 100 - 170 µm thick microscope cover glass (BK7) with refractive index $n = 1.52$. For the fabrication of these samples different techniques have been applied. As these fabrication techniques are sometimes crucial for the conducted investigations, they will be discussed in more detail in context with the respective experiments.

The samples investigated in this work have two features in common. Firstly, the metal particles are always located on top of the cover glass as shown in Fig. 3.1. In this configuration, the layout allows for the excitation of the samples and the detection of their optical response by means of an inverted optical microscope from below, while the sample can be manipulated, e.g. chemically or mechanically, from above (see Fig. 3.2). Secondly, the particles have a lateral distance of at least 10 µm from each other so that it is pos-

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1 The thickness of the cover glass is dictated by the working distance of the microscope objective. For the ZEISS objective used here the maximum thickness amounts to 210 µm.
3 Experimental techniques

Fig. 3.1: Typical sample layout for single-particle experiments. Metal particles are situated on top of a BK7 cover glass and are well separated from each other (10 µm minimum distance). It is therefore possible to optically address single particles.

Possible to optically address a single particle without affecting the neighboring ones. Such single-particle samples are investigated by means of the setups described below.

3.2 Scanning far-field optical microscopy

3.2.1 Confocal microscopy

The key component of the optical setup used in this work is an inverted optical microscope, ZEISS AXIOVERT 200. Illumination of the sample and detection of its optical response are carried out in a confocal setup as depicted in Fig. 3.2. The light source is either a collimated laser beam or a xenon arc lamp. The light is directed through an electro-optical modulator (EOM) and a GLAN-THOMPSON polarizer. This combination allows for the control of both the polarization direction and the light intensity. The beam is then reflected from a beam splitter into the microscope objective. For all experiments, a ZEISS α-PLANFLUAR 100x oil immersion objective with a high numerical aperture (N.A.) of 1.45 has been used.\(^2\)

In case of laser illumination, this objective creates a diffraction-limited spot on the sample the lateral extension of which depends on the laser wavelength [59]:

\[
\Delta x \approx 0.61 \frac{\lambda}{N.A.} = 0.42\lambda
\]

\(^2\)The complete parameter set of the objective: 100x/1.45/∞/0.17. Focal length: 1.645 mm, entrance pupil diameter: 4.79 mm, free working distance with a 0.17 mm BK7 cover glass: 0.11 mm, field of view: 23 mm, position of backfocal plane: -4.99 mm. The opening angle of the detection cone amounts to 144°.
3.2 Scanning far-field optical microscopy

Fig. 3.2: Confocal microscopy setup. **Green**: Excitation light (either laser or white-light) passing an electro-optical modulator (EOM) and a polarizer, and finally being focused onto the sample. **Yellow**: Scattered light gathered in a confocal detection path.

A laser of 532 nm wavelength thus creates a spot size of approximately 220 nm. Although the objective is well corrected for chromatic imaging errors, the white-light beam is focused to a much larger spot of approximately 5 µm which is due to the limited collimation of the beam. Nevertheless, with both illumination sources it is easily possible to address one single particle as the particles are at least 10 µm separated from each other.

Two major light-sample interaction processes are observed in this configuration: while one portion of the incident beam is scattered from the addressed particle, another part is reflected from the oil-glass and glass-air interfaces of the sample. All signal components stemming from the sample and propagating into the lower half space are collected by the same objective that is used for illumination. After passing the beamsplitter, a second
lens focuses the collected light onto a slit aperture in front of a detector. The aperture rejects out-of-focus components from the collected light, i.e., light not originating from the focus will not pass the aperture and, hence, can not reach the detector. Laterally displaced beams will be directly blocked by the aperture, and beams stemming from points displaced along the optical axis are not focused onto the detection plane and will therefore be strongly attenuated by the slit.

Closing the aperture thus means reducing the investigated sample area and increasing the spatial resolution within the diffraction limit. However, at the same time the number of photons entering the detector is drastically reduced, necessarily leading to longer exposure times for spectroscopic measurements. A slit width of 100 µm turned out to render a reasonable compromise between these two competing processes. As the slit length is fixed to approximately 100 µm as well and a 100x objective is used, the investigated sample area amounts to approximately 1 µm$^2$. This area again fulfills the prerequisite of single-particle addressing. The detector following the slit aperture in the optical beam path is a combination of a 75 mm$^{-1}$ grating spectrometer and a CCD camera cooled to -60°C by means of a Peltier element.

As in this confocal setup the sample is illuminated by a diffraction-limited spot, the cover glass has to be raster-scanned through the focus in order to obtain a full image. Thus, the sample is mounted onto a piezo scanning stage, which is operated via a home-built computer software for scanning purposes. As this software is run on the same computer which also reads the CCD camera, the signal from the camera can be directly attributed to the respective sample location. In addition to scanning, the sample position can be manipulated by a manual offset.

This setup was used for both optical imaging and spectroscopic measurements. For the former, the CCD signal of a rather small spectral window is integrated and converted into a corresponding pixel image color. The spectral window might either include the excitation wavelength only (for determining scattering properties), or it may span some other range (e.g. the fluorescence spectrum of certain dye molecules). The spectral integration of the photons counted within the selected range offers the advantage of low exposure times (approx. 0.1 sec per pixel), i.e., high scanning speed. However, any spectral information within this range is “lost“ in the integral value. This information is retained in spectroscopy experiments, where no spectral integration is carried out. In these cases, a single particle is moved into the optical focus by means of the manual position control.

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3 Spectrometer: SOLAR TII MS7504. Camera: ANDOR DU440.
4 PXY 101 CAP, PIEZOSYSTEM JENA, Germany
5 “SPMM“ by Tobias Otto.
3.2 Scanning far-field optical microscopy

and a single spectrum $I(\lambda)$ is acquired. The recorded spectrum is then normalized to the signal of the reflection $I_{\text{ref}}(\lambda)$ from the glass surface according to the formula

$$I_{\text{norm}}(\lambda) = \frac{I(\lambda)}{I_{\text{ref}}(\lambda)} \cdot 100.$$ (3.1)

To measure the reflection spectrum, the sample was moved by means of the piezostage to a position where the incident light did not hit any particle.

### 3.2.2 Wide-field excitation

In the confocal setup described above the collimated beam has a linear polarization and a Gaussian intensity profile. The polarization direction can be freely rotated by the combination of EOM and polarizer, but always stays uniform over the beam cross section. However, focusing such a Gaussian beam leads to an effect called depolarization: the focal region contains field components with polarizations different from the input beam [60, 61]. Fig. 3.3 depicts the focal polarization components as simulated by MMP [62]. Besides the original polarization ($x$ direction), a weak component with four-fold symmetry is generated in $y$ direction, and in $z$ direction a two-lobe contribution can be seen.

Fig. 3.3: MMP-calculated polarization components of a focused Gaussian beam (originally polarized in $x$ direction) in the focal region ($\lambda = 700$ nm, $n = 1.52$, N.A. = 1.45). a) $x$ component. b) $y$ component (intensity x 1000). c) $z$ component. d) Sum of all components. Taken from [62] with permission.

These additional polarization components can excite processes in the sample not induced by purely linearly polarized light. Especially in non-spherical particles the additional polarization components may excite unwanted LSP modes and therefore complicate the optical response of the particle. To circumvent this problem, a different illumination modes was installed (see Fig. 3.4). In this so-called wide-field mode, an additional
lens is introduced into the white-light beam to better determine the scattering spectrum of single particles. This lens focuses the input light onto the backfocal plane of the objective, resulting in a beam which leaves the objective nearly collimated (divergence angle $< 10^\circ$). Thus, the sample is illuminated on a circular area with 20 $\mu$m diameter and uniformly distributed power. This configuration provides essentially plane-polarized incident light, as out-of-plane components of the electric field can be neglected in the object plane. Furthermore, as the detection path is not influenced by introducing the additional lens into the excitation path, it retains its confocal character.

Fig. 3.4: Combined wide-field white-light excitation and confocal laser microscopy setup. In comparison to Fig. 3.2, the white-light beam (depicted in red) is not focused onto the sample but leaves the objective as a collimated beam. It thus provides plane-polarized excitation light for determining the scattering properties of the sample.
3.2 Scanning far-field optical microscopy

3.2.3 The role of immersion media

As mentioned above, an oil immersion objective has been used in this work for both illuminating the samples and collecting their optical response. However, not only the space between the front lens of the objective and the cover glass has been filled with immersion oil. An immersion medium has also been applied on top of the specimen to embed the MNPs under investigation. This technique, introduced as “homogeneous immersion” by STEPHENSON already in 1878 [63], offers several benefits. Due to the large difference of the refractive indices at the air-glass interface, a sizeable portion of the incident light is reflected even under wide-field illumination. The intensity of this reflected light is typically much higher than the light scattered by a single metal particle, thus preventing single-particle detection. Therefore the interface is virtually removed by applying an index-matching liquid on top of the sample. Under such conditions, only very low reflection occurs, and the contrast between scattered and reflected light is augmented. In addition to this optical effect, even more advantages arise from the use of an immersion liquid:

- As has been discussed in detail in section 2.3, the plasmonic response of the particle, i.e., the scattering cross section, is increased due to the high $\varepsilon_m$ of the surrounding medium, further easing the optical measurements. In fact, in the eyepiece of the microscope the particles appear as very bright scattering centers in front of a dark background.

- The immersion medium strongly suppresses degradation of samples, e.g. photooxidation of certain metals such as copper [64] or organic molecules [65]. Due to diffusion inside the liquid medium, heat is effectively transported away from single particles, further preventing optically induced damage.

- The medium might be used as a solvent, for example for fluorescent dyes or charged ions, which might either be the substance under investigation or in some other way important for the experiment.

- A theoretical modeling of the optical particle response becomes much easier when the particle environment is homogeneous. The presence of an interface not only leads to a change of the effective dielectric constant of the surrounding medium, but can also heavily distort emission patterns, e.g. that of a dipole [66]. These effects are suppressed by the homogeneous immersion method.
3 Experimental techniques

However, the abovementioned advantages are accompanied by some drawbacks. The immersion medium itself might be harmful to the sample under investigation, and it often turns out that it is difficult to remove the liquid without also rinsing off the particles. Evaporation of the medium (or of components) might cause further complications. However, these problems did not occur with the liquids used in this work. The space between objective and cover glass was always filled with ZEISS IMMERSOL 518 F\(^6\), which is the standard immersion liquid recommended by the producer of the objective. For homogeneous sample immersion, CARGILLE #1160\(^7\) was typically used, an oil especially designed to exhibit low viscosity. This low viscosity is a crucial condition for several experiments. For example, it allows to operate a near-field scanning optical microscope in homogeneous immersion (see next section).

3.3 Scanning near-field optical microscopy

As mentioned above, conventional (far-field) microscopy has diffraction-limited spatial resolution in the order of half the wavelength. To circumvent this restriction, several other optical microscopy techniques have been developed which provide sub-wavelength resolution [67]. One way to push the resolution to smaller length scales is to increase the spectrum of spatial frequencies \(k = \omega/c\) involved in the imaging process. In far-field microscopy, the \(k\)-spectrum is limited to the range \(k \in [0...N.A. \cdot \omega/c]\), reaching a strict limit for \(N.A. = n\) [21]. However, such far-field considerations ignore the spatial frequencies associated with evanescent waves. In fact, evanescent waves can increase the \(k\)-spectrum drastically and resolution can - aside from experimental complications - be improved arbitrarily [68]. The optical near-field in the vicinity of a nanostructure is such an evanescent wave and can be accessed and exploited by different techniques. One of them is the so-called apertureless scanning near-field optical microscopy (ASNOM), which is briefly presented here.\(^8\)

ASNOM relies on the fact that any material under far-field illumination exhibits a near-field in its vicinity. Depending on the material properties, the strength of the near-field can be higher than that of the incident light, e.g. due to a LSP resonance. Thus, intense research has been devoted to the fabrication of near-field probes with high field enhancement and strong confinement. As a result, pointed metal tips or metal-coated dielectric tips are typically used to raster-scan the sample under far-field irradiation, cre-

\(^{6}\)\(n = 1.518 \ @ \ \lambda = 589\ nm\)

\(^{7}\)\(n = 1.517 \ @ \ \lambda = 589\ nm\)

\(^{8}\)A detailed discussion of other methods can be found in textbooks on the topic [69, 70].
3.3 Scanning near-field optical microscopy

ating a near-field illumination only in the vicinity of the sub-wavelength tip apex. In case the contrast between the sample response due to far-field illumination and the response due to the enhanced near-field of the probe is too weak, modulation or other techniques might be applied to suppress the far-field background signal [71].

Fig. 3.5: Block diagram of the ASNOM. The shear-force feedback mechanism is used to position the tip at a desired height above the sample.

The home-built ASNOM system\(^9\) used here consists of a quartz tuning fork driven at its resonance frequency of 32.8 kHz, to which the near-field probe is glued [72] - [74]. When the tip is approached to the sample surface, shear forces occur and damp the oscillation of the tip-fork system. This leads to a phase change between the driving sine voltage and the piezoelectric response voltage of the tuning fork. The phase change is

\(^9\)The described system was set up by Phillip Olk between 2004 and 2005.
Experimental techniques

read-out electronically as depicted schematically in Fig. 3.5 and fed back for positioning the tip at a desired distance above the sample surface.

The manipulation of the tip on the nanometer scale is carried out by means of a piezostage\textsuperscript{10} with a strain-gauge-based positioning control loop. The entire setup is mounted on top of the inverted optical microscope, allowing for raster-scanning the sample under far-field illumination from below. It is possible to cover the sample with a liquid medium and operate the ASNOM tip in the liquid (see Fig. 3.5). The low-viscosity immersion liquid CARGIL#1160 turned out to be well suited to operate the ASNOM in homogeneous immersion as it does not damp the tip oscillation too heavily.

\textsuperscript{10}TRITOR SG 100, PIEZOSYSTEM JENA, Germany.
4 Applications of metal nanoparticles

The unique physical and chemical properties of metal nanoparticles are exploited in various fields of nanotechnology. Especially in nano-optics, a vast number of applications has been reported in the last decade, and the topic is an ever-growing one. To address all application fields is way beyond the scope of this work. This chapter therefore aims at giving the reader only a general idea on the use of metal particles in nano-optics. To this end, two examples are described. Firstly, exploiting the far-field properties of MNPs is demonstrated experimentally by using the high scattering cross section of a gold particle for signal enhancement in an optical microscope. To this end, the particle is attached to the apex of an ASNOM probe. Secondly, particle-mediated near-field light-matter interaction is discussed theoretically using the example of molecular fluorescence enhancement in the vicinity of a single MNP. Finally, this chapter describes how such nano-optical applications can benefit from a method which allows the optical (plasmonic) tuning of single particles.

4.1 Metal nanoparticles as scanning probes

The high scattering cross section of noble metal particles may be used to augment the signal levels in nano-optical experiments. How to achieve such signal enhancement by appropriately using suitable particles has bothered scientists for more than 20 years now [75]. In most cases, a rather large number of particles was distributed in either a 2D or a 3D fashion in a sample. Then, either a large number of measurements was carried out on single particles [14], or - vice versa - a single measurement on a large number of particles in order to obtain statistically relevant optical data [76, 77].

In recent years, a small community of researchers has devoted considerable effort to conduct nano-optical experiments with a single particle attached to the apex of a scanning probe tip, i.e., a particle mobile in 3D space (see Fig. 4.1). Although experimentally demanding, such a mobile particle supersedes the need for multi-particle measurements in certain experiments and allows to circumvent complications such as signal broadening or difficult sample preparation. In particular, mobile particles can be used to determine distance dependences of optical signals both in the near-field and in the far-field [78, 79].
Besides the advantages of such scanning particle probes, the difficulty of attaching the particle to the tip apex remains. It turned out that an optical control of the fabrication process increases the reproducibility of the tips (see Appendix B for a short description of the fabrication of particle-decorated scanning probes).

In order to demonstrate the capabilities of this experimental tool, a particle-tip was mounted on the ASNOM (see Fig. 3.5 on page 31) and positioned centrally in the focus of the optical microscope. By means of the shear-force distance control it was kept at a height of approximately 10 nm above the sample surface. The latter was a cover glass equipped with an inhomogeneous layer of fluorescent molecules (Nile Blue, SIGMA-ALDRICH, Germany) of low topography (< 10 nm).\footnote{The molecular layer was prepared by spin-coating a 10-µl droplet of a 1mM solution of Nile Blue in ethanol under low rotation speed (500 rpm) onto the cover glass.}\footnote{As the confocal scan was performed before the tip-enhanced image was acquired, bleaching of the molecules is not responsible for the observed signal enhancement. Furthermore, no enhancement effect was observed when a fiber tip without a MNP was used.} CARGILLE #1160 was used for homogeneous immersion. The sample was raster-scanned through the 532-nm laser focus, while the particle-decorated tip remained at its lateral position. The resulting fluorescence image is depicted in Fig. 4.2 b). As a comparison, the fluorescence image acquired beforehand with the tip retracted (tip-sample distance 5 µm) is shown in Fig. 4.2 a). A sizeable increase of the fluorescence signal is observed when the particle is located inside the focal region.\footnote{As the confocal scan was performed before the tip-enhanced image was acquired, bleaching of the molecules is not responsible for the observed signal enhancement. Furthermore, no enhancement effect was observed when a fiber tip without a MNP was used.}
Fig. 4.2: a) Fluorescence image acquired by a confocal scan of a thin layer of Nile Blue molecules with retracted tip. b) Fluorescence image of the same area scanned with the particle-tip approached to the fluorescent layer (same color scale as in a) ). In the latter case, a sizeable increase of the signal is observed.

focus and affected by direct far-field excitation. This leads to a low near-field signal compared to a strong far-field contribution. In fact, it has been shown [45] that when a particle is approached to such a layer of fluorescent molecules, the signal enhancement is predominantly due to far-field effects.\(^3\) The experiment demonstrates that signal enhancement can be achieved with a properly positioned single MNP used as a “particle mirror”. Such a mirror has the same optical properties for each pixel of the image. In this arrangement, the increase of the signal level will be the higher the better the plasmonic spectrum of the particle overlaps with both the fluorescence spectrum of the molecules and the laser excitation.

\(^3\)As several far-field processes occur simultaneously, their individual contributions are difficult to separate. The particle not only scatters fluorescence light into the microscope objective, but also redirects excitation light back to the sample, which again induces fluorescence. Subsequently, higher-order scattering processes can occur.
4 Applications of metal nanoparticles

4.2 Particle-mediated enhancement of molecular fluorescence

The ratio between the far-field and the near-field contribution to the optical signal changes drastically when a single fluorescent molecule is considered instead of an extended molecular layer. In this case, the near-field interaction between the molecule and the particle dictates the overall fluorescence signal. Experimental investigations of this interaction have been described in several reports (see, for example, \[80\] and \[81\]). In these experiments, particle-decorated ASNOM probes were applied to control the distance between a single molecule and the particle, and enhanced fluorescence was found for certain distances between the two. However, these experiments were conducted with a limited set of parameters. In particular, it remained unaddressed how changing the plasmonic particle properties affects the fluorescence enhancement. In this section, this issue is discussed theoretically, facilitating several conclusions on how to optimally implement particle probes experimentally.

In particular, the influence of a single gold nanosphere on a single fluorescent molecule is discussed in what follows. The latter is considered a two-level system influenced by the LSPs in the particle. These LSPs can

- enhance the molecular excitation rate by increasing the local electric field,
- lower the emission efficiency by offering nonradiative decay channels for the molecular dipole, and
- increase the fluorescence by coupling radiative molecular emission to a radiative LSP mode.

The processes above exhibit different dependences on the separation between the particle and the molecule. As a consequence, the fluorescence emission from the molecular dipole shows a non-trivial distance dependence and demands careful computation. Results of a MMP-based approach are presented in this section. They originate from a study carried out in cooperation with Philipp Reichenbach who conducted the respective MMP programming.
4.2 Particle-mediated enhancement of molecular fluorescence

4.2.1 Distance-dependent interaction of a single fluorophore and a single nanosphere

The geometrical configuration most relevant for the fluorophore-particle interaction is depicted in Fig. 4.3. The fluorophore is represented by an electric point dipole \( p \) oriented radially with respect to the particle center, and it is pointing onto one of the “poles” of the particle. Thus, when a plane wave is incident from the left and polarized in the plane of projection, the dipole is optimally excited and located in the area of maximum field enhancement.\(^4\)

MMP allows to calculate the emission of the single point dipole (referred to as fluorescence in what follows) at a variable distance from the gold nanoparticle. The analysis relies on the computation of the electromagnetic field distribution in the coupled particle-dipole system. It can be shown that this classical electrodynamic approach leads to the same results as a quantum electrodynamic treatment for all quantities involved in the fluorescence emission [81]. The fluorescence emission rate \( \gamma_{em} \) of the coupled particle-dipole system can be expressed as

\[
\gamma_{em} = q \cdot \gamma_{exc} \propto q \cdot |E_{exc} \cdot p|^2
\]

with \( q \) the emission quantum efficiency of the coupled particle-dipole system, \( \gamma_{exc} \) the molecular excitation rate, \( E_{exc} \) the electric field vector at the position of the dipole, and \( p \) the dipole moment of the molecular transition giving rise to the fluorescence emission. An intrinsic quantum efficiency of unity was assumed for the molecule, as well as weak excitation so as to be far from saturation.

The calculation was carried out in a two-step process. In the first step, the electric field \( E_{exc} \) at the position of the dipole was calculated so as to account for the excitation of the fluorophore. The electric field arises from the superposition of a linearly polarized plane wave incident on the particle and the induced particle polarization field. In the second step, a classical HERTZian dipole emitter was used to excite the system from the position of the molecule, which describes the emission of the latter.

This emission was taken to occur with the same polarization as the excitation field, but at a different wavelength \( \lambda_{em} \). The system was evaluated by a 3D Poynting vector integration over the spherical surfaces depicted in Fig. 4.3. The time-averaged radiative energy flux \( P_{rad} \) out of sphere \( S_1 \) enclosing the entire particle-dipole system is given by

\(^4\)Other orientations and locations of the fluorophore lead to less optimal excitation conditions and consequently to less fluorescence emission. An overview over other configurations can be found in [82].
Fig. 4.3: Geometry considered for the fluorophore - particle interaction model. The fluorophore is represented by a point dipole moment $\mathbf{p}$ oriented radially with respect to the particle center, and it is pointing onto one of the “poles” of the particle. For excitation, a plane wave polarized in the paper plane is incident from the left. The radiated power $P_{\text{rad}}$ as well as the power $P_{\text{nr}}$ dissipated in the particle are calculated by 3D Poynting vector integration over the spherical surfaces $S_1$ and $S_2$, respectively.

\[
P_{\text{rad}} = \frac{1}{2} \int_{S_1} \Re(\mathbf{E}_{\text{exc}} \times \mathbf{H}^*_{\text{exc}}) \hat{s}_r \, ds,
\]

(4.2)

with $\mathbf{E}_{\text{exc}}$ and $\mathbf{H}^*_{\text{exc}}$ being the electromagnetic field components at the surface of integration, and $\hat{s}_r$ a unit vector pointing radially away from $S_1$. Furthermore, the nonradiative power $P_{\text{nr}}$ dissipated by Ohmic losses within the MNP can be calculated in the same way:

\[
P_{\text{nr}} = \frac{1}{2} \int_{S_2} \Re(\mathbf{E}_{\text{exc}} \times \mathbf{H}^*_{\text{exc}}) \hat{s}_r \, ds.
\]

(4.3)

Here, $\hat{s}_r$ denotes a unit vector pointing radially into sphere $S_2$ enclosing only the MNP. The emission quantum efficiency of the entire system is then given by the relation [83]

\[
q = \frac{P_{\text{rad}}}{P_{\text{rad}} + P_{\text{nr}}}.
\]

(4.4)

Thus, the necessary quantities $q$ and $\gamma_{\text{exc}}$ for the calculation of the emission rate $\gamma_{\text{em}}$ according to Eq. 4.1 are at hand.
4.2 Particle-mediated enhancement of molecular fluorescence

Fig. 4.4: Dependence of the normalized dipolar emission rate \( \gamma_{em}/\gamma_{em}^0 \), excitation field \( E_{exc}/E_{exc}^0 \), and quantum efficiency \( q \) on the distance between particle and fluorophore. Two different particle diameters (30 nm and 80 nm) were considered. The emitted signal strength results from a competition between the excitation field and the emission quantum efficiency. In case of the 30-nm particle, the field enhancement is not high enough to outweigh the low quantum efficiency, while for an 80-nm particle this is the case in a distance range of approximately 10 - 100 nm.

The distance-dependent behavior of \( \gamma_{em}, E_{exc} \) and \( q \) are depicted in Fig. 4.4 for a plane wave excitation at \( \lambda_{exc} = 532 \) nm and emission at \( \lambda_{em} = 560 \) nm. These spectral values approximate a single Rhodamine 6G molecule, for example. Two different values for the particle diameter were considered (30 nm and 80 nm), and the surrounding medium of the system was assumed to be air (\( \varepsilon_m = 1 \)). All curves are normalized to the values obtained for an infinite distance between dipole and particle, i.e., the situation of a free molecule.

Obviously, the emitted signal strength results from a competition between the enhancement of the excitation field and the decrease in quantum efficiency. As a consequence, fluorescence enhancement is obtained under certain conditions only. In the case of the 30-nm particle, the field enhancement is generally too low to outweigh the decrease in emission quantum efficiency. Thus, quenching of the fluorescence signal takes place in the entire distance range. The 80-nm particle causes a different situation: at a certain distance between particle and fluorophore (approx. 10 - 100 nm for the parameters considered here), the fluorescence signal is indeed enhanced. For closer distances, however, the drastic decrease in quantum efficiency again causes the fluorescence to be quenched.
### 4.2.2 Influence of the surrounding medium on fluorescence enhancement

The sphere-molecule separation is not the only parameter influencing the interaction between the two. As the surrounding dielectric medium drastically influences the plasmonic behavior of the particle (see section 2.3), it also affects the fluorescence enhancement. In particular, the maximum field enhancement factor experiences a spectral shift when the system is embedded in different media. This behavior becomes important when optical imaging or spectroscopy are carried out in homogeneous immersion as described in section 3.2.3.

![Normalized fluorescence rate](image)

Fig. 4.5: Normalized fluorescence rate $\gamma_{em}/\gamma_{em}^{0}$ at 560 nm, 590 nm, and 650 nm for air ($\varepsilon_m = 1.00$), water ($\varepsilon_m = 1.77$), and immersion oil ($\varepsilon_m = 2.25$), plotted as a function of distance $d$ and excitation wavelength $\lambda_{exc}$. Particle diameter 80 nm. Note that the $x$-scale is different for each row.

To shine light on the effect, three different dielectrics (air, water, and immersion oil with $\varepsilon_m = 1, 1.77,$ and $2.25$, respectively) were considered. The emission rate $\gamma_{em}$ for...
4.3 Benefits from the in-situ manipulation of optical particle properties

different emission wavelengths ($\lambda_{\text{em}} = 560$ nm, 590 nm, and 650 nm) was calculated assuming excitation wavelengths varying from 450 nm up to the respective emission wavelength. Results are shown in Fig. 4.5.

The fluorescence intensity increases towards larger emission wavelengths, which is due to the increase of the emission quantum efficiency [82]. The latter is caused by decreasing damping of the particle plasmon modes towards longer wavelengths, i.e., less energy is dissipated in the nanosphere. This finding is in accordance with other reports concerning the spectral position of the radiative decay peak [78, 84].

The fluorescence yield also increases with higher $\varepsilon_m$, although $q$ diminishes for higher dielectric constants at the emission wavelengths considered here. The increase in field enhancement due to the high $\varepsilon_m$ outweighs the latter effect. Finally, the distance $d$ for maximum fluorescence enhancement for a fixed $\varepsilon_m$ also decreases slightly in the vicinity of the resonance due to the enhanced excitation field in this spectral region.

In conclusion, the fluorescence output for fixed excitation and emission wavelengths can be maximized by optimizing the refractive index of the surrounding medium. Vice versa, for a given environmental refractive index, one can either tune the excitation wavelength or the dipole emission wavelength (by choosing a suitable fluorophore) to obtain a maximum fluorescence signal. The results presented in Fig. 4.5 allow one to make the optimum choice of excitation and emission wavelengths in order to achieve maximum fluorescence signal intensity for particle-enhanced fluorescence microscopy or ASNOM.

4.3 Benefits from the in-situ manipulation of optical particle properties

The findings of the previous section show that the fluorescence signal stemming from a single fluorophore can indeed be enhanced in the vicinity of a metal nanoparticle. However, a net enhancement occurs only under certain conditions. A sufficiently large particle volume is one of these conditions, as the field enhancement induced by too small particles is not able to outweigh the decrease of the quantum efficiency. In this case, fluorescence quenching dominates the fluorophore-particle interaction. Furthermore, changes in the local dielectric surrounding of the coupled particle-dipole system can lead to drastic spectral shifts of the maximum fluorescence enhancement factor, and thus induce either an increase or a decrease of the fluorescence signal level.

It was suggested to optimize the fluorescence signal by proper choice of either the dielectric medium or/and the excitation and emission wavelengths for the respective experiment. However, this often turns out to be less straightforward than it sounds as in
most cases a lot of experimental restrictions apply. It is often impossible to vary even only one of these parameters. In particular, problems might occur when changing

- the fluorophore (due to the existence of specific binding sites, chemical compatibility with other sample materials, etc.)

- the excitation wavelength (due to the demands of the fluorophore or simply due to practical availability restrictions of a different laser source)

- the surrounding medium (many biological samples only survive in aqueous solution [45]).

These experimental difficulties can be circumvented by the correct initial choice of the particle in use and consequently the correct spectral distribution of the enhancement factors. However, also this obvious condition might not be simple to be fulfilled as particle solutions exhibit particle size distributions, and the optical properties of the particles might be altered by changes in the local dielectric environment during the experiment. The latter effect could for example be due to the coverage of the particle by organic molecules with high refractive index. Thus, it seems advantageous to have a method at hand which allows to spectrally tune the optical properties (especially the LSP resonance) of single particles in situ.

This train of thoughts triggered the search for a possibility to intentionally manipulate the optical particle properties in a controlled way. Of course, this predominantly means manipulating the LSP resonance in these particles. Besides being applicable to individually addressed single particles, the method should be simple, reproducible, and – most importantly – in situ, i.e., it should be possible to tune the particles in the same experimental environment in which they are to be applied later.

Several methods of tuning the LSP resonances in metal nanoparticles can be found in the literature. Among others, they include the electrochemical deposition of material onto immobilized particles [85] or their electrochemical oxidation [86], charging of MNPs to change their electron density [87, 88], and manipulating the pH of the embedding medium [89]. Also the tuning of the MNP size and, hence, the LSP resonance by photothermal evaporation of particle material was reported [90] - [92]. Last but not least, photochemical and radiochemical protocols were used to change the sizes of particles in solutions [93] - [95]. However, all these approaches do not fulfill the conditions stated above. They are either inapplicable in situ as they require special environments such as ultrahigh vacuum or conductive substrates, or they can not be carried out on the single-particle level. In addition, some of them rely on sophisticated experimental equipment such as a γ-ray source.
4.3 Benefits from the in-situ manipulation of optical particle properties

The way around these problems was inspired by photography, i.e., the scientific heritage of the Institute of Applied Photophysics. The central idea was to exploit the autocatalytic growth of nanoparticles as it occurs during the development of a photographic emulsion. In other words, the abovementioned photochemical metal deposition [95] was to be made applicable on the single-particle level.

It turned out that this method fulfills all of the requirements. By photochemically depositing metal onto individually addressed MNPs, their size, shape and material composition can be manipulated, and, hence, the spectral position of their LSP resonance. This method, its versatility and its application to several nanooptical systems is described in the second part of this book.
Part II

Photochemical manipulation of surface plasmon resonances in metal nanoparticles
5 Photochemical metal deposition

The photochemical properties of metal salts have been employed in technical applications for centuries. A very prominent application – perhaps the most successful one – is photography. Its advent in the 19th century triggered detailed investigations of the photochemistry of metals and their salts. The textbooks of those times document the rapid advancement of both science and technology in the field [8, 96], and a good part of the work presented in this book relies on the knowledge gained already in those days. Considerable contributions to this development were also made at the Technische Universität Dresden [97]. From this point of view, the results presented in this chapter bridge more than a century of scientific research by introducing the photochemical activity of metal salts into nanooptics on the single-particle level.

This chapter is organized in the following way: The optically induced reduction of salt complexes for the deposition of metal from solution is described in sections 5.1 and 5.2. By depositing metal onto preformed nanostructures, especially onto single metal particles, the optical properties of these structures can be freely manipulated. The advantages of such in-situ particle manipulation have been outlined in the previous chapter. To tune the optical structure properties in a targeted way, a precise deposition control is of utmost importance. Such process monitoring is a challenging task, but can be achieved with the approach presented in section 5.3.

5.1 Photochemical reduction of tetrachloroaureate (HAuCl₄)

In the context of photochemical activity, silver salts are known to show highest optical sensitivity [98], and they are therefore predominantly used for photographic applications. However, for nearly every metal a photochemically active salt can be found [7], and here the work horse material was tetrachloroaureate (HAuCl₄). Although its photochemical activity is much lower than that of most silver salts, the reduction product, i.e., pure gold, is much more stable and chemically inert in comparison to silver. This is of importance when the deposited material is to be analyzed, e.g. by means of electron microscopy, which includes the exposure of the deposit to air. In this regard, a chemically stable material is highly advantageous.
5 Photochemical metal deposition

The photochemical reaction underlying the gold deposition process is the disproportionation of the salt complex [95, 99]. As a first step, the following redox reaction is induced by illuminating a HAuCl$_4$ solution [100]:

\[
2\text{AuCl}_4^- \xrightarrow{h\nu} 2\text{AuCl}_3^- + 2\text{Cl}^0
\]

\[
2\text{AuCl}_3^- \rightarrow \text{AuCl}_4^- + \text{AuCl}_2^-
\]

\[
\text{AuCl}_2^\rightarrow \xrightarrow{h\nu} \text{Au} + \text{Cl}^0 + \text{Cl}^-.
\]

The chloride ions originating in the reaction are compensated by scavengers in the solution or the solvent itself. In a second step, the neutral gold atoms agglomerate to small clusters which then act as nucleation centers and catalyze the reduction of further salt complexes. Thus, nano-sized gold particles are formed in the illuminated solution and finally precipitate.

![Fig. 5.1: Transmittance spectrum of HAuCl$_4$ in CARGILLE #1160 (1 mm, 50 mM). Transmittance losses in the solvent have been substracted.](image)

The energy of the incident photons plays a crucial role for the initialization of the reaction. Only photons with sufficiently high energy can promote electrons of the gold complex into an excited state and thus trigger the reduction. Fig. 5.1 shows the transmittance spectrum of 1 mm of a 50 mM HAuCl$_4$ solution.\(^1\) The gold complexes strongly absorb light in the UV and blue wavelength region, which explains the yellowish tinge

\(^1\)The solvent (CARGILLE #1160) shows 95% transmittance over the entire observed wavelength range. The curve in Fig. 5.1 has been corrected for this solvent effect.
of the salt solution. Consequently, a short illumination wavelength will cause a much higher reaction and deposition rate than a long-wavelength excitation.

In order to prove that the gold deposition is really due to illumination, a simple control experiment was designed. Three different gold salt solutions were prepared: solution A and B contained a mixture of HAuCl₄, 80-nm gold particles, potassium iodide (KI), and starch, while solution C contained only KI, starch and the 80-nm particles. In all three cases, the immersion oil CARGILLE #1160 served as the solvent, as it was also used in the deposition experiments described later. Solution A was exposed to an unfocused 532-nm laser beam (50 mW) for 8 hours, while solution B was stored in the dark.

![Fig. 5.2: Results of a control experiment concerning the photochemical reduction of HAuCl₄. Solution A (left) and B (middle) contained a mixture of HAuCl₄, 80-nm gold particles, potassium iodide (KI), and starch, while solution C (right) contained only KI, starch and the 80-nm particles. CARGILLE #1160 was used as solvent in all cases. Solution A and C were exposed to an unfocused 532-nm laser beam for 8 hours, while solution B was stored in the dark. The expected violet color occurred only with solution A, which indicates the optically induced reduction of the gold salt.](image)

After the exposure time, solution A showed a pronounced violet shade (see Fig. 5.2). This color is a clear indication of chloride in the solution, which originates from the disproportionation reaction and oxidizes the iodide ions to elemental iodine. The iodine, in turn, causes the well-known color change of the starch. To prove that this color change was not induced by ozon generated during laser irradiation, solution C (not containing HAuCl₄) was illuminated in the same way as solution A. Both solutions B and C showed
5 Photochemical metal deposition

no change in color, which gives evidence of the reaction being triggered by the absorption of incident photons and the subsequent reduction of gold complexes.\(^2\)

As the reduction is part of a disproportionation, no further chemicals than the gold salt are necessary. This furthermore means that all process parameters (except the salt concentration) such as the wavelength and the intensity of the incident light are optical parameters. The latter can easily be controlled and altered \textit{in situ}. Finally, the method is applicable with a wide range of different solvents: water, glycol, and various types of immersion oil all led to identical experimental results. Thus, the method is not limited to a special experimental environment.

5.2 Nanoparticles as catalytic seeds

In the experiments described in the next chapters, the second step of the deposition process, i.e., the formation of nucleation centers, is redundant, as seeds are already given by the nanoparticles onto which the metal is to be deposited. In this case, metal deposition results in the autocatalytic growth of the seed, very similar to what is know as “development” in the context of photography.

The initial presence of seed particles is of high importance, as the reduction potential of the system \(\text{Au}^\text{III}_{\text{aq}} / \text{Au}^\text{atom}_{\text{aq}}\) is highly negative (-1.5 eV), while the potential of the \(\text{Au}^\text{III}_{\text{aq}} / \text{Au}_{\text{particle}}\) has a less negative value (between -1.5 eV and 1.5 eV) [95]. The formation of new nucleation centers in the solution is therefore much more unlikely compared to the reduction of salt complexes in the vicinity of an already existing seed. Thus, neutral metal atoms accumulate at the surface of the illuminated particle, leading to a homogeneous increase of the particle size The entire process is depicted schematically in the inset in Fig. 5.3.

5.3 Experimental procedure

In detail, the deposition of metal onto individually addressed nanoparticles was carried out as follows: A cover glass equipped with the desired seed nanoparticles was mounted onto the inverted microscope. Wide-field excitation and confocal detection were used as depicted in Fig. 5.3 to address and monitor single particles.

\(^2\)In fact, solution \(B\) did not show any hints of a reaction even after several months in the dark. Additionally, a photothermal mechanism for the reduction can be ruled out, as the temperature change due to light absorption in the solution - even in the presence of particles - is only on the order of 10 K [92, 101].
5.3 Experimental procedure

Fig. 5.3: Combined wide-field excitation and confocal setup for metal deposition onto individually addressed particles. Inset: Scheme of the optically induced metal deposition. Due to irradiation, the reduction of gold salt complexes is induced in the solution. Elemental gold precipitates, while residual ionic compounds are compensated by scavengers in the solution or by the solvent itself. The process takes place preferentially in the vicinity of a seed particle, as the presence of such a particle alters the reduction potential of the chemical system.
A 5-µM gold salt solution was produced by dissolving HAuCl₄ in the low-viscosity immersion oil CARGILLE #1160. Typically, a 20-µl droplet of the solution was applied on the particle sample.

The deposition process was initiated by exposing single seed particles to the diffraction-limited 532-nm laser spot (1 mW). Each particle was illuminated for a period of approximately one minute. Then, the laser was blocked and the white-light beam was directed into the microscope by means of a flip mirror. This rendered possible to measure the scattering spectrum of the particle as described in section 3.2.1. With increasing exposure time, i.e., growing deposition layer thickness, the scattering spectrum shows characteristic changes and therefore provides comprehensive information on the state of the deposition process. After the spectrum was recorded, the next laser exposure, i.e., deposition step, followed. This procedure was iterated several times until the particle showed the desired scattering properties. A control experiment verified that the 10-µW unfocused white-light beam is not able to initiate the reaction.

The low concentration of the gold salt leads to a weak absorption of 532-nm laser energy in the solution. However, the energy absorbed by the solution in the vicinity of the addressed particle is certainly higher than far away from the particle, as the LSP excited in the particle leads to an electric field enhancement even in the nonresonant case [17]. This process may additionally promote particle “growth”. Due to this effect and the influence of the seed on the reduction potential, metal is only deposited onto the individual particle intentionally addressed by the laser focus. Adjacent unexposed particles show no change in the scattering spectrum, and there is no precipitation of metal on the cover glass. However, increasing either the salt concentration or the laser power leads to these unwanted effects [102]. In that sense, the process parameters are crucial and have to be well adjusted.

In the next chapters, this experimental procedure is applied to several sample systems. These experiments show that it is indeed possible to achieve a precisely in-situ controlled manipulation of the optical particle properties by photochemically tuning their size, shape, or material composition.
6 Manipulation of plasmon resonances I:
Effects of size and shape

As described in section 2.3, the plasmonic properties of metal nanoparticles strongly depend on their size and shape. In the experiments described here, these two parameters are intentionally manipulated using optically induced metal deposition. Thus, the LSP resonances in single gold nanospheres and elongated nanodisks are photochemically tuned. Since this manipulation is carried out under in-situ monitoring, these proof-of-concept experiments lead to a better control of the optical properties of metal nanoparticles.

6.1 Photochemical tuning of the plasmonic properties of single gold nanospheres

6.1.1 Experiment

In the first experiment, the autocatalytic particle growth by metal deposition is demonstrated with single spherical Au particles of 30 nm diameter. These particles were extracted from a commercially available solution by blow-drying a droplet on a clean cover glass. The technique results in a homogeneous particle distribution with approximately 10 - 15 µm interparticle distance as postulated in section 3.2.1. Single particles were exposed to the focused 532-nm laser light and monitored as described in the previous chapter.

The scattering spectra recorded for increasing exposure times are depicted in Fig. 6.1 a). A monotone redshift of the LSP resonance and an increase of the scattering intensity are observed, indicating the gold deposition on the sphere, i.e., the growth of the particle.

6.1.2 Conclusions concerning the deposition process

From the peak wavelength of the scattering spectrum, the respective particle diameter for each deposition step can be calculated using Eq. 2.35. Although the presence of the substrate will inhibit a completely isotropic growth, considering the grown particles as

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Fig. 6.1: a) Scattering spectra of a single spherical particle recorded at different stages of the growth process; b) Linear evolution of the particle diameter with exposure time. The diameters (black diamonds) were calculated from the respective resonance wavelength according to Eq. 2.35. The red curve represents a linear fit of the experimental data.

spheres seems justified (see next section). Thus, Eq. 2.35 allows to evaluate the growth more quantitatively. Its application to the measured data reveals a linear growth of the particle diameter as a function of time (Fig. 6.1 b)).

The linear increase of the diameter with time and the symmetric shape of the resonance curves allow several conclusions concerning the deposition process:

- Firstly, under the experimental conditions described above, the number of excited ions in the solution is not a limiting factor for the deposition rate. If this was the case, the deposition process should slow down with increasing particle size, as the larger particle surface area would extract more ions from the solution. This was not observed.

- By the same argument, it can be deduced that the change of the resonance wavelength of the LSP excited on the particle is of minor importance. While growing, the particle becomes less and less resonant with the 532-nm excitation. However, this also has no effect on the deposition rate.

The error bars consider the spectral step width of the calculations for Eq. 2.35 (1 nm), its propagation in this equation, and the error of the measured resonance wavelength (3 nm). Due to the decreasing noise level and lower slope of Eq. 2.35 for larger particles, the error bars decrease for increasing diameter. Note that errors due to nonspherical growth have not been included here (see next section).
• The same experimental results as depicted in Fig. 6.1 a) were obtained with single particles attached to a tapered glass fiber tip, thus rendering an ASNOM probe with tunable optical properties. Consequently, one can deduce that the substrate has only minor influence on the LSP resonance of the exposed particle (see also next section).

• The slope of the curve in Fig. 6.1 b), i.e., the speed of the particle growth, can be controlled by either the laser power, the exposure time, or the salt concentration. However, it turned out that more intense irradiation or more concentrated solutions lead to precipitation of gold next to the addressed particles. On the other hand, a decrease of these two parameters makes longer exposure times necessary, but seems to facilitate higher reproducibility of the “particle growth”. For gold deposition onto single spherical particles the parameter values given in section 5.3 are sufficient. For other structures, the process parameters may have to be adjusted.

• The polarization of the focused laser light has no influence on the shape of the growing particle. This is confirmed by the finding that scattering spectra taken with polarized white light after laser exposure exhibit the same resonance wavelength for any polarization direction. Different peak wavelengths would render an indication for elongated particles, which was not observed.

• Finally, applying the wide-field excitation mode also for the laser light, i.e., initiating the deposition process with purely linearly polarized light, led to the same experimental results as described above. In particular, the particles again preserved their circular projection which was tested with different white-light polarization directions. To trigger the reduction, only the laser power had to be adjusted according to the lower power density in the unfocused beam.

All these findings were also confirmed by scanning electron microscopy (SEM) measurements as shown in Fig. 6.2. The left curve in the diagram shows the scattering spectrum of the depicted 33-nm particle (upper left corner), while the right spectrum stems from the sphere shown in the upper right corner. The latter has been grown from its original size to 85 nm in diameter. The relation between the final size of the grown particle and its resonance wavelength is in good agreement with Eq. 2.35. There is only a slight misfit of the peak resonance wavelength of approximately 5 nm between measured and calculated data, which is within the error margin of the experiment.
6 Manipulation of plasmon resonances I: Effects of size and shape

6.1.3 Nonspherical particle growth

The vast majority of treated particles shows a single peak in the LSP spectrum and a spherical projection in SEM images. However, the presence of the substrate inhibits a completely isotropic growth, as no gold can be deposited in the region of contact between the seed particle and the substrate. To quantify how this effect influences the plasmonic properties of the particle, the scattering spectrum of a spherical calotte was calculated using MMP. In the model, a long axis of 100 nm was considered, while the diameter of the short axis amounted to 65 nm (see Fig. 6.3 a)). These values correspond to a layer of 35 nm thickness deposited onto a 30-nm seed particle.

The calculations yield a resonance wavelength which differs from the one of a 100-nm sphere only within the error margin of the experiment (Fig. 6.3 b)). This result shows that the diameter of the long particle axis is the crucial parameter for the spectral position of the LSP resonance wavelength. In the experiment, this particle axis is the predominantly excited one, and as the projection of the particle is circular, it is sufficient to account for this parameter in a spherical model [40].

The scattering cross section of the calotte is clearly smaller than that of the sphere, which is caused by the smaller volume of the former. However, the LSP resonance wavelength of both geometries is the same for the rather low aspect ratios considered here. As this resonance wavelength is the main matter of interest concerning plasmonic tuning, the influence of the substrate does not render problematic, and to model the
Besides the substrate, further parameters such as the initial geometry of the particles and their crystallinity influence the final shape after exposure. However, as the particles from the purchased solution show high uniformity, cases with extremely asymmetric particle shapes occurred rarely and were sorted out. The 30-nm seed particles are typically poly-crystalline, and thus the deposited material also shows poly-crystalline structure, i.e., no large-scale crystal facettes were observed in SEM images.

In conclusion, the experimental results described so far demonstrate the principle of LSP tuning in single nanoparticles by photochemical metal deposition. In order to demonstrate the versatility of the technique, the next section deals with particles of different shape and fabrication.

6.2 Photochemical tuning of the aspect ratio of single ellipsoidal nanodisks

To broaden its application range, the bottom-up photochemical deposition method was combined with the top-down approach of electron beam lithography (EBL). With the latter technique, elongated nanodisks as depicted in Fig. 6.4 a) were fabricated by Yury Alaverdyan in the group of Mikael Käll (Chalmers University of Technology Göteborg.
Manipulation of plasmon resonances I: Effects of size and shape

Sweden). The disks had a 100 nm long and a 50 nm short axis, and a height of 20 nm. The projection of these particles onto the substrate plane is no longer circular, and such particles therefore exhibit two LSP modes oscillating in parallel to the substrate. The observable long-wavelength mode corresponds to electron oscillations along the long axis of the particle, while a short-wavelength mode oscillates along the short axis [44, 103, 104].

Fig. 6.4: a) SEM images of an untreated ellipsoidal nanodisk (left) and a treated one (right). b) Evolution of the scattering spectrum of the short axis due to particle growth and c) of the long particle axis due to the shape change. d) Calculated long-axis scattering spectra of two spheroidal particles with different aspect ratios according to a).

Details concerning the fabrication process can be found in Appendix C.
6.2 Photochemical tuning of single ellipsoidal nanodisks

The nanodisks were exposed to the focused 532-nm laser light in the same way as the spheres, but the scattering spectrum was now measured with white light polarized along either the short ("a") or the long ("b") axis of the particle. A comparison between Fig. 6.4 b) and c) shows that the spectral evolution is now anisotropic.

The short-axis resonance behaves similarly to the case of a sphere: the LSP resonance redshifts and increases in intensity with increasing particle size. However, the long-axis resonance instead exhibits a sizeable blueshift, although the intensity increases in a similar fashion as the short-axis response. These observations are due to three effects: the overall increase in particle size is accompanied by both a decrease of the aspect ratio and an increase of the radius of curvature at the ends of the long axis (see Fig. 6.4 a)). Thus, the particle becomes more isotropic as the photochemical growth proceeds. The latter two effects obviously outweigh the redshift due to the growth of the long axis, and a blue-shifted long-axis resonance results.

This blueshift is in accordance with other reports on the role of the particle size [35] and the radius of curvature, e.g. of the end caps of nanorods [105]. The impact of the aspect ratio on the spectral LSP position has, however, been disputed recently [106]. It seems that no dependence at all exists for long particles (nanorods) with high aspect ratios. In contrast, such a dependence was found for nearly round particles as investigated here. In this case, a smaller aspect ratio leads to a shorter LSP resonance wavelength [105].

As all three effects occur simultaneously, it is difficult to evaluate their respective contribution. However, the SEM images displayed in Fig. 6.4 a) confirm the interpretation given above. Both particles shown in the image had the same scattering properties before exposure. The left, untreated one shows an aspect ratio \( r = b/a = 1.65 \) (\( a = 54 \) nm, \( b = 89 \) nm), while for the right one the ratio has decreased to \( r = 1.49 \) (\( a = 71 \) nm, \( b = 106 \) nm), as the particle has grown by about the same amount of 17 nm along both axes. Such a behavior was recorded and confirmed for many particles, and MMP calculations with these parameters also reproduced the LSP blueshift quantitatively (see Fig. 6.4 d)).

The same results were found for excitation by light polarized either along the short or the long axis during growth. This again shows that the gold deposition is independent from the polarization of the incident laser light. Furthermore it turned out that the cit-
rate protection layer present on the surface of colloidal particles (as investigated in the previous section) has no influence on the reduction reaction. This can be deduced as the EBL-fabricated samples are citrate-free and no pronounced difference in growth speed was observed between both types of particles.

In conclusion, the proof-of-concept experiments describe in this chapter yielded suitable process parameters for the photochemical deposition of gold onto single Au particles. Furthermore, ample experience concerning the experimental procedure was gained, which allows the application of the technique to more complex structures. As an example, the photochemical tuning of particle pairs is described in the next chapter.
7 Application: Tunable plasmonic nanoresonators

Far-field optical resonators can induce high optical field densities inside a cavity formed e.g. by two parallel mirrors. These high fields are due to standing waves which demand a cavity length of at least half the wavelength of light (so-called microcavities). A further miniaturization can be achieved by using the high electric fields induced in the gap between two plasmonically coupled nanoparticles. Such particle pairs are denoted as plasmonic nanoresonators in what follows. The resonance wavelength of such nanoresonators is very sensitive to the interparticle distance, i.e., it can be tuned in the same manner as in macroscopic far-field resonators, namely by manipulating the cavity length.

This chapter describes how such a manipulation of the interparticle distance can be achieved by photochemical metal deposition onto the particles constituting the resonator. These tunable nanoresonators are then applied to shape the fluorescence spectra of organic molecules. Thus, the direct application of photochemical metal deposition is demonstrated for both nanostructure fabrication and nanooptical signal manipulation.

7.1 Plasmonic coupling in particle pairs

If two illuminated metal nanoparticles are brought close to each other (to a distance smaller than their respective diameter), their LSP modes can couple and form hybridized modes. This leads to extraordinarily enhanced optical fields inside the interparticle gap (see Fig. 7.1 c) and [107] - [114]). As these fields are even more promising for the manipulation of field-sensitive optical processes (e.g. fluorescence, Raman scattering) than the fields induced by single particles, thorough theoretical and experimental investigations of the plasmonic mode coupling have been carried out [115] - [124]. As a result, there is a good understanding of the LSP coupling process based on a relatively simple dipole-dipole interaction model (see Appendix D). A decreasing distance between two particles (each represented by an electric dipole) leads to a redshift of the resonance wavelength for the LSP mode oscillating in parallel to the center-to-center axis of the dimer. The charge distribution in a particle pair exposed to such an excitation is depicted in Fig. 7.1 c). Vice versa, the coupling of the modes oscillating perpendicular to the central dimer axis leads to a blueshift of the resonance wavelength compared to the uncoupled case.
The strong dependence of the resonance wavelength of the coupled system on the interparticle distance implies both advantages and drawbacks. On the one hand, it offers a possibility to tune the resonator if one has a method at hand which allows to manipulate the interparticle distance. On the other hand, a very precise technique is required to fabricate such coupled particle pairs, as already minor deviations from a desired dimer gap width entail drastic variations of the coupled LSP resonance. The decision for a suitable fabrication technique is therefore an important issue.

In the last decade, considerable effort has been devoted to the controlled fabrication of particle-based nanostructures. Thus, elaborate fabrication techniques exist and include top-down approaches such as focused ion beam (FIB) milling, electron beam lithography (EBL), purely chemical routes for metal deposition and particle fabrication [56, 125], as well as self-assembly-based bottom-up methods [126, 127]. One of the major advantages of EBL and FIB milling is that they allow for the fabrication of arbitrary structure layouts, which are often unachievable with bottom-up strategies. The latter, however, facilitate control over structure dimensions well below the 10-nm range, a limit still challenging the reproducibility of top-down techniques. However, it is this length scale which is relevant for the nanoresonator gap width.

To achieve such high precision in the fabrication of particle pairs, photochemical metal deposition was again combined with the versatility of EBL. To this end, pairs of gold nanodisks of 50 nm in diameter, 20 nm in height, and 30 nm spacing were EBL-fabricated on a cover glass (see Fig. 7.1 a) and d)). Photochemical metal deposition was then used to “grow” the particles, i.e., to reduce the gap between the two. Besides the tuning of the plasmonic nanoresonator spectrum - which was the main goal of the experiment - the results described in the next section also show that the deposition method is capable to create nanostructure feature sizes below 10 nm in a highly reproducible manner.

### 7.2 Photochemical tuning of single plasmonic nanoresonators

The photochemical deposition of gold onto the particle pairs was carried out in the same way as detailed in section 5.3, i.e., the particle pairs were exposed to the gold salt solution, addressed by focused 532-nm laser light and monitored by means of a white-light beam. This experimental approach differs considerably from other investigations of coupled particle pairs [115] - [124], as in those studies the particle size was always kept...
Photochemical tuning of single plasmonic nanoresonators

**Fig. 7.1:** a) SEM image (top view) of a gold particle pair fabricated by electron beam lithography. b) Charge distribution in the dimer due to excitation light polarized along the center-to-center axis. The coupling of the LSP modes leads to a high charge concentration around the gap. The electric field distribution is depicted in c) (MMP calculation, geometry according to d), $\lambda = 633$ nm, $n = 1.5$. d) Scheme of the disks (side view).

constant for decreasing interparticle distance. In the experiment described here, however, both the particle separation and the particle size change simultaneously during laser exposure. This effect was accounted for by investigating the evolution of the LSP modes oscillating either perpendicularly or in parallel to the center-to-center axis of the dimer separately. To this end, the polarization direction of the white-light excitation was turned accordingly by means of a polarization filter. This procedure helps to better understand the optical response of the sample by separating the effects of increasing particle size and decreasing gap width. In the experiment, the evolution of the plasmonic spectrum of single particle dimers with gap widths decreasing from 30 to 0 nm was analyzed. Besides measuring the LSP resonance wavelength of the perpendicular ($\lambda_\perp$) and the parallel ($\lambda_\parallel$) LSP mode, the respective particle diameters and gap sizes were determined by means of SEM. The obtained spectra and electron micrographs are depicted in Fig. 7.2 a) - e). For increasing exposure time, a redshift of the backscattering peaks is observed for both modes (column I and II in Fig. 7.2). For the parallel mode, a second, shortwavelength peak emerges during exposure. This peak is caused by a higher-order LSP mode typically observed on larger particles [29].

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Fig. 7.2: Evolution of the LSP resonance during the deposition process for the center-to-center particle axis (column I), as well as perpendicular to it (column II). Column III: SEM images of the dimer in the respective growth state. The length of the scale bar is 100 nm.
7.2 Photochemical tuning of single plasmonic nanoresonators

The images in column III show clear and reliable gap sizes down to 5 nm, whereas smaller gaps are blurred due to limited resolution in SEM. Sufficiently long exposure finally leads to the formation of an electric contact between the nanodisks (Fig. 7.2 e)). The redshift of the scattering peak during the formation of the metallic contact is smooth, and no jump or splitting of the plasmonic spectrum is observed. Here, gold is again deposited onto the particles only, and no precipitation is observed on the substrate next to the seeds.

Evolution of the perpendicular LSP mode

In Fig. 7.3, the red triangles show $\lambda_\perp$ as a function of the particle diameter. For increasing exposure time, i.e., increasing particle diameter, $\lambda_\perp$ redshifts due to stronger retardation of the incident electric field over the particle. For comparison, the evolution of the LSP resonance wavelength during the growth of single disks fabricated in the same way as the particle pairs is shown (black squares). Obviously, $\lambda_\perp$ shows the same linear dependence on the particle size as found for the resonance wavelength of the single particles. Thus, the growth of the dimers is highly comparable to the growth of single particles.

For this direction of excitation, the dipolar coupling between two particles is expected to result in a marginal blueshift of $\lambda_\perp$ compared to the single particle resonance wavelength [22]. However, for particles of constant size this shift is in the order of only 3 - 5 nm for the relatively short interparticle distance range of 30 nm covered in the experiment [119, 124]. As Fig. 7.3 shows, the redshift of $\lambda_\perp$ due to the increase in particle size is much stronger and the weak dipole coupling effect can be neglected here. Thus, for the perpendicular LSP mode, the optical response of the sample to the increase in particle size is separated from dipolar coupling effects in the dimer.

Evolution of the parallel LSP mode

The near-field of the dipolar LSP oscillation decays with the third power of the inverse distance (see section 2.2.2) [23]. The strength of the plasmonic coupling of two particles (dipoles) also exhibits a $1/d^3$ dependence. Jain et al. have shown that this dependence can be approximated by an exponential decay, and dubbed the empirical equation describing this behavior “plasmon ruler equation” [128]. The equation connects the ratio of the relative LSP resonance peak shift ($\Delta \lambda_\parallel = \lambda_\parallel - \lambda_\parallel^0$) to the initial, uncoupled LSP resonance wavelength $\lambda_\parallel^0$ with the ratio of the particle distance $d$ to the particle diameter $D$:

$$
\frac{\Delta \lambda_\parallel}{\lambda_\parallel^0} = a \cdot \exp \left( -\frac{d}{b \cdot D} \right),
$$

(7.1)
Fig. 7.3: Resonance wavelength $\lambda_\perp$ of the LSP mode oscillating perpendicularly to the center-to-center axis of the dimer for increasing particle diameter (red triangles). As a comparison, the evolution of the resonance wavelength $\lambda_{\text{res}}$ during the growth of single particles fabricated in the same way as the dimers is shown (black squares).

where $a$ and $b$ are fit parameters. It was also shown that this equation holds independently of the particle size, as the coupling strength depends on the same powers of the separation $d$ and the particle diameter $D$ and therefore allows for dimensional scaling. However, this dimensional scaling is only valid if also the free resonance wavelength $\lambda_0^\parallel$ is corrected for the change of the particle dimensions. As the particle diameter changes for every exposure step in the experiment described here, adjusting $\lambda_0^\parallel$ is extremely important.

The required correction has been carried out using the results presented in Fig. 7.3. As the resonance wavelength of a single particle and the peak position of the perpendicular mode of a dimer show the same dependence on the particle size, $\lambda_0^\parallel$ can be substituted in Eq. 7.1 by $\lambda_\perp$. The latter was determined experimentally for every growth state. Taking this correction into account and inserting the respective data into Eq. 7.1 yields the results depicted in Fig. 7.4 a). The fit parameters amount to $a = 0.33 \, (\pm 0.01)$ and $b = 0.25 \, (\pm 0.01)$.

These experimental results were again cross-checked by means of MMP calculations. The model pairs consisted of disks with initial parameters of 20, 25, and 30 nm for height, radius and edge-to-edge separation, respectively. Height and radius were increased in steps of 5 nm, thus the gap was gradually reduced. The respective scattering spectra were calculated as the response to a plane-wave illumination, and $\lambda_\parallel$ and $\lambda_\perp$ were determined
7.2 Photochemical tuning of single plasmonic nanoresonators

Fig. 7.4: a) Ratio $\Delta\lambda_0/\lambda_\perp$ indicating the relative shift of the resonance wavelength during particle growth vs. gap/diameter (squares). (Minimum gap width 5 nm. The data points at $d/D = 1.6$, 3, and 4 stem from unexposed dimers of 50 nm particle diameter and gap widths of 80, 150, and 200 nm, respectively.) The exponential decay fit to the data according to Eq. 7.1 is plotted as a solid line. b) Calculated data (squares) and their exponential fit (solid line) with parameters.

as described above. Results are depicted in Fig. 7.4 b). The fit parameters for these calculated data amount to $a = 0.16$ ($\pm 0.01$) and $b = 0.29$ ($\pm 0.01$).

Both the experimental and the calculated decay constants $b$ excellently reproduce the value of 0.27 ($\pm 0.03$) reported in [128] for particle pairs embedded in a medium with dielectric constant $\varepsilon_m = 2.25$. The same is true for the experimentally determined amplitude $a$, which is in good agreement with the value of 0.29 ($\pm 0.03$) from the same reference. The calculated amplitude is somewhat smaller, but well within the range given in [128] for different particle geometries.

Photochemical particle welding

The SEM images in Fig. 7.2 show a clear separation of the individual particles down to a gap width of 5 nm. Only below this value an influence of the plasmonic coupling on the metal deposition was observed. For such a small interparticle separation, extremely high electric fields are induced inside the gap region, which finally lead to an observable increase of the gold complex reduction rate. This causes the formation of a thin metal bridge on the cover glass already before the radii of the particles actually overlap, i.e., the particles get photochemically welded. Under further exposure, the bridge grows both in thickness and height. The SEM micrograph in Fig. 7.2 e) supports this finding.
This effect, which is driven by the high electric field in the gap region, limits the smallest obtainable particle separation to approximately 5 nm. The spectra in Fig. 7.2 a) - e) demonstrate that the transition from the LSP mode of the separated particles to the electrically connected case takes place gradually, as the connection between the particles is formed by a metal bridge with increasing conductivity. No splitting of the plasmonic modes upon contact formation into so-called touching modes was observed. Such a mode splitting was reported by ATAY for broken contacts [129] and computed by ROMERO [130] for spherical particles with a singular contact point. However, due to the smooth creation of the contact nanobridge, such touching modes are not induced here, as they only exist in dimers with much smaller separation.

7.3 In-situ read-out of the nanoresonator geometry

The modification of Eq. 7.1 allows for the optical far-field determination of the interparticle separation. As the center-to-center distance of the disks is kept constant, the gap width \( d \) naturally is a function of the particle diameter \( D \) reading \( d = l_0 - D \), where \( l_0 \) is the center-to-center distance of 80 nm. Therefore, the disk diameter \( D \) can be substituted in Eq. 7.1 and the gap width can be directly calculated from

\[
d = \frac{l_0 \cdot \kappa}{1 + \kappa} \quad \text{with} \quad \kappa = -b \cdot \ln \left( \frac{\Delta \lambda_{\|}}{a \cdot \lambda_{\perp}} \right). \tag{7.2}
\]

The separation between the particles can be determined at every growth state by measuring the resonance wavelength of both the LSP modes oscillating along the center-to-center axis and perpendicular to this axis, calculating \( \Delta \lambda_{\|} \), and finally using the fit parameters \( a \) and \( b \) from Fig. 7.4 a). This in-situ procedure is a valuable tool, as it can not only be applied for the characterization of the nanostructure under investigation, but also to evaluate the growth process itself. For example, metal deposition rates and their dependences on parameters such as laser wavelength or intensity can be determined all-optically.

The results presented so far demonstrate that a plasmonic nanoresonator can be tuned by photochemical metal deposition. Moreover, the influence of the particle growth and increased coupling can be well separated by changing the polarization of the excitation light, and the change in resonance wavelength can be read-out in situ. In what follows,
such tunable nanoresonators are used to manipulate the emission spectra of organic fluorescent molecules.

7.4 Tuning of molecular fluorescence spectra

Theoretical background

A plasmonic nanoresonator can be used to selectively enhance the emission rate $\gamma_{em}$ (see Eq. 4.1) of a fluorescent molecule. Selectively means that – in contrast to the considerations in chapter 4 – $\gamma_{em}$ of a molecule inside the nanoresonator is a function of the wavelength. At the resonance wavelength of the nanoresonator, the excited molecule is offered a large number of decay channels (radiative and nonradiative plasmonic modes). While the molecule is in the excited state, its electronic configuration fluctuates due to the fluctuating liquid environment [131]. Seen over time, the molecule is more likely to emit when one of its fluctuating transition wavelengths hits the plasmonic resonance. At any point in time, an excited molecule is therefore more likely to relax into a vibrational sublevel of the electronic ground state if the transition to that level is in resonance with the plasmonic resonator.

Two consequences of the presence of a nanoresonator are to be expected. Firstly, the emission spectrum of molecules inside the resonator will change, as the molecules are “forced” to emit at the resonators resonance wavelength. Secondly, an electronic two-level system as applied in chapter 4 for the theoretical treatment of fluorescence is not sufficient anymore to describe the behavior of the molecules. A full theoretical description has to take more electronic levels into account, which is, however, not further detailed here. Such a comprehensive treatment can be found in [132].

Experiment

To investigate the influence of the nanoresonators onto the emission spectrum of organic molecules, several EBL-fabricated particle pairs were tuned to different resonance wavelengths $\lambda_\parallel$ as described in section 7.2. After the gold deposition, the salt solution was rinsed off and the resonators were embedded in a 10 nM solution of Rhodamine 6G in immersion oil Cargille #1160. Single resonators were addressed again by focused 532-nm laser light, and the generated fluorescence light was collected in a confocal detection scheme as shown in Fig. 3.2. The excitation light was removed from the detection beam path by means of a notch filter. After the fluorescence spectra were recorded, the

\[^3\text{Semrock, USA}\]
molecular solution was again rinsed off and the pure immersion liquid was applied on top of the sample. The procedure of addressing the resonators with the laser beam was repeated, now recording the autofluorescence of the gold particles. The obtained autofluorescence was subtracted from the respective molecular fluorescence spectrum. Finally, the latter was normalized to its maximum value.

**Experimental results**

The number of molecules inside the resonator is generally much smaller than the number of “free“ emitters in the rest of the focal volume. Consequently, the measured fluorescence spectrum is dominated by the free molecules in the solution outside the resonator.

![Emission and Scattering Spectra](image)

Fig. 7.5: a) Emission spectra of Rhodamine 6G (R6G) molecules without the influence of a resonator (black curve), as well as in the presence of nanoresonators A - C with different resonance wavelengths. The latter spectra have been corrected for the gold autofluorescence. b) Scattering spectra of the applied nanoresonators. The arrows indicate the respective resonance wavelength.

The strong emission from these unaffected molecules covers up any effects induced by the resonator in the fluorescence range of the undisturbed molecules (550 nm - 650 nm). However, sizeable changes of the spectra are observable where the free molecules ex-
hibit only weak emission (650 nm - 800 nm). Fig. 7.5 a) shows a comparison between such spectra in the presence of a nanoresonator and the emission spectrum of the free molecules (black curve). In Fig. 7.5 b), the scattering spectrum of the respective nanoresonators are depicted. The molecules inside the resonator show an enhanced emission at the resonance wavelength of the coupled particle pair. Remarkably, in the most extreme case (blue curve), the molecules show fluorescence emission in a spectral range were the free molecules show practically no emission.

In conclusion, this experiment demonstrates how plasmonic nanoresonators can be tuned by photochemical metal deposition, and how this tuning can be applied to manipulate the fluorescence emission of fluorophores inside the resonator. The deposition method is therefore not only a mere structure fabrication technique, but an interesting tool for controlling optical processes on the nanoscale.
8 Manipulation of plasmon resonances II: Material effects

Naturally, the plasmonic spectrum of a nanoparticle is strongly influenced by the particle material. As described in detail in section 2.3, this concerns the specific material structure in terms of crystallinity, as well as the material composition. Both alter the effective dielectric function $\varepsilon_{\text{eff}}(\omega)$ and, hence, the optical response to illumination. This chapter deals with both aspects: On the one hand, the influence of the material structure is investigated using platinum spheres with high surface roughness. On the other hand, the effect of different material compositions is illustrated by the fabrication of bimetallic core-shell particles, again by means of photochemical metal deposition.

8.1 Platinum particles with rough surface

In terms of LSP resonances in metal nanoparticles, it is difficult to reach the short-wavelength region of the optical spectrum with particles made from gold or silver, the two materials most commonly used in nanooptics. Platinum is an interesting alternative, as Pt nanoparticles show resonances typically below 450 nm and exceed this value for large diameters only. Although their LSP curves are rather broad and field enhancement is lower than found for gold or silver particles [17], they are promising candidates for nanooptical applications in the UV region.

Furthermore, there is a variety of other application fields specifically for Pt nanoparticles. Large and monodisperse high-refractive-index particles are needed, e.g. for photonic crystals, where Pt spheres can complement the already existing Ag, Pd, Bi, Pb spheres and other monodisperse shapes [133] - [135]. Also in catalysis, Pt nanocrystals play a key role due to their large surface area and chemical potential, which has been proven for several systems [136].

Thus, the past decade has witnessed huge activities concerning Pt nanoparticle synthesis (see [57] and references therein). However, especially for spheres larger than 5 nm in diameter, an easy-to-follow synthesis route to monodisperse Pt particles of controlled size at small standard deviation was still missing to date. Such a facile route for Pt nanospheres ranging from 5 to 100 nm in diameter was developed in a cooperation with
8 Manipulation of plasmon resonances II: Material effects

Fig. 8.1: a) Size distribution for the four different batches of nanoparticles. b) Transmission electron micrographs of Pt nanospheres with mean diameters of 29, 48, 73, and 107 nm, respectively.

the group of Alexander Eychmüller at Physikalische Chemie und Elektrochemie of the Technische Universität Dresden. In particular, Pt particles of 29, 48, 73, and 107 nm in diameter have been synthesized by Nadja Bigall [57]. Besides the synthesis, also the optical properties of the synthesized particles were of interest in the cooperation, as the observed LSP resonances of the particles differed from those initially expected.

The transmission electron microscopy (TEM) images depicted in Fig. 8.1 b) and Fig. 8.2 show that the Pt particles exhibit a high surface roughness. Their outer surface consists of small crystallites ranging from 3 - 8 nm in diameter. The presence of these crystallites results in a peak-to-valley roughness of approximately 5 nm. Nevertheless, the overall diameter distributions of the outer diameters is very narrow with standard deviations as small as 3% for the larger spheres (Fig. 8.1 a)).

In Fig. 8.3 a), experimentally determined extinction spectra of the aqueous solutions containing spheres with mean diameters of 29 nm, 48 nm, 73 nm, and 107 nm, respectively, are presented. With increasing sphere diameter, the LSP resonance, i.e., the extinction peak, shifts to larger wavelengths from 248 nm for 29-nm particles to 494 nm for the largest spheres (squares in Fig. 8.3 c)).

[1] The wet-chemical synthesis protocol is presented in Appendix E.
[2] TEM imaging in the medium resolution regime was performed using a FEI Tecnai 10 (LaB6-source) microscope. High-resolution TEM experiments were carried out with a field emission microscope, CM 200 FE/ST-Lorentz (FEI COMPANY, Eindhoven, NL). TEM work by Paul Simon.
[3] The spectra have been measured using a Cary 5000 spectrophotometer.
The extinction spectra of these particles were calculated by means of two methods. For the smallest particle size (29 nm), the computation was carried out using the quasi-static approximation, as the diameter of the particle is small enough compared to the wavelength of the incident light. The extinction cross section $\sigma_{\text{ext}}$ is given by the sum of the scattering and the absorption cross section ($\sigma_{\text{sca}}$ and $\sigma_{\text{abs}}$, respectively; see Eq.s 2.26 and 2.28 on page 15). For larger spheres, the quasi-static model becomes more and more erroneous as retardation effects occur on the particles due to their increasing diameter. Therefore, the MMP method was used for computing the extinction spectra of these particles. In a first approach, the particles were modeled as homogeneous poly-crystalline Pt spheres, using the data of Weaver for the dielectric function $\varepsilon_{\text{Pt}}$ of the material [28]. The resulting peak positions are represented by circles in Fig. 8.3 c).

In Fig. 8.3 c), a very good agreement between the slope of the measured and the calculated curves can be seen. However, the computed values show a sizeable offset compared to the measured data. This effect can be attributed to the crystallinity and roughness of the sphere surface, which leads to a dielectric function slightly different from the bulk material.

To account for this effect, the modeling was refined by treating the spheres as core-shell systems as depicted in Fig. 8.4. For such a geometry, the particle polarizability in the quasi-static limit is given by [20]
8 Manipulation of plasmon resonances II: Material effects

Fig. 8.3: (a) Experimentally determined extinction spectra of the Pt particles in aqueous solution. (b) Extinction peaks calculated with a core-shell Pt sphere model. (c) Extinction peak positions of the experimental data (squares) and calculated values for massive platinum spheres (circles), as well as for core-shell particles (triangles). All lines depict linear fits to the respective data points.
8.1 Platinum particles with rough surface

Fig. 8.4: a) TEM image of a single nanosphere. b) Core-shell model used for the electrodynamical calculations. The surface roughness of the particles is accounted for by a shell of effective dielectric function $\varepsilon_2$.

\[
\alpha = 4\pi\varepsilon_0 R_1 \frac{(\varepsilon_1 - \varepsilon_3)(\varepsilon_1 + 2\varepsilon_2) + f(\varepsilon_1 - \varepsilon_2)(\varepsilon_3 + 2\varepsilon_2)}{2\varepsilon_2 + 2\varepsilon_3}(\varepsilon_1 + 2\varepsilon_2) + f(2\varepsilon_2 - 2\varepsilon_3)(\varepsilon_1 - \varepsilon_2)} \tag{8.1}
\]

with

\[
f = \frac{R_1}{R_2} = \frac{R_1}{R_1 - 5\text{ nm}}. \tag{8.2}
\]

Here, $R_1$ and $R_2$ denote the outer and the inner radius, respectively, while $\varepsilon_1$ and $\varepsilon_2$ are the dielectric functions of the core and shell, and $\varepsilon_3$ the dielectric constant of the surrounding medium. Using expression 8.1 for the polarizability, the extinction cross section for the core-shell system can be obtained from Eqs 2.26 and 2.28. The actual particle size measured by TEM was taken as the outer shell diameter $R_1$. The peak-to-valley surface roughness of 5 nm was taken into consideration by treating the outermost 5 nm of the particle as a shell with an effective dielectric function. This function was obtained by weighting the dielectric data $\varepsilon_{\text{Pt}}$ of platinum and $\varepsilon_{\text{H}_2\text{O}}$ of water, while the particle core again was treated as being pure poly-crystalline platinum. The larger particles were treated with the MMP method.

Finding an effective dielectric function which properly describes the optical properties of the particle shell is not an easy task, as deviations from the bulk data can occur due to several effects. On the one hand, the crystallites at the particle surface are smaller than the mean free path of the electrons in Pt (11 nm, see Table 2.1). Hence, surface scattering of the electrons is high in these crystallites, which leads to higher damping of the electron motion and consequently to longer LSP resonance wavelengths. On the other hand, the rough particle shell consists of much less metal than a massive Pt layer, which may lead one to the assumption of a smaller effective particle radius. This would
Manipulation of plasmon resonances II: Material effects

result in a shorter LSP resonance wavelength. Furthermore, the TEM images provide no indication on how the transition from the rough surface towards the massive particle core takes place in terms of crystallinity.\(^4\)

It is difficult to decide which effect dominates the behavior of the particle shell and, hence, which of the many kinds of effective medium models applies best [137]. Vice versa, it will be difficult to deduce any structural properties of the particles from the \(\varepsilon_{\text{eff}}(\omega)\) of choice. To achieve at least a proper simulation of the optical particle properties, the dielectric functions were weighted by means of the very simple power law

\[
\varepsilon_{\text{eff}}^\beta = f\varepsilon_P^\beta + (1 - f)\varepsilon_{H_2O}^\beta
\]

called the Silberstein formula [138]. Here, \(\beta\) was choosen to be 1 and the volume fraction of the different materials was assumed to be \(f = 0.5\). With this approach, a very good agreement was obtained between the calculations for single particles and the experimental data measured for the aqueous Pt nanoparticle solutions. The resulting extinction spectra are shown in Fig. 8.3 b), and the respective peak positions are depicted as triangles in Fig. 8.3 c). Due to this effective core-shell structure, the particles show LSP resonances which are red-shifted by \(\approx 25\) nm compared to their massive pendants.

The example of Pt nanospheres with rough surfaces shows the importance of the material structure for the plasmonic behavior of the particles. However, in addition to the shift of the LSP resonances, also the linear dependence between particle diameter and LSP resonance wavelength is interesting. In contrast to other materials, especially gold and silver, this linearity holds even for small particle sizes and makes platinum a highly interesting material for size-dependent nano-optical experiments [139].

8.2 Bimetallic core-shell particles

The material composition of nanoparticles is a key parameter which defines not only their optical, but for example also their magnetic and catalytic properties. This section deals with the manipulation of this composition through optically induced metal deposition. The approach is demonstrated by the fabrication of Pt-core Au-shell (Au@Pt) particles with in-situ controlled optical and chemical properties.

For this experiment, platinum particles were chosen as seeds. Pt particles with 30 nm diameter were prepared in aqueous solution according to the protocol described in Appendix E [57] and then treated as described in section 5.3. In particular, the same gold salt solution and optical setup were used.

\(^4\)A massive particle core is indicated by microtome cuts (data not shown).
8.2 Bimetallic core-shell particles

![Fig. 8.5: a) Experimentally determined scattering spectra during gold deposition on Pt nanospheres. b) Calculated scattering spectra of Au@Pt particles. A gold layer of respective thickness $L$ was assumed in the calculations performed for the nanoegg geometry depicted in c).](image)

The evolution of the plasmonic spectrum of a single Pt particle for increasing Au shell thickness due to exposure to laser light is depicted in Fig. 8.5 a). The LSP resonance of the Pt seeds is located at approximately 250 nm and is therefore not observable in the visible regime. As a consequence, the scattering signal exhibits only a slight increase towards the UV region, and the particles are barely visible when observed through the eyepiece of the microscope. Upon illumination, a gold shell is formed around the illuminated platinum seeds. This shell is responsible for the peak which emerges around 540 nm in the scattering spectrum and causes the addressed particle to appear in a bright yellow color.

The scattering spectrum of a single core-shell particle was again calculated using MMP. In the model, a 30-nm Pt particle was covered with an Au shell of increasing
thickness, while being homogeneously embedded in a dielectric material of $n = 1.52$. Presumably, again no gold can be deposited in the region of contact between the particle and the substrate. The core and the shell were therefore considered to be non-centrosymmetric in a so-called nanoegg geometry as introduced by Wang et al. [140] and depicted in Fig. 8.5 c). On the upper particle hemisphere, the layer thickness was considered to be constant. It amounts to the values depicted next to the calculated scattering spectra shown in Fig. 8.5 b). On the lower hemisphere, the layer thickness decreases to zero at the contact point between the substrate and the particle. The theoretical curves obtained with this model reproduce the features of the experimental spectra, especially the increasing peak around 540 nm.5

In conclusion, these results demonstrate that in the context of photochemical deposition gold can also be combined with other seed materials to fabricate multi-composite core-shell particles. The experimental spectra are well reproduced by theoretical calculations using a bimetallic core-shell nanoegg model. Thus, the presented photochemical technique allows not only the manipulation of the optical properties, but it can be applied to tune also the material composition of single MNPs.

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5 The spectral deviation of the curves calculated on the basis of the nanoegg model from those obtained with a concentric core-shell model are marginal (data not shown). It would actually be sufficient to take the latter, far simpler model into account.
9 Conclusion

Instead of rounding off the respective topics, the results of this thesis open up several paths for further scientific inquiries, both fundamental and application-oriented. However, these paths will be followed in future work, and before some continuative ideas are discussed, this book closes with a brief summary of the hitherto existing findings.

9.1 Summary

In nano-optics, single metal nanoparticles (MNPs) are applied to optically induce, control, and monitor processes below the diffraction limit. Two such MNP applications were discussed in Part I of this book. Firstly, the use of single particles as optically active probes for scanning near-field optical microscopy was demonstrated. Secondly, fluorescence enhancement in the vicinity of a single MNP was described theoretically with a focus on how the particle diameter and the surrounding medium influence the enhancement. It turned out that in these two examples the optical signal levels can be improved by manipulating the spectral LSP resonance position of the particles. This finding motivated the author to search for a method allowing the in-situ manipulation of LSP resonances in single metal particles.

As the method of choice and, hence, the central element of Part II of this book the optically induced metal deposition from solution was used and made applicable on the nanoscale. In a given dielectric environment, the LSP resonance of a particle depends on its size, shape, and material. All three parameters were manipulated with the presented technique in a targeted way. The exploited chemical processes and a detailed protocol for the deposition of metal onto single, individually addressed particles were described in chapter 5. Applying this protocol to different types of particles yielded the following results:

- The deposition of gold onto spherical gold particles extracted from a colloidal solution leads to an expected increase of the particle size, and thus to a redshift of the LSP resonance in the particle. As the particles work as seeds for the deposition process, the metal precipitates exclusively onto the particle surface. The area on the substrate next to the addressed particle and neighboring, unexposed particles
Conclusion

remain unaffected.

• In the same manner, single gold particles attached to the scanning probe of a near-field optical microscope were manipulated. Thus, scanning probes with in-situ tunable optical properties were obtained. With this it was also shown that the influence of a substrate onto the deposition process is marginal.

• Besides an increase in size, a decrease of the aspect ratio was observed during the exposure of ellipsoidal seed particles. This shape change manifests itself in a blueshift of the LSP resonance of the long particle axis. Under the excitation parameters used here the deposition process is independent from both the LSP resonance of the seed and the polarization of the incident light. The procedure is therefore not limited to specific types of seed particles or materials.

• After having gained experience with the photochemical procedure in the above-mentioned proof-of-principle experiments, the method was applied to tune single plasmonic nanoresonators formed by pairs of gold nanodisks. Photochemical gold deposition was used to increase the particle size, i.e., to reduce the interparticle gap space and augment the plasmonic coupling in the pair. It was found that with the presented procedure the coupled LSP mode of the dimers can be tuned over a broad spectral range, and that several geometrical parameters of these resonators can be read-out in situ by monitoring this LSP shift. Finally, the tunable resonators were applied to manipulate the fluorescence spectrum of organic molecules located inside the interparticle gap space.

• The influence of material effects on the LSP resonance in single particles was discussed in chapter 8. In particular, Pt particles fabricated with a novel synthesis protocol were investigated. Due to the crystallinity of their surface, these particles exhibit unexpected plasmonic properties. A theoretical description of this material effect was achieved by means of a core-shell model geometry. The calculations revealed that the rough surface feigns a smaller particle diameter.

• Finally, the manipulation of the surface material composition of single particles was shown by the fabrication of gold shell - platinum core (Au@Pt) particles. Again, this manipulation was monitored in situ by single-particle LSP resonance analysis. As a consequence, photochemical metal deposition renders possible the fabrication of single bimetallic MNPs with custom-designed optical and chemical properties.
9.2 Prospects

Especially the findings of the last chapter connect nano-optics with other fields of nanotechnology, such as research into catalysis, local surface modification, nano-structure fabrication, and so forth. Consequently, photochemical metal deposition may foster novel applications in these fields. To this end, the deposition of other metals has to be made possible, as well as a controlled deposition onto surfaces without seed particles.

As an initial step into this direction, the following proof-of-concept experiment was conducted. In order to alter the deposited material, a copper salt was chosen as the precursor. In particular, copper(II)chloride was dissolved in ethylene glycol\(^1\) with \(n = 1.43\), resulting in a 10-mM solution. Single gold particles of 80 nm diameter were used as seeds. They were again supported by a cover glass and embedded in the CuCl\(_2\) solution. For the exposure of these seeds to laser light, the setup depicted in Fig. 3.4 was used.

Upon irradiation, elemental copper precipitated from the solution. The deposition was again bound to the presence of a seed particle, as no reaction was initiated on the bare substrate. In contrast to previous experiments, the substrate was now moved laterally by means of the piezo stage while the sample was illuminated. Thus, the precipitated material worked as the seed for the area next to the particle into which the the deposition was now extended. As a result, a thin copper wire was fabricated on the glass surface (see Fig. 9.1). Interestingly, the deposition stopped immediately when the end of the wire was moved out of the focal region, e.g. by moving the substrate too fast. This effect corroborates the importance of a seed for the metal precipitation.

The solvent played a crucial role in this experiment, as no deposition was achieved with other solvents than glycol. These experimental observations allow the conclusion that due to its strong reducing character glycol converts Cu\(^{2+}\) into elemental Cu in the presence of an illuminated particle [141]. No such reaction was observed in the absence of a particle or on a non-irradiated seed. An analysis of the deposited material by means of energy-dispersive x-ray spectroscopy (EDX) further verified the deposition of copper, as the precipitated material did not contain any chloride (see Fig. 9.2).\(^2\) Presumably, oxidation of the material does not occur during deposition, as the process takes place in solution and under exclusion of air. However, this has to be examined further, for example by conductivity measurements.

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\(^1\)99.5\%, Sigma Aldrich, Germany
\(^2\)Chloride would appear in the spectrum as a peak between 2.6 and 2.7 keV.
9 Conclusion

Fig. 9.1: A copper wire deposited from solution. The deposition was initiated by a seed particle (80-nm gold sphere) and extended laterally by moving the substrate.

Fig. 9.2: EDX spectrum of the material deposited from the CuCl$_2$ solution under illumination. As no peak is observed between 2.6 keV and 2.7 keV, it can be excluded that the precipitated material contains any chloride.
The fabrication of copper wires demonstrates that the seed-mediated photochemical metal deposition from solution can be extended to other metals than gold, and very different structures can be manufactured. Further applications can range from the deposition of magnetic alloys, materials for the improvement of adhesion coefficients, catalytically active elements, and combinations thereof.

The importance of a seed in connection with the abovementioned process parameters has already been pointed out. This effect offers a route to confine structure dimensions such as the width of metal wires to length scales below the diffraction limit. The confinement was demonstrated for the deposition of metal onto particles; for extended structures it remains to be shown. However, already in the case of particles this confinement effect represents an advantage over existing laser direct-write approaches [142] - [144] and makes the photochemical method a valuable nanoscale fabrication and manipulation tool.

Besides these application-oriented prospects, the presented technique also facilitates to conduct rather fundamental studies. Especially the possibility to monitor the deposition process in situ is a virtue in this context. As an example, the effective dielectric function of alloy particles or exotic bimetallic core-shell systems can be directly determined by measuring their optical response during the deposition of the respective materials. The method therefore constitutes a way to access the optical properties of many different material combinations and ratios of components.

These and many other investigations can be launched on the experimental basis established in this work. The author therefore hopes that the presented results will contribute to a better understanding and a more precise control of the nanoworld.
Part III

Appendix
The multiple-multipole technique (MMP)

MMP is a semi-analytical method developed for the computation of electromagnetic problems. It relies on optimizing domain-boundary conditions and is therefore very well suited for the theoretical investigation of the structures dealt with in this work. In particular, it circumvents the problems of finite-elements-based methods such as the proper meshing of geometries with small feature sizes or the error propagation. A short overview over the principles of MMP are given below.

Theoretical background

Under the assumption of a linear, homogeneous, and locally responding medium without free charges and currents, the HELMHOLTZ equations can be derived from MAXWELL’s equations in media [23]:

\[(\nabla^2 + k^2)E = 0 \quad \text{and} \quad (\nabla^2 + k^2)H = 0.\] (A.1)

The material properties are contained in the wavenumber \(k\): \(k^2 = \varepsilon\mu\omega^2/c^2\). In a MMP model, the 3D model geometry can be freely subdivided into several domains in each of which the respective \(\varepsilon\) and \(\mu\) is homogeneous.

The fields \(E\) and \(H\) can be considered the sum of the incident and the scattered field, respectively:

\[E = E_{in} + E_{sca} \quad \text{and} \quad H = H_{in} + H_{sca}.\] (A.2)

As a consequence, Eq.s A.1 can be transposed in such a way that incident excitation field (which is known) and the field induced by the light-matter interaction are located on different sides of the equal sign. The excitation field thus resembles an inhomogeneity. The solutions of this set of differential equations have to fulfill the boundary conditions for their parallel and perpendicular components, respectively.

The MMP principle

MMP solves the prepared set of equations by discretizing the domain boundaries pre-assigned in the respective geometrical model. It is assumed that within a domain, an
A The multiple-multipole technique (MMP)

exact electromagnetic solution exists, whereas the conditions imposed by the boundary
can only be fulfilled within an error margin. As a consequence, the numerical effort is
much smaller than when using other methods such as FDTD, where the entire space is
discretized.

The field contained within a domain is described by a set of multipoles outside this
domain. Hence, the main task of the MMP code is to calculate and optimize the multipole
coefficients such that they fulfill the boundary conditions within a specified margin of
error.

The entire procedure may sound simple. However, the pitfalls are ubiquitous and range
from the design of the geometry via the proper choice of the boundaries’ matching points
to the correct implementation and location of multipoles. Nevertheless, the designers of
MMP around Christian Hafner have managed to allow the user to quickly become
acquainted with handling the program, which together with the short computation times
made MMP the technique of choice for the electromagnetic problems encountered in this
work. Much more details concerning MMP can be found in [38].
B Fabrication of particle-decorated probes for aperturless scanning near-field optical microscopy (ASNOM)

The central idea for the fabrication of ASNOM probes decorated with single metal particles goes back to the work of Kalkbrenner [145]. The scanning probe tip in use is coated with a monolayer of bifunctional chain-like molecules. These molecules are equipped with one functional end group preferentially binding to the tip material. As the probe is either a tapered glass fiber or a silicon AFM tip, a silane is used. The other molecular end group is chosen in such a way that it shows high binding strength to metals. Thus, aminopropyl-trimethoxy-silane (APTMS) turned out to be the molecule of choice.

Monolayer coverage of the tip is achieved by dipping it into a 10 mM aqueous APTMS solution for approximately 30 seconds and subsequent rinsing with deionized water. The tip is then mounted into the scanning probe microscope and scanned over a cover glass carrying the desired nanoparticles in non-contact mode. Once a particle is identified, the tip is lowered onto the particle, i.e., it gets “pecked” up. Rescanning the same sample area then yields information on the success of the attachment process.

It turned out to be extraordinary helpful to optically monitor the fabrication process, e.g. by means of an inverted microscope and homogeneous immersion as described in section 3.3. In this configuration, a suitable particle is directly visible as a bright scattering center. This makes scanning the sample before and after particle attachment dispensable, thus speeding up the process and making it more reliable. More details and practical hints on the entire fabrication process can be found in [62].
C Fabrication of gold nanoparticles by electron beam lithography (EBL)

The EBL-manufactured samples used in this work were fabricated by Yury Alaverdyan in the group of Mikael Käll at Chalmers University of Technology in Göteborg, Sweden. In particular, the elongated particles and the particle pairs described in chapters 6 and 7, respectively, were prepared there. In what follows, the fabrication protocol is given.

The respective particles were fabrication on glass substrates (VWR, 150-m-thick microscope cover slides). Prior to the electron beam exposure, the substrates were plasma-cleaned, spin-coated with the resist ZEP520 (diluted 1:2 in anisole) at 6000 rpm, baked at 170°C for 10 min, and finally covered by 10 nm of resistively evaporated gold. The exposure to the electron beam, which was performed using a JEOL9300XS high-resolution EBL system at 100 kV, 500 pA, was followed by removal of the 10-nm gold film in an aqueous solution of 4 g of KI and 1 g of I₂ in 150 ml of deionized water, a development step in hexylacetate (30 s), evaporation of a 0.5 nm Ti adhesion layer, and finally evaporation of a 20-nm gold film. The remaining resist, with gold on its surface, was removed in Shipley 1165 at 55°C, before the sample was rinsed with deionized water and dried in pure N₂. The nanoparticles were arranged in a grid with 15 µm interparticle spacing. In comparison to the colloidal nanoparticles, the EBL structures possess no citrate capping layer.
Dipolar coupling model

Here, an approximative description of the plasmonic coupling between two identical gold spheres (each represented by a point dipole) is sketched. In particular, the behavior of the LSP resonance for different coupling configurations is analyzed. As the particle shape has minor influence on the dipole-dipole coupling, the formalism can easily be extended to non-spherical particles (see the more detailed description in [128]).

In section 2.2.1 it was shown that in the quasi-static approximation the scattering field $\mathbf{E}_{\text{ sca}}$ induced by a nanosphere equals the one of an electric dipole moment $\mathbf{p}$ of the form

$$\mathbf{p} = \alpha \varepsilon_m \mathbf{E}_{\text{exc}}$$  \hspace{1cm} (D.1)

with $\mathbf{E}_{\text{exc}}$ the excitation field, $\alpha$ the polarizability of the sphere, and $\varepsilon_m$ the dielectric constant of the surrounding of the particle. In case of a particle pair with interparticle separation $d$ smaller than the sphere radius $R$, each particle feels the sum of the excitation field $\mathbf{E}_{\text{exc}}$ and the near-field of the other particle. The latter decays as the cube of the distance $d$ (see section 2.2.2), and the sum of the fields reads

$$\mathbf{E}' = \mathbf{E}_{\text{exc}} + \frac{\eta \mathbf{p}'}{4\pi \varepsilon_m \varepsilon_0 d^3}. \hspace{1cm} (D.2)$$

Here, $d$ represents the interparticle separation (from surface to surface), and $\eta$ denotes a factor which depends on the orientation of the two single-particle dipoles [22, 128]. For the dipoles aligned in a head-to-tail configuration, $\eta$ amounts to 2. This situation is caused by incident light polarized along the center-to-center axis of the particles and leads to a plasmon resonance denoted as $\lambda_\parallel$ in section 7.2. Light polarized perpendicularly to the center-to-center dimer axis causes a parallel orientation of the dipoles and a resonance wavelength $\lambda_\perp$. This situation is described by $\eta = -1$. Finally, the polarizability of the two-particle system is given by

$$\alpha' = \alpha \left(1 - \frac{\eta \alpha}{4\pi \varepsilon_0 d^3}\right)^{-1}. \hspace{1cm} (D.3)$$

Using the single-particle polarizability

$$\alpha = 4\pi \varepsilon_0 R^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m}, \hspace{1cm} (D.4)$$
D Dipolar coupling model

the two-particle polarizability reads

$$\alpha' = \frac{4\pi\varepsilon_0 [\varepsilon(\omega) - \varepsilon_m]}{\varepsilon(\omega) \left(1 - \frac{\eta R^3}{d^3} \right) + \varepsilon_m \left(2 + \frac{\eta R^3}{d^3} \right)}. \quad (D.5)$$

The resonance of the collective electron oscillation of the coupled particles equals a maximum of the polarizability which occurs under the condition

$$\varepsilon(\omega) \left(1 - \frac{\eta R^3}{d^3} \right) + \varepsilon_m \left(2 + \frac{\eta R^3}{d^3} \right) \rightarrow \text{min.} \quad (D.6)$$

In the special cases of $|\varepsilon_2(\omega)| \ll 1$ or a small $\partial\varepsilon_2/\partial\omega$, the LSP resonance condition $D.6$ can be approximated as

$$\varepsilon_1^{\text{res}}(\omega) = -\varepsilon_m \left(2 + \frac{\eta R^3}{d^3} \right). \quad (D.7)$$

The near-linear dependence of the real part $\varepsilon_1$ of gold on the wavelength between 500 and 800 nm (see Fig. 2.1) can be approximated to $\varepsilon_1 = (464.4 - \lambda)/14.3 \ [128]$. Inserting this relation into Eq. $D.7$ finally yields the LSP resonance wavelength

$$\lambda_{\text{res}} = 14.3\varepsilon_m \left(2 + \frac{\eta R^3}{d^3} \right) + 464.6. \quad (D.8)$$

For the two possible values of $\eta$, the fraction in Eq. $D.8$ takes on the form

$$\left(2 - \frac{R^3}{d^3} \right) \ (\eta_\perp = -1) \quad \text{and} \quad \left(2 + \frac{2R^3}{d^3} \right) \ (\eta_\parallel = 2). \quad (D.9)$$

From the above equations, the experimental observations described in chapter 7 can be understood. On the one hand, due to the different signs of $\eta$ for the two different coupling configurations, the LSP resonance of the interacting particle pair shifts into different directions for decreasing interparticle separation $d$. On the other hand, the different absolute values of $\eta_\parallel$ and $\eta_\perp$ lead to different amounts of the shift when the particles approach each other.
E Synthesis of platinum nanospheres

Platinum particles of different sizes were fabricated by Nadja Bigall in the group of Alexander Eychmüller at the Technische Universität Dresden. The wet-chemical protocol of the fabrication is given below.

Synthesis of small platinum seeds

Pt nanoparticle seeds of 5 nm in diameter were prepared according to Brown et al. [146]. Briefly, 36 mL of a 0.2% solution of chloroplatinic acid hexahydrate (SIGMA-ALDRICH, ACS reagent) was added to 464 mL of boiling deionized water. After 1 minute, 11 mL of a solution containing 1% sodium citrate and 0.05% citric acid was added, followed half a minute later by a quick injection of 5.5 mL of a freshly prepared sodium borohydride (0.08%) solution containing 1% sodium citrate and 0.05% citric acid. After 10 minutes, the product was cooled down to room temperature.

Synthesis of 29-nm platinum particles

To 29 mL of deionized water, 1 mL of the platinum seed solution was added at room temperature. A 0.045 mL portion of a 0.4 M chloroplatinic acid solution (VEB BERGBAU-UND HÜTTENKOMBINAT ALBERT FUNK, Hexachloroplatin(IV)säure, reinst) was added, followed by the addition of 0.5 mL of a solution containing 1% sodium citrate and 1.25% L-ascorbic acid. Under stirring, the temperature was slowly increased to the boiling point (≈ 10°C/min). The reaction time was 30 minutes in total. By varying the amount of chloroplatinic acid, particles with diameters from 10 to 30 nm in diameter (as obtained from transmission electron microscopy (TEM) measurements) were synthesized.

Synthesis of large-diameter platinum spheres

To obtain Pt spheres with diameters larger than 29 nm, the particles described above were used as seeds. By adding 4 mL of the 29-nm Pt-particle solution to 26 mL of deionized water together with 0.045 mL of the chloroplatinic acid solution, followed by the addition of 0.5 mL of the solution containing 1% sodium citrate and 1.25% L-ascorbic acid and slowly increasing the temperature to the boiling point, spheres with 48 nm diameter were
obtained. The same procedure using 1 and 0.25 mL of seed solution in 29 mL of water resulted in spheres of 73 and 107 nm diameter, respectively.

**Post-treatment of the particles**

All nanoparticles were washed three times by precipitation in the centrifuge (EPPENDORF MINI SPIN, operated at 1000-13400 rpm depending on the nanoparticle size), exchanging the supernatant against deionized water, and redispersion of the nanoparticles.
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Publications, presentations, and patents related to this thesis


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Other publications


Patents


- German patent: DE 10 2007 037 201.0 “Element zu oberflächenverstärkten Spektroskopie und Verfahren zur Herstellung eines Elements“ (with R. Kullock, L. M. Eng, R. Pollard, and P. Evans)
List of symbols and abbreviations

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<thead>
<tr>
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<th>Description</th>
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<tr>
<td>$\alpha(\omega)$</td>
<td>polarizability of a nanoparticle</td>
</tr>
<tr>
<td>$\delta(\omega)$</td>
<td>penetration depth</td>
</tr>
<tr>
<td>$\varepsilon(\omega)$</td>
<td>dielectric function of a material</td>
</tr>
<tr>
<td>$\varepsilon_1(\omega)$</td>
<td>real part of the dielectric function</td>
</tr>
<tr>
<td>$\varepsilon_2(\omega)$</td>
<td>imaginary part of the dielectric function</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>vacuum permittivity</td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>dielectric constant of the surrounding medium</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>vacuum wavelength of light</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity</td>
</tr>
<tr>
<td>$\sigma_{sca}$</td>
<td>scattering cross section</td>
</tr>
<tr>
<td>$\sigma_{abs}$</td>
<td>absorption cross section</td>
</tr>
<tr>
<td>$\tau$</td>
<td>mean time between electron-electron scattering events</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>plasma frequency</td>
</tr>
<tr>
<td>$\chi$</td>
<td>dielectric susceptibility</td>
</tr>
<tr>
<td>$D$</td>
<td>nanoparticle diameter</td>
</tr>
<tr>
<td>$d$</td>
<td>distance measured from the nanoparticle surface</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field vector</td>
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<tr>
<td>$e_0$</td>
<td>elementary charge</td>
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<td>$H$</td>
<td>magnetic field vector</td>
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<tr>
<td>$k$</td>
<td>wave vector</td>
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<tr>
<td>$l_m$</td>
<td>electron mean free path</td>
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List of symbols and abbreviations

\( m_e \)  effective electron mass
\( n \)  refractive index
\( n_e \)  electron density
\( p \)  electric dipole moment
\( r \)  position vector
\( R \)  nanoparticle radius
AFM  atomic force microscope / microscopy
APTMS  aminopropyl-trimethoxy-silane
ASNOM  apertureless scanning near-field optical microscope / microscopy
CCD  charge-coupled device
EBL  electron beam lithography
EDX  energy-dispersive x-ray spectroscopy
EOM  electro-optical modulator
IR  infrared
LSP  localized surface plasmon
MLWA  modified long wavelength approximation
MMP  multiple-multipole (method)
MNP  metal nanoparticle
N.A.  numerical aperture
R6G  Rhodamine 6 G
SEM  scanning electron microscope / microscopy
TEM  transmission electron microscope / microscopy
UV  ultraviolet
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