Photothermal properties of gold nanorods and their application to five-dimensional optical recording

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I, Peter Zijlstra, declare that this thesis entitled:

“Photothermal properties of gold nanorods and their application to five-dimensional optical recording”

is my own work and has not been submitted previously, in whole or in part, in respect of any other academic award.

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Dated this day, 25 June 2009
Abstract

The development of controllable synthesis methods in the 1990s has sparked an enormous interest in gold nanorods, both fundamentally and application driven. Their anisotropic shape induces a splitting of the surface plasmon resonance (SPR) into a transverse and a longitudinal component, of which the latter occurs in the near-infrared wavelength range and is extremely sensitive to the wavelength and polarization of the impinging light. At the longitudinal SPR wavelength, gold nanorods exhibit strong light absorption, which makes them ideal photothermal energy converters. In this thesis we investigate the photothermal properties of gold nanorods, and apply them to achieve five-dimensional optical recording. In the past decades many optical recording techniques have been proposed which exploit the wavelength, polarization or the three spatial dimensions for multiplexed recording. However, the lack of a suitable recording medium has hampered the integration of these techniques to achieve a five-dimensional recording method, which could increase the information capacity by orders of magnitude. We used the photothermal properties of gold nanorods to achieve for the first time five-dimensional optical recording.

To achieve this goal we developed a high-yield synthesis method which is viable at high temperatures. Elevating the reaction temperature increased the growth rate by almost three orders of magnitude, resulting in a synthesis protocol which enables rapid synthesis of gold nanorods on a large scale.

We studied the photothermal properties of these nanorods using a combination of electron microscopy, white light spectroscopy, and ultrafast laser spectroscopy.
To remove ensemble averaging in the experiments, we performed experiments on single gold nanorods. We measured the electron-phonon decay in single particles, and found that the electron-phonon coupling constant agrees well with the literature value. We also detected the acoustic vibrations of the nanorod and, in contrast to previous studies on ensembles of gold nanorods, we found that the acoustic mode frequencies compare well to theoretical predictions.

Doping of the nanorods into a matrix is key to successful application in optical recording. We doped the nanorods into a polyvinyl alcohol (PVA) matrix, which provides a flexible and stable matrix for the nanorods. We investigated the thermal properties of the polymer nanocomposite, and found significant accumulation of heat caused by the high repetition rate of commercial femtosecond laser systems. We show that this heat accumulation can be prevented by employing single laser pulses, resulting in a thermally stable nanocomposite suitable for optical recording.

Using a combination of white light spectroscopy and electron microscopy we studied the melting and reshaping of single gold nanorods in a PVA matrix. Unlike previous ensemble experiments, we find good agreement between the theoretical and experimental melting energy of a single nanorod. Higher aspect ratio particles were found to be thermodynamically less stable, leading to more pronounced partial reshaping at lower pulse energies.

Finally, we employed this photothermal reshaping to achieve five-dimensional optical recording. The narrow longitudinal SPR linewidth combined with the dipolar optical response allowed us to optically address only a small subpopulation of nanorods in the laser irradiated region. Using this technique we achieved aspect ratio and orientation selective photothermal reshaping, which allowed us to incorporate three wavelength channels and two polarization channels. The distinct energy threshold required for the photothermal reshaping provided the axial selectivity required to record in multiple layers. We demonstrate that two-photon luminescence detection has an enhanced wavelength and angular selectivity compared to conventional linear readout mechanisms, which enabled cross-talk free recording and readout.
Acknowledgments

In 2004 I completed my internship in the CMP under supervision of Dr. James Chon. While I was back in The Netherlands to finish my Masters degree, James contacted me again to let me know there was a Ph.D. position available which would allow me to continue the work I did during my internship. After some deliberation, I decided to take the step and come back to Melbourne for four years.

I never regretted this decision, and I have truly enjoyed working in the CMP. I was given a lot of freedom to fill in my project as I wished, for which I am grateful to James. I always thought our discussions were stimulating and resulted in many new ideas, sometimes so many I didn’t know where to start! The scope of your knowledge is impressive and has certainly helped a lot in compiling this thesis. I would also like to thank Prof. Min Gu for the opportunities I have been given in the CMP, which is truly a world-class facility. From Min I quickly learned that doing research is not only about conducting experiments, but publishing your results is critical to survive and progress.

The development of a new recording medium starts with the preparation of samples, in my case these samples consisted of gold nanorods. At the start of my PhD, my knowledge on the synthesis of nanoparticles was very limited, but the enthusiasm and knowledge of Dr. Craig Bullen got me interested. I rapidly acquired all the chemistry skills I needed and used these throughout my PhD to prepare samples. Thanks Craig, for all your help! I am also grateful to Lintec Corporation for kindly supplying us with the pressure sensitive adhesive we used in Chapter 5 of this thesis.
The work presented Chapter 3 of this thesis was done in the Single Molecule Optics group at Leiden University in The Netherlands. I am very thankful to Prof. Michel Orrit and Dr. Anna Tchebotareva for having me in Leiden. Thanks to Michel for the stimulating scientific discussions, I didn’t know I could learn so much in only 8 weeks. Anna spent a lot of time with me in the lab, both to set up and conduct the experiments, for which I’m grateful.

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This thesis reflects the results of 3.5 years of research in the Centre for Micro-Photonics at Swinburne University of Technology in Melbourne. During this time we tried to develop an understanding of the optical and thermal properties of gold nanorods, and applied this knowledge toward novel optical recording techniques. There was not much prior knowledge about the synthesis and properties of gold particles in the Centre, which made this project even more challenging. The objective was to develop a next generation optical data storage medium capable of storing more information on a single disc than is currently possible. One way to achieve this is to make the recording bits on the disc smaller, which could increase the storage capacity by a factor of two or three. Instead, we chose a more ambitious approach, which potentially increases the capacity by one-hundred or even one-thousand times.

This recording technique is called multiplexing or multidimensional recording. By cleverly using the polarization and color of the laser light, it is possible to record two or more bits on the same spot. Multiplexing had been demonstrated with either the polarization or the wavelength of the recording light, but never have these two been integrated together because of limitations of the recording medium. We decided to try and achieve this by using gold nanorods.

Gold nanorods are cylinder shaped clusters of gold atoms, typically with a size below 100 nm. The conduction electrons in gold can freely move within the nanorod, which gives rise to a strong interaction with the electromagnetic field of light. As a result gold nanorods possess a strong absorption in a narrow wavelength region,
which is the origin of the vibrant colors displayed by nanoparticle solutions. The recording mechanism we choose was aimed at irradiating the nanorods at their absorption band with a femtosecond laser pulse. With enough laser power we can melt the rods (melting requires a temperature of $\sim 1000 \, ^\circ C$), and reshape them to spherical particles. This changes their absorption spectrum, which can be detected as a color change. Multiplexing was possible by exploiting the optical properties of nanorods, which allowed us to selectively excite and melt only the nanorods with a certain aspect ratio which are aligned to the laser light polarization. The remaining rods were unaffected by the laser light, and can be used to record another piece of information.

The first challenge we faced was the reproducible synthesis of gold nanorods. In order to develop an attractive recording medium, we have to be able to synthesize its building blocks on a large scale. Several techniques existed to prepare gold nanorods, but all of these were quite slow: it takes up to one hour to grow the rods in water solution. We decided to try and speed this process up by increasing the temperature during the synthesis. Indeed, by elevating the reaction temperature to just under the boiling point of water we could synthesize rods within one second, a huge improvement. In Chapter 2, the method and results of this experiment are described in more detail.

To better understand the process of exciting the rod and heating its lattice, we collaborated with Prof. Michel Orrit, Dr. Anna Tchebotareva, and Dr. Meindert van Dijk from the Single-Molecule Optics group at Leiden University in The Netherlands. They have expertise in studying these processes using pump-probe spectroscopy. In pump-probe spectroscopy a pump pulse heats the nanorod, and a probe pulse detects the relative change in transmission due to this heating. Both pulses arrive at the sample with a tunable mutual time delay that can be changed by simply changing the optical path length of one of the beams. This allowed us to probe the heating and cooling dynamics with a time resolution of one picosecond. Because all nanorods in a solution are generally different, we decided to remove the ensemble averaging by studying a single nanorod. Using this technique we studied the electron-phonon decay (which is a measure of the rate at which the
particle heats up after absorption of the laser pulse) and the heat dissipation to the environment. We also detected the acoustic vibrations of a single gold nanorod: when a pump-pulse increases the electron and lattice temperature in the particle, the lattice expands rapidly. This has the same effect on the nanoparticle as striking a tuning fork: it will start to resonate with a frequency that depends on the size and shape of the particle/fork. As we will explain in Chapter 3, these acoustic vibrations contain important information about the elastic properties of the nanorods.

The use of nanorods in a recording medium requires them to be doped into a matrix material. Our initial choice was a glass matrix; glass is a rigid material that can successfully withstand the high temperatures generated in the gold nanorods. Unfortunately, this proved to be complicated as the solvents used to prepare the glass matrix rapidly aggregate the nanorods. In order to prevent aggregation, we had to overcoat the nanorods with a capping layer, which is very laborious and difficult to implement on a large scale. So we changed the matrix material to a polymer, in which the rods are more stable. However, polymers have very poor thermal properties, which turned out to be critical for our photothermal recording mechanism. The femtosecond laser we used for recording emitted one light pulse of 100 fs every 12 ns. Initially, we used an exposure time of 25 ms, which is roughly 2 million light pulses. The problem we encountered was that after absorption of a laser pulse, the polymer in the focal spot did not cool down to room temperature before the next pulse arrived, 12 ns later. As we describe in the first part of Chapter 4, heat builds up in the focal volume causing damage to the matrix material. To overcome the issues of heat buildup we decided to install an electro-optic modulator, which is capable of picking a single laser pulse from the pulse train. Recording with a single pulse not only prevented the buildup of heat, but it also increased our recording speed by a factor of 2 million (instead of 25 ms, the exposure time is only 12 ns).

Now that we were able to record without damaging the matrix, we decided to have a closer look at the reshaping of the gold nanorods. These experiments are described in the second part of Chapter 4. We measured the scattering spectrum of a single nanorod before and after absorption of a laser pulse, from which we determined the melting energy of a single gold nanorod. The melting energy for a large ensemble
of nanorods was reported in literature before, but the value did not match the expected theoretical melting energy, possibly due to errors caused by ensemble averaging. By removing the ensemble averaging, we found good agreement with the expected theoretical melting energy. We also recorded the electron microscope image of the nanorods after irradiation, from which we extracted the evolution of the particle shape at different stages of the reshaping.

In Chapter 5 we apply our knowledge to achieve, for the first time, five-dimensional optical recording. We recorded images in three spatial dimensions (i.e. multiple layers), the wavelength domain and the polarization domain by exploiting the unique optical properties of gold nanorods. We first tried to record images in a thick polymer sample homogeneously doped with gold nanorods. Unfortunately, we observed quite some cross talk between neighboring layers. To reduce the cross talk we used a type of “sticky tape” with a thickness of just 10 µm and a refractive index exactly the same as our polymer. We spin coated thin polymer layers with nanorods, separated by this spacer layer. When we still observed cross talk in the readout, we were convinced it did not originate from the recording, but from the readout mechanism we employed. Until now we had been detecting the recordings in transmission with laser diodes as a light source. This is a linear readout mechanism, which means that out-of-focus light (i.e. light absorbed by other layers) is also detected. We decided to try a non-linear readout mechanism, namely the two-photon induced luminescence from the gold nanorods. This completely removed the cross talk between the layers, and we found that the non-linear character of the excitation also significantly reduced the cross talk between neighboring polarization and color channels. This allowed us to record and read data in five dimensions with no noticeable cross talk.

The ultrafast spectroscopy and melting experiments described in this thesis provide a powerful method to study the thermal and physical properties in individual, nanometer sized objects. These experiments provide a first step toward experimentally exploring the scale on which the thermal and physical properties of a nanoparticle start to differ from bulk values. In the future, perhaps with even more sensitive detection equipment, these experiments will be conducted on
objects of several nanometers or less in diameter, and will be able to reveal shape and size effects in a variety of materials. We applied the acquired knowledge toward multiplexed optical recording, and we developed the first recording medium which is capable of five-dimensional recording with simultaneous polarization and wavelength multiplexing.

The physics of metal nanoparticles is described in Chapter 1 of this thesis. We will give an overview of the optical and thermal properties of gold nanorods, and describe how these can be employed toward multiplexed optical recording. We also review the current state of the art in multiplexed optical data storage. Whether you come from a background related to physics, nanoparticles or optical recording, we hope you enjoy reading this thesis.
Small metal particles exhibit complex optical and physical properties. Their small sizes (< 100 nm) cause strong confinement of the electrons, giving rise to fascinating effects not observed in the bulk material. The most striking phenomenon encountered in metal nanoparticles are electromagnetic resonances due to the collective oscillation of the conduction electrons. These so-called localized surface plasmon resonances (SPR) induce a strong interaction with light, and the wavelength at which this resonance occurs depends on the local environment, shape, size and orientation of the particle.\textsuperscript{1–3} Fundamental aspects and potential technological applications have been widely investigated in the past decade, and metal nanoparticles have been used for catalysis,\textsuperscript{4, 5} sub-wavelength optical devices,\textsuperscript{6–8} surface enhanced Raman spectroscopy,\textsuperscript{9, 10} biological imaging and sensing,\textsuperscript{11, 12} and photo activated cancer treatment.\textsuperscript{13, 14}

At the SPR wavelength metal particles exhibit strong light absorption, which is the origin of the vibrant colors displayed by media containing these particles. Because their absorption cross section is orders of magnitude higher than that of a non-metallic object of the same size, they are efficient converters of photon energy to thermal energy. A particularly appealing application of this energy conversion is photothermal optical recording.\textsuperscript{15–18} The thermal energy generated in the particle can be used to induce a change in the particle(s) or in their environment. This results in a local color change, which represents a recording mark in the medium.
Currently a huge effort is directed toward increasing the information capacity of optical recording media. The most efficient method to achieve this is a technique called multiplexed optical recording. Multiplexing exploits the wavelength or polarization sensitivity of the recording medium to record multiple bits in the same volume, and can potentially increase the storage capacity of a recording medium by several orders of magnitude. The unique wavelength and polarization properties of the SPR make gold nanoparticles a promising material for multiplexed optical recording. Especially gold nanorods with their narrow, wavelength tunable and polarization dependent SPR hold great potential for multiplexing.

In this Chapter we will review and explore the optical and photothermal properties of gold nanorods, and we highlight their suitability for wavelength and polarization multiplexed optical recording. In Section 1.1 we will discuss how the SPR resonance depends on particle shape, size and orientation. We start by shortly discussing the absorption of light by spherical particles in the context of Mie theory. We will then focus on the wavelength and polarization dependent optical properties of gold nanorods. In Section 1.2 we will describe the steps involved in the photothermal energy conversion process, where we shall focus on excitation with a short laser pulse. Next, we review previous efforts in metal nanoparticle assisted optical recording in Section 1.3. Finally we review the current state of the art in multiplexed optical recording in Section 1.4, and we will illustrate how gold nanorods can play an important role in this application.

1.1 Optical properties of metal nanoparticles

In this Section we describe the optical properties of metal nanoparticles, in particular gold. We focus on the optical properties relevant to multiplexed optical recording, namely the wavelength and polarization sensitivity of the SPR. We also discuss the factors that influence the linewidth of the SPR absorption band. The SPR linewidth ultimately determines how many recording channels we can achieve in the wavelength domain, and we will see that gold nanorods have a much reduced linewidth compared to spheres. In the final Section we describe a phenomenon which is strongly correlated to the SPR of a metal nanoparticle, namely photoluminescence.
1.1.1 Absorption of light by spheres

The problem of absorption and scattering of light by spherical particles of arbitrary size was first treated by Gustav Mie in 1908.\textsuperscript{19} The Mie theory describes the absorption of a plane wave by a homogeneous sphere of arbitrary radius. Posing the right boundary conditions at the sphere’s surface and at infinity, Maxwell’s equations can be solved.\textsuperscript{20,21} The optical properties of the sphere depend on the radius of the sphere $R$ and on the dielectric function of both the sphere, $\epsilon_l$, and the surrounding medium, $\epsilon_m$. We can then express the scattering and extinction cross sections as\textsuperscript{20}

$$\sigma_{sca} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) (|a_n|^2 + |b_n|^2), \quad \text{and} \quad (1.1)$$

$$\sigma_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \Re(a_n + b_n), \quad (1.2)$$

where $k$ is the wavenumber in vacuo, and $a_n$ and $b_n$ are the scattering coefficients defined by

$$a_n = \frac{m\psi'_n(mx)\psi_n(x) - \psi_n(mx)\psi'_n(x)}{m\psi'_n(mx)\zeta_n(x) - \psi_n(mx)\zeta'_n(x)}, \quad \text{and}$$

$$b_n = \frac{\psi'_n(mx)\psi_n(x) - m\psi_n(mx)\psi'_n(x)}{\psi'_n(mx)\zeta_n(x) - m\psi_n(mx)\zeta'_n(x)}, \quad (1.3)$$

where the variable $x = \sqrt{\epsilon_m k R}$ is the size parameter of the system, $m = \sqrt{\epsilon_l/\epsilon_m}$, and $\psi_n$ and $\zeta_n$ are the Riccati Bessel functions of order $n$.\textsuperscript{20} The prime denotes differentiation with respect to the argument. The absorption cross section can be obtained from the optical theorem\textsuperscript{20}

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca}. \quad (1.4)$$

The size parameter $x$ determines the optical properties of the sphere. Note that, as we expect, the scattering coefficients and thus the scattered field disappears if there is no particle present ($\epsilon_l = \epsilon_m$).
In order to calculate the absorption cross section, we require the dielectric function of the particle. The dielectric function of metals can be calculated using models such as the Lorentz model and the Drude model. These models treat the electrons and ions of matter as simple harmonic oscillators (i.e., "springs") subject to the driving force of applied electromagnetic fields. However, the complex electronic structure of metals is not described very accurately by these models. Therefore most calculations involving metals use a dielectric function known from measurements. The measurements by Johnson and Christy are generally considered to be most reliable, and will be used in this thesis. These dielectric functions were measured on metal films under high vacuum conditions. In Figure 1.1 we plot the real and complex parts of the dielectric function of gold as measured by Johnson and Christy. They have proved to accurately reproduce the optical properties of metal particles. However, to reliably obtain quantitative optical cross sections for very small particles ($R < 5 \text{ nm}$) the effects of electron surface scattering have to be taken into account.

The above formalism enables us to calculate the optical cross sections of arbitrarily sized spherical particles. As an example, in Fig. 1.2a we show the absorption cross section of a gold sphere, which was calculated using Eq. 1.4. To illustrate the effect of the particle size on the absorption properties we have varied the radius of the sphere in the calculation. The spectra are characterized by a rather broad plasmon resonance around 530 nm, and display a pronounced asymmetry.
This broad linewidth and the asymmetry are caused by the interband transitions of the bound electrons in gold. This interband absorption is clearly observed as a sharp increase in the imaginary part of the dielectric function of gold around 400 nm (see Fig. 1.1). As expected, the absorption cross section increases with particle size. We also observe a weak red-shift of the plasmon resonance as the particle size increases. This red-shift is observed for sizes greater than approximately 10 nm and is caused by electromagnetic retardation.\textsuperscript{20}

In Fig. 1.2b we illustrate the dependence of the absorption cross section on the polarization of the incoming light. The symmetric particle does not possess any polarization sensitivity due to the monopole character of the excitation of the surface plasmon. This absence of polarization sensitivity, the rather broad absorption cross section and the limited wavelength tunability restricts the usefulness of gold spheres for multiplexing applications.

Figure 1.2: Calculated optical cross sections of a gold sphere (a) Calculated absorption cross sections of gold spheres of various radii, embedded in a medium with $\epsilon_m = 2.25$. (b) Illustration of the dependence of the absorption cross section on the linear polarization angle of the excitation light evaluated at the peak wavelength of the SPR.
1.1.2 Absorption of light by nanorods

Contrary to the case of spheres, the theoretical description of scattering of light by cylinders of finite length is complicated due to the lack of symmetry in the problem. We will therefore approximate the shape of a nanorod with a very small ellipsoid, for which a simple solution to the scattering problem was developed in 1912 by Gans.\textsuperscript{25}

Let us consider a smooth ellipsoidal particle with two different semi-axes lengths ($a > b = c$) in an elliptical coordinate system. For simplicity we restrict ourselves to particles which are much smaller than the wavelength of the incident light. The particle can then be approximated as an ideal dipole, and the field outside the particle is a superposition of the incoming field and the field of the ideal dipole. The polarizability in a field parallel to one of its principal axes can be expressed as\textsuperscript{20}

$$\alpha_p = 4\pi abc \frac{\epsilon_l - \epsilon_m}{3\epsilon_m + 3L_p(\epsilon_l - \epsilon_m)},$$  \hspace{1cm} (1.5)

where $p=(1,2,3)$ denotes the polarization of the incoming field, aligned to one of the axes of the particle. The geometrical depolarization factors $L_p$ describe the shape of the particle. For prolate spheroids the geometrical factors can be expressed as\textsuperscript{20}

$$L_1 = \frac{1 - e^2}{e^2} \left( -1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right), \text{ and}$$

$$L_2 = L_3 = \frac{1 - L_1}{2},$$ \hspace{1cm} (1.6)

where $e^2 = 1 - b^2/a^2$ is the eccentricity of the particle. The optical cross sections for spheroids can then be expressed as\textsuperscript{20}

$$\sigma_{ext} = k \text{ Im}(\alpha)$$ \hspace{1cm} (1.7)

$$\sigma_{sca} = \frac{k^4}{6\pi} |\alpha|^2,$$ \hspace{1cm} (1.8)

and the absorption cross section can be obtained from Eq. 1.4.
The shape of the prolate spheroid ranges from a needle ($e = 1$) to a sphere. Note that for a sphere $e^2 = 0$, and all geometrical factors $L$ reduce to $\frac{1}{3}$. In this special case the polarizability can be expressed as

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

allowing the computation of optical cross sections for spheres much smaller than the wavelength of light.

In Fig. 1.3 we show the cross sections of a gold spheroid with a semi-minor axis length of 15 nm and a semi-major axis length of 45 nm. In this calculation the incoming field was aligned to the long particle axis, and thus only the longitudinal SPR is visible. We observe a narrow plasmon resonance around 800 nm. An important difference with the cross sections for spherical particles is the fact that the longitudinal SPR of a spheroid is significantly narrower, and symmetric. This is because the longitudinal SPR is far away from the interband absorption, which occurs close to the plasmon resonance for spheres at 500 nm (see Fig. 1.1b). We will describe the importance of the SPR linewidth later in this section.

Electron microscopy studies have revealed that most nanorods are more like spherically-capped cylinders than ellipsoids. However, an analytical solution

![Figure 1.3: Calculated optical cross sections of a gold spheroid Absorption, scattering and extinction cross sections for a spheroid with a semi-major axis length of 45 nm and a semi-minor axis length of 15 nm. The spheroid was embedded in a medium with $\epsilon_m = 2.25$.](image)
for such shapes is not possible. Recently, Mulvaney and co-workers\textsuperscript{30} employed the direct-dipole approximation (DDA) to calculate the optical properties of spherically capped cylinders. By fitting the Gans-theory to the DDA spectra, they obtained approximate values for $L$ which can be used to obtain the optical cross sections of spherically capped cylinders in a limited range of sizes and aspect ratios. Although the fitted values of $L$ represent the longitudinal SPR wavelength more accurately, we will use the above described analytical approach because it reliably predicts the general trend of the optical properties, including the aspect ratio and polarization sensitivity.

The theory developed by Gans predicts that the SPR would split into two modes, the transverse and the longitudinal SPR, due to the independent polarizability along the respective particle axes. Because of the difficulty in preparing non-spherical particles, little experimental work to support Gans formulation existed until the 1950s. In the 1960s, Stookey \textit{et al}.\textsuperscript{31} stretched glasses containing small silver spheres, and they found that the small particles were elongated in the glass and exhibited red-shifted absorption spectra. More recently, it has become possible to prepare large amounts small gold rods in aqueous solution.\textsuperscript{18,26–28,32} By varying the chemical composition in the solution the aspect ratio can be tuned from 2 to as much as 50. In the vast majority of these studies Gans’ theory has successfully explained the qualitative optical properties of gold nanorods.

\textbf{The effect of aspect ratio}

The longitudinal SPR of a gold spheroid occurs when the denominator of Eq. 1.5 is zero. The denominator is a function of the eccentricity (or aspect ratio) of the particle, inducing a broad tunability of the longitudinal SPR wavelength by varying the aspect ratio of the particle. In Fig. 1.4a we show the absorption cross sections of three spheroids with a different aspect ratio. Changing the aspect ratio from 2 to 4.7 induces a shift of the longitudinal SPR wavelength from 620 nm to 920 nm. We also observe an overall increase in the absolute cross section, which is mainly caused by the increase in the volume of the particle.

In Fig. 1.4b we take a closer look at how the longitudinal SPR depends on the aspect ratio of the spheroid. For comparison we also show the peak of the absorption
cross section for spherical particles within the same range of radii, which was calculated using Eq. 1.4 and the full Mie solution. In the case of spheres we observe a very limited tunability of the absorption peak induced by the aforementioned retardation effects due to the large volume of the particles. In contrast, we find that the spheroids exhibit a large tuning range when the aspect ratio is varied. Such a large range of accessible wavelengths combined with the narrow Lorentzian linewidth of the longitudinal SPR makes gold nanorods the ideal building block for multiplexing applications.

The fact that gold nanorods exhibit a longitudinal SPR in the near-infrared has drawn interest from the biophysical community to use the particles in cells. Because cells strongly scatter light at wavelengths <700 nm, gold spheres are not easily detected inside tissue. However, the large near-infrared optical cross section of gold nanorods provides excellent contrast, and was quickly adopted for imaging and sensing in cells. Notably, in 2007 Yu et al. presented a multiplexed biosensor consisting of a mixture of gold nanorods with aspect ratios varying from 2 to 5. They coated different aspect ratios with a different ligand to achieve three independent sensing channels. Cells were probed directly using dark field microscopy, and
integration with a spectral imager allowed for simultaneous detection of up to three different biomolecules.

The tunability of the longitudinal SPR was exploited by Xu et al.\textsuperscript{40} in 2005 to achieve glass coatings for solar control on windows. They showed that such coatings can attenuate solar radiation effectively, even with a low density coating. This could be used as window coatings in buildings to prevent heating of the interior by the transmitted near-infrared solar radiation.

\textbf{The effect of orientation}

Another unique feature of nanorods is the dependence of their optical cross sections on the relative orientation of the particle with respect to the light polarization. In Fig. 1.5 we show the absorption cross section for a spheroid which is aligned parallel (dotted line) and perpendicular (solid line) to the polarization of the incoming light. When the spheroid is aligned parallel to the polarization of the incoming light, we observe the longitudinal absorption band. When the spheroid is aligned perpendicular to the light polarization we only observe the weak transverse resonance, which occurs at around 530 nm as it does for spherical particles. In Fig. 1.5b we show the calculated absolute value of the absorption cross section versus polarization angle. The angular absorption cross section follows a cosine dependence, as is expected for a perfect dipole.

This unique cosine dependence of the longitudinal SPR was used as an orientational sensor by Sönnichsen et al.\textsuperscript{41} in 2005. They illuminated a solution of gold nanorods with randomly polarized white light using a darkfield microscope. The scattered light was collected and passed through a birefringent calcite crystal, which splits two orthogonal polarization directions for each gold rod into two spots. The intensity of these spots was simultaneously monitored on a charge coupled device, allowing for continuous monitoring of the orientational diffusion of a large number of nanorods. Because the SPR does not blink or bleach, these nanorod based orientational probes could rapidly replace commonly used anisotropic fluorescent probes such as dyes.

In 2005 Pérez Juste et al. demonstrated the use of aligned gold nanorods in a polymer film as a polarized light filter.\textsuperscript{18} Randomly oriented gold nanorods were
firstly doped into a polymer film, and upon stretching of the heated film, the embedded gold nanorods aligned along the stretching direction. When viewed in transmission, the stretched film displayed a green color when the light polarization was aligned to the nanorod’s long axis. When the polarization was rotated by 90 degrees only a faint red color, caused by the transverse SPR, was visible. They found good agreement between the measured polarization dependent optical response and the theory developed by Gans (see section 1.1.2).

The longitudinal plasmon linewidth

The linewidth of the SPR is of crucial importance for multiplexing applications. Multiplexing in the wavelength domain can only be achieved when the separation between the different color channels is more than the linewidth of the SPR. As such, a narrow plasmon linewidth allows for the implementation of multiple channels over a small wavelength range.

The finite plasmon linewidth is a result of the dephasing of the electron cloud oscillation. The initial oscillating electron population can decay through radiative and non-radiative channels.\textsuperscript{42} Non-radiative decay occurs through electron-hole
excitations, which are either intraband excitations within the conduction band or interband excitations due to transitions between other bands (for example the $d$ bands of noble metals). The interband excitations require a minimum photon energy of about 2 eV and can be clearly observed in the imaginary part of the dielectric function of gold around $\sim$ 400 nm (see Fig. 1.1). Radiative decay on the other hand occurs through transformation of plasmons into photons (i.e. scattering). Because the scattering cross section scales as $R^6$, radiative decay mainly occurs in large particles. Also other minor effects can contribute to the dephasing of the electron oscillation, most notably electron-surface scattering in very small particles ($< 10$ nm) and interaction of electrons with surface adsorbates (e.g. interface damping).44

In Fig. 1.6 we show the calculated linewidth $\hbar \Omega_{SPR}$ of the scattering cross sections of spheroids and spheres, as a function of the surface plasmon resonance energy (for spheroids the linewidth of the longitudinal SPR is plotted). The linewidth of the sphere SPR was calculated using the full Mie-theory (Eq. 1.1), where we used the dielectric function as measured by Johnson and Christy (see Fig. 1.1). For rods we employed the electrostatic approximation for spheroidal particles (Eq. 1.8), and we corrected the dielectric function of Johnson and Christy to account for
radiation damping. The calculation for spheres and spheroids gives approximately the same linewidth for a (near) spherical particle (\( \sim 300 \) meV). We observe a drastic increase in linewidth for a sphere SPR with the same resonance energy as that of a spheroid. The linewidth increases to as much as 1 eV. This significant increase in linewidth is caused by radiation damping. Because the wavelength tunability of the sphere SPR is limited, a large increase in radius is required to shift the SPR to longer wavelengths. This is accompanied by a large increase in the radiative decay rate, which scales as \( R^6 \).

However, when the length of the spheroids is increased we observe a narrowing of the linewidth, to about 100 meV. This reduced linewidth is caused by the fact that the longitudinal SPR energy for aspect ratios \( > 2 \) moves away from the interband transition in gold, thus reducing the interband damping. In contrast to the sphere SPR, radiative decay does not play a significant role in the linewidth of the longitudinal SPR due to the small volume of the spheroids. The linewidth of the longitudinal SPR stays more or less constant up to an aspect ratio of 6 (the limit of our calculation).

The lack of sensitive spectroscopy techniques has not allowed for the experimental verification of the homogeneous linewidth of SPRs until 10 years ago. Since then, the homogeneous linewidth of different shaped metal particles has been measured using single particle white light spectroscopy techniques. In 2002, Sönichsen et al. compared the linewidth of single gold spheres to gold nanorods, and found strong evidence that radiation damping determines the linewidth in larger gold spheres. In 2005, Berciaud et al. experimentally confirmed the intrinsic size effects caused by electron surface scattering in very small gold spheres. In 2006, Novo et al. measured homogeneous linewidths of individual gold nanorods in a large range of sizes. They found evidence of electron surface scattering in small nanorods and radiation damping in large nanorods. Their measured linewidths were in good agreement with predictions from the theory by Gans (see section 1.1.2).
1.1.3 Photoluminescence

Photoluminescence from noble metals was first reported in 1969 by Mooradian.\textsuperscript{47} Single-photon luminescence from metals has been described as a three-step process: (1) excitation of electrons from the $d$- to the $sp$-band to generate electron-hole pairs, (2) scattering of electrons and holes on the picosecond timescale with partial energy transfer to the phonon lattice, and (3) electron-hole recombination resulting in photon emission.\textsuperscript{47} Two-photon luminescence (TPL) of gold surfaces was characterized by Boyd \textit{et al}.\textsuperscript{48} and is considered to be produced by a similar mechanism as single-photon luminescence, but the relatively weak TPL signal can be amplified by several orders of magnitude when produced from roughened metal substrates. This amplification was attributed to the presence of a large electric field enhancement in the near-field of the nanoscale grains on the metal surface. This observation was confirmed in studies on nanoparticle dimers, where the strongest TPL signal originated from the gap region where this electric field enhancement is large.\textsuperscript{49,50}

Among other nanoparticle shapes, gold nanorods exhibit a particular large local field enhancement due to a reduced interband damping.\textsuperscript{42} For this reason gold nanorods possess a bright TPL, and recent studies have shown the TPL brightness is strongly correlated with their SPR.\textsuperscript{51–54} In 2005, Bouhelier \textit{et al}. reported on the TPL emission spectrum of large single gold nanorods.\textsuperscript{52} They showed that the TPL emission spectrum strongly resembles the scattering spectrum of the individual rod, and exhibits a clear peak around the longitudinal SPR. Moreover, Wang \textit{et al}. have shown that the excitation polarization dependent TPL signal of a gold nanorod exhibits a $\cos^4$ dependence,\textsuperscript{53} which suggests a longitudinal SPR mediated two-photon excitation process. They also reported that the TPL action cross section of individual rods is almost 60 times higher than that of a single Rhodamine 6G molecule. The main advantage for imaging applications however is the fact the TPL from metals does not blink or bleach, and thus overcomes one of the major hurdles faced with dyes and semiconductor nanoparticles.

For this reason TPL from gold nanorods has been widely employed for imaging in biological tissue, including cancer cells.\textsuperscript{14,55,56} Because TPL is most efficiently
excited with a short pulsed laser, the excitation of TPL gives rise to simultaneous generation of thermal energy due to non-radiative decay of the particle plasmon. This notion was exploited in 2008 by Li et al., who achieved simultaneous TPL imaging and photothermal cancer treatment using gold nanorods.

Because of the strong correlation with the wavelength and polarization properties of the longitudinal SPR, TPL provides a suitable detection mechanism for multiplexing applications. Further, as we will show in Chapter 5 of this thesis, the wavelength and polarization selectivity of the TPL is significantly higher than that of the (linear) absorption or scattering, thereby providing an extremely selective readout mechanism in which cross-talk can be prevented altogether.

1.2 Excitation dynamics

In this section we will describe the excitation dynamics of small metal particles, in which the photon energy of a short laser pulse is converted to thermal energy and acoustic vibrations. The excitation dynamics of metals on picosecond timescales has been widely studied using ultrafast spectroscopic techniques. Since the 1980s, a wide range of pump-probe studies on metal films and ensembles of metal nanoparticles of various shapes and compositions have revealed a complex interaction between the excitation light source (most often a femtosecond laser

![Figure 1.7: Schematic of excitation and relaxation dynamics](image-url)  
Illustration of the excitation and relaxation dynamics in metals. The pump pulse firstly interacts with the conduction electrons, which transfer their kinetic energy to the lattice through electron-phonon coupling. The particle heats up and transfers its thermal energy to the environment. At the same time acoustic vibrations can be launched in the nanoparticle by the sudden thermal expansion of the electron cloud and the lattice.
pulse) and the conduction electrons and lattice of the particle. A generic series of events has been found in these studies, which largely applies to both metal films and nanoparticles. A sketch of the steps involved is shown in Fig. 1.7. Firstly the excitation pulse sets the free electron cloud into oscillation, and increases the electron temperature. The kinetic energy of the electrons is then conveyed to the lattice through electron-phonon coupling. When the excitation light pulse has sufficient energy, the lattice temperature increases to above the threshold melting temperature and the particle melts. The rapid rise in electron and lattice temperature is also responsible for the launching of a lattice oscillation in nanoparticles, most commonly referred to as acoustic vibrations. As a last step in the process the nanoparticle reaches thermal equilibrium with its environment through heat dissipation.

In this Section we will briefly describe the above mentioned processes. In Section 1.2.1 we discuss the ultrafast excitation of the electron cloud and its subsequent equilibration with the lattice phonons. In Section 1.2.2 we discuss the launching of acoustic vibrations, where we shall focus on the vibrational modes in gold nanorods. The interaction of the hot nanoparticle with its environment through heat dissipation will be described in Section 1.2.3, followed by a discussion on the melting of the particle in Section 1.2.4.

1.2.1 Electron dynamics and electron-phonon coupling

When a short laser pulse strikes a metal nanoparticle, surface plasmons are excited. These surface plasmons almost instantaneously lose their coherence through electron-electron collisions.\textsuperscript{60} Within 100 fs the initially non-thermal distribution of electrons has equilibrated and creates a hot electron gas. Through electron-phonon coupling these hot electrons transfer their energy to the phonon system, thus heating the lattice of the particle.\textsuperscript{59–63} Depending on the excitation pulse energy, the electrons and phonons are in thermal equilibrium within 5-15 ps. The hot particle will then transfer its heat to the environment, which we will discuss in more detail in section 1.2.3.

The coupling between the electrons and the lattice can be described by the two-temperature model.\textsuperscript{64,65} We start with a hot electron gas with temperature $T_e$. The
thermalization with the lattice with an initial temperature of $T_l(0) = T_0$ can then be described by two coupled differential equations:\textsuperscript{64,65}

$$\frac{\delta T_e}{\delta t} = -\frac{g(T_e - T_l)}{C_e(T_e)}, \quad (1.10)$$

$$\frac{\delta T_l}{\delta t} = \frac{g(T_e - T_l)}{C_l} - \frac{(T_l - T_0)}{\tau_s}, \quad (1.11)$$

where $g$ is the electron-phonon coupling constant ($g \approx 3 \times 10^{16}$ Wm\(^{-3}\)K\(^{-1}\) for gold\textsuperscript{66}), $\tau_s$ is the characteristic time for heat dissipation to the environment, and $C_e(T_e) = \gamma T_e$ is the temperature dependent heat capacity of the electron gas ($\gamma = 66$ Jm\(^{-3}\)K\(^{-2}\) for gold\textsuperscript{66}). The temperature dependence of $C_e(T_e)$ means that the timescale for electron-phonon coupling depends on the initial electronic temperature, and leads to a non-exponential decay of the electron temperature.

Calculated changes in the electronic and lattice temperatures for gold with an initial $T_e$ of 3000 K are shown in Fig. 1.8. The characteristic time for heat decay to the environment was set to 300 ps. The calculation shows that the energy deposited into the electrons is transferred to the lattice within about 10 ps. Due to the large difference in heat capacity between the electrons and the phonons, the lattice only heats up to a maximum temperature of $\sim 400$ K. We will present a detailed study of the electron phonon coupling in single gold nanorods in Chapter 3.
1.2.2 Acoustic vibrations

The heating of the lattice described in the previous paragraph causes the particles to undergo rapid thermal expansion. For particles larger than a few nanometers the timescale for heating is faster than the lattice expansion, which causes the lattice expansion to overshoot.\textsuperscript{66–68} Additionally, the surge in electron pressure induces a force on the lattice, which can contribute to the lattice expansion.\textsuperscript{67,69} These effects launch a vibration in the particle, which were optically observed for the first time in the late 90’s in both metallic\textsuperscript{70,71} and semiconductor nanoparticles.\textsuperscript{72} Because the timescale of the vibration is related to the sound velocity in the material of the particle, these vibrations are often referred to as acoustic vibrations.

For spherical particles only the radially symmetric breathing mode is excited.\textsuperscript{66,73} The frequency of these modes can be accurately described using a model developed by Lamb in 1882.\textsuperscript{74} However, in the case of gold nanorods the symmetry is broken and also the extension modes can be excited.\textsuperscript{67,69} The breathing and extension vibrational frequencies of a freestanding cylinder were calculated by Hu et al.\textsuperscript{75} The vibrational frequencies of a free standing, elastically isotropic, long cylinder can be expressed in terms of the elastic moduli and dimensions of the nanorod as\textsuperscript{75}

\begin{equation}
\nu_{ext} = \frac{m}{2L} \sqrt{\frac{E}{\rho}},
\end{equation}

where the positive integer \( m \) indicates the extensional mode number (note that Hu et al. considered only extensional modes in which the rod’s center is fixed), and

\begin{equation}
\nu_{br} = \frac{\tau_n}{2\pi a} c_l,
\end{equation}

where the positive integer \( n \) indicates the radial mode number, \( a \) and \( L \) are the radius and length of the nanorod, \( c_l \) is the longitudinal speed of sound in gold \((c_l = \sqrt{(K + 4/3\mu)/\rho})\), where \( K \) and \( \mu \) are the bulk and shear moduli, and \( \rho \) is the density), and \( E \) is the Young’s modulus. The parameter \( \tau_n \) is the \( n \)-th root of \( \tau J_0(\tau) = \frac{1 - 2\sigma}{1 - \sigma} J_1(\tau) \), where \( \sigma \) is Poisson’s ratio. For the fundamental breathing mode, \( \tau_1 = 2.28 \).\textsuperscript{67} The ratio between the breathing and extensional frequency is directly related to the aspect ratio \( AR \) of the particle through \( \nu_{br}/\nu_{ext} = 2.32 \times AR \).
Chapter 1. Introduction

Figure 1.9: Vibrational mode shapes of a long cylinder

Diagram showing the fundamental extensional and breathing modes of a long cylindrical rod. The breathing mode exhibits a pure radial expansion and contraction without a change in length. In the extensional mode, an increase in length is accompanied by a decrease in width.

(for simplicity the properties of the nanorod are assumed to be the same as those of polycrystalline bulk gold: \( E = 78.5 \) GPa, \( \nu = 0.42 \), \( \rho = 19300 \) kg m\(^{-3}\), and \( c_l = 3300 \) m s\(^{-1}\)).

In Fig. 1.9 we show a sketch of the breathing and extension mode shapes according to this model. The breathing mode mainly modulates the width of the particle whilst maintaining the length. This causes a periodic change in aspect ratio, and the change in volume induces a modulation of the plasma frequency of the gold through a change in the electron density. In the case of the extensional mode the volume is maintained while the aspect ratio of the particle is modulated by the acoustic vibration. The described effects induce a periodic change in energy, linewidth and intensity of the surface plasmon resonance. These acoustic vibrations can be detected by conventional pump-probe spectroscopy, in which the pump pulse excites the acoustic vibration. A time-delayed probe pulse (tuned to the plasmon absorption band) can then be used to detect the change in transmission caused by the periodic change in particle shape and volume.

In recent pump-probe studies it was shown that the period of the acoustic vibration is strongly correlated to the size, shape, stiffness, and crystallinity of the particles. The frequency can therefore be used to characterize geometrical, mechanical and crystallographic properties of metal nanoparticles which are not easily accessible with other far field optical microscopy techniques. Recent developments in single particle spectroscopy have allowed the investigation of acoustic vibrations in single gold and silver nanoparticles. Investigating
single metal nanoparticles removes inhomogeneous broadening and allows for the measurement of homogeneous damping times of the acoustic vibrations. These homogeneous damping times can reveal valuable information about the coupling of the nanoparticle to its local environment. In Chapter 3 we will present an in-depth study of the acoustic vibrations in single gold nanorods.

1.2.3 Dissipation to the environment

The next aspect we will discuss is the dissipation of heat to the environment of the hot nanoparticle. For this purpose let us consider a small particle in an infinite, homogeneous medium. As we described in section 1.2.1 the lattice of a particle excited by an ultrafast laser pulse will reach its maximum temperature on a timescale of several picoseconds. The heat dissipation to the environment occurs on the scale of hundreds of picoseconds. This large discrepancy in timescales allows us to assume that the particle at \( t=0 \) has a constant temperature \( T_{1i} \). This initial temperature can be considered constant within the particle’s volume due to the high thermal conductivity of metals. At \( t=0 \) the particle starts the cooling process by conducting heat to its surroundings. For simplicity we shall assume the particle to be spherical and we will neglect any interface effects. The radial temperature profiles for the conduction heat transfer problem of having a sphere of radius \( R \) initially at temperature \( T_{1i} \) inside an infinite medium with initial temperature \( T_{2i} \) is then given by the conduction equations:

\[
\frac{\delta T_1}{\delta t} = \alpha_1 \frac{\delta^2}{\delta r^2} [rT_1(r,t)], \quad \text{and} \\
\frac{\delta T_2}{\delta t} = \alpha_2 \frac{\delta^2}{\delta r^2} [rT_2(r,t)],
\]

(1.14)  
(1.15)

where \( \alpha = k/(\rho c_p) \) is the thermal diffusivity of the respective material (with \( k \) the thermal conductivity, \( \rho \) the density, and \( c_p \) the specific heat capacity, see Table 1.1 for typical values). The boundary conditions at the interface \( R \) are

\[
T_1 = T_2, \quad k_1 \frac{\delta T_1}{\delta r} = k_2 \frac{\delta T_2}{\delta r}.
\]

(1.16)
These equations can be solved either numerically or analytically to yield the time dependent temperature profile at any place inside or outside the sphere. To illustrate the effect of the environment on the cooling of a metal nanoparticle, we have calculated the temperature decay for an $R=20$ nm gold sphere immersed in different environments (see Fig. 1.10). The sphere was initially at $T_1=1000$ K in an environment initially at $T_2=293$ K. The temperature of the particle was evaluated at $r=2R/3$. The results are displayed in Fig. 1.10, where we observe a strongly non-exponential energy relaxation process. As expected, the cooling time of the particle strongly depends on the thermodynamic properties of the environment. The characteristic cooling time in silica and water are very similar and has a $1/e$ decay time of $\approx 100$ ps. In a polyvinyl alcohol (PVA) matrix however, the cooling time is significantly longer and approaches $\approx 500$ ps, which is caused by the low thermal conductivity of the PVA environment. As we will see in Chapter 4, these variations in cooling time in different matrices has profound effects on applications such as optical recording.

The cooling time of the sphere also strongly depends on the size of the particle. As was reported by Hu et al. the characteristic cooling time scales as $R^2$. They found that for very small particles the cooling time competes with the time scale for electron-phonon coupling, which indicates that a significant amount of energy is lost to the environment already before the electrons and the lattice are in thermal equilibrium. Wilson et al. used ultrafast spectroscopy to deduce the thermal interface conductance of the nanoparticle/fluid interface by comparing the cooling time of metal nanoparticles in a solvent. They measured the cooling times of gold, platinum, and gold-palladium nanoparticles and found that the measured interface conductance was in good agreement with theoretical predictions.
In 2005 Ge et al. demonstrated that the cooling time of gold spheres strongly depends on the surface chemistry. The addition of a cosolvent induced swelling of a polymer coating layer, and the change in the microstructure of the shell increased the effective thermal conductivity of the shell. The corresponding time scale for the cooling of the nanoparticle decreased from 200 ps to approximately 100 ps, thus demonstrating that the cooling time can be controlled in-situ by a polymer coating layer. Similarly, in 2008 Schmidt et al. reported on the thermal interface conductance of the gold nanorod/surfactant/water interface. They varied the concentration of the surfactant commonly used for the preparation of gold nanorods, and found that the thermal interface conductance increases by a factor of 3-4 when the surfactant is (partially) removed from the solution. This was attributed to the formation of a surfactant bilayer on the surface of the nanorod for high surfactant concentrations, which strongly inhibits the transport of thermal energy from the nanorod to the aqueous environment. A similar conclusion was reached by Horiguchi et al. in 2008, who performed femtosecond laser illumination studies on aqueous gold nanorods. They found a pronounced effect of the surface capping on the reshaping behavior of the gold nanorods, which was attributed to the thermal conductance of the surface capping which determines the rate at which the particles cool.

Figure 1.10: Cooling of a sphere in different environments Time dependent cooling of an $R=20$ nm gold sphere immersed in different environments. The particle was initially at $T_{1i}=1000$ K in an environment initially at $T_{2i}=293$ K. The parameters used for the calculation can be found in Table 1.1.
1.2.4 Melting

Much research has been devoted to the melting and reshaping of nanoparticles, where both fundamental and applied aspects have drawn significant attention. Fundamentally the melting of small nanoparticles (both metal and semiconductor) is interesting because they form a natural transition between atoms and the bulk material. Their melting behavior therefore differs from both the molecular and the bulk material. For very small particles this has profound implications on their melting behavior due to the large fraction of surface atoms. Indeed, a significant reduction in both the melting temperature\textsuperscript{89–92} and the latent heat of fusion\textsuperscript{93,94} have been reported for small enough particles.

The melting of small particles starts at the surface. Such surface melting occurs in a continuous manner over a broad temperature range, and involves the formation of a thin liquid layer at temperatures well below the melting point.\textsuperscript{89–95} This melting point reduction occurs due to the surface tension difference between the liquid and solid phases,\textsuperscript{89–92} and for particles < 5 nm the melting temperature is inversely proportional to the radius of the particle.\textsuperscript{90,92,94} In 1992, Goldstein \textit{et al.} found that the melting temperature of $R=1.2$ nm CdSe nanoclusters is as much as 1000 K below the bulk melting point.\textsuperscript{91}

In contrast to surface melting, the homogeneous melting of the solid core occurs abruptly at the critical melting temperature.\textsuperscript{94,95} ($T_{\text{melt}} \sim 1300$ K for bulk gold\textsuperscript{85}). The core melting involves a sudden disordering of the lattice structure, which was recently studied by ultrafast electron\textsuperscript{96–100} and x-ray diffraction.\textsuperscript{101} The metal is heated with a femtosecond optical pulse, and the subsequent structural changes are monitored in the diffraction patterns. In contrast to all-optical pump-probe methods, these techniques provide direct information about the atomic structure of the material. Probing the structure can reveal when and to what degree the material melts by monitoring the long range order of the lattice. Using this technique Ruan \textit{et al.} studied the melting of small gold particles.\textsuperscript{99} They observed significant structural changes within the first 100 ps after excitation, which were attributed to reversible surface melting and full melting of the optically excited nanoparticles. Plech \textit{et al.} used ultrafast x-ray diffraction to monitor the lattice expansion and thermal decay.
in gold nanoparticles.\textsuperscript{101} At high temperatures they observed a loss of long-range lattice order, which was attributed to pre-melting of the particles. At the bulk melting point complete melting was observed within 100 ps after excitation.

The acoustic vibrations described in section 1.2.2 were also used as a probe for phase transitions. The stiffness of a material depends on its temperature, and thus the vibrational spectrum can be used to study heating and melting in nanoparticles. In 2003 Hartland \textit{et al.} reported an intensity dependent breathing mode period,\textsuperscript{102} which was attributed to softening of the elastic properties due to laser-induced heating. However, due to absorption saturation they did not observe any abrupt changes owing to the melting transition of the particles. In 2007 Plech \textit{et al.} performed a similar experiment, but they heated the nanoparticles continuously with a resistive heater.\textsuperscript{103} They found a sudden change in the phase and damping time of the breathing mode when the 60 nm particles were heated above 104 °C, which was attributed to the onset of surface melting below the bulk melting point.

In 2006, Petrova \textit{et al.} studied the melting behavior of gold nanorods by monitoring the extensional mode vibration excited with femtosecond laser pulses.\textsuperscript{104} They found no abrupt changes in the phase or period of the vibration mode up to lattice temperatures of \textasciitilde 1230 K, indicating that the particles maintained their integrity. They compared these observations to continuous heating of the nanorods in an oven. Under continuous heating, they observed a shift of the longitudinal SPR at temperatures of \textasciitilde 40% of the melting point of the bulk metal, which was attributed to surface melting. This large difference between laser-induced heating and continuous heating was attributed to thermal diffusion to the environment of the rod: in the laser experiments the rods do not stay hot for long enough after excitation for significant structural changes to occur. Similarly, when nanosecond laser pulses are used, the photothermal heating process already competes with the dissipation of heat to the environment, which occurs on a similar timescale as the pulse width (see section 1.10). Energy that could contribute to the reshaping process is now lost to the environment, which significantly decreases the efficiency of the reshaping process. This was confirmed in 1999 by Link \textit{et al.}, who found that reshaping of gold nanorods with nanosecond laser pulses requires a higher threshold pulse energy than in the case of femtosecond laser pulses.\textsuperscript{105}
1.2.5 Applications of photothermal energy conversion

The conversion of photon energy to thermal energy we discussed in the previous sections is particularly efficient in metal nanoparticles because of the low radiative decay rate of electron-hole pairs. The photothermal energy conversion efficiency then mainly depends on the absorption cross section of the respective particle geometry. Gold nanospheres in the size range commonly employed (∼40 nm) exhibit an absorption cross-section 5 orders of magnitude higher than conventional absorbing dyes. However, as we discussed in section 1.1.1, the poor tunability of the plasmon wavelength in nanospheres (roughly from 520 to 580 nm) limits their use in many photonics and (in vivo) biological applications. Silica-gold nanoshells were found to have optical cross-sections much higher than nanospheres. Additionally, their optical resonances lie in the near-infrared region, where scattering by tissue is reduced. The SPR wavelength in nanoshells can be tuned from the visible to the near-infrared by changing the thickness of the gold shell, which makes them useful probes for many applications.

Gold nanorods however show optical cross-sections comparable to nanoshells, but at much smaller volumes. As we described in section 1.1.2 their longitudinal SPR can tuned across the near-infrared region by simply changing the aspect ratio of the particle. Because of their large cross sections at a reduced size, gold nanorods have been widely employed as photothermal energy converters in both physical and biological applications.

The photothermal properties of near-infrared absorbing gold nanorods have been most notably used in photo activated treatment of antibiotic resistant bacteria, infectious parasites, and cancer cells. In such treatment a femtosecond laser pulse heats the nanoparticles which are selectively attached to malignant cells, allowing for the treatment of infected tissue while keeping the surrounding healthy tissue intact. Upon excitation with a short pulsed laser source, the nanoparticles heat up and dissipate their thermal energy into the environment. The targeted cells are then destroyed by irreversible damage to the cell membrane. Traditionally such treatment was conducted with dyes, but the high absorption cross section and photothermal energy conversion efficiency of gold nanorods has reduced the
required laser power to below the medical safety level,\textsuperscript{14} enabling the technique to be implemented clinically. In a different medical application, hollow nanoparticles have been employed for targeted drug delivery.\textsuperscript{109–111} The hollow nanoparticles act as a delivery capsule for the drugs. Through surface modification, the capsules can be targeted to specific cell types. Upon arrival, an intense laser pulse heats and melts the capsule, thus delivering the drugs to the targeted tissue.

In photonics, the photothermal properties of metal nanoparticles have also led to the development of a multitude of active nanostructures and materials.\textsuperscript{112–114} In these materials, the photothermal properties of metal nanoparticles were used to efficiently heat a thermo-responsive material. This allowed for the controlled shrinking and swelling of the respective material. In particular, this technique was used to deactivate the fluorescence of quantum dots bound to the surface of gold nanoparticles by thermo-responsive peptides.\textsuperscript{114} Upon irradiation, the peptide chain length increased, and the fluorescence efficiency of the coupled quantum dots could be modulated through distance-dependent fluorescence modification by the near-field enhancement around the metallic nanoparticles. This technique provides a new means to manipulate optical properties such as fluorescence, without the need to disassemble the material.

Recently, photothermal heating has enabled the far field optical detection of very small single gold nanoparticles in a strongly scattering background.\textsuperscript{115, 116} In this case the nanoparticles were heated with a continuous wave light source, and the temperature change of a small nanoparticle and its environment was detected by differential interference contrast microscopy. Because the (non-absorbing) scatterers in the background do not heat up significantly compared to the gold particles, it was possible to detect the gold particles even in a strongly scattering background. Combined with high frequency modulation, nanoparticles as small as 2.5 nm in diameter could be detected.

1.3 Photothermal optical recording

A particularly interesting application exploiting the photothermal properties of metal nanoparticles is optical recording and patterning. Many groups have
devoted research into photothermal optical recording using metal nanoparticles, and generally we can classify the employed recording mechanisms by considering the induced temperature rise in the nanoparticles. In Fig. 1.11 we sketch the possible photothermal recording mechanisms according to this classification. When low excitation powers are employed the nanoparticles will heat up and distribute thermal energy to their environment, thus acting as heat sensitizers. With an intermediate excitation level, the nanoparticles heat up to above their melting temperature, and recording is accomplished by melting or reshaping the excited particles. With even higher excitation powers the temperature increases to above the boiling point and optical recording is achieved through fragmentation. In the next sections we will describe these recording mechanisms in more detail.

1.3.1 Nanoparticles as photothermal sensitizers

When the excitation laser induces temperatures in the nanorod well below their melting temperature ($T_{\text{melt}} \sim 1300$ K in the case of bulk gold\textsuperscript{85}), the nanorods can act as nanoscale heat generators to sensitize optical recording. The generated heat can be used to sensitize another thermal recording mechanism, such as phase change recording in traditional CDs and DVDs. In a phase change recording media the

**Figure 1.11:** Photothermal optical recording mechanisms Optical recording mechanisms classified according to the average particle temperature reached during recording.
recording of data bits is governed by a transition in the recording material from the amorphous to a crystalline phase. A short pulse of a focused, high-intensity laser beam locally heats the phase-change material above its melting temperature. Rapid cooling of the alloy quenches the liquid-like state into a disordered, amorphous phase. A pronounced optical reflectivity change is obtained because the atomic arrangement differs considerably between the two states. It was shown by Chon et al. that the recording in phase change materials such as Ge$_4$Sb$_1$Te$_5$ (more commonly referred to as GST) can be significantly improved by deposition of gold nanorods on the surface of the phase change material. For this purpose they tuned the longitudinal SPR of gold nanorods to the recording laser wavelength (658 nm). They achieved more than double the reflectivity change, and observed a significantly faster rate of phase change when nanorods were present on the surface.

Optical recording by micro explosion and void generation in a solid dielectric material such as glass or polymer has been widely employed to fabricate waveguide structures, photonic crystals, and microfluidic channels. Recently this technique has also been applied to optical data recording. This technique comprises the non-linear absorption of a tightly focused femtosecond laser pulse, which causes bond breaking, decomposition and evaporation of the matrix material. This in turn causes a micro explosion due to an immense increase in both temperature and pressure gradient. Recently, gold nanoparticles and in particular gold nanorods have been integrated in this technique. The ability to dope any transparent material with strongly absorbing nanoparticles significantly increases the number of materials which can be employed for optical recording in transparent materials. Most importantly, the pulse energy required for fabrication is lowered from $>10$ nJ to less than 0.5 nJ, thus eliminating the need for a regenerative amplifier for fabrication.

In void generation the gold nanoparticles again act as passive sensitizers by aiding the photothermal decomposition and evaporation of the matrix material. Over the course of the millions of pulses absorbed during the exposure, the embedded gold nanorods mediate the buildup of heat in the focal volume. When the average temperature in the focal volume reaches the polymer decomposition temperature,
large amounts of gas are released, thus creating a pressure gradient and subsequently
a void. Choi et al. demonstrated that a single nanorod per focal volume is
sufficient to reduce the required energy for void generation by almost one order
of magnitude. Using gold nanorod assisted void generation they demonstrated
three-dimensional optical recording in a polyvinyl alcohol matrix material.

1.3.2 Fragmentation

In a more radical recording mechanism, photothermal fragmentation occurs
when the temperature in the nanoparticles is elevated to above the boiling point
($T_{\text{boil}} \sim 2600$ K in the case of bulk gold). Fragmentation of metal particles
can occur through near-field ablation, vaporization, or through Coulomb
explosion caused by electron ejection induced by thermionic or multiphoton
ionization processes. Fragmentation using short laser pulses has been widely
used to control the size and shape distribution in a colloidal solution of metal
particles. In these schemes a femtosecond pulse laser or super continuum
light source is employed after the synthesis to narrow down the initially broad
range of sizes through fragmentation of the colloidal nanoparticles.

In 2001 Koda et al. developed a recording medium exploiting laser induced
fragmentation of gold nanoparticles. Gold nanoparticles were fabricated in-situ by
a photo reduction method in a sol-gel matrix. Upon irradiation with 532 nm laser
light, which corresponds to the transverse surface plasmon resonance absorption
of the gold particles, the absorption spectrum of the film showed a blue shift.
Transmission electron microscope images supported that the change in absorption
spectrum was due to a size reduction of the embedded particles due to evaporation
of gold atoms on the surface. The energy threshold for the recording was 300 mJ
$\text{cm}^{-2}$, which agreed well with the calculated fluence required for vaporization of
gold. Using this method they created a nanoparticle based recording material and
recorded holograms in the film.
Chapter 1. Introduction

1.3.3 Photothermal reshaping

When the initial particle shape is non-spherical, the particles will reshape to the energetically more favored spherical geometry when the particle temperature exceeds the melting temperature. Consequently, gold nanorods can be efficiently reshaped due to their large absorption cross sections and high energy geometry. Link et al.\textsuperscript{130} and Chang et al.\textsuperscript{27} have studied laser induced reshaping of gold nanorods using UV-VIS spectroscopy. They found that laser irradiation depletes the population of nanorods which exhibit a non-zero absorption cross section at the laser illumination wavelength. This causes a bleach in the extinction profile around the laser wavelength and a pronounced color change can be observed. Because the longitudinal SPR of gold nanorods is very sensitive to the particle geometry, reshaping of gold nanorods results in large spectral changes which can be detected with straightforward spectroscopic techniques.

Mulvaney et al. reported on the application of photothermal reshaping of metal nanorods to optical patterning.\textsuperscript{18,131} They prepared polymer films embedded with metal nanorods, and aligned the nanorods by stretching the film.\textsuperscript{132} A pronounced color change was observed when the film was irradiated with a nanosecond laser pulse. Electron microscope studies confirmed that the nanorods reshaped to the energetically lower spherical geometry, which induced a bleach in the longitudinal plasmon extinction profile. Because the nanorods were aligned in the film, the contrast of the pattern depended on the polarization of the white light used for imaging, i.e. a maximum contrast was obtained when the polarization was parallel to the long particle axes.

This polarization dependent contrast was used in a slightly different way by Niidome et al.\textsuperscript{17} They employed a polymer film embedded with gold nanorods, but in this case the gold nanorods were randomly oriented. They illuminated the film with linearly polarized laser light. They observed that the majority of the reshaped rods were initially aligned to the laser light polarization, indicating that orientation selective reshaping is possible. They demonstrated that this technique can be used to induce dichroism in a gold nanorod doped matrix.
Figure 1.12: Wavelength multiplexing using gold nanorods. Illustration of wavelength multiplexing in gold nanorods. The narrow longitudinal plasmon absorption band of the nanorods is employed to selectively excite and reshape only one population of rods. The other population of shorter aspect ratio rods remains unaffected and can be used to record another piece of information. Figure adapted with permission from Ref. [133].

The large area patterning performed by Mulvaney et al.\textsuperscript{18,131} and Niidome et al.\textsuperscript{17} provide the background required to develop a more versatile optical recording medium based on photothermal reshaping of gold nanorods. The first experiments on such a recording medium were conducted in 2006 by Chon \textit{et al.}\textsuperscript{133} They demonstrated that wavelength multiplexing is possible in a gold nanorod doped silica sol-gel film. The sol-gel film was doped with two distinct distributions of aspect ratios (longitudinal SPR centered around 720 nm and 920 nm respectively) which could be independently reshaped by employing the proper laser wavelength (see Fig. 1.12). They demonstrated that only gold nanorods that possess a longitudinal SPR on resonance with the laser light undergo reshaping, thus leaving the other nanorods available to record another piece of information in the same focal volume. These experiments indicated that the unique optical properties of the longitudinal SPR of gold nanorods could provide the ultimate building block to achieve multiplexed optical recording.
1.4 Multiplexed optical recording

Multiplexing is a very powerful method to efficiently increase the storage capacity of a medium by orders of magnitude. The number of recording states in binary recording scales as $2^n$, where $n$ is the number of individually addressable recording channels. When several channels can be multiplexed into the same recording volume it is possible to significantly increase the storage capacity without reducing the bit-size or increasing the sample thickness to support more recording layers. In the next section we will discuss the current state of the art in multidimensional optical recording, and we will illustrate how gold nanorods can play an important role in multiplexed recording.

We will start by describing the current state of the art in three-dimensional recording in Section 1.4.1, where we focus on bit-by-bit storage technologies because of their compatibility with current drive technology. In Section 1.4.2 we discuss polarization multiplexing, where different polarization states of the recording laser light are employed for recording. Multiplexing in wavelength space will be addressed in Section 1.4.3.

1.4.1 Three-dimensional recording

Instead of recording on the surface of a medium as is done in phase-change recording, three-dimensional recording uses the whole volume of a recording medium to store information. The most efficient way to achieve three-dimensional recording is to employ a two-photon excitation recording mechanism. Two-photon excitation involves the simultaneous absorption of two photons of identical or different frequencies in order to excite a molecule from one state (usually the ground state) to a higher energy electronic state. The energy difference between the involved lower and upper states of the molecule is equal to the sum of the energies of the two photons. The excitation strength depends on the square of the intensity, and the optical sectioning property of two-photon excitation\textsuperscript{134} limits the excitation volume to the focal plane (unlike single photon excitation, where the out of focus laser light also induces excitation). Three-dimensional recording has been extensively studied
and was demonstrated in photochromic and photorefractive materials, as well as photopolymers and transparent materials.

Three-dimensional recording in photochromic materials was proposed in 1989 by Rentzepis et al.¹³⁵ A photochromic material is characterized by its ability to alternate between two different isomers having different absorption spectra, in response to irradiation by light of the appropriate wavelength.¹³⁶ Several photochromic molecules have been employed for recording, such as spirobenzopyran,¹³⁵ diarylethene,¹³⁷–¹³⁹ and azo-dyes.¹⁴⁰–¹⁴³ Non-destructive readout can be achieved through differential interference contrast microscopy, where a small change in refractive index of the photochromic isomers in the near-infrared is detected.¹⁴⁴ Alternatively, this change in refractive index can be detected by reflection confocal microscopy.¹³⁷

In 1995 Kawata et al. reported rewritable multi-layer optical recording in a photorefractive material.¹⁴⁵ In the photorefractive effect, the photo-excited electrons are re-trapped in vacant donor sites after movement in the conduction band. The movement of the excited electrons results in a non-uniform distribution of charges. The charge distribution produces an electric field and modulates the refractive index by the Pockels effect. Photorefractive materials allow rewriting of data by uniform illumination, which excites the electrons in the donor level which then recombine with vacant donor sites uniformly. The photorefractive effect can be induced using single-photon¹⁴⁵ and two-photon¹⁴⁶,¹⁴⁷ excitation schemes. The resulting refractive index change in the irradiated region can be detected using reflection confocal microscopy or differential interference contrast microscopy.

In 1991 Strickler et al. reported three-dimensional storage in a transparent photopolymer.¹⁴⁸ Data was recorded by creating submicrometer volume elements of increased refractive index by two-photon excitation of a photoinitiator, which induces photopolymerization. In 1999 Cumpston et al. devised a more efficient photoinitiator allowing recording of information using low laser pulse energy.¹⁴⁹ The information stored using these methods could be read out using either differential interference contrast microscopy or single-photon induced fluorescence readout.¹⁴⁹ In 1996, Glezer et al.¹⁵⁰ reported three-dimensional storage in a transparent material.
where bits were recorded in multiple layers by tightly focusing a picosecond laser pulse. This induces a microexplosion and creates a structurally altered region with a high contrast in index of refraction. By employing a two-photon excitation process they were able to create voids as small as 200 nm in diameter.

1.4.2 Polarization multiplexing

Polarization multiplexing makes use of polarization state of the recording laser light to record multiple, individually addressable bits in the same focal volume. To achieve polarization multiplexing one requires a compound which exhibits a polarization dependent optical response. Photochromic dyes (see Section 1.4.1) are such a compound and have been widely employed for polarization encoding.

Polarization encoding is achieved through optically induced birefringence in photochromic dyes.\textsuperscript{140,141} The induced birefringence is based on the two possibilities for the \textit{cis-trans} photoisomerization.\textsuperscript{140–142} Initially the azo dye of the \textit{trans} state absorbs the light whose polarization direction is parallel to the dipole moment of the azo dye, and then it changes to the \textit{cis} isomer. The \textit{cis} isomer also absorbs the light and photo-isomerizes again, generating one of the two possible \textit{trans} states: one is a state which is the same state as before illumination, and the other is an inversion process generating a \textit{trans} state whose axis is rotated $90^\circ$ from the initial state. This process continues until the whole population of \textit{trans} state molecules with a dipole parallel to the laser light polarization has depleted. The increase in the number of azo dye molecules whose axis is perpendicular to the direction of the illuminated polarization generates an optically anisotropic refractive index distribution. Polarization multiplexing can now be achieved by repeating this process for different laser light polarizations. Recording at two polarizations that are perpendicular to each other is not possible because they will deplete each others population of azo dye molecules, thus erasing the recorded data.

Using this mechanism Alasfar \textit{et al.} demonstrated three-state polarization encoding\textsuperscript{142} using angles of 0, 60, and 120 degrees. Two state polarization encoding was also achieved in photochromic bacteriorhodopsin doped polymer films,\textsuperscript{151} where
polarization angles of 0 and 45 degrees were used for recording. In 2007 Li et al. demonstrated three-dimensional polarization multiplexed recording by employing two-photon induced isomerization in azo-dye doped polymer.\textsuperscript{143} They showed rewritable two-state polarization encoding in three layers spaced by approximately 30 $\mu$m.\textsuperscript{143}

1.4.3 Wavelength multiplexing

Another dimension of the recording laser light which has been employed for multiplexing is the wavelength or frequency of the laser light. A widely studied phenomenon that can be employed for wavelength multiplexing is persistent spectral hole burning.\textsuperscript{152} Persistent spectral hole burning involves the selective bleaching of impurity centers or dye molecules by laser irradiation, thus creating a “hole” in the spectral emission profile. The linewidth of the emission of this impurity center has to be narrow to allow spectral hole burning at multiple frequencies in the inhomogeneously broadened emission profile. For this reason very low temperatures (i.e. liquid helium temperatures) are required to counter thermal broadening of the emission profile of a single impurity center. By varying the laser irradiation wavelength multiple “holes” can be burned in the emission profile, allowing the storage of data at different wavelengths in the same focal volume. Persistent spectral hole burning was even detected in a single impurity molecule, suggesting that optical recording on a single molecule level could be possible.\textsuperscript{153} The major problem with the application of spectral hole burning to optical recording is that recording and readout has to be done at liquid helium temperatures.

In a similar technique employing selective bleaching of photochromic dyes, Irie et al.\textsuperscript{139} employed multiple dyes with a large frequency separation between their respective emission spectra. The large frequency separation between the dye molecules allows for recording and readout at room temperature because thermal broadening is not an issue. They demonstrated wavelength multiplexing by selectively bleaching three photochromic dyes embedded in a polymer matrix.\textsuperscript{139} Upon UV irradiation, each derivative changed to their closed-ring isomers having a different color. Upon irradiation with visible light of the appropriate wavelength, each closed-ring isomer was selectively bleached, and three-bits eight-states recording
was demonstrated. The eight states could be read out non-destructively by using infrared light (≈ 5 μm) of appropriate wavelengths. The long readout wavelength limits the resolution achievable with this technique though. Furthermore, the data is erased when exposed to room light.

In 2004 Kumacheva et al.\textsuperscript{154,155} demonstrated wavelength multiplexing by selective bleaching of normal dye molecules. These dye molecules were stable under ambient light and data could be read out at visible wavelengths. They employed core-shell particles comprised of different dyes in the core and in the shell to produce a multidye nanostructured material with a periodic structure. Physical separation of the dyes prevented energy transfer between the dyes. Patterns were recorded by photobleaching at 488 nm and 633 nm, and were read out by detecting the single photon fluorescence using the same laser wavelengths.

As we have outlined above, wavelength and polarization multiplexing have been successfully implemented in individual recording media. However, spatial, wavelength, and polarization multiplexing have never been implemented into a single recording material, simply because there is no material available that can provide orthogonality in all recording dimensions. Recently, plasmonic gold nanorods have attracted much attention due to their tunable longitudinal plasmon resonance wavelength, polarization dependent optical properties, large optical cross section, and chemical stability. Most importantly, metal nanoparticles are photostable and do not blink or bleach, in contrast to the dyes and photochromic materials employed in the current multiplexing technologies. This ambient stability combined with the unique spectral and polarization dependent properties makes this material uniquely suitable for application in multidimensional optical recording and patterning.

\section*{1.5 This thesis}

The aim of this thesis is to investigate the photothermal properties of gold nanorods, and to employ their efficient photothermal reshaping toward optical recording. More specifically we aim to develop a recording medium which supports five-dimensional encoding by exploiting the three spatial dimensions, the wavelength

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and the polarization of the laser light all at once. For this purpose the recording medium has to exhibit several critical optical properties.

1. The material has to be sensitive to the polarization of the recording laser.

2. The material has to be sensitive to the wavelength of the recording laser.

3. Both the recording and the readout mechanism have to possess optical sectioning to allow for three-dimensional encoding.

4. The readout mechanism has to be nondestructive.

We show that the unique optical and photothermal properties of gold nanorods fulfill all these criteria. We explore a versatile method in which the wavelength and polarization of light are simultaneously exploited for multiplexed recording, leading to the first reported medium to provide five-dimensional optical storage. Unlike prior investigations into multiplexed recording the thermal and optical stability of gold nanoparticles will provide a recording medium which is extremely stable in ambient conditions and allows for non-destructive readout through surface plasmon mediated two-photon luminescence. Toward this aim, several key steps are required which will be discussed in this thesis:

- **Chapter 2:** In order to develop a nanoparticle based recording medium, we require a synthesis protocol which allows for rapid synthesis of large quantities of gold nanorods. To this end we developed a seed-less, wet-chemical synthesis protocol which is viable at high temperatures. We will characterize the final reaction products and establish the activation energy for the formation of gold nanorods.

- **Chapter 3:** Understanding the thermal and mechanical properties of gold nanorods is crucial for many of their future uses, including optical recording. In contrast to a polycrystalline bulk metal, nanoparticles often are single crystals, or are composed of very few single crystals. Their large surface to volume ratio introduces size effects which can significantly alter their thermal and elastic properties. In this Chapter we investigate the excitation dynamics and the
Chapter 1. Introduction

elastic moduli of single gold nanorods using ultrafast spectroscopy. We find that, unlike previously reported, the mechanical properties agree well with the reported values for bulk gold.

- **Chapter 4:** The interaction of the embedded nanoparticles with the matrix material is crucial in achieving a reliable storage medium. As we showed in section 1.10 the thermal properties of the environment can significantly affect the cooling dynamics and thus the reshaping behavior of the embedded gold nanorods. In the first part of this Chapter we investigate the effect of the repetition rate of the patterning laser on the thermal stability of the polymer matrix. The thermal stability is explained in terms of heat accumulation in the focal volume due to the low conductivity of the polymer matrix. Secondly, we take a closer look at the femtosecond laser pulse induced reshaping of single gold nanorods inside a polymer matrix. We measure the optical properties of single gold nanorods before and after reshaping, and we identify the melting energy of a single gold nanorod.

- **Chapter 5:** Here we demonstrate true five-dimensional optical recording in a polymer matrix doped with gold nanorods. We outline a fabrication procedure to produce multi layered samples comprising active layers embedded with gold nanorods and transparent spacer layers with a well defined refractive index and thickness. Both the recording and reading mechanism exploit the unique properties of the longitudinal surface plasmon resonance. By combining photothermal reshaping and plasmon mediated two-photon luminescence we demonstrate for the first time cross-talk free five-dimensional optical recording.

- **Chapter 6:** We will conclude this thesis and provide suggestions for future research toward a continuation of the work presented here.
Gold nanorod synthesis

In order to study gold nanorods and use them in any application a reliable
and large scale synthesis method is required. Various methods have been
established for the synthesis of metal nanorods. A templated method was
first introduced by Martin and co-workers. This method is based on the
electrochemical deposition of gold within the pores of nanoporous polycarbonate or
aluminium template membranes. The gold nanorods were contained in the template
to form a nanocomposite in which the aspect ratio of the nanorods can be controlled
by varying the size of the pores. Van der Zande and co-workers later showed
that a colloidal solution of nanorods could be obtained by redissolving the template.

The fundamental limitation of the template method is the low yield, which
makes it commercially unattractive. Larger scale synthesis can be accomplished
by the widely used wet chemical synthesis method. Wet chemical synthesis includes
electrochemical, seeded and seed-less growth methods. These methods
are conducted in aqueous surfactant media which direct the nanoparticle growth by
providing anisotropic micellar templates. Here we will restrict ourselves to the
seeded and seed-less growth method because they are more attractive methods for
large scale synthesis. We will show that the seed-less growth method provides a
commercially attractive route toward rapid large scale synthesis of gold nanorods.
Chapter 2. Gold nanorod synthesis

2.1 Seeded growth

The seeded growth method was developed by the groups of Murphy et al.\textsuperscript{32,160,162} and El-Sayed et al.\textsuperscript{28,163,164} It was derived from the seeded method used to grow large gold nanospheres.\textsuperscript{18,165} The seed particles were 3.5 diameter in diameter prepared by borohydrate reduction of gold salt. By controlling the growth conditions in aqueous surfactant media it was possible to synthesize gold nanorods with tunable aspect ratio using this method. The surfactant generally used to synthesize gold nanorods is cetyltrimethylammonium bromide (CTAB), which forms rod shaped micelles above the second critical micelle concentration ($\sim 20$ mM).\textsuperscript{166} The surfactant forms a bilayer on the surface of the nanorod and directs the nanorod growth by preferentially binding to the crystal faces along the length of the particle.\textsuperscript{164,166}

It was found that addition of AgNO\textsubscript{3} influences not only the yield and aspect ratio control of the gold nanorods but also the mechanism for gold nanorod formation and correspondingly its crystal structure.\textsuperscript{18,29,167} Subsequent reports have found that gold nanorods prepared in the presence of AgNO\textsubscript{3} are single crystalline with a [100] growth direction.\textsuperscript{29,77,167} When no AgNO\textsubscript{3} is present the rods grow in the [110] direction and exhibit a multiply twinned crystal structure.\textsuperscript{168} Liu et al. recently reported that silver acts as a surface structure specific surfactant.\textsuperscript{29} They concluded that silver deposits selectively on the more open $\{110\}$ facet of the gold rod, slowing down the growth of this facet which results in better control over the final aspect ratio.

The seeded growth method in the presence of AgNO\textsubscript{3} yields gold nanorods with a controllable aspect ratio up to $\sim 4.5$ (longitudinal SPR $\sim 825$ nm). The group of El-Sayed et al.\textsuperscript{28} later modified this method to allow synthesis of higher aspect ratios. Instead of using a single surfactant they proposed a binary surfactant mixture composed of CTAB and Benzyldimethylhexadecylammonium Chloride (BDAC), yielding nanorods with an aspect ratio up to $\sim 10$ (longitudinal SPR $\sim 1300$ nm).

2.1.1 Experimental

Ascorbic acid, AgNO\textsubscript{3}, and NaBH\textsubscript{4} were purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB) was purchased from Alfa-Aesar. Benzyl-
dimethylhexadecylammonium Chloride (BDAC) was purchased from TCI America. HAuCl₄ · H₂O was purchased from ProSciTech. All chemicals were used without further purification. Distilled water was used for the preparation.

**Preparation of CTAB capped gold seeds:** Gold seeds were prepared in a 10 mL aqueous solution containing 0.1 M CTAB and 0.25 mM HAuCl₄. To this solution was added 0.6 mL of a 16 mM ice-cold, aqueous NaBH₄ solution under vigorous stirring. Stirring was continued for 30 seconds after which the seed solution was put aside for 1 hour to ensure removal of excess NaBH₄.

**Preparation of gold nanorods with aspect ratios <4.5:** Gold nanorods were prepared using a AgNO₃ assisted, seed-mediated growth method, based on the system developed by El-Sayed *et al.* To the growth solution ([CTAB] = 0.1 M, [HAuCl₄] = 0.5 mM) we added a certain amount of AgNO₃ depending on the required aspect ratio, and 0.75 mM freshly prepared ascorbic acid. Initiation of the nanorod growth was achieved by adding 6 µL per mL of the growth solution while stirring.

**Preparation of gold nanorods with aspect ratios >4.5:** These particles were prepared using a binary surfactant mixture. To the growth solution ([CTAB] = 0.025 M, [BDAC] = 0.075 M, [HAuCl₄] = 0.5 mM) we added different amounts of AgNO₃ and 0.75 mM freshly prepared ascorbic acid. Initiation of the nanorod growth was achieved by adding 6 µL per mL of the seed solution while stirring.

**Preparation of large volume gold nanorods:** Larger volume nanorods were prepared using a low seed concentration. To the growth solution ([CTAB] = 0.1 M, [HAuCl₄] = 0.5 mM) we added different amounts of AgNO₃ and 0.6 mM freshly prepared ascorbic acid. Initiation of the nanorod growth was achieved by adding 1 µL per mL of the seed solution while stirring.

### 2.1.2 Results

In Fig. 2.1a we show the extinction spectrum of gold nanorods prepared with a single surfactant (CTAB) and [AgNO₃] = 0.12 mM. From the temporal evolution of the longitudinal plasmon wavelength we find that the rods form within approximately 20 minutes and do not change appreciably after 40 minutes. We can tune the final aspect ratio of the rods by changing the concentration of metal ions, see Fig. 2.1b. The longitudinal plasmon wavelength achievable with this method
Chapter 2. Gold nanorod synthesis

Figure 2.1: Seeded growth of short nanorods (a) Extinction spectrum and transmission electron micrograph of gold nanorods prepared with a single surfactant and $[\text{AgNO}_3] = 0.12 \text{ mM}$. The inset shows the temporal evolution of the longitudinal plasmon wavelength during the synthesis. The scalebar indicates 50 nm. (b) Longitudinal plasmon wavelength 24 hours after preparation for different gold and AgNO$_3$ concentrations. The crosses indicate the acquired data points.

is $\sim 650 - 830$ nm, with typically $< 1 \%$ by-products. The typical width of the particles is 8-12 nm, with a length that varies between 35-60 nm, respectively.

In fig. 2.2a we show the extinction spectrum of gold nanorods prepared in a binary surfactant mixture with a AgNO$_3$ concentration of 0.04 mM. The final aspect ratio can be controlled by varying the AgNO$_3$ concentration, as is indicated in Fig. 2.2b. With this preparation method we could achieve a surface plasmon wavelength

Figure 2.2: Seeded growth of long nanorods (a) Extinction spectrum and transmission electron micrograph of gold nanorods prepared with a binary surfactant mixture and 0.04 mM of AgNO$_3$. The scalebar indicates 50 nm. (b) Longitudinal plasmon wavelength 24 hours after preparation for different AgNO$_3$ concentrations.
ranging from $\sim 800 \text{ nm} - 1 \mu\text{m}$. Synthesis with a binary surfactant mixture typically results in the formation of 5-10% of by-products. The growth rate of the rods grown in a binary surfactant mixture is significantly slower than in a single surfactant solution, and we found that no appreciable growth takes place after $\approx 12$ hours. The typical width of the particles synthesized in a binary surfactant system is 4-10 nm, with a length that varies between 45-70 nm, respectively.

The combination of the above single and binary surfactant systems allows us to synthesize gold nanorods with a longitudinal SPR ranging from 650 nm - 1000 nm. We will employ these synthesis methods in Chapter 5 to achieve optical recording in multiple wavelength channels spread across the wavelength range of a femtosecond pulse laser system tunable between 700–1000 nm.

As described in Section 1.1.2 the absorption cross section of individual nanorods

![Graphs and images demonstrating the seeded growth of large nanorods.](image)

**Figure 2.3: Seeded growth of large nanorods** Extinction spectra in water, transmission electron micrographs, and particle statistics of large gold nanorods prepared with the seeded growth method using a AgNO$_3$ concentration of 0.047 mM (a),(b) and 0.12 mM (c),(d). Scale bars 50 nm.
Chapter 2. Gold nanorod synthesis

scales with the volume $V$, and the scattering cross section even scales as $V^2$. Therefore, when one aims to spectroscopically study individual particles, it is desirable to employ rods with a larger volume to ensure a sufficient signal-to-noise ratio with acceptable acquisition times. For this purpose we synthesized larger gold nanorods by employing a low seed concentration. When fewer nucleation centers are available to form gold nanorods, the amount of gold monomer per nucleation center is larger which results in larger volume particles. The results of this procedure are shown in Fig. 2.3, where we show extinction spectra, transmission electron microscope (TEM) images, and statistics for these particles. Instead of using 6 µL seed solution per mL of growth solution as we did for the nanorods in Fig. 2.1 and 2.2, we now employed only 1 µL seed solution per mL of growth solution. As can be seen from the statistics in Fig. 2.3, these rods have a width of $\sim 20-30$ nm, which is significantly larger than the $\approx 8-12$ nm we achieved in Fig. 2.1 and 2.2. By varying the silver concentration we synthesized rods with an average aspect ratio of $2.1 \pm 0.4$ ([AgNO$_3$] = 0.047 mM) and $3.2 \pm 0.4$ ([AgNO$_3$] = 0.12 mM), with a longitudinal SPR at 620 nm and 730 nm, respectively.

2.2 Seedless growth

Most reported methods, including the seeded method described above, involve synthesis at temperatures close to room temperature. However, to increase the growth rate and make the protocol more suitable for commercial applications one may want to increase the solution temperature during the reaction. Jana et al.$^{160}$ recently concluded for their system that CTAB micelles break down at high temperature and indicated that nanorods only form at temperatures below 50 °C. Similarly, Pérez-Juste et al.$^{169}$ reported that reaction temperatures close to room temperature are more favorable for higher nanorod yields.

To perform a systematic study of the effect of temperature on rod growth the initial conditions for each reaction should be identical. This is hard to accomplish when using a seeded growth method because the properties of seed solutions are not easily reproducible and are also temporally labile. To avoid these effects a seedless...
growth method comparable to the method previously reported by Jana et al.\textsuperscript{160} was adopted for this study. A seedless growth method involves \textit{in situ} formation of seeds, in contrast to seeded growth where seeds are formed \textit{ex situ}.

### 2.2.1 Experimental

Gold nanorods were prepared using a seedless growth method in aqueous solution, comparable to the method previously reported by Jana et al.\textsuperscript{160} A 5 mL aqueous solution containing CTAB (0.1 M) and HAuCl\textsubscript{4} (0.5 mM) was prepared. Various concentrations of AgNO\textsubscript{3} were added to this solution, depending on the experiment. Au(III) was reduced to Au(I) by adding 30 µL of an ascorbic acid solution (0.1 M) under vigorous stirring. Nucleation and growth were initiated 5 seconds after adding the ascorbic acid by quickly injecting 2 µL of a NaBH\textsubscript{4} solution (1.6 mM) under vigorous stirring.

Temperature control during the nucleation and growth of the particles was achieved by immersing the sample vials in a heat bath. Depending on the experiment a water bath (Memmert WB-10) or an oil bath was used. The vials were immersed in the heat bath throughout the experiment (including injection of ascorbic acid and NaBH\textsubscript{4}) to ensure a constant temperature during the growth. Temperatures listed in the next section are temperatures of the growth solution just before the injection of ascorbic acid. Vials were kept in the heat bath until the end of the reaction and at room temperature thereafter.

### 2.2.2 Results

The inclusion of AgNO\textsubscript{3} in the growth solution was found to be essential for nanorod synthesis at elevated temperatures. In Fig. 2.4 we show photographs of the final reaction products we obtained by varying temperature and AgNO\textsubscript{3} concentration. A solution with a blue color indicates formation of short nanorods with a longitudinal SPR around 700 nm (aspect ratio $\sim$3). A brownish color is from nanorods absorbing in the near infrared (aspect ratio 4-5). A red color indicates the presence of spheres in the solution. As can be seen from Fig. 2.4 choosing an optimum AgNO\textsubscript{3} concentration becomes crucial at higher temperatures. High AgNO\textsubscript{3} concentration resulted in a low rod yield and mainly spheres at temperatures
Figure 2.4: Reaction products seed-less growth method Photographs of reaction products obtained as a function of AgNO$_3$ concentration and temperature. The optimum AgNO$_3$ concentration is highlighted. A blue color indicates formation of short nanorods of aspect ratio $\sim$3, a brownish color is caused by nanorods with aspect ratio $\sim$4-5 whereas a red color indicates the presence of spheres in the solution.

above 50 °C. A low AgNO$_3$ concentration resulted in short rods throughout the temperature range. The optimum AgNO$_3$ concentration (0.12 mM, highlighted in Fig. 2.4) resulted in formation of nanorods throughout the temperature range. We used the optimum AgNO$_3$ concentration in the remainder of the experiments described here.

In Fig. 2.5 we show the extinction spectra of the solutions synthesized at different temperatures ([AgNO$_3$] = 0.12 mM). It is apparent from the extinction spectra that the amount of spherical by-products with extinction $<520$ nm is relatively low for all temperatures. As can be seen from Fig. 2.5 the longitudinal surface plasmon resonance shifts to shorter wavelengths as the synthesis temperature increases, indicating formation of particles with a lower aspect ratio. Within our temperature range we obtained nanorods with an longitudinal SPR peak ranging from 825 nm at
Figure 2.5: Temperature dependent final extinction spectra Extinction spectra of gold nanorod solutions ([AgNO\(_3\)] = 0.12 mM) synthesized at different temperatures, the spectra are offset for clarity. The normalization factors are: 1.27 for 25 °C, 1.93 for 30 °C, 1.70 for 35 °C, 1.92 for 40 °C, 1.20 for 50 °C, 1.57 for 60 °C, 1.77 for 80 °C, and 1.95 for 97 °C.

25 °C to 670 nm at 97 °C, yielding nanorods which are useful in for example optical recording\(^{133}\) and imaging applications.\(^{13,53}\)

In Fig. 2.6 we show TEM images of samples synthesized at (a) 25 °C, (b) 50 °C, and (c) 97 °C. The scalebar indicates 50 nm. As can be observed from the TEM images the width of the particles is constant throughout the temperature range. The length however decreases at higher temperatures, resulting in lower aspect ratio particles. This is confirmed by the shift of the longitudinal SPR to shorter wavelengths at high temperatures as is shown in Fig. 2.5. In Fig. 2.6d we show the evolution of the length and width of the nanorods as a function of temperature. The values for length and width are obtained by analyzing approximately 150 particles for each individual temperature.
Figure 2.6: Dimensions of the reaction products of seed-less growth TEM images obtained from gold nanorods synthesized at (a) 25 °C, (b) 50 °C, and (c) 97 °C. The scalebars indicate 50 nm. (d) Particle dimensions as obtained from TEM analysis. The error bars represent the error in the mean value of the distribution of the respective dimension.

The formation of lower aspect ratio particles at higher temperatures might be related to the number of nuclei forming upon injection of NaBH$_4$. When more are nuclei present at the start of the nanorod growth, less gold monomer is available per nuclei resulting in lower aspect ratio nanorods. Using the theory describing scattering off a small spheroid shaped particle$^{20}$ we calculated the extinction cross sections for the particles formed at room temperature and at 97 °C. Using the particle dimensions depicted in Fig. 2.6 we found that the ratio of extinction cross sections is $\sim 3$. If the number of particles in the final reaction product was equal, we expected to see a factor of 3 decrease in extinction between room temperature and 97 °C. We did not observe this significant extinction decrease, suggesting that the number of particles formed at elevated temperatures is higher than at room temperature. The nanorod yield we obtained was nearly 100 % at all temperatures. Generally we did not observe any by-products at temperatures below 40 °C. Less than 1 % of by-products was present at temperatures between 40 °C and 80 °C. The reaction at 97 °C resulted in approximately 5 % by-products.
To study the effect of temperature on the growth rate we recorded extinction spectra during the synthesis of the gold rods. In Fig. 2.7 we show typical extinction spectra recorded during synthesis of gold nanorods at a temperature of 97 °C. The time interval between each subsequent recorded extinction spectrum shown in Fig. 2.7 is 15 ms. Initially the longitudinal SPR red-shifts during the growth of the nanorod, indicating anisotropic growth in the longitudinal direction. During later stages of the reaction, we observed an increase in extinction without a significant shift in the longitudinal SPR peak wavelength. This may be because the anisotropic growth stalls and the particles grow relatively isotropically to their final volume. We observed similar growth behavior at all temperatures.

In Fig. 2.8 we show the evolution of the integrated area of the extinction spectrum versus time for nanorods synthesized at different temperatures. The obtained temporal evolution of the integrated extinction was fitted with a sigmoidal growth function, which we can use to obtain the growth rate during the synthesis. A sigmoidal growth function has an inflection point after which the growth rate decreases to asymptotically approach a finite value.

Fig. 2.8 shows three orders of magnitude increase in nanorod growth rate by increasing the temperature from 25 to 97 °C. At 97 °C we obtained the final reaction product within less than 2 seconds, whereas for synthesis at room temperature
we observed a reaction time of about 1500 seconds. From the rate at which the extinction area increases we obtain the rate at which gold atoms adsorb on the particle. Because the extinction area is proportional to particle volume, the rate of gold atom adsorption on the nanorod surface is proportional to the rate at which the extinction area increases. From TEM images we obtained an average final particle volume of 1600 nm$^2$, which is roughly 6×10$^4$ gold atoms. Considering the volume of a gold atom and the maximum rate at which the extinction area increases, we obtain a maximum deposition rate of 6.25×10$^4$ gold atoms per nanorod per second at 97 °C.

From the time resolved rod growth at different temperatures we obtain the activation energy for the reaction. For this purpose we use the rate equation, given by

$$k = A e^{-E_a/RT}, \quad (2.1)$$

where $k$ is the reaction rate, $A$ is a constant, $E_a$ is the activation energy, $R$ is Avogadro’s number, and $T$ is the temperature at which the reaction takes place (in K). We obtain the activation energy from the slope $-E_a/R$ in the relation between $\ln(k)$ and $1/T$. In our experiments we relate the rate constant to the 1/e time $\tau_{1/e}$ of the time resolved extinction area (Fig. 2.8). We obtained $\tau_{1/e}$ from the sigmoidal

![Figure 2.8: Time dependent extinction](image)

**Figure 2.8: Time dependent extinction** Evolution of the integrated area of the extinction spectrum versus time for nanorods synthesized at different temperatures. The extinction area was integrated between 450 and 1100 nm and normalized to the peak value. The solid lines are sigmoidal fits to the experimental data points.
fits to the time traces as shown in Fig. 2.8. In Fig. 2.9 we show the relation between \( \ln(1/\tau_c) \) and \( 1/T \). The solid line is a linear fit to the experimental data points. The slope we obtained from the linear fit is \(-11 \pm 1 \times 10^3\) K. Multiplication with \( R \) leads to a measured activation energy \( E_a = 90 \pm 10\) kJ mol\(^{-1}\).

We have demonstrated that growth in the systems is not diffusion limited, but activated. The presence of an activation barrier in gold nanorod synthesis has been suggested previously by Pérez-Juste et al.\(^{169}\) who estimated the growth rate to be many orders of magnitude lower than the diffusion limited rate. The activation energy represents a significant energy barrier for the deposition of Au atoms onto the surface of the nascent particles, and is expected to depend on the affinity of CTAB with the gold different gold facets. It is important to stress that the activation energy is an average value for all faces of the growing nanorods. Considering the convergence of particle length and widths with increasing temperature (Fig. 2.6), the fast growing end facets have a lower \( E_a \) than the side faces. The average value of \( 90 \pm 10\) kJ mol\(^{-1}\) obtained here should prove useful as a reference point for modeling the anisotropic growth of Au nanorods.

High temperature gold nanorod synthesis opens the door to resolving two important issues which have not been addressed in literature so far. Firstly, something which severely limits the potential commercial application of gold
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nanorods is the restriction to slow batch synthesis. Ultrafast high temperature synthesis presents a better system for rapid production of gold nanorods for potential commercial applications. In our experiments high temperature synthesis resulted in formation of gold nanorods on a timescale of several seconds, which might allow for development of rapid flow based nanorod synthesis.

Secondly, the fact that gold nanorods form at high temperatures suggests that using a thermally activated reducing agent is possible. Thermal activation of reducing agents has been used in for example the polyol process,\textsuperscript{172,173} in which metal nanoparticles are synthesized in ethylene glycol at elevated temperatures. Most reports on gold nanorod synthesis so far utilize NaBH\textsubscript{4} to initiate the formation of gold nanorods.\textsuperscript{28,32} NaBH\textsubscript{4} reacts with water and has to be used immediately after preparation, which compromises reproducibility. Using a thermally activated reducing agent would avoid the use of the unstable NaBH\textsubscript{4} resulting in stock growth solutions which are stable at room temperature. We suggest that sodium citrate or glucose could serve as a thermally activated reducing agent for reduction of Au(I).

2.3 Conclusion

We have studied two methods to synthesize gold nanorods on a large scale. These methods allow us to synthesize gold nanorods in the spectral range from 630-1000 nm, which is the wavelength range required to achieve multiple wavelength channels within the wavelength range of a femtosecond pulsed laser (typically 700-1000 nm). The seeded growth method allows for more control over the aspect ratio and a greater range of aspect ratios is accessible by changing to a binary surfactant system. We have shown that seedless nanorod synthesis gives high yields of nanorods and can be used for high-speed synthesis at high temperatures, which makes this method more commercially attractive. We have performed a kinetics study of the seedless nanorod synthesis in which the reaction temperature was varied between 25 and 97 °C. We found that using the correct AgNO\textsubscript{3} concentration is crucial for the formation of rod shaped particles at high temperatures. Transmission electron microscopy (TEM) images of the final products demonstrate a decrease in rod length at high temperatures while the width stays constant. We observed an increase in
growth rate of three orders of magnitude when the temperature was raised from room temperature to 97 °C, presenting a more attractive method for large scale production of gold nanorods. Additionally, from the temperature dependence of the growth rate we obtain the average activation energy for the growth on all nanorod facets.
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Chapter 3

Excitation dynamics in single gold nanorods

Understanding the thermal and elastic properties of gold nanorods is crucial for many of their future uses, including optical recording. In contrast to a polycrystalline bulk metal, nanoparticles often are single crystals, or are composed of very few single crystals. Defects are rare or absent because they easily anneal at nearby surfaces. As size decreases, the surface-to-volume ratio increases, and surface effects (such as surface tension or melting) become significant. At small enough scales, the thermal and mechanical properties are expected to differ from those of bulk materials. Electronic confinement and atomic discreteness may also play a role.

The excitation dynamics in gold and silver nanoparticles has been studied extensively on ensembles using ultrafast spectroscopy and time-resolved x-ray scattering. It appears that the excitation dynamics depend in unique ways on the size, shape, crystal structure, and local environment of a nanoparticle. In ensemble measurements, however, differences from bulk properties are likely to be screened by the differences between the individual particles. Recent ultrafast spectroscopic measurements on single gold nanospheres and single silver nanocubes demonstrated how to remove this heterogeneity. They revealed stark differences in the local environment between individual particles. Here we study the excitation dynamics, and in particular the
acoustic vibrations and mechanical properties of single gold nanorods. Previous studies have reported on acoustic vibrations in a single nanoparticle, but they did not directly yield the mechanical properties. This can only be achieved when the precise morphology and dimensions of each individual particle are known, which requires electron microscopy and ultrafast spectroscopy of the same single nanoparticle.\cite{78}

Here, we measure the acoustic responses and electron micrographs of the same single gold nanorods, from which we derive their elastic constants. Contrary to previous reports\cite{76, 77} on ensembles of gold nanorods, we find the elastic moduli of single nanorods to agree well with bulk values, confirming theoretical estimates.\cite{183–185}

\section{3.1 Experimental}

\subsection{3.1.1 Sample preparation}

The gold nanorods used in this study were prepared by the silver assisted seed mediated growth method discussed in Section 2.1. The extinction spectrum in water, transmission electron micrographs, and particle statistics are displayed in Fig. 2.3c and d. The average length of the nanorods is $92 \pm 9$ nm, with an average width of $30 \pm 3$ nm (averaged over $\sim75$ particles). After preparation, the remaining solutes were diluted by four orders of magnitude through centrifugation. This dilution ensured a minimum of surfactant remaining on the surface of the rod without inducing any noticeable aggregation. After this, the bare nanorod solution was spin-coated on a clean fused silica glass coverslip. The coverslip was marked by femtosecond laser writing to help locate the same nanorods for spectroscopy and electron microscopy.

\subsection{3.1.2 White-light scattering}

Single particle white-light scattering microscopy\cite{46} was performed in a home built optical microscope (see Fig. 3.1). The reflected light from a fibre coupled high-power Xenon lamp was collected by the focusing objective (0.95 NA air spaced, coverslip corrected) and directed to an avalanche photodiode (APD, PerkinElmer). The spot was raster-scanned over the sample surface. To increase the visibility of the rods, the reflected light was bandpass-filtered ($638 \pm 45$ nm) before detection. The unfiltered scattering spectrum of each individual nanorod was dispersed by
a spectrograph (Acton Instruments, SpectraPro 500i) on a liquid nitrogen cooled
CCD-camera (Princeton Instruments, Spec-10).

If an incident field $E_i$ is focused onto the sample, it undergoes reflection at
the glass-air interface. The field that reaches the detector can be expressed as
$E_r = r E_i e^{-i\pi/2}$. The quantity $r$ takes into account the effective reflectivity of
the interface ($r = 0.04$ for the glass-air interface). The phase $\pi/2$ has been introduced to
account for the Gouy phase shift. For a nanoparticle with an effective radius $R \ll \lambda$
the scattered field at the detector is $E_s = s E_i$, where $s = |s(\lambda)| e^{i\phi(\lambda)}$ is proportional
to the polarizability $\alpha$ of the particle, i.e. $s = \eta \alpha(\lambda)$ where $\alpha$ is given by Eq. 1.5.
Here $\eta$ takes into account the detection efficiency. The measured intensity $I_m$
at the detector is a superposition of the reflected light off the interface and the light
scattered by the particle, and can be expressed as

$$I_m(\lambda) = |E_r + E_s|^2 = |E_i|^2 \left[ r^2 + |s(\lambda)|^2 - 2r |s(\lambda)| \sin \phi(\lambda) \right],$$  \hspace{1cm} (3.1)

where the first and second term indicate the reflection off the interface and the
pure scattering signal by the particle, and the last term indicates the interference
signal between the reflected and scattered fields. The pure scattering signal scales
as $R^6$ and is the dominant term for large ($R > 20$ nm) particles. The last term
however scales as $R^3$ and therefore does not drop as fast. This term results in an
inversion of the contrast in raster scans for decreasing particle size, and allows for
the detection of very small particles with a scattering cross section much smaller
than the absorption cross section.

\begin{figure}[ht]
\centering
\includegraphics[width=0.7\textwidth]{setup.png}
\caption{{\bf Sketch of the white-light setup} Schematic drawing of the
experimental setup used for white-light scattering spectroscopy on single gold
nanoparticles.}
\end{figure}
Chapter 3. Excitation dynamics in single gold nanorods

In the experiment, in order to correct for the spectral characteristics of the Xenon white-light source we normalize each measured spectrum to a reference spectrum $I_r(\lambda)=|E_r(\lambda)|^2$ which was recorded several microns away from the particle:

$$
\sigma(\lambda) = \frac{I_m(\lambda) - I_r(\lambda)}{I_r(\lambda)},
$$

(3.2)

where $\sigma(\lambda)$ is the parameter we plot in the remainder of this Chapter.

### 3.1.3 Pump-probe spectroscopy

The pump-probe spectroscopy was performed in the same setup as the white-light scattering spectroscopy to facilitate measurements on the same particle. A sketch of the optical setup used for the pump-probe spectroscopy measurements is displayed in Fig. 3.2. The ultrafast spectroscopy study was performed in transmission and probed the extinction by the particle. The laser light was focused onto the sample with a 0.95 NA objective lens (coverslip corrected), and was collected in transmission by a 0.9 NA condenser lens (no coverslip correction). The sample was mounted on a three-dimensional computer controlled translation stage. Acoustic oscillations of the nanoparticles were excited with the pulsed output ($\sim 300$ fs pump pulses) of a Ti: Sapphire laser ($\lambda_{pump} = 800$ nm), modulated by an acousto-optic modulator. The

![Figure 3.2: Sketch of the pump-probe setup](image-url)  
Schematic drawing of the experimental setup used for ultrafast spectroscopy on single gold nanoparticles.
Chapter 3. Excitation dynamics in single gold nanorods

Relative transmission change was probed with the frequency-doubled signal beam of an optical parametric oscillator (OPO), tunable between 520 and 700 nm. The transmitted light was collected by the condenser lens and detected by an APD coupled to a lock-in amplifier. For all particles, the probe wavelength was tuned to the longitudinal plasmon absorption band. The pump-probe delay time was scanned by a delay line. In all measurements, the pump and probe pulse energies at the back aperture of the objective were 2 pJ and $\sim 0.1$ pJ (average powers 160 $\mu$W and 8 $\mu$W), respectively. Except for polarization measurements, both the pump and the probe pulses were circularly polarized.

3.2 Imaging single nanorods

The sample surface was imaged by scanning electron microscopy (SEM), single-particle white-light scattering, and pump-probe spectroscopy at zero time delay (i.e. the pump and the probe pulse overlap in time). Fig. 3.3a shows an SEM

![Figure 3.3: Imaging single gold nanorods](image)

(a) Scanning electron micrograph showing three gold nanorods (bar length 1 $\mu$m). (b) White-light scattering scan showing isolated rods. The box encloses the area of (a) (bar length 1 $\mu$m). (c) Scattering spectrum of two individual gold nanorods in unpolarized white light. Solid lines are Lorentzian fits. Inset: polarized scattering versus angle, with dipolar cosine fits (solid lines).

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image of a small area on the sample, from which we identify single nanorods and extract their accurate dimensions.

Fig. 3.3b shows a white-light scattering raster scan of the same area, where diffraction-limited spots correlate well with the position of the single rods in the SEM image. Some nanorods appear dimmer because part of their scattering spectrum falls outside the filter band. We measured the white-light scattering spectra of more than 30 individual particles and found longitudinal plasmon energies distributed between $\hbar \Omega_{LSP} = 1.8 - 2 \text{ eV} \ (\lambda \sim 690 - 620 \text{ nm})$. The intrinsic line width is $\Gamma_{intr} = 112 \pm 15$ meV, in good agreement with earlier reports. These Lorentzian lines help us select individual nanorods, and optimize the probe wavelength for each rod. In all cases, the polarized scattered intensity followed the expected dipolar angle dependence.

### 3.3 Electron-phonon decay in single gold nanorods

When a short laser pulse strikes a metal nanoparticle, surface plasmons are excited. These surface plasmons almost instantaneously lose their coherence through electron-electron collisions. Within 100 fs the initially non-thermal distribution of electrons has equilibrated and creates a hot electron gas. Through electron-

![Figure 3.4](image-url)

**Figure 3.4:** Electron-phonon decay in a single gold nanorod (a) White light scattering spectrum of the gold nanorod. The pump and probe wavelengths used for the ultrafast spectroscopy are indicated in the figure. (b) Initial stages of the timetrace, showing the time dependent decay of the longitudinal SPR bleach due to electron-phonon scattering.
phonon coupling these hot electrons transfer their energy to the phonon system, thus heating the lattice of the particle.\textsuperscript{59–63} Depending on the excitation pulse energy, the electrons and phonons are in thermal equilibrium within a few picoseconds. The hot particle will then transfer its heat to the environment.

To illustrate the electron-phonon relaxation in a single gold nanorod we show the initial stages of a pump-probe trace in Fig. 3.4. For reference, the measured scattering spectrum of the same nanorod is shown in Fig. 3.4a. This particular nanorod was excited with circularly polarized pump pulses (\(\lambda = 800\) nm, pulse energy 2 pJ), whereas the wavelength of the probe laser pulses was tuned to the longitudinal SPR peak (\(\lambda = 650\) nm, pulse energy 20 fJ, circular polarization). A transient bleach is observed when the pump and probe laser pulses overlap (\(t=0\)). This bleach (which we will call the electronic response) is caused by a large broadening and shift of the surface plasmon resonance induced by the pump laser pulse. As the electrons transfer their energy to the lattice, the longitudinal SPR bleach decays quickly. The offset we observe for \(t>5\) ps is due to the elevated lattice temperature, which decays on a typical timescale of hundreds of picoseconds.

In Fig. 3.5a we show a raster scan of the same area as in Fig. 3.3b. However, this raster scan was obtained by imaging the surface of the sample with the pump and probe pulses, with the time delay set to \(t=0\) (so we detect the peak of the electronic response). We observe a large spread in the sign and amplitude of the electronic response. This is caused by the nature of the transient SPR, which involves a broadening and a shift of the longitudinal SPR,\textsuperscript{66} which is sketched in Fig. 3.5a. As we can see, the sign and amplitude of the electronic response strongly depends on the probe photon energy with respect to the longitudinal SPR energy. When probed on the blue side of the longitudinal SPR, we observe a transient bleach due to the broadening of the SPR, whereas probing on the red side results in a transient absorption due to the red shift of the SPR.

In Fig. 3.5b we show the amplitude of the electronic response as a function of probe photon energy. The curve is very well represented by the difference between two Lorentzian line shapes with a slightly different frequency, line width and intensity. Besides a small change in the intensity of the longitudinal SPR (\(\Delta I_{SP}\))
Figure 3.5: Probe photon energy dependence of the electronic response
(a) Pump-probe raster scan of the surface of the sample (same area as in Fig. 3.3a). The time delay between the pump and probe pulses was set to t=0, so as to detect the amplitude of the electronic response. Bar length 1 µm. The bottom sketch illustrates the red-shift and broadening of the surface plasmon due to the hot electrons (the effect is exaggerated). When probed on the red side, the relative transmission decreases, when probed on the blue side, the relative transmission increases. (b) Probe photon energy dependence of the amplitude of the electronic response. The lines represent the difference between two Lorentzian line shapes with a different frequency $\hbar\Omega_{LSP}$, line width $\Gamma$ and intensity $I$ (Lorentzian fitting parameters: $\hbar\Omega_{LSP,1}=1.91152$ eV, $\Gamma_1=133.059$ meV, $I_1=0.04004$, $\hbar\Omega_{LSP,2}=1.91128$ eV, $\Gamma_2=133.408$ meV, $I_2=0.040028$). The measured surface plasmon energy is indicated by the vertical line.

$= 0.03 \%$, we find that the plasmon bleach is dominated by a line broadening ($\Delta \hbar\Omega_{LSP}/\Delta \Gamma \sim 0.05$). This line broadening is due to an increase in the electron scattering rate of the hot electrons, which supplies additional decay channels for the plasmon oscillation.\(^{60}\)

As was noted in section 1.2.1 the effective rate constant for the decay of the electronic temperature $g/\gamma T_e$ decreases as the initial electronic temperature increases due to the temperature dependent electron heat capacity $C_e(T_e)$. This implies that longer decay times are expected for higher pump pulse energies. In Fig. 3.6 we show the dependence of the electron phonon decay on the pump pulse energy. We observe a clear increase in the decay time when the pump power is increased. We also find a relatively linear relation between the pump pulse energy and the amplitude of the electronic response, indicating that the particle is not undergoing any radical shape changes when we employ higher pump pulse energies. In Fig. 3.6b we show the
Figure 3.6: Pump pulse energy dependence of the electron-phonon decay
(a) Normalized electronic response as a function of pump pulse energy. The inset shows the amplitude of the electronic response versus pump pulse energy. (b) Electron-phonon decay time as a function of pump pulse energy. The decay time was obtained by fitting the curves in (a) with a single exponential.

extracted electron-phonon decay times, which were obtained by fitting the curves in Fig. 3.6a with a single exponential (in the low excitation regime we employed, the e-ph decay fitted well with a single exponential decay curve; however, for strong excitation a highly non-exponential decay is expected and the two-temperature model should be employed to fit the e-ph decay).

The electron-phonon coupling constant can be determined by fitting the electronic response with the two-temperature model. This approach requires the initial electron temperature as a parameter in the two-temperature model. However, there is always uncertainty in the initial temperature in the simulations. A more accurate approach is to extrapolate the measured electron phonon decay times displayed in Fig. 3.6b to zero pump pulse energy. In the two-temperature model (see section 1.2.1) the electron-phonon decay time is given by \( \tau = \gamma T_e/g \), where \( T_e \) is the initial electron temperature, \( g \) is the electron phonon coupling constant, and \( \gamma = \pi^2 k_B^2 \mathcal{N}_F / 3 \) with \( k_B \) Boltzmann's constant, and \( \mathcal{N}_F \) is the electronic density of states at the Fermi level.\(^{186}\) The appropriate value for gold is \( \gamma = 66 \text{ Jm}^{-3}\text{K}^{-2} \).\(^{186}\) In the limit of low excitation power (i.e. \( T=T_0 \)) the decay time reduces to \( \tau_0 = \gamma T_0/g \), with \( T_0 \) room temperature. When we linearly extrapolate the curve in Fig. 3.6b to zero pump pulse energy, we find a limiting electron-phonon decay time of \( \tau_0 = 550 \pm 50 \text{ fs} \).
This gives us a value of $3.5 \pm 0.3 \times 10^{16}$ Wm$^{-3}$K for the electron phonon coupling constant, which is in good agreement with previous measurements on ensembles of gold particles$^{187}$ and gold films.$^{186}$

### 3.4 Acoustic oscillations in single gold nanorods

The creation of a hot electron gas and the subsequent transfer of energy to the lattice phonons excites mechanical vibrations of the particle by two distinct mechanisms.$^{67,69}$ First, the sudden surge in electron temperature applies additional pressure on the particle surface. Second, as the electronic energy is transferred to the lattice, equilibrium inter-atomic distances increase because of anharmonicity. Electron-lattice relaxation being fast (1-3 ps) compared to acoustic oscillations (provided the particle is not too small), the particle is suddenly brought out of mechanical equilibrium, and coherent oscillations are launched. A rod’s (non-torsional) vibrational modes are labeled by two integers, $n$, the radial number, and $l$, the angular momentum number.$^{66,188}$ Spherical particles only show the radially symmetric breathing mode $(n,l) = (0,0)$. $^{66,68}$ As the spherical symmetry is broken in nanorods, they additionally display the fundamental extensional $(n,l) = (0,2)$ mode.

![Figure 3.7](image_url)

**Figure 3.7**: Single nanorod vibrational trace (a) Vibrational trace of a single gold rod. Inset: zoom on the highlighted part, fitted with Eq. 3.3. (b) Power spectral density of the trace in (a) after Fourier transform (inset: zoom on the high-frequency peak). (c) Polarization dependence of the optical response $\delta T_k(0)$ for the breathing (squares) and the extensional mode (circles), with cosine fits (solid lines).
In Fig 3.7a we show the vibrational trace of the bottom right rod in Fig. 3.3a obtained by pump-probe spectroscopy. The particle dimensions are $90 \times 29 \text{ nm}$ and $\hbar \Omega_{LSP} \sim 1.94 \text{ eV} \ (\sim 643 \text{ nm})$. For this particle, we tuned the probe laser frequency to $\hbar \omega = 1.86 \text{ eV} \ (670 \text{ nm})$. We observe a complex vibrational trace which exhibits two distinct vibrations with a long life time. This is confirmed by the power spectrum of the Fourier transform shown in Fig. 3.7b, where we find two distinct Lorentzian resonances. These two oscillations were observed for all the rods we investigated. Following Hu et al., we attribute the low frequency peak to the fundamental extensional mode, and the high frequency peak to the fundamental breathing mode.

The inset of Fig 3.7a shows the early part of the vibration trace fitted with a sum of damped oscillating terms:

$$\delta \tau(t) = A \exp(-t/\tau_{cool}) + \sum_{k=(\text{ext,br})} \delta \tau_k(0) \exp(-t/\tau_k) \cos(2\pi \nu_k t - \phi_k), \quad (3.3)$$

where $\delta \tau$ is the relative transmission change $\Delta \tau/\tau$. The initial electronic response was omitted. The first term represents the cooling of the particle, where $A$ characterizes the change of optical response due to the initial lattice heating, and $\tau_{cool}$ is a characteristic cooling time. In the second oscillating term, $k=(\text{ext,br})$ refers to the $(n,l)=(0,2)$ extensional and $(n,l)=(0,0)$ breathing modes. $\delta \tau_k(0)$ is the initial amplitude of the vibrational modes in the optical response, and $\nu_k$, $\tau_k$, $\phi_k$ are their respective frequency, damping time, and phase. Fitting Eq. 3.3 to the vibrational trace of Fig. 3.7 gives the extensional frequency $\nu_{ext} = 9.78 \pm 0.01 \text{ GHz}$ and damping time $\tau_{ext} = 1 \pm 0.06 \text{ ns}$. The breathing mode has a frequency of $\nu_{br} = 80.6 \pm 0.1 \text{ GHz}$ and the damping time is $\tau_{br} = 122 \pm 8 \text{ ps}$. Fig. 3.7c shows the probe laser polarization dependence of $\delta \tau_k(0)$. For both the breathing mode and the extensional mode, $\delta \tau_k(0)$ follows the expected dipolar dependence, which arises from that of the optical response.

The quality factors of the modes, $Q_k = 2\pi \nu_k \tau_k/2$, for about 20 measured particles are $Q_{ext} = 28 \pm 9$ for the extensional mode, and $Q_{br} = 37 \pm 6$ for the breathing mode (the errors are the standard deviations). These values are significantly higher than...
Figure 3.8: Probe photon energy dependence (a) Vibrational traces of a single gold nanorod for three different probe photon energies. The nanorod has dimensions $86 \times 30$ nm and $\hbar \omega = 1.92$ eV (648 nm) (b) Probe photon energy dependence of $\delta \tau_k(0)$. The lines represent the difference between two Lorentzian line shapes with a different plasmon frequency $\hbar \Omega_{LSP}$, line width $\Gamma$ and intensity $I$. The measured surface plasmon energy is indicated by the vertical line. Lorentzian fit parameters, extensional mode: $\hbar \Omega_{LSP,1} = 1.91152$ eV, $\Gamma_1 = 133.059$ meV, $I_1 = 0.04004$, $\hbar \Omega_{LSP,2} = 1.91148$ eV, $\Gamma_2 = 133.064$ meV, $I_2 = 0.0400401$, breathing mode: $\hbar \Omega_{LSP,1} = 1.91152$ eV, $\Gamma_1 = 133.059$ meV, $I_1 = 0.04004$, $\hbar \Omega_{LSP,2} = 1.91154$ eV, $\Gamma_2 = 133.059$ meV, $I_2 = 0.0400406$.

those of ensembles,$^{75}$ and agree well with those of breathing modes of single gold nanospheres$^{68}$ and single silver nanocubes.$^{79}$

In Fig. 3.8a we show vibrational traces of a single gold nanorod for three different probe photon energies. The mechanical oscillations induce a periodic modulation of the energy, line width and intensity of the surface plasmon band, $I_{SP}$, giving rise to a strong dependence of the optical response on the probe photon energy with respect to the surface plasmon band. In Fig. 3.8b we show $\delta \tau_k(0)$ (obtained from fits with Eq. 3.3) as a function of probe photon energy. The measured $\delta \tau_k(0)$ is very well represented by the difference between two Lorentzian line shapes with a slightly different frequency, line width and intensity. From the Lorentzian fits we find that the breathing mode vibration mainly modulates the energy of the longitudinal surface plasmon ($\Delta I_{SP} = 0.01 \%$, $\Delta \hbar \Omega_{LSP}/\Delta \Gamma \sim 12$), whereas the extensional mode vibration induces a line broadening comparable to the shift in energy ($\Delta I_{SP} = 0.01 \%$, $\Delta \hbar \Omega_{LSP}/\Delta \Gamma \sim 1$).
3.4.1 Excitation mechanism

The vibrational modes are launched by two distinct excitation mechanisms: the surge in electron pressure after the absorption of a short pump pulse, and the lattice anharmonicity. Because the corresponding stress profiles have a distinct time dependence\(^{69}\) we can extract the dominant launching mechanism from the observed phase \(\phi_k\) of the individual vibrational modes (see Eq. 3.3). Theoretically \(\phi_k\) can be estimated using a simple harmonic oscillator model.\(^{67,69}\)

In Fig. 3.9 we show the correlation between vibrational frequency and measured phase obtained by fitting the vibrational traces with Eq. 3.3. The measured phase is compared to theoretical estimates obtained from a simple harmonic oscillator description.\(^{69}\) For the breathing mode we find that the phase corresponds well to a launching mechanism mediated by both lattice anharmonicity and the surge in electron pressure.

For the extensional mode we find reasonable agreement between the measured and calculated phase of the vibration. The electron pressure has a minor effect on the launching of the extensional mode due to the large frequency mismatch between

![Figure 3.9: Phase of the vibrational modes](image)

Correlation between the vibrational frequencies and the measured phase of the oscillation for (a) the breathing mode and (b) the extensional mode vibrations. The dotted and dashed lines are the theoretical estimates of the phase for the individual electron and lattice contributions, calculated using a simple harmonic oscillator model. The solid line is the calculated phase of the vibration launched by both electron pressure and lattice anharmonicity. The open square symbols indicate the nanorods which have a Young’s modulus close to the bulk value. (Note: this figure also contains data points for rods which were not imaged in the electron microscope.)
the impulse heating of the electron cloud and the extensional mode vibration. It has to be noted that for the extensional mode the nanorod vibrations cannot be easily approximated using the simple isotropic harmonic oscillator model. The complex initial stress and displacement fields should be spatially and temporally decomposed onto the normal mode shape to yield a reliable estimate of $\phi_{ext}$.

### 3.4.2 Elastic moduli of single gold nanorods

As we described in Section 1.2.2, Hu et al. calculated the vibration frequencies of a polycrystalline free rod in a simple classical model and compared the results with a finite element method. They found a breathing frequency which scales with the bulk longitudinal speed of sound $c_l$ and the inverse particle width. The bulk longitudinal speed of sound can be expressed as a function of the bulk ($K$) and shear ($\mu$) moduli of the nanorods ($c_l = \sqrt{(K + 4/3\mu)}/\rho$, where $\rho$ is the density of bulk gold). The extensional frequency scaled with the inverse length and the square root of the Young’s modulus. Although the obtained analytical relations strictly hold only in the limit of infinite aspect ratio, Hu et al. found an excellent agreement with finite element calculations down to aspect ratios as small as $\sim 2.5$, with an error smaller than 1 %.

Because our rods are single-crystalline, the Young’s modulus probed by the extensional mode $E_{long}$ depends on their growth direction. We determined the growth direction of our nanorods by high resolution transmission electron microscopy (TEM). The TEM image in Fig. 3.10a shows that the particles are perfect single crystals without any defects. From the crystal plane spacing and orientation we deduce the growth direction, [100], and the relevant Young’s modulus for the extensional mode, $E_{long} = E_{[100]} = 42$ GPa.

When decomposing the breathing mode shape onto the atomic arrangement in the nanorod we find that the breathing mode involves motion of atoms along crystal directions perpendicular to [100]. It is therefore not straightforward to generalize Eq. 1.13 to single crystal cylinders. However, Eq. 1.13 can still be used to calculate the approximate vibrational frequencies of our single crystal rods. The error in frequency entailed by this approximation can be estimated by considering the dependence of
c\textsubscript{l} on the crystal direction. For the bulk modulus \( K \), the crystal growth direction is irrelevant. However, the shear modulus of a single crystal depends on the shear axes, and the direction dependent shear modulus \( \mu_{[hkl]} \) can be expressed in terms of the direction dependent Young’s modulus \( E_{[hkl]} \) as

\[
\mu_{[hkl]} = \frac{3E_{[hkl]}K}{9K - E_{[hkl]}},
\]

where the crystal direction dependence is explicitly noted. We obtained \( \mu_{[hkl]} \) by substituting the known values for the single crystal Young’s modulus\textsuperscript{77} into Eq. 3.4. The crystal direction dependent values for \( E_{[hkl]} \), \( \mu_{[hkl]} \) and \( c_{l,[hkl]} \) are tabulated in Table 3.1.

In the expressions derived by Hu et al.,\textsuperscript{75} the breathing mode involves a pure radial expansion while the length of the cylinder is fixed. Therefore, in order to estimate the error in the calculated breathing mode frequency we consider the average speed of sound in the directions perpendicular to the long axis of the nanorod, the [100] and [110] directions. We find a crystal direction averaged speed of sound of 3175 m/s. Considering that the speed of sound in polycrystalline gold is 3242 m/s, we estimate the error in the breathing mode frequency to be \( \sim 2\% \).

Fig 3.10(b) shows the correlation between breathing frequency \( \nu_{br} \) and the rod diameter (width). The dotted line represents the analytical approximation to \( \nu_{br} \) from Eq. 1.13. We find good agreement between the theoretical and experimental breathing frequencies, indicating that the bulk and shear moduli of the nanorods are close to the values for bulk gold.

As reported by Hu et al.,\textsuperscript{75} frequency ratio \( \nu_{br}/\nu_{ext} \) only depends on the aspect ratio \( AR \). They found that \( \nu_{br}/\nu_{ext} = 2.32 \times AR \) for polycrystalline gold nanorods. We now generalize this frequency ratio to single crystal gold nanorods by assuming

<table>
<thead>
<tr>
<th>crystal direction</th>
<th>( E_{[hkl]} ) (GPa)\textsuperscript{77}</th>
<th>( K ) (GPa)\textsuperscript{190}</th>
<th>( \mu_{[hkl]} ) (GPa)</th>
<th>( c_{l,[hkl]} ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>42</td>
<td>171</td>
<td>14.4</td>
<td>3098</td>
</tr>
<tr>
<td>[110]</td>
<td>81</td>
<td>171</td>
<td>28.5</td>
<td>3252</td>
</tr>
<tr>
<td>[111]</td>
<td>115</td>
<td>171</td>
<td>41.5</td>
<td>3387</td>
</tr>
<tr>
<td>polycrystalline</td>
<td>78.5\textsuperscript{190}</td>
<td>171</td>
<td>27.6</td>
<td>3242</td>
</tr>
</tbody>
</table>

\textbf{Table 3.1}: Crystal direction dependent Young’s modulus, shear modulus and longitudinal speed of sound for gold.
Chapter 3. Excitation dynamics in single gold nanorods

Figure 3.10: Elastic moduli (a) High resolution TEM image showing the single crystalline structure of the gold nanorods with a [100] growth direction (bars are 5 nm long). (b) Correlation between diameter (width) and breathing frequency $\nu_{br}$. The dotted line is the calculated $\nu_{br}$ for a free rod. The error in measured frequency is smaller than the symbol size. (c) Correlation between the measured aspect ratio and the frequency ratio $(\nu_{br}/\nu_{ext})/\text{AR}$. The dotted line indicates the calculated ratio of 3.24 for a free rod with the [100] Young’s modulus in the longitudinal direction. The green solid data points indicate the particles that have a Young’s modulus close to the value of bulk gold, the open square symbols indicate the nanorods which display a large deviation from the bulk Young’s modulus. (d) Correlation between the frequency and damping rate for the breathing mode. (e) Correlation between the frequency and damping rate for the extensional mode. Color of the data points is as in (c).
the single crystal Young’s modulus in Eq. 1.12 and approximating the breathing mode vibration with the frequency in a polycrystalline gold nanorod. We rewrite this ratio as

\[
\frac{\nu_{br}}{\nu_{ext}} = \frac{\tau_n}{2\pi a} c_A \left( \frac{1}{2L} \sqrt{E_{[100]}/\rho} \right) = 3.24 \times AR. \tag{3.5}
\]

In figure 3.10(c) we plot this frequency ratio as a function of the measured aspect ratio. For a sub-population of the rods we find a frequency ratio close to the theoretically expected ratio. Therefore, the Young’s modulus of these rods is close to the bulk value for a macroscopic cylinder with axis in [100] direction. Our finding agrees well with nano-indentation experiments on micron sized silver\textsuperscript{191} and gold nanowires,\textsuperscript{192} reporting Young’s moduli close to bulk values. Hence, we conclude that surface and size effects on elastic properties are still negligible in the size regime we studied. Indeed, theoretical arguments suggest that size effects are insignificant for widths larger than 5 nm.\textsuperscript{183–185} Previous pump-probe studies on ensembles of gold nanorods\textsuperscript{76, 77} have reported elastic moduli which were $\approx \text{25 - 40}\%$ lower than the bulk values. As suggested by the authors, the discrepancy may have resulted from a population bias by the optical signal strength.\textsuperscript{77}

For a larger portion of the rods we find a frequency ratio which is 15 - 25\% lower than expected. The corresponding Young’s modulus is $\sim 60$ GPa, 42 \% higher than the expected [100] value. We propose that the apparent stiffening is caused by coupling to the substrate. Van der Waals interactions\textsuperscript{193} favor contact of the nanorods to the substrate with their \{001\} or \{110\} long facets\textsuperscript{77} for a majority of rods. Considering the symmetry of the extensional mode oscillation with respect to the substrate, the additional restoring force is supplied by shear deformation of the substrate surface. The spring constant of a rod with a Young’s modulus $E_{long}$ can be expressed as $k_{ext} = E_{long} A/L$, with $A$ the radial sectional area of the nanorod. For a typical freestanding rod with a bulk Young’s modulus in the [100] growth direction of 42 GPa, a length of 85 nm and a radius of 15 nm we find a spring constant of $k_{ext} \sim 300$ N/m. The average spring constant of the nanorods
coupled to the substrate can be expressed as $k_{\text{total}} = k_{\text{ext}} + k_{\text{cpl}}$, where $k_{\text{cpl}}$ is the additional spring constant caused by the coupling. As described in the manuscript the average Young’s modulus of a nanorod coupled to the substrate is $\sim 60$ GPa, corresponding to $k_{\text{total}} = 510$ N/m. We estimate that the coupling of the extensional mode vibration to the substrate adds $k_{\text{cpl}} = 210$ N/m to the spring constant of the system.

We propose that some of the nanorods do not rigidly adhere to the surface, due to local adsorbates such as residual surfactant. These uncoupled nanorods would show an extensional frequency close to that of free rods. This hypothesis is supported by the significant phase delay we found for the extension mode of rods interacting with the substrate, from $\phi_{\text{ext}} = -0.3 \pm 0.1$ rad for the ’free’ rods to $\phi_{\text{ext}} = -0.1 \pm 0.1$ rad for the ’sticking’ rods. We found $\phi_{\text{br}} = 0.65 \pm 0.15$ rad for the breathing mode of all rods, with no difference between the two above-mentioned sub-populations. This was expected for this mode, which does not involve large shear displacements with respect to the substrate.

In Fig. 3.10 (d) and (e) we show the scatter plots of the measured damping rates vs. the corresponding vibrational frequencies. A simple model for the damping of the acoustic vibrations of a sphere in a homogeneous medium predicts that both the period and the damping time should be proportional to the size of the particle.\textsuperscript{175} Measurements on a larger number of particles are needed to explore a possible correlation between the coupling of the rods to the substrate and the damping rates of the extensional mode. However, the absence of a clear correlation between the damping rates and the oscillation frequencies indicates that there is a significant heterogeneity in the micro environment of the nanorods.

### 3.5 Conclusion

Understanding the thermal and elastic properties of gold nanorods is crucial for their application in optical recording. To this end we have measured the excitation dynamics and acoustic vibrations in single gold nanorods. From the electron-phonon decay time we found an electron phonon coupling constant in single gold nanorods which is in good agreement with reported values for ensembles of
gold nanoparticles and gold films. We have also determined the elastic moduli of individual gold nanorods from their vibration modes and precise dimensions. Contrary to earlier reports, we find that continuum elasticity theory is compatible with the measured vibrations of large free nanorods, and with bulk gold’s elastic moduli. Deviations in frequencies $\nu_{\text{ext}}$ or $\nu_{\text{br}}$ can be attributed to effects of the local mechanical environment. The sensitivity of the extensional frequency to interaction with the substrate could be exploited to probe the contact of the nanoparticle with its local environment and its elastic properties. Our results are the first step toward experimentally exploring the scale on which the elastic moduli of a nanoparticle start to differ from bulk values.
Chapter 3. Excitation dynamics in single gold nanorods
Doping of the nanorods into a matrix is key to successful application of the particles in optical laser writing and patterning. Herein the nanorods are embedded in a dielectric matrix and the anisotropy of the embedded particles is exploited by inducing a morphological change from a rod shape into the energetically favored spherical geometry by pulsed laser excitation. In such applications the laser pulse energy is the primary source of shape control, but other factors such as the thermal and mechanical properties of the dielectric matrix also play an important role (see for example Section 1.10).

In this Chapter we will study the photothermal reshaping of gold nanorods embedded in a polymer matrix. In Section 4.1 we study the interaction between the polymer and the nanorod, where we focus on heat accumulation induced by the high repetition rate of the recording laser combined with the low thermal conductivity of the polymer matrix material. In Section 4.2 we take a closer look at the melting and reshaping of the embedded nanorods. To remove ensemble averaging we will investigate single gold nanorods using white light scattering spectroscopy and electron microscopy.
4.1 Accumulative heating in a gold nanorod doped nanocomposite

In previous studies soft polymer materials such as polyvinyl alcohol (PVA)\textsuperscript{131,194} and ureasils\textsuperscript{195} as well as more rigid materials such as silica sol-gel glasses\textsuperscript{133} were employed as the matrix material. Each of these nanocomposites is stable under unique pulsed laser irradiation conditions. Even though gold nanorod doped dielectrics have been under intense investigation\textsuperscript{131,133,194,195} there has been no attempt to study the thermal stability of these nanocomposites, let alone explore ways to improve this property imperative to patterning applications. While a polymer such as polyvinyl alcohol (PVA) is an attractive matrix because of its mechanical properties and ease in doping, its low glass transition temperature and softness compared to other dielectric materials warrants a low damage threshold. Furthermore, its low thermal conductivity means that it is prone to heat accumulation upon irradiation with a high repetition rate laser source, which significantly reduces the damage threshold. These issues need to be resolved for the reliable use of the nanocomposite in optical laser writing and patterning applications.

Here we study both experimentally and theoretically the laser writing in a gold nanorod doped PVA film for various laser spot sizes and laser source repetition rates. We show indeed that a high repetition rate laser source induces heat accumulation in the nanocomposites. We find that the size of the focal spot strongly influences the degree of accumulative heating, which is confirmed by a simple theoretical model in which the nanorods were modeled as instantaneous point sources of heat. We show that accumulative heating can be limited by lowering the repetition rate of the laser source, and can be ultimately prevented by recording with single laser pulses.

4.1.1 Experimental

Gold nanorods with an aspect ratio of \(~4.4\) were prepared using a silver nitrate assisted, seed mediated growth method, as described in Section 2.1. The average dimensions of the nanorods are 52 nm x 12 nm with an average aspect ratio of \(4.4 \pm 0.5\) (distribution obtained by analyzing >200 particles in TEM micrographs). The
nanorods were then homogeneously dispersed in a PVA film by mixing a purified nanorod solution (particle concentration $\sim 2 \text{nM}$) with a 10% PVA solution, after which 10 $\mu$L of the mixture was dropcast on a cover slip and dried at 70°C. This resulted in a PVA film of about 30 $\mu$m thickness with a homogeneous nanorod concentration of $\sim 25 \text{nM}$ ($\sim 1.5 \times 10^{13}$ nanorods per cm$^3$).

Laser writing of patterns was achieved by femtosecond pulsed laser illumination at 850 nm (Spectra-Physics Tsunami, 100 fs pulse width, 82 MHz repetition rate). The pulse train was focused through a 0.7 NA objective lens. All patterning was conducted 12 $\mu$m below the surface. The exposure time was controlled by a mechanical shutter and was 25 ms per exposure in all experiments (equivalent to $2.05 \times 10^6$ laser shots per exposure). All pulse energies and laser fluences mentioned in the remainder are the values in the focal plane of the objective. Laser fluences indicated are spatially and temporally averaged over a single laser pulse. The patterns were imaged using low power continuous wave illumination at the recording wavelength with a laser scanning microscope operated in transmission (Olympus BX300, 1.2 NA water immersed objective lens). The recording threshold was determined by the lowest laser pulse fluence for which contrast was observed. The damage threshold was identified using a microscope equipped with a white light source and a 100x magnification objective, in which damage was identified as deformation at the surface of the sample.

Absorption spectra of a written bit pattern were measured using a homebuilt micro spectrophotometer. Light from a collimated white light source (Oriel Apex Quartz Tungsten Halogen source) was focused onto the sample through a 1.2 NA water immersed objective and collected in transmission using a 0.8 NA infrared enhanced objective lens. The light was redirected to a spectrograph (Acton Spectrapro 300i) and dispersed onto a charge coupled device (Princeton Instruments PIXIS 100).
4.1.2 Effect of the laser spot size

In Fig. 4.1 we show the extinction spectrum of a PVA film doped with gold nanorods, together with a TEM micrograph of the gold nanorods on a copper grid. The inset shows the change in extinction spectrum upon pulsed laser irradiation. Recording was done through a 0.7 NA objective lens using a laser fluence of 6 mJcm$^{-2}$. A clear decrease in extinction is observed around the laser wavelength, whereas the extinction at shorter wavelengths increases. This is consistent with a recording mechanism based on a shape transformation of the nanorods to lower aspect ratio particles, which is caused by femtosecond laser induced heating and melting of the nanorods.$^{27,105,133}$

When the pulse energy was further increased we observed significant damage to the nanocomposite upon irradiation. This is displayed in Fig. 4.2, where we show patterns recorded through a 0.7 NA objective lens using (a) 6 mJcm$^{-2}$ and (b) 7.5 mJcm$^{-2}$. Using a 0.7 NA objective lens we observe significant deformation in and around the focal volume when the laser fluence exceeded 7.1 mJcm$^{-2}$.

To investigate the origin of the observed damage we varied the laser spot size by systematically reducing the back aperture of the 0.7 NA objective lens, and

![Figure 4.1: Sample extinction before and after recording](image)

The extinction spectrum of a PVA film doped with gold nanorods. The TEM micrograph shows the gold nanorods on a copper grid. The scale bar indicates 50 nm. The inset shows the change in optical density within the focal volume upon pulsed laser irradiation (irradiation parameters: NA 0.7, $\lambda = 850$ nm, $t_{\text{exp}}=25$ ms, pulse energy density 6 mJcm$^{-2}$.)
identified the recording and damage threshold fluences for each NA value. The results are shown in Fig. 4.2c. One would expect that the recording and damage thresholds occur at similar energy densities for all recording NA lenses. Surprisingly, the results in Fig. 4.2c suggest that a higher recording NA requires a higher energy density for recording and damage to occur, i.e., smaller laser spot sizes (high NA focusing) require higher laser fluence to record. Secondly, from simple thermodynamic considerations\textsuperscript{133} we found that the pulse energy densities employed for recording are not sufficient to cause melting of the embedded gold nanorods. Link et al.\textsuperscript{130} reported that it requires $\sim 65$ fJ of absorbed photon energy to heat up a similar sized nanorod to its melting temperature of 1300 K, and Petrova et al.\textsuperscript{104} reported that at laser induced temperature increase of 1000 K the nanorods show signs of reshaping. However, we found that the maximum energy absorbed per nanorod to reach the recording threshold (NA 0.7, I$\sim 5.3$ mJcm$^{-2}$) is $\sim 27$ fJ, which corresponds to a maximum temperature rise of $\sim 500$ K. This is well below the melting temperature of gold nanorods for all recording NAs.

Both observations are indicative of accumulation of heat inside the focal volume by absorption of sequential laser pulses from the high repetition rate laser source.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_2.png}
\caption{Recording and damage thresholds with a high repetition rate laser source} Bit patterns recorded through an 0.7 NA objective lens using pulse energies of (a) 6 mJcm$^{-2}$ and (b) 7.5 mJcm$^{-2}$. The size of the pattern is 30 $\mu$m $\times$ 30 $\mu$m. (c) Recording threshold (open circles) and damage threshold (solid circles) as a function of NA of the recording lens. The error bars indicate the standard deviation of the spread in contrast obtained from all 16 recorded bits. The error bars for the damage threshold are of the order of the symbol size.
\end{figure}
The embedded nanorods act as nanoscale absorbers of the laser energy and transfer their energy to the environment via phonon-phonon interactions. The energy transfer from the nanorods to their environment causes an increase in temperature within the focal volume. The energy then dissipates out of the focal volume into the bulk medium. The time interval between sequential laser pulses is 12.5 ns, which is significantly shorter than the time required for heat to diffuse out of the focal volume (simulated to be $\sim 2 \mu s$ for a spherical focal volume in PVA with a radius of 1 $\mu m$ using Cooper’s heat dissipation model\textsuperscript{82}). Hence over time, the energy from successive laser pulses accumulates in and around the focal volume and causes the PVA to heat up.

Accumulative heating also explains the fact that the rise in temperature of the gold nanorods caused by the laser pulses is not enough to reach their melting temperature. The temperature of the nanorods embedded in the nanocomposite is governed by both the temperature of the surrounding matrix and the temperature rise induced by the pulsed laser illumination. If the matrix surrounding the nanorods heats up, the additional absorbed laser energy could elevate the temperature inside the nanorods above their melting point. The maximum temperature of the surrounding matrix for recording without damage is limited by the decomposition temperature of PVA, which is $\sim 540$ K.\textsuperscript{196} The combined effect of the locally hot matrix and the pulsed laser irradiation (inducing $\Delta T \sim 500$ K, see above) results in a maximum nanorod temperature of $\sim 1040$ K, which is close to the expected melting temperatures for gold nanorods.\textsuperscript{77,130} The fact that the recording and damage thresholds do not occur at a constant energy density for different NAs (Fig. 4.2c) indicates that the size of the focal volume plays a critical role in the accumulative heating process. A more quantitative theoretical validation of this observation is discussed in the next section.

### 4.1.3 A simple model

To obtain a better insight into the accumulative heating process in a nanoparticle doped dielectric we employed a simple three dimensional heat dissipation model in which the embedded nanorods were modeled as point absorbers, which is a reasonable assumption on the length scale of several microns. The nanoparticles
Chapter 4. Photothermal reshaping

absorb photon energy, which is converted to thermal energy and dissipated into the surrounding medium. The nanoparticles thus act as point sources of thermal energy. These point sources were homogeneously distributed within an infinite (non-absorbing) PVA matrix with an inter-particle distance of \( \sim 400 \text{ nm} \) (calculated from the particle concentration in our experiment). The relevant timescales involved\(^{60} \) are the electron-phonon relaxation time \( \tau_{\text{e-ph}} \) (typically \(< 5 \text{ ps} \)) and the phonon-phonon relaxation time \( \tau_{\text{ph-ph}} \) (typically \(> 300 \text{ ps} \) for particles embedded in PVA, see section 1.2.3). Because \( \tau_{\text{e-ph}} \ll \tau_{\text{ph-ph}} \) it is reasonable to assume that the absorbed energy is released instantaneously by the point source. The generation and dissipation of thermal energy from an instantaneous point source into the PVA matrix gives rise to a time and position dependent temperature change \( \Theta \) which can be expressed as\(^{197} \)

\[
\Theta(r,t) = T(r,t) - T_0 = \frac{Q}{8\rho c_p(\pi \alpha t)^{3/2}} \exp \left[ \frac{-(r - r_0)^2}{4\alpha t} \right], \tag{4.1}
\]

where \( T_0 \) is the initial temperature (293 K), \( Q \) is the amount of thermal energy released by the point source, \( \rho \) is the density of PVA (1200 \( \text{kgm}^{-3} \)), \( c_p \) is the specific heat capacity of PVA\(^{198} \) (1650 \( \text{Jkg}^{-1}\text{K}^{-1} \)), \( r - r_0 \) is the radial distance away from the point source, and \( \alpha \) is equal to \( k / \rho c_p \) where \( k \) is the thermal conductivity of the nanocomposite. The value for the thermal conductivity depends on the volume fraction of nanorods present in the polymer nanocomposite. As in our experiment the volume fraction of gold is less than 0.1\% we assumed a value for \( k \) equal to that for PVA (0.21 \( \text{Wm}^{-1}\text{K}^{-1} \)).\(^{198} \)

To model the experimentally observed homogeneous dispersion of the nanorods, the point sources were distributed on a hexagonal grid. To simulate the random alignment of the nanorods in the polymer matrix we assigned a randomly generated \( Q \) to each individual nanoparticle. This distribution of \( Q \) values was spatially multiplied by a Gaussian function to account for the intensity distribution inside the focal volume. The nanoparticles in the area bounded by twice the full width at half maximum of the Gaussian intensity distribution were included in the calculations.

The time dependent temperature distribution after absorption of a single laser pulse by an ensemble of nanoparticles can be obtained by superposing the solutions for \( n \) individual particles. The absorption of subsequent laser pulses at a fixed interval can be calculated by incorporating a temporal offset in Eq. 4.1.
A typical temperature map of the focal volume obtained from Eq. 4.1 is shown in Fig. 4.3a. The temperature distribution in and around the focal volume was evaluated 12.5 ns after absorption of 200 consecutive laser pulses at a repetition rate of 82 MHz. The random value for $Q$ was set to a maximum of 50 fJ for a nanorod fully aligned to the laser light polarization. Assuming a typical absorption cross section for nanorods of $5 \times 10^{-12} \text{ cm}^2$ this corresponds to an experimental laser fluence of 10 mJcm$^{-2}$. This amount of absorbed energy is insufficient to completely melt the gold nanorods and thus closely represents our experimental conditions. The Gaussian intensity distribution is shown at the top, the radius $r_{\text{foc}}$ was set to 1 $\mu$m in this particular case. One can observe a significantly elevated average temperature within $r_{\text{foc}}$ due to accumulative heating.

In our experiments we observed that the laser spot size had a profound effect on the degree of accumulative heating (Fig. 4.2c). To verify this observation we varied the theoretical parameter $r_{\text{foc}}$ and simulated the temperature profile within the focal volume while keeping the laser pulse fluence and nanorod concentration constant. The average temperature, defined as the mean temperature within the focal volume

![Figure 4.3: Calculated temperature profile in the focal volume](https://example.com/figure4.3.png)

(a) Typical calculated temperature distribution in and around the focal volume 12.5 ns after absorption of 200 laser pulses at a repetition rate of 82 MHz. The intensity distribution within the focal volume is shown at the top ($r_{\text{foc}} = 1 \mu m$). (b) Calculated average temperature within the focal volume 12.5 ns after absorption of a number of laser pulses for different $r_{\text{foc}}$. The repetition rate of the laser source was 82 MHz (closed symbols) or 1 kHz (open symbols). The results for different $r_{\text{foc}}$ for the low repetition rate laser source overlap. The error bars were obtained by performing fifteen independent calculations for which a new distribution of random $Q$ was defined. The error bars indicate the standard deviation of the spread in $T_{\text{avg}}$. 

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bounded by $r_{\text{loc}}$ is then plotted against the number of laser pulses and the results are shown in 4.3b. The simulation clearly indicates that a larger focal size induce more heat accumulation. This is in good agreement with our experimental data presented in Fig. 4.2c. We also simulated the temperature profiles for a low repetition rate (1 kHz) excitation laser source. The simulation did not show any accumulative heating for any $r_{\text{loc}}$ or number of laser shots, which confirms our experimental result in the preceding section.

In the initial stages of heat accumulation ($< 100$ laser pulses or $t < 1 \mu s$) we do not observe a significant difference in the rate at which the average temperature increases. This is an effect caused by the spacing between the embedded gold nanoparticles. Thermal energy dissipates away from the gold nanoparticles but due to the low thermal conductivity of PVA the rate at which this thermal energy diffuses is limited. The small heat baths surrounding the nanoparticles have not merged yet and do not interact. Once the small heat baths merge and form a large heat bath the size of the focal volume we observe a significant difference in the rate at which the thermal energy accumulates. A smaller focal spot size has a larger surface to volume ratio and thus has more surface area available for heat to dissipate to the matrix surrounding the focal volume. This results in a lower rate of accumulative heating for smaller focal spot sizes. This confirms our experimental observation that the higher NAs require a higher pulse fluence to obtain a resolvable bit contrast.

### 4.1.4 Recording with lower repetition rate or a single pulse

For laser writing applications it would be highly beneficial to prevent the accumulative heating we observed with a high repetition rate laser source. To this end we repeated the above experiment using a low repetition rate laser source (Spectra Physics Spitfire, repetition rate 1 kHz, wavelength 800 nm). Here the inter-pulse separation (1 ms) is significantly longer than the characteristic time for diffusion of heat out of the focal volume ($\sim 2 \mu s$), thus excluding accumulative heating. The recording and damage thresholds obtained using the low repetition rate laser are shown in Fig. 4.4. The exposure time in this experiment was adjusted so that the number of laser pulses per exposure is the same as for the high repetition rate laser source. The highest NA we used was 0.3 because our power meter did
Chapter 4. Photothermal reshaping

Figure 4.4: Low repetition rate laser source Recording threshold (open circles) and damage threshold (solid circles) as a function of NA of the recording lens, using a low repetition rate laser source. The error bars for the recording threshold are of the order of the symbol size.

not allow measurement of the extremely low average powers required for the higher NA objective lenses. We observe that the recording and damage threshold occur at similar energy densities for all recording NAs, thus confirming that accumulative heating does not affect the laser writing using a low repetition rate laser source.

Ultimately one would like to record bits or pixels with a single femtosecond laser pulse. In that case the recording speed is only limited by the repetition rate of the laser source, which can be as high as 1 GHz for modified laser cavities. We performed single pulse recording by employing an electro-optic modulator (ConOptics Inc., 350-160) to select single pulses on demand from the pulse train of our 82 MHz femtosecond laser source. An example of a pattern recorded with single pulses per pixel is shown in Fig. 4.5. The pattern was recorded at a wavelength of 850 nm with a pulse energy density of 125 mJ cm$^{-2}$ (the maximum we could achieve with our laser source). Note that, even though this pulse energy density is ten-fold higher than the values we employed with the low repetition rate laser source (see Fig. 4.4), we still do not observe any damage to the polymer matrix.

This observation strongly suggests that the damage to the polymer matrix we observed is a multiple pulse effect, whereas the reshaping of the nanorods is achieved at the very start of the exposure time with one or a only few laser pulses. The nanorod reshaping results in a bleach of the longitudinal plasmon within the first couple of pulses, after which the absorption decreases dramatically. However, it is
this first pulse absorption which makes a critical difference in the final steady state temperature profile. This observation is in good agreement with previous reports on void generation in gold nanorod doped polymers.\textsuperscript{121}

Now that we have developed a better understanding of the thermal properties of the nanocomposite as a whole, we will take a closer look at the melting and reshaping of the embedded nanorods. To prevent the accumulative heating and thermal damage we observed here, we will employ a single laser pulse to heat up, melt and reshape a single gold nanorod.

### 4.2 Photothermal reshaping of single nanorods

The excitation of the SPR by an electromagnetic field such as laser light creates a free electron oscillation which decays through radiative and non-radiative decay channels.\textsuperscript{42} In metal particles, non-radiative decay is prevalent and releases thermal energy through electron-phonon scattering,\textsuperscript{60} causing an increase in particle temperature. The extent of the temperature increase depends on the laser pulse energy and the absorption cross section at the laser wavelength. Because the time constant of heat dissipation to the environment is on the order of hundreds of picoseconds,\textsuperscript{83} the laser pulse width also plays a role in the photothermal energy conversion process.\textsuperscript{200} When enough photon energy is conveyed to the lattice, the particle reaches its melting temperature and undergoes a phase transition.
Theoretical studies have predicted that the melting and reshaping of gold nanorods depends in unique ways on the size and aspect ratio.\textsuperscript{201–203} Bouhelier \textit{et al.} measured the angular photoluminescence of a single molten gold nanorod, but did not report a systematic study of the thermodynamic reshaping properties of the particle.\textsuperscript{52} Other reports on the melting and reshaping of gold nanorods have so far only been conducted on ensembles.\textsuperscript{27, 104, 130, 200, 204} In ensemble measurements however, the different dimensions of the individual particles are likely to screen any effects of size and aspect ratio, and large discrepancies between the calculated and the measured melting energy have been observed.\textsuperscript{130} Recent advances in far-field microscopy have allowed for the detection and spectroscopy of single metal nanoparticles.\textsuperscript{42, 46, 205, 206} Studying a single nanorod removes the heterogeneity in the sample and allows one to study the size and shape effects of the melting transition. Here we study the melting and reshaping of single gold nanorods embedded in a polyvinyl alcohol matrix. We collected scattering spectra of individual gold nanorods before and after irradiation, and correlated these with electron microscope images. We find a melting energy which is in good agreement with theoretical predictions assuming thermodynamic values for bulk gold. We observed that higher aspect ratio particles are thermodynamically less stable, leading to a greater reduction of the aspect ratio at lower laser pulse energy densities.

\subsection*{4.2.1 Experimental}

Gold nanorods were prepared using the wet-chemical synthesis method described in Section 2.1. The rods have an ensemble average size of $92 \times 30$ \text{nm}, and an ensemble average volume of $5.8 \times 10^4$ \text{nm}^3, see Fig. 2.3c and d. To ensure that the nanorods are in a homogeneous environment, we first spincoated a thin layer of polyvinyl alcohol (PVA) on an indium tin oxide (ITO) coated coverslip. A dilute solution of the nanorods was mixed with a 3\% PVA solution, and spincoated onto the initial PVA layer. The sample was then sealed with another pure PVA layer identical to the first layer. With an atomic force microscope we measured the thickness of the individual layers to be 80 nm, 30 nm, and 80 nm respectively. We fabricated grids in the PVA layer by femtosecond laser writing to help locate the same nanorods for spectroscopy and electron microscopy.
Single particle white-light scattering microscopy\textsuperscript{46} was performed in a home built optical microscope (see Fig. 4.6). The output from a high power quartz tungsten halogen light source was spatially filtered using a 30 \( \mu \text{m} \) pinhole, and was focused onto the sample through a 1.4 NA oil immersed objective lens. The reflected light was collected by the same objective and directed to a photomultiplier tube (PMT, Oriel Instruments 77348). To increase the visibility of the rods, the reflected light was bandpass-filtered (760 \( \pm \) 60 nm) before detection. The unfiltered scattering spectrum of each individual nanorod was dispersed by a spectrograph (Acton Instruments, SpectraPro 300i) on a charge coupled device (Princeton Instruments, PIXIS 100). Except for polarization measurements, the white light was randomly polarized.

To induce melting and reshaping, the nanorods were illuminated with a femtosecond pulse laser source (SpectraPhysics Tsunami, pulse width 100 fs, repetition rate 82 MHz, tunable 700-1000 nm). An electro-optic modulator (ConOptics Inc., 350-160) selected single pulses on demand from the 82 MHz pulse train. A half wave plate was used to rotate the polarization of the linear excitation source to match the orientation of the nanorod on the sample surface. Unless stated explicitly, all the nanorods were irradiated with a laser wavelength corresponding to the peak of their longitudinal SPR, and with a polarization parallel to the long axis of the nanorod.

In the white-light scattering measurements the measured intensity \( I_m \) at the detector is a superposition of the reflected field off the interface \( E_r \) and the light

Figure 4.6: Sketch of the setup Schematic drawing of the experimental setup used for white-light scattering spectroscopy and laser illumination of single gold nanoparticles.
field $E_s$ scattered by the particle\textsuperscript{46} (see Eq. 3.1). The pure scattering signal scales as $R^6$ and is the dominant term for our large nanorods ($r_{\text{eff}} \sim 25$ nm). The detected intensity can then be expressed as

$$I_m(\lambda) = |E_i|^2 [r^2 + |s(\lambda)|^2], \quad (4.2)$$

where the reflection term was included to correct for the weak reflection of the oil-polymer-glass interface. In the experiment, we correct for the reflection signal by subtracting a background spectrum $I_{bg}$, which was recorded several microns away from the particle. The spectral characteristics of the white light profile were taken into account by normalizing each spectrum to $I_{WL}$, which was recorded at the glass-air interface at the back of the coverslip. We then extracted the absolute scattering cross section $\sigma_{sca}$ by taking into account the focal spot size $A_{foc}$ and the collection efficiency $\phi$ of the setup using

$$\sigma_{sca}(\lambda) = \frac{A_{foc}}{\phi} \frac{I_m(\lambda) - I_{bg}(\lambda)}{I_{WL}(\lambda)}. \quad (4.3)$$

We note that this approach is only valid in an index matched geometry where $I_{bg}(\lambda)$ is much smaller than the scattered intensity. If this is not the case, the interference between the scattered and reflected waves should be included in Eq. 3.1.

To enable comparison between the individual nanorods, we applied several selection criteria before including each respective nanorod in our final analysis:

1. We only analyzed nanorods with a comparable area under the longitudinal SPR in the scattering spectrum (standard deviation $\approx 12\%$). Because the total scattered field scales as $V^2$, this selects a subpopulation with a standard deviation of $\approx 7\%$ in volume.  
2. We only considered nanorods with a peak value of $\sigma_{sca} = 1.55 \pm 0.2 \times 10^{-15}$ m$^2$ in randomly polarized light (standard deviation 12%). Because $\sigma_{sca}$ scales as $V^2$ and $\sigma_{abs}$ scales as $V$, this criteria isolates nanorods with a standard deviation of 5.8% in $\sigma_{abs}$.  
3. We finally split the irradiated nanorods into two separate populations according to their longitudinal SPR energy, corresponding to average initial aspect ratios of $2.5 \pm 0.2$ (longitudinal SPR 750 $\pm$ 20 nm) and $3 \pm 0.2$ (longitudinal SPR 805 $\pm$ 15 nm).
4.2.2 Correlation between structural and optical properties

To locate the nanorods, the white light spot was raster scanned over the sample surface. We then acquired white light scattering spectra of the individual gold nanorods before irradiation. In Fig. 4.7 we show a selection of scattering spectra of individual gold nanorods in unpolarized white light. On the vertical axis in Fig. 4.7 we have plotted the absolute scattering cross section of the nanorods, \( \sigma_{sca} \), extracted from Eq. 4.3.

In the scattering spectra we observe a longitudinal SPR ranging from 1.4-1.7 eV (equivalent 840-740 nm). The Lorentzian linewidth is \( \Gamma = 105 \pm 20 \) meV, which is in good agreement with previous reports.\(^{24,206}\) In all cases, the polarized scattered intensity followed the expected dipolar angle dependence (see the inset in Fig. 4.7). These scattering spectra help us locate isolated gold nanorods, determine their orientation on the sample surface, and select the appropriate irradiation wavelength for each individual nanorod.

To establish a correlation between the physical and optical properties, we acquired the scattering spectrum and the scanning electron microscopy (SEM) image of \( \sim 20 \) nanorods. The correlation between aspect ratio and longitudinal SPR energy for all the particles is displayed in Fig. 4.8, together with two typical SEM
Correlation between structural and optical properties

Correlation between the aspect ratio (measured from SEM images of each rod) and the longitudinal SPR energy (measured from the scattering spectrum of each rod). The error bars indicate the uncertainty in the dimensions obtained from the SEM images. The dotted line is the calculated longitudinal SPR energy for spherically capped cylinders embedded in a medium with $\epsilon_m = 2.25$ (see text for more details). Insets: scanning electron microscope images of two individual nanorods with a different aspect ratio. The scale bars are 50 nm.

Images of nanorods with a different aspect ratio. As expected, we find a strong correlation between aspect ratio and longitudinal SPR energy. The small spread of the data points is caused by differences in the (effective) refractive index of the local environment around each nanorod, possibly caused by impurities or local air/water content in the polymer matrix. The dotted line in the figure indicates the calculated longitudinal SPR energy for a spherically capped cylinder with a width of 30 nm, as reported by Prescott et al. We find good agreement between the calculated and measured SPR energy, indicating that the rods can be accurately modeled as spherically capped cylinders.

The stark dependence of the longitudinal SPR energy on aspect ratio makes gold nanorods the ideal system to study melting and reshaping. Even small changes in particle geometry are straightforward to detect by simply extracting the energy of the longitudinal SPR from the scattering spectrum. The exact particle shape can be extracted from SEM images obtained from the same rods after illumination. We will now employ this technique to study the melting and reshaping transitions in single gold nanorods.
4.2.3 Melting and reshaping of single gold nanorods

Individual gold nanorods were then irradiated with a single femtosecond laser pulse, which is shown in Fig. 4.9. In Fig. 4.9a we show $\sigma_{\text{sca}}$ of a nanorod with an initial longitudinal SPR at 1.68 eV (745 nm). Using the correlation displayed in Fig. 4.8, we estimate the initial aspect ratio of the particle to be 2.5±0.2 (we could not obtain SEM images of the rods before irradiation, because the electron beam induced damage to the PVA film made it impossible to obtain scattering spectra after electron microscope imaging). This rod was irradiated with a single laser pulse

![Graph showing scattering cross sections and polar plots before and after irradiation](image)

**Figure 4.9:** Melting and reshaping single gold nanorods (a) Scattering cross sections in unpolarized white light, before and after irradiation with a single laser pulse at 745 nm with an energy density of 1.93 mJ cm$^{-2}$. The polar plot shows polarized scattering versus angle before (squares) and after (circles) irradiation, with dipolar cosine fits (solid lines). Inset: SEM image of the nanorod after irradiation, scale bar 50 nm. (b) Same as (a), only this nanorod was irradiated with 2.5 mJ cm$^{-2}$. 

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with a pulse energy density of 1.93 mJ cm\(^{-2}\) in the focal plane (\(\lambda = 745\) nm). After irradiation, we find that the longitudinal SPR energy has blue-shifted to 1.96 eV (640 nm). We also observe a significant broadening of the longitudinal SPR, which is caused by the interband transitions in gold which have an onset energy of \(\sim 2\) eV. The polarized scattered intensity did not change significantly from the initial particle due to the remaining elongated particle shape. From the SEM image acquired after irradiation we find that the dimensions of the particle are 73 nm \(\times\) 40 nm, with an aspect ratio 1.6. The volume of the particle is approximately 61000 nm\(^3\), which is close to the ensemble averaged volume of 58000 nm\(^3\).

In Fig. 4.9b we show \(\sigma_{\text{scat}}\) for another gold nanorod (initial longitudinal SPR at 1.67 eV or 750 nm, aspect ratio 2.5\(\pm\)0.2). We illuminated this rod with a higher pulse energy density of 2.5 mJ cm\(^{-2}\) (\(\lambda = 745\) nm), upon which it completely relaxed to the spherical geometry. From the SEM image acquired after reshaping we observe a spherical particle with a radius of 24 nm (V = 58000 nm\(^3\)). As expected, the scattering spectrum after irradiation displayed a peak at 2.3 eV (540 nm), corresponding to the sphere SPR. The initial dipole character of the polarized scattered intensity now displays a monopole character due to the loss of anisotropy in the particle shape.

**Figure 4.10: Intermediate particle shapes** Sketch of the intermediate particle shapes observed at different pulse energy densities. The dimensions of all SEM images are 200\(\times\)150 nm.
As expected, upon melting the nanorods (partly) reshape to the energetically favored spherical geometry. The particle shape we observed for three different particles after irradiation with an increasing laser pulse energy is displayed in Fig. 4.10. The particles had an initial aspect ratio of 2.5±0.2, and were illuminated with a laser wavelength on resonance with their longitudinal SPR peak. We observe a gradual shape change from a long nanorod to a shorter and wider nanorod, before the particle finally relaxes to the spherical shape.

We repeated the experiment displayed in Fig. 4.9 on approximately 20 nanorods which fall within the selection criteria outlined in the Experimental section. In Fig. 4.11 we show the longitudinal SPR after irradiation versus the amount of absorbed energy (corrected for laser spot size and objective transmission at the laser wavelength). We determined the amount of energy absorbed by a nanorod by considering the pulse energy density $I$ in the focal plane, and the absorption cross section $\sigma_{\text{avg}}^{\text{abs}}$, where the superscript indicates that the value is averaged over the narrow sub-population we considered. The amount of energy absorbed by the rod can then be expressed as $Q_{\text{abs}} = I \times \sigma_{\text{avg}}^{\text{abs}}$. We obtain an estimate for $\sigma_{\text{avg}}^{\text{abs}}$ from the theoretical ratio between the scattering and absorption cross section. We calculated this ratio in the electrostatic approach, for which we employed Gans’ theory with the estimated shape factors $L$ reported by Prescott et al. for a spherically capped cylinder with a width of 30 nm. Using typical parameters for our nanorods embedded in PVA with an aspect ratio of 2.7 we find $\sigma_{\text{avg}}^{\text{abs}} / \sigma_{\text{avg}}^{\text{sca}} = 4.3$. The expression relating $Q_{\text{abs}}$ and $I$ is then

$$Q_{\text{abs}} = 4.3 \times I \times \sigma_{\text{sca}}^{\text{avg}}.$$ \hspace{1cm} (4.4)

The relative error entailed in this approach is largely determined by the relative error in $\sigma_{\text{sca}}^{\text{avg}}$, which is twofold. Firstly, our approximation to neglect the interference term in Eq. 3.1 introduces an error determined by the measured value of $r^2/|s|^2 = 0.08$. Secondly, our averaging over an ensemble with a standard deviation of 12% in $\sigma_{\text{sca}}$ introduces an additional error. We estimate the total error in $Q_{\text{abs}}$ to be approximately 20%.
From Fig. 4.11 we find that both aspect ratios require \( \sim 260 \) fJ to completely relax to the spherical geometry. From thermodynamic considerations we can express the amount of energy required to just melt a nanorod as\(^{197}\)

\[
Q_{\text{melt}} = \rho V [c_p(T_{\text{melt}} - T_0) + \Delta H_{\text{fus}}],
\]

where \( \rho \) is the density of bulk gold, \( V \) is the volume of the nanorod, \( c_p \) is the specific heat capacity of bulk gold\(^{85}\) (129 J/kg/K), \( T_{\text{melt}} \) is the melting temperature of bulk gold\(^{85}\) (1330 K), \( T_0 \) is the ambient temperature, and \( \Delta H_{\text{fus}} \) is the heat of fusion for bulk gold\(^{85}\) (6.5\( \times \)10\(^4\) J/kg). Employing the ensemble average volume of 5.8\( \times \)10\(^4\) nm\(^3\) we find \( Q_{\text{melt}} = 225 \pm 15 \) fJ for a typical nanorod in our experiment (the error originates from the uncertainty in the typical volume of the rods of 4.8%, see the Experimental section). In our experiment we find a melting energy which is \( \approx 15\% \) larger than the theoretical prediction. This could be due to the viscoelasticity of the polymer matrix, which counters the surface energy driven migration of the molten gold atoms to form a spherical particle. This is expected to increase the amount of

\[\text{Figure 4.11: Final longitudinal SPR versus absorbed energy}\] Dependence of the longitudinal SPR energy after irradiation on the amount of absorbed laser energy, for two populations with an initial aspect ratio of 2.5\( \pm \)0.2 (solid symbols) and 3.0\( \pm \)0.2 (open symbols). The errors indicate the uncertainty in the amount of absorbed energy (s.d.), see the text for details. The lines are a guide to the eye. The vertical dashed lines indicate the calculated energy range associated with no melting \((T<1330\text{ K})\), partial melting \((T = 1330\text{ K})\), and full melting \((T>1330\text{ K})\).
energy required for structural changes to occur. Also effects of the cooling of the particle during reshaping could contribute to the observed discrepancy. Ruan et al. reported that a gold sphere undergoes full melting within 100 ps. In combination with an estimated 1 ns cooling time, this implies that approximately 10% of the heat has dissipated before melting, which may explain the difference between the measured and calculated melting energies.

The initial stages of the reshaping at energies below $\approx 200 \text{ fJ}$ exhibit a gradual structural change into shorter aspect ratio particles. In this pulse energy regime the nanorod undergoes partial melting, and only a thin shell of surface atoms migrates to form a lower energy geometry. When the nanorod absorbed more than $\approx 220 \text{ fJ}$, the particles suddenly collapsed to a spherical geometry. This behavior is similar to previous molecular dynamics studies performed by Wang et al., who modeled the melting and reshaping of a small, freestanding gold nanorod. The authors simulated the continuous heating of gold nanorods from 5-1300 K, and analyzed the equilibrium atomic structure at different temperatures. They reported that the nanorods initially undergo a gradual shape transition to a shorter and wider particle. Around the bulk melting point the internal atomic structure of the nanorod suddenly became disordered and the nanorod collapsed to the spherical geometry, which is similar to the behavior we observe in our experiment.

Their simulations also indicated the formation of an intermediate, stable particle with a lower aspect ratio. This intermediate shape was the result of a surface reorganization from \{110\} and \{100\} facets to the energetically more stable \{111\} facets. The intermediate product covered with \{111\} facets was found to be stable up to the bulk melting point of gold. The temperature at which this intermediate geometry occurred was found to increase with increasing particle size and approached the homogeneous melting temperature for large systems. As a consequence, the intermediate stable particle shape was precluded in large nanorods, which is probably why we do not observe this in our experiment.

Interestingly, we find that partial structural changes occur at a lower pulse energy density for longer aspect ratio particles. For example, for $Q_{\text{abs}} \approx 220 \text{ fJ}$, the particles with an initial aspect ratio of 3 underwent significant structural changes to an aspect
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ratio of $\sim 1.8$, but the particles with an initial aspect ratio of 2.5 were hardly affected, exhibiting an aspect ratio of $\sim 2.2$. Because of our selection criteria outlined in the Experimental section, this effect cannot be caused by differences in particle volume or absorption cross section. We suggest that the observed difference in energy required for reshaping is due to the difference in surface energy between the two aspect ratios. The shape of the particle after laser induced heating is driven by the tendency of surfaces to reduce their surface energy. Surface energy being proportional to surface area, the total surface energy difference, relative to the lowest energy geometry of a sphere, is almost 20% larger for an aspect ratio of 3 compared to an aspect ratio of 2.5 (assuming a constant volume). Due to this difference in surface energy, an aspect ratio 3 particle may exhibit a higher rate of reshaping in order to minimize its surface energy. The homogeneous melting temperature still occurs at a similar temperature for both aspect ratios because this is determined by the bulk melting temperature of gold.

4.3 Conclusion

In this Chapter we studied laser writing by photothermal reshaping of gold nanorods embedded in a polyvinyl alcohol film. We showed that, when a high repetition rate laser source is employed, the nanocomposite exhibits accumulative heating inside the focal volume. The rate at which heat accumulates strongly depends on the size of the focal volume, which was confirmed by theoretical simulations. Lowering the repetition rate reduced the damage to the nanocomposite because accumulative heating is prevented. When a single laser pulse was employed for recording, we did not observe any damage to the nanocomposite, even for energy densities which were ten-fold higher than we employed with the low repetition rate laser source. This confirmes that the damage to the matrix is a multiple pulse effect, whereas the reshaping of gold nanorods occurs within a few, if not one, laser pulse.

In the second part of this Chapter we have studied the melting and reshaping of single gold nanorods using a combination of white-light scattering spectroscopy and electron microscopy. We measured a melting energy of 260 fJ for nanorods with an average size of $92 \times 30$ nm, which is in good agreement with the theoretical value.
of 225 fJ. We observed that higher aspect ratio particles are thermodynamically less stable, leading to a greater reduction in aspect ratio upon partial melting. Our technique is capable of accurately determining the melting energy of individual nanoscale objects, which can give valuable insight in size and shape effects on the melting transition. Accurate knowledge about the melting threshold should also prove useful to photothermal applications of gold nanorods, where shape transitions need to be limited or prevented altogether.
Chapter 4. Photothermal reshaping
Five-dimensional optical recording mediated by surface plasmons in gold nanorods

MULTIPLEXED OPTICAL RECORDING provides an unparalleled approach to increase the information density beyond 1 Tbits/cm$^3$ by storing multiple, individually addressable patterns within the same recording volume. Although wavelength, polarization and spatial dimensions have all been exploited for multiplexing, these approaches have never been integrated into a single technique which could ultimately increase the information capacity by orders of magnitude. The major hurdle is the lack of a suitable recording medium which is extremely selective in the wavelength, polarization and the 3 spatial domains in order to provide orthogonality in all 5 dimensions. Here we show true five-dimensional optical recording by exploiting the unique properties of the longitudinal surface plasmon resonance (SPR) of gold nanorods. The longitudinal SPR exhibits an excellent wavelength and polarization sensitivity, whereas the distinct energy threshold required for the photothermal recording mechanism provides the axial selectivity. The recordings were detected using longitudinal SPR mediated two-photon luminescence (TPL) which we demonstrate to possess an enhanced wavelength and angular selectivity compared to conventional linear detection mechanisms. Combined with the high
TPL action cross section, this enabled nondestructive, cross-talk free readout. This technique can be immediately applied to optical patterning, encryption and data storage, where higher data densities are pursued.

The concept of five-dimensional patterning is illustrated in Fig. 5.1. The sample consists of a multilayered stack in which thin recording layers are separated by a transparent spacer. In both the wavelength and polarization domains three-state multiplexing is illustrated to provide a total of nine multiplexed states in one recording layer. The key to successfully realizing such five-dimensional encoding is a recording material that 1) is orthogonal in all dimensions, in both recording and readout, 2) is able to provide multiple recording channels in each dimension, 3) is stable in ambient conditions and can be read out nondestructively. Existing multiplexing techniques are only orthogonal in one dimension (either wavelength, or polarization), and often ambient conditions and readout degrades the recorded patterns through unwanted isomerization or photobleaching.

We show that a recording material based on plasmonic gold nanorods exhibits all the above criteria, and can be employed for cross talk free recording and readout in five dimensions. Gold nanorods have been extensively used in a wide range of

![Figure 5.1: Sketch of the sample structure](image)

The sample consists of thin recording layers of spin coated polyvinyl alcohol (PVA) doped with gold nanorods, on a glass substrate. These recording layers were spaced by a transparent pressure sensitive adhesive with a thickness of 10 µm. In the recording layers we patterned multiple images using different wavelengths and polarizations of the recording laser. When illuminated with unpolarized broadband illumination a convolution of all patterns will be observed in the read-out. However, when the right polarization and wavelength is chosen the patterns can be read out individually without cross talk.
applications because their unique optical and photothermal properties. The narrow longitudinal SPR linewidth of a gold nanorod (100–150 meV, or ≈ 45–65 nm in the near-infrared, see section 4.2.2) combined with the dipolar optical response allows us to optically address only a small subpopulation of nanorods in the laser irradiated region. We use this selectivity to achieve surface plasmon mediated five-dimensional optical recording and readout.

5.1 Experimental

The gold nanorods were prepared by the silver-assisted seed-mediated growth method described in section 2.1. By varying the silver concentration and surfactant composition, gold nanorods with different average aspect ratios were prepared. In Fig. 5.2 we show the transmission electron microscope (TEM) images and the extinction profiles of the three distributions of gold nanorods which we used in the recording layers. From TEM image analysis we found average aspect ratios of 2.3 ± 1 (average size 37×19 nm), 4.3 ± 1 (average size 50×12 nm), and 6 ± 2 (average size 50×8 nm). After preparation, the remaining solutes were diluted by three orders of magnitude through centrifugation.

Figure 5.2: Nanorod extinction spectra Normalized extinction spectra of the as-prepared gold nanorod solutions. The insets show transmission electron micrographs of the gold nanorods on a copper grid. The average sizes of the nanorods are, from left to right, 37×19 nm (aspect ratio 2 ± 1), 50×12 nm (aspect ratio 4.2 ± 1), and 50×8 nm (AR 6 ± 2). The scale bars are 50 nm. Each recording layer in the multi-layered sample is doped with a mixture of these gold nanorods to form an inhomogeneously broadened extinction profile.
The nanorod solutions were then mixed to obtain a “flat” extinction profile in the 700–1000 nm wavelength range. This nanorod solution was mixed with a 15% wt. polyvinyl alcohol solution and spincoated on a glass coverslip. The thickness of this layer was $1 \pm 0.2 \, \mu m$, measured using an atomic force microscope. The approximate nanorod concentration in the film was $400 \pm 50 \, nM$, which is equivalent to a total of $\approx 200$ nanorods in the focal volume of the 0.95 NA objective lens used for recording and readout. A transparent pressure sensitive adhesive (LINTEC Co.) with a thickness of $10 \pm 1 \, \mu m$ and a refractive index of 1.506 was laminated onto the spincoated layer. Subsequently, another recording layer was spincoated on top of the spacer layer. This process was repeated until the desired number of layers was reached.

In Fig. 5.3 we show the increase in the extinction of the sample after subsequent spincoating of three recording layers. We observe a linear increase in extinction, indicating a consistent layer thickness and nanoparticle concentration for each layer. We measured the exact layer spacing by exciting the two-photon luminescence (TPL) of the gold nanorods at 760 nm and scanning the sample in the $z$-direction. The TPL

![Figure 5.3: Sample characterization](image)

(a) Extinction profiles after the subsequent spin coating of three recording layers. The PVA layers were doped with the broad distribution of gold nanorods depicted in Fig. 5.2. The lower panel shows the extinction spectra of the as prepared aqueous gold nanorods. (b) Depth profile of the spin coated sample. The TPL was excited at 760 nm while scanning the sample in the $z$-direction. The three curves represent a $z$-scan at three different positions in the sample, spaced by approximately 5 mm. The curves are offset for clarity.
z-scan is shown in Fig. 5.3b. The highest peak in the z-profile corresponds to TPL from the first recording layer. We measured z-scans on three different positions in the sample spaced by ~5 mm (shown as three curves in Fig. 5.3). The layer spacing did not vary by more than 0.5 µm over this distance.

The peak TPL intensity is reduced by approximately 50 % when moving from the first to the third and deepest recording layer. This reduction in TPL intensity is caused by a combination of spherical aberration and extinction by previous recording layers. The extinction of a recording layer is 0.07 at the excitation wavelength of 760 nm, and thus each recording layer reduces the light transmission by approximately 15%. Considering the two-photon nature of the excitation, the extinction by a recording layer will reduce the TPL intensity by ≈30% per layer, or ≈50% by two layers. This implies that the reduction in TPL intensity can be fully explained by the extinction by previous recording layers, and spherical aberration does not play a significant role for the three layers spaced by 10 µm employed here.

Recording of the patterns was conducted in a home built microscope. For patterning, an electro optical modulator (ConOptics Inc., 350-160) selected single pulses on demand from the pulse train of a broadband tunable femtosecond pulse laser (SpectraPhysics Tsunami, 100 fs pulse duration, 82 MHz repetition rate, tunable between 690 and 1010 nm). Using single laser pulses prevents the adverse accumulative thermal effects on the matrix which were observed in section 4.1, where a high repetition rate pulse train was employed. The laser pulses were focused onto the sample through a high numerical aperture objective lens (Olympus 0.95 NA 40x, coverslip corrected). The sample was scanned through the laser focus on an automated translation stage (Physik Intrumente).

5.2 Recording mechanism

During recording, the absorption of a laser pulse induces a temperature rise in the selected nanorods with a longitudinal SPR on resonance with the laser light wavelength and polarization. For sufficiently high laser pulse energy the selected nanorods will heat up to above the threshold melting temperature, and transform their shape into shorter rods or spherical particles. This results in a
depleted population of nanorods with a certain aspect ratio and orientation (see Fig. 5.4a), and hence a polarization dependent bleaching occurs in the extinction profile. Despite the single photon excitation of the longitudinal SPR, the threshold of the photothermal melting confines the writing process axially to within the focal volume and provides the ability to record three-dimensionally. This is in stark contrast to single photon recording by photobleaching or photo-isomerization, where the out of focus laser light would still induce recording.

To directly confirm the selective reshaping, a mixture of the gold nanorods depicted in Fig. 5.2 was spin coated on an indium tin oxide coated glass coverslip. The nanorods were embedded in a very thin PVA film (estimated <20 nm). The polymer layer was marked by femtosecond laser writing to help locate the same area before and after irradiation. We acquired scanning electron microscope (SEM)

**Figure 5.4:** **Recording mechanism** (a) A schematic illustration of the patterning mechanism. The patterning is governed by aspect ratio and orientation selective photothermal reshaping of the gold nanorods in the focal volume of the focusing objective. A linear polarized laser pulse will only be absorbed by gold nanorods which are aligned to the laser light polarization and which exhibit an absorption cross section which matches the laser wavelength. In the upper panel, the s-polarized laser light with a wavelength of 840 nm will only affect the nanorods with an intermediate aspect ratio which are aligned to the laser polarization. In the lower panel, the p-polarized laser light with a wavelength of 980 nm only reshapes the high aspect ratio gold nanorods aligned to the laser light polarization. (b),(c) SEM image of gold nanorods spin coated on an indium tin oxide coated glass coverslip (b) before and (c) after irradiation with a single femtosecond laser pulse of 840 nm with a horizontal polarization. The rods that were affected by the laser pulse are indicated with arrows. The scale bars are 100 nm.
images of gold nanorods before (Fig. 5.4b) and after (Fig. 5.4c) irradiation with a single, linearly polarized femtosecond laser pulse ($\lambda = 840$ nm and pulse energy 0.28 nJ in the focal plane of the objective). We find that only nanorods with an aspect ratio of $3.4 \pm 0.9$ within an angular range of 25 degrees with respect to the horizontal laser light polarization were affected by the laser pulse (averaged over 20 reshaped particles). As can be seen in Fig. 5.4c some of the rods were propelled from the glass interface due to a rapid change in the center of mass during the melting process, which was observed before for gold triangles. Such lift-off is prevented in our recording medium because the nanorods are embedded in a thick polymer layer.

5.3 Readout mechanisms

5.3.1 Transmission

The reshaping of the nanorods induces a bleaching in the extinction profile due to a reduction in the number of nanorods in the focal volume. To demonstrate this bleaching, we performed white light transmission spectroscopy of an individual recorded pixel. For this purpose, the spatially filtered output from a quartz tungsten halogen light source was focused onto the sample through a 0.95 NA objective lens, and collected in transmission by a condenser. The transmitted light was dispersed on a charge coupled device by a spectrograph. The transmission of the film in an unrecorded region was taken as the background, and a pixel (size at full width at half maximum $\approx 450$ nm) was recorded using a single laser pulse with a linear polarization.

In Fig. 5.5 we show the change in extinction caused by the recording laser pulse. A bleaching occurred in the extinction spectrum centered around the recording laser wavelength (indicated by the arrows in Fig. 5.5). As expected, the polarized transmission profile followed a dipolar angle dependence caused by the orientation selective reshaping of only the nanorods which are aligned to the laser light polarization. The linewidth of this bleaching is $\approx 80$–$90$ nm, which is about twice the homogeneous absorption linewidth of a typical gold nanorod. Cross talk free recording and readout can thus be achieved when the recording wavelengths are spaced by twice this linewidth, or $\approx 150$ nm.
Figure 5.5: Transmission spectroscopy of a recorded pixel. Change in extinction after irradiation with a linearly polarized, single femtosecond laser pulse of 710 nm (dark blue line) and 840 nm (light yellow line). The spectrum was measured on a single recorded pixel (size at full width at half maximum $\approx 450$ nm) by illuminating with tightly focused, linearly polarized white light. The inset shows the polarization dependent extinction modulation, with a dipolar cosine fit (solid line).

To illustrate the readout in transmission we first recorded a single image using vertically polarized laser pulses with a wavelength of 840 nm (pulse energy 0.3 nJ at the backaperture of the objective lens). The sample was then wide-field illuminated with a quartz tungsten halogen white light source. The light was narrow band filtered around the recording wavelength ($840 \pm 5$ nm) and directed toward a charge coupled device (CCD, Silicon Imaging 1920HD). The resulting background corrected image is shown in Fig. 5.6a. As expected, the recorded pixels exhibit a higher transmission due to the depleted nanorod population with a longitudinal SPR in resonance with the imaging light. We do not observe any contrast when the polarization is rotated to horizontal, (see Fig. 5.6b) or when the filter band is changed to 710$\pm 5$ nm (see Fig. 5.6c). This indicates that only the subpopulation of nanorods with a longitudinal SPR in resonance with the laser light has reshaped.

5.3.2 Two-photon luminescence

In this section we will demonstrate the SPR characteristics of TPL, and its use to the readout of multiplexed optical recordings. In Fig. 5.7a we show the TPL spectrum from an ensemble of gold nanorods (average size $45 \times 12$ nm, longitudinal
Figure 5.6: Widefield transmission readout on a CCD (a) One shot transmission readout of a pattern recorded at 840 nm with a vertical polarization. The white light was filtered around 840±5 nm, and was vertically polarized. The pattern is 75x75 pixels. The insets show the images when the white light is filtered at (b) 840±5 nm with a horizontal polarization, and (c) 710±5 nm with a vertical polarization. All scale bars are 20 µm.

SPR peak at 800 nm) in water solution excited with the femtosecond pulsed output from a Titanium Sapphire laser source (λ_{exc}= 780 nm). To confirm the two-photon excitation process, we increased the excitation power from 50 μW to 130 μW and recorded the emitted TPL intensity, see Fig. 5.7b. On a log-log scale we find a slope of 1.94, which is indicative of a two-photon excitation process.

In Fig. 5.8 we present a study on the SPR characteristics of two-photon induced luminescence (TPL) in single gold nanorods. For this purpose we spin coated a dilute solution of gold nanorods (average size 45×12 nm) in a 1% PVA solution onto a glass coverslip. The nanorod concentration was adjusted to yield ≈ 15 nanorods per 100 µm². The TPL was excited and collected by the same 0.95 NA objective lens. The TPL signal was detected by a PMT (Hamamatsu H7422-40P) in the 400–600 nm wavelength region.

In Fig. 5.8a we show a raster scan of the sample surface where diffraction limited spots indicate the location of well separated gold nanorods. In Fig. 5.8b we show the normalized TPL excitation profiles for four individual gold nanorods, which was obtained by scanning the same area on the sample with different excitation wavelengths and recording the peak intensity of single spots in Fig. 5.8a. The
peak position indicates the longitudinal SPR energy\textsuperscript{53} of the individual rods (the ensemble peak position in aqueous solution was found to be 730 nm, which is in good agreement with the single particle peak position in PVA we find here). The TPL excitation profile linewidth we find is 70±10 meV (average over 10 particles). In Fig. 5.8c we also show the excitation polarization dependence of the TPL intensity for three individual nanorods. As expected for TPL from gold nanorods, the intensity follows a $\cos^4$ dependence.\textsuperscript{210}

The TPL brightness of individual gold nanorods (average size $45 \times 12$ nm) was characterized by calculating their TPL action cross section ($=\eta \sigma_2$, where $\eta$ is the luminescence quantum yield and $\sigma_2$ is the two-photon absorption cross section). The TPL action cross section was measured directly using the formalism described by Xu and Webb.\textsuperscript{211} For a single nanoparticle, the number of fluorescence photons detected can be expressed as\textsuperscript{211}

$$F = g \phi \eta \sigma_2 I^2,$$

where $g$ is the degree of second-order temporal coherence of the excitation source,
Figure 5.8: Two-photon luminescence of single gold nanorods (a) Raster scan of the sample surface showing diffraction limited spots indicating the location of isolated single gold nanorods. The TPL was excited with circularly polarized laser light at 760 nm, and detected at 400–600 nm. Bar length 3 µm. (b) Normalized excitation profile of the TPL intensity of four individual gold nanorods obtained by raster scanning the sample surface with different excitation wavelengths. The TPL intensity was obtained by integrating the photomultiplier tube voltage over the individual spots in (a). (c) TPL intensity versus polarization angle of the excitation laser light, with cos^4 fits.

\( \phi \) is the collection efficiency of the setup, \( I \) is the incident photon flux (in photons/s/cm^2), and \( \eta \sigma_2 \) is the two-photon action cross section (in cm^4 s/photon), with \( \eta \) the fluorescence quantum yield and \( \sigma_2 \) the two-photon absorption cross section. Typical values in our experiment are \( g = 1.9 \times 10^5 \), \( \phi = 0.17 \), and \( I = 1 \times 10^{23} \) photons/s/cm^2. The number of detected fluorescence photons \( F \) was extracted from the peak value in the TPL excitation profile (see for example Fig. 5.8b) by considering the sensitivity of the photomultiplier tube.

We estimate the TPL action cross section of a single gold nanorod to be \( \sim 3 \times 10^4 \) GM for excitation on resonance with the longitudinal SPR. From the TPL action cross section, the two-photon absorption cross section \( \sigma_2 \) can be calculated if the luminescent quantum yield \( \eta \) is known. Previous reports on photoluminescence of gold nanoparticles\(^{212-214} \) suggest that the quantum yield of the nanorod geometry is drastically increased compared to spherical particles\(^{213} \) or films.\(^{47} \) The so-called "lightning rod effect" around a nanorod is known to enhance the local field strength and the radiative decay rate via coupling to the surface plasmon resonance, and
has been used to explain the observed increase in quantum yield from $10^{-10}$ for a film to $\sim 10^{-4}$ for rods with a size and aspect ratio similar to the ones studied here. Assuming the reported quantum yield, we estimate that the two-photon absorption cross section $\sigma_2$ is $\sim 3 \times 10^8$ GM. This is to our best knowledge the highest $\sigma_2$ ever observed, with the previous report being $3.5 \times 10^6$ GM for a 4 nm gold nanoparticle. We propose that this drastic increase is caused by the two orders of magnitude larger volume and intrinsically higher optical cross section of our nanorods compared to the 4 nm diameter gold nanoparticles used in the study by Ramakrishna et al. The current direct measurement of the TPL action cross section is also one order of magnitude larger than the value of $2.3 \times 10^5$ GM as reported by Wang et al., which was indirectly determined by comparing the brightness of a single Rhodamine 6G molecule to a single gold nanorod. The large TPL action cross section allows us to nondestructively image the recordings by using very low excitation powers.

Previous reports on patterning in gold nanoparticles all employed linear detection processes based on scattering or extinction. However, a nonlinear detection process such as TPL has a significantly higher angular and wavelength sensitivity. To demonstrate this, we compared the scattering and TPL excitation profiles of a single gold nanorod (average aspect ratio 3, average size 90×30 nm) both as a function of wavelength and polarization (see Fig. 5.9a and b). Firstly, the nonlinear character of the TPL induces an excitation profile linewidth which is almost 60% narrower than the linewidth of the linear scattering spectrum (see Fig. 5.9a). Furthermore, we find a reduction of almost 50% in the width of the angular excitation profile (see Fig. 5.9b), which is in good agreement with previous observations. The observed narrowing of the spectral and angular excitation profiles significantly reduces interference in the readout between neighbouring recording channels. Even more so, the axial sectioning induced by two-photon excitation allows for crosstalk free readout of closely spaced layers. The most fascinating property of TPL is that it is most efficiently excited on resonance with the linear plasmon absorption band, enabling single photon recording and multiphoton readout using the same wavelength.
To demonstrate the TPL readout, we again imaged the pattern in Fig. 5.6. The recorded pattern (displayed in Fig. 5.9c) was retrieved by raster scanning the sample and detecting the TPL signal from the gold nanorods. The TPL was excited with the same wavelength and polarization which was used for the patterning. The pixels exhibit a lower TPL signal due to a depleted population of nanorods with an longitudinal SPR in resonance with the readout laser light.

Figure 5.9: Two-photon luminescence readout (a) Normalized white light scattering spectrum (solid line) and TPL excitation profile (circles) of individual gold nanorods with approximate dimensions of 90×30 nm. The profiles were centered around the longitudinal SPR peak. (b) Polarized scattering (open squares) and TPL intensity (solid circles) versus the polarization of the excitation light. (c) Normalized TPL raster scan of an image patterned using single laser pulses per pixel with a wavelength of 840 nm and a vertical polarization. The TPL was excited with the same wavelength and polarization as was used for the patterning. The pattern is 75×75 pixels, with a pixel spacing of 1.33 μm. The inset shows a high magnification image of the recording (size 7×7 μm). The figures on the right show the images when the TPL is excited at (d) 840 nm with a horizontal polarization, (e) 710 nm with a vertical polarization, and (f) 980 nm with a vertical polarization. All scale bars are 20 μm.
average pixel size from high resolution TPL raster scans, and found a full width at half maximum of $500 \pm 100$ nm after deconvolution with the point spread function of the imaging objective lens. This value is close to the diffraction limited spot size of $470$ nm for focusing of $840$ nm light through a $0.95$ NA objective lens. The contrast (defined as $|I_{\text{pixel}} - I_{\text{background}}|/(I_{\text{pixel}} + I_{\text{background}})$) of the imaged pixels using TPL readout was $0.7$. When this image was read in transmission mode (see Fig. 5.6) the contrast was found to be $0.05$. Considering the nanorod concentration (see section 5.1), we estimate that this contrast arises from the reshaping of $\approx 30$ nanorods in the focal volume. We do not observe any contrast when the TPL is excited with a horizontally polarized laser beam (see Fig. 5.9d) or when the wavelength is tuned to $700$ nm or $980$ nm (see Fig. 5.9e and f). This indicates that only the subpopulation of nanorods with a longitudinal SPR in resonance with the laser light has reshaped.

### 5.4 Five-dimensional recording

Using the longitudinal SPR mediated recording and TPL readout mechanisms we achieved for the first time five-dimensional optical recording. In Fig. 5.10 we show TPL raster scans of eighteen images, all patterned in the same area. The patterning was done using single femtosecond laser pulses per pixel of $700$ nm, $840$ nm, and $980$ nm, with both horizontal and vertical polarization. Images were patterned in three layers with a layer spacing of $10 \, \mu \text{m}$ and a pixel spacing of $1.33 \, \mu \text{m}$. The laser pulse energy and the patterning wavelengths were optimized to minimize cross talk between the different patterning channels. The images in the first layer were patterned using pulse energies of $0.21$ nJ at $700$ nm, $0.22$ nJ at $840$ nm, and $0.32$ nJ at $980$ nm (all pulse energies in the focal plane). For patterning in subsequent (deeper) layers, the pulse energy was increased by $20\%$ per layer to compensate for extinction by previous layers.

We have also performed three-state polarization encoding, which potentially increases the number of independent recording channels to as many as nine. The recording was done using single femtosecond laser pulses at $840$ nm with a pulse energy of $0.16$ nJ in the focal plane of the objective. Patterns were recorded using linear laser light polarizations of $0$, $60$, and $120$ degrees relative to the laboratory...
Chapter 5. 5D optical recording

Figure 5.10: Five dimensional patterning and readout Normalized TPL raster scans of eighteen patterns encoded in the same area using two laser light polarizations and three different laser wavelengths. Patterns were written in three layers spaced by 10 µm. The recording laser pulse properties are indicated. The recordings were retrieved by detecting the TPL excited with the same wavelength and polarization as employed for the recording. The size of all images is 100x100 µm, and the patterns are 75x75 pixels.

frame. The recorded patterns were imaged by detecting the TPL excited with the same wavelength and polarization as was used for the recording. The result is shown in Fig. 5.11, where we observe cross talk free recording and readout.

Figure 5.11: Three state polarization encoding Three state polarization encoding with single femtosecond laser pulses (λ = 840 nm, pulse energy 0.16 nJ.) The patterns were imaged by exciting the TPL at 840 with a linear polarization and detecting the TPL at 400-600 nm. The images are 75×75 pixels and measure 100×100 µm.
While we used a femtosecond pulse laser for patterning, the recording can also be done with a continuous wave (CW) laser or laser diode, paving the way for a low-cost patterning apparatus. To demonstrate this, patterning was performed using a titanium sapphire laser source, operating in continuous wave mode. The CW laser power was 80 mW at the back aperture of the 0.95 NA objective lens (60 mW in the focal plane). The exposure time on the sample was controlled by an electro-optic modulator, and was 10 ns per pixel. In Fig. 5.12 we show TPL raster scans of two polarization multiplexed images, recorded at 840 nm with a linear polarization (indicated by the arrows). The TPL was excited using the pulsed output from the titanium sapphire laser and was excited with the same wavelength and polarization as was used for recording.

Compared to recording with femtosecond laser pulses, the pulse energy required for CW recording at 840 nm has increased from 0.22 nJ to 0.8 nJ. This sharp increase is caused by the competition between laser induced heating and dissipation to the environment. In the case of femtosecond laser pulses the nanorod reaches its maximum temperature after less than 5 ps (see Section 3.3). The timescale for dissipation to the environment is several hundreds of picoseconds in PVA (see Section 1.2.3), so in the case of femtosecond laser irradiation the two timescales are decoupled. However, in the case of excitation with a nanosecond exposure time, a significant amount of heat has dissipated to the environment before the end of the

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\text{Figure 5.12: Patterning with a continuous wave laser source} \quad \text{Polarization encoding with a continuous wave laser source of 840 nm. The laser power was 80 mW at the back aperture of the objective lens, and the exposure time per pixel was } \approx 10 \text{ ns. The patterns were imaged by exciting the TPL at 840 with a linear polarization and detecting the TPL at 400–600 nm. The images are } 75 \times 75 \text{ pixels and measure } 100 \times 100 \mu \text{m.}
\]
Figure 5.13: Recording in many layers Polarization multiplexed recording in ten layers spaced by 10 µm. The recorded patterns were detected by exciting the TPL at 840 nm, and detecting in the 400–600 nm window. The inset on the right shows a 6×6 µm high magnification image of the area indicated by the square.

laser pulse. This heat loss is compensated for by the higher pulse energy required for patterning.

To demonstrate the feasibility of our technique for high density optical data storage on a disc, we demonstrate optical recording in ten layers spaced by 10 µm. The patterns in Fig. 5.13 (100×100 µm, 75×75 pixels) were recorded using single femtosecond laser pulses at 840 nm. The recording pulse energy for each layer was optimized to yield the best contrast without noticeable cross talk. As is shown by the inset in Fig. 5.13, we can record in the tenth layer without noticeable loss of spatial resolution and sensitivity.
5.5 Conclusion

We have for the first time achieved true five-dimensional optical recording by exploiting the unique properties of the longitudinal surface plasmon resonance (SPR) of gold nanorods. The longitudinal SPR was shown to exhibit excellent wavelength and polarization sensitivity, whereas the distinct energy threshold required for the photothermal recording mechanism provided the axial selectivity required for recording in close spaced layers. We employed two-photon luminescence detection because of the enhanced wavelength and angular selectivity compared to conventional linear readout mechanisms. Combining these techniques we patterned 18 images in one recording volume (three wavelength states and two polarization states per layer, in three layers spaced by 10 μm).

Using this technique, improved security imprinting and encryption can be realized, where the added dimensions can act as an extended and counterfeit proof encryption key. In such practical applications one can obtain immediate access to the patterns by wide-field transmission readout on a CCD. This technique allows for one-shot readout of patterns, and when multiple CCDs are employed it can provide instant and simultaneous readout of all recorded patterns. Additionally, the modulation of the transmission introduced by the patterns can be employed as a polarization and wavelength dependent signal modulator for optical devices. For example, the large extinction of gold nanorods allows for customized modulation in multiple wavelength bands of a super continuum light source. This can be accomplished in a single (on chip) filter, which does not suffer from bleaching and exhibits a high damage threshold of > 10 mJ cm^{-2} (based on the recording/reshaping threshold we found in the presented experiments).

Most importantly, the presented technique could be highly beneficial for high density optical data storage. As demonstrated in Fig. 5.10, incorporation of two polarization and three wavelength channels, a 10 micron spacer layer, and a bit spacing equal to the bit diameter of 0.75 μm mounts to a bit density of 1.1 Tbit/cm^{3}. This results in a disk capacity of 1.6 Tbyte for a DVD sized disk. We have performed recording and readout in ten layers, demonstrating the feasibility of our technology for application on a disk. Further improvement in data capacity is warranted if three-
state polarization encoding is combined with a thinner spacer. A three-fold reduction in spacer layer thickness is feasible considering the recording layer thickness of 1 µm, resulting in a disk capacity of 7.2 Tbyte. Our bit-by-bit recording technique is fully compatible with existing drive technology and allows for recording speeds up to 1 Gbit/s when a high repetition rate laser source is employed.
Chapter 6

Conclusion

6.1 Thesis conclusion

In this thesis we have studied the photothermal properties of gold nanorods, and we employed the efficient photothermal reshaping to achieve for the first time five-dimensional optical recording.

For a recording medium to be commercially attractive one requires an efficient synthesis protocol which can rapidly produce the required building blocks, preferably at a large scale. To this end we have developed a wet-chemical synthesis protocol which produces gold nanorods at elevated temperatures. We eliminated the need for preparation of a seed solution, which dramatically increases the reproducibility of the method because the properties of seed solutions are not easily repeated, and are also temporally labile. Our seed-less growth method is ultimately suitable for continuous flow synthesis, and combined with the viability at high temperature allows for the rapid and reproducible synthesis of large amounts of gold nanorods. Such a synthesis protocol paves the way for commercialization of gold nanorod based devices.

The recording mechanism we proposed to achieve five-dimensional recording entails photothermal melting and reshaping of gold nanorods in the laser focus. To obtain a better understanding of the processes involved in femtosecond laser pulse excitation we have studied the excitation dynamics in single gold nanorods. The electron-phonon coupling was visualized using an ultrafast spectroscopic technique,
which probes the transient bleach of the longitudinal surface plasmon resonance caused by the increased scattering rate of the hot electrons. After absorption of the pump laser pulse by the electrons we observed electron-phonon energy transfer on a timescale of several picoseconds. Using this technique we determined the electron-phonon coupling constant in single gold nanorods, which was found to be in good agreement with previous reports on ensembles of gold nanoparticles and gold films.

The process of electron excitation and electron-phonon relaxation also excites mechanical vibrations in the particle. The frequency of these vibrations contains valuable information about the exact shape and size of the particle, but most importantly they can reveal the particle’s elastic moduli. Recently, experiments on mechanical vibrations of semiconductor nanoparticles have shown that their elastic properties are strongly size-dependent. Such size-effects have also been predicted in theoretical studies on the elastic properties of metal nanoparticles. However, contrary to semiconductor nanocrystals, the synthesis protocols for metal colloids often result in a large size dispersion. Therefore, when measurements are conducted on ensembles of nanoparticles the size effects are likely to be screened due to effects of inhomogeneous broadening. Our single particle results are the first step toward experimentally exploring the effects of particle size on the elastic moduli of metal nanoparticles. Contrary to earlier reports on ensembles of nanoparticles, we found that continuum elasticity theory is compatible with the measured vibrations of large free nanorods and with bulk gold’s elastic moduli. Deviations in measured frequencies were attributed to effects of the local mechanical environment.

These fundamental spectroscopic studies were performed on gold nanorods deposited on a substrate. Doping of the nanorods into a matrix is key to successful application of the particles in optical recording. When a femtosecond pulse laser source is applied, we often deal with high pulse energies and a high repetition rate. While a polymer such as polyvinyl alcohol (PVA) is an attractive matrix because of its mechanical properties and ease in doping, its low $T_g$ and softness compared to other dielectric materials warrants a low damage threshold. We have studied both experimentally and theoretically the laser writing in a gold nanorod doped polyvinyl alcohol (PVA) film for various laser spot sizes at two different laser pulse repetition
rates. The recording mechanism we employed was photothermal reshaping, in which the permanent bleach of the extinction profile around the laser wavelength was detected in a transmission microscope. We found that a high repetition rate laser source induces heat accumulation in the PVA matrix and caused damage to the matrix, even when low numerical apertures were employed. The accumulative heating was caused by the low cooling rate of the focal volume compared to the repetition rate of the employed laser source. This study indicated that reshaping of the gold nanorods is a single pulse process, whereas the damage to the matrix was a multiple pulse effect. This study indicated that single laser pulses would be the most suitable for stable optical recording in a polymer matrix.

To gain more insight into the reshaping of gold nanorods in a polymer matrix, we studied this process on single gold nanorods. With increasing pulse energies, we observed a gradual shape change from a long nanorod to a shorter and fatter nanorod, before the particle finally relaxed to the spherical shape. We found that the energy required for complete melting and reshaping into a spherical particle is in good agreement with the expected value for bulk gold, indicating that size effects do not play a role in these particles. Furthermore, we observed that higher aspect ratio particles are thermodynamically less stable, leading to a more pronounced partial reshaping. These experiments demonstrated that single gold nanorods constitute an attractive system to study melting and reshaping of small metal particles, and could reveal size effects on a single particle level when small particles are employed.

We have applied this photothermal reshaping of gold nanorods toward multidimensional optical recording. We achieved for the first time five-dimensional optical recording by exploiting the unique properties of the longitudinal surface plasmon resonance of gold nanorods. The longitudinal surface plasmon resonance was shown to exhibit excellent wavelength and polarization sensitivity, whereas the distinct energy threshold required for the photothermal recording mechanism provided the axial selectivity required for recording in closely spaced layers. We employed two-photon luminescence detection because of the enhanced wavelength and angular selectivity compared to conventional linear readout mechanisms. Combining these techniques we patterned 18 images in one recording volume (three wavelength states and two polarization states per layer, in three layers spaced by 10 µm).
Chapter 6. Conclusion

Using this technique, improved security imprinting and encryption can be realized, where the added dimensions can act as an extended and counterfeit proof encryption key. In such practical applications we showed that one can obtain immediate access to the patterns by wide-field transmission readout on a CCD. This technique allows for one-shot readout of patterns, and when multiple CCDs are employed it can provide instant and simultaneous readout of all recorded patterns. Additionally, the modulation of the transmission introduced by the patterns can be employed as a polarization and wavelength dependent signal modulator for optical devices. For example, the large extinction of gold nanorods allows for customized modulation in multiple wavelength bands of a super continuum light source. This can be accomplished in a single (on chip) filter, which does not suffer from bleaching and exhibits a high damage threshold of \( > 10 \text{ mJ cm}^{-2} \) (based on the recording/reshaping threshold we found in the presented experiments).

Most importantly, the presented technique could be highly beneficial for high density optical data storage. We have demonstrated a bit density of 1.1 Tbit/cm\(^3\), resulting in a disk capacity of 1.6 Tbyte for a DVD sized disk. We have performed recording and readout in ten layers, demonstrating the feasibility of our technology for application on a disk. Further improvement in data capacity is predicted if three-state polarization encoding is combined with a thinner spacer, which could increase the disk capacity to 7.2 Tbyte. Our bit-by-bit recording technique is fully compatible with existing drive technology and allows for recording speeds up to 1 Gbit/s when a high repetition rate laser source is employed.

6.2 Outlook

The research in this thesis can be further extended towards a more comprehensive understanding of the photothermal properties of small metal nanoparticles, and their application in a commercially available recording disc.
6.2.1 Size effects on photothermal and elastic properties

A logical continuation of the experiments described in Chapters 3 and 4 is the extension to smaller nanoparticles. As we discussed, pronounced size effects are expected when the dimensions of the particle are below 10 nm. Size effects on thermal and elastic properties of single particles remain elusive because it is challenging to optically detect a particle smaller than 10 nm, even with the recently reported photothermal detection techniques. Gold nanorods are therefore ultimately suitable to explore these size effects, because their optical cross sections are much larger than for gold spheres, enabling detection of particles with a significantly smaller volume.

Also, the experiments should be extended to nanoparticles which are embedded in a completely homogeneous medium. The experimental observation and isolation of environment effects on the thermal and elastic properties remains extremely challenging. This is mainly caused by the difficulty of creating a completely homogeneous environment (even when embedded in polyvinyl alcohol we observed sizable effects of the local environment in this thesis). One attractive approach may be to optically trap the nanoparticles in water solution. This would eliminate any environmental defects, and allows one to easily change the environment by trapping the particle in a different solvent.

Interestingly, the reduction of the melting temperature for small particles may have drastic effects on the photothermal recording mechanism we proposed. When smaller particles are employed, a higher number density can be achieved in the recording medium, resulting in an enhancement of the pixel contrast. A higher particle concentration would also allow for super-resolution recording by, for example, near-field excitation using a scanning near-field optical microscope. More importantly, the reduced melting temperature would lead to a reduction in pulse energy required for the recording of a pixel. This reduces the specifications of the laser source for recording, and results in a lower energy consumption of the commercial device. Therefore, exploration of synthesis protocols to controllably achieve smaller particle sizes, and their application in photothermal recording is an attractive continuation of the research presented in this thesis.
6.2.2 Recording with a supercontinuum laser source

Owing to the low recording pulse energy (< 0.5 nJ per pulse), a drastic increase in recording speed can be achieved when a supercontinuum light source is employed for simultaneous recording in all channels. A supercontinuum source is capable of generating wavelengths ranging from 500 nm into the near infrared, which covers the wavelength range employed for recording in this thesis. The pulse duration of a generated white light is generally under a picosecond, so adverse effects from the competition between particle heating and dissipation to the environment are not expected. When such a source is employed to simultaneously record in all nine channels (three polarization channels and three wavelength channels), the recording speed can be increased to 9 Gbit/s when a 1 GHz source is employed.

6.2.3 Dynamic testing

In order to test the suitability of our proposed recording medium to be used in an optical drive, dynamic testing in a prototype drive with the appropriate error correction algorithms is required. This will ultimately determine the signal to noise ratio and error rates, and allows us to optimize these parameters to meet market standards. Dynamic testing requires a circular disc on a solid substrate like polycarbonate. Although not reported in this thesis, we have explored the spin coating on large area substrates, and found that the quality of the spin coating is proportional to the substrate area. This indicates that fabrication of a multi-layered disc structure is feasible, which would allow for dynamic testing and ultimately the design of a commercial drive exploiting photothermal recording using plasmonic nanoparticles.
Bibliography


List of publications

Publications related to this thesis


Publications not related to this thesis


Conference proceedings and abstracts (presenter underlined)


