Synthesis and Alignment of Volume and Shape Controlled Gold Nanorods

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Recently, gold nanoparticles (AuNPs), have been widely used in surface-enhanced Raman scattering (SERS)\cite{1,2}, fluorescence enhancement\cite{3,4}, biological imaging and sensing\cite{5,6}, and photo activated cancer treatment\cite{7,9}, because of their unique optical and physical properties that result from their small size. The most intriguing optical feature is electromagnetic resonance, also known as surface plasmon resonances (SPR), of the conduction electrons in the gold nanorods. These SPRs give rise to a strong interaction with light. In this chapter, I will theoretically explain that the wavelength where the surface plasmon resonances occur depends on the local environment, shape, and size of the gold nanoparticles.

1.1 Surface Plasmon Resonance of Gold Nanospheres

To describe the optical properties of gold nanorods, it is better firstly to discuss the optical properties, the absorption and scattering in particular, of gold nanospheres, due to the simple symmetric shape in 3 dimensional space. The absorption and scattering of light by spherical particles of arbitrary size was first studied by Gustav Mie\cite{10} in 1908, and is known as Mie theory. The Mie theory describes the absorption of a plane wave by a homogeneous sphere with arbitrary size. Employing the suitable boundary conditions on the sphere’s surface and at infinity, Maxwell’s equations can be solved\cite{11}.

Accordingly, the optical properties of the sphere depend on the radius of the sphere $R$, the dielectric function of both the sphere $\epsilon_l$ and the surrounding medium $\epsilon_m$. The scattering and extinction cross-sections can be written as\cite{11}

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

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

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

$$
a_n = \frac{m\psi_n^\prime(mx)\psi_n(x) - \psi_n(mx)\psi_n^\prime(x)}{m\psi_n^\prime(mx)\zeta_n(x) - \psi_n(mx)\zeta_n^\prime(x)}, \quad \text{and}
$$

$$
b_n = \frac{\psi_n^\prime(mx)\psi_n(x) - m\psi_n(mx)\psi_n^\prime(x)}{\psi_n^\prime(mx)\zeta_n(x) - m\psi_n(mx)\zeta_n^\prime(x)},
$$

where $x = \sqrt{\epsilon_m k R}$ is the size parameter of the system, $m = \sqrt{\epsilon_l/\epsilon_m}$, and $\psi_n$ and $\zeta_n$ are the Bessel functions of order $n$. The prime indicates the first order differentiation of these functions. The absorption cross-section, can be obtained according to\cite{11}
\( \sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{sca}}. \)  

(1.5)

The dielectric function of gold, which is required to calculate the cross-sections, was measured by Johnson and Christy\(^{[12]}\). Using their measurements and according to equation (1.5), the absorption cross-section of gold nanospheres with different sizes can be calculated. Fig. 1.1 shows the calculated results for nanospheres with a radius ranging from 10 nm to 40 nm (by P. Zijlstra\(^{[13]}\)). With the increasing of sphere size, the absorption cross-section increases significantly but the surface plasmon resonance stays nearly constant around 530 nm.

![Figure 1.1: Calculated optical cross-section of gold spheres with a radius ranging from 10 nm to 40 nm. The dielectric constant of the surrounding medium \( \epsilon_m \) is 2.25 in this calculation. This figure is taken from the PhD thesis by P. Zijlstra\(^{[13]}\).](image)

1.2 Surface Plasmon Resonance of Gold Nanorods

In contrast to the case of nanospheres, the theoretical solution of absorption and scattering by cylinders with finite length is too complicated to calculate directly. Therefore, the rods are treated as very small ellipsoids. The solution has been developed by Gans in 1912\(^{[14]}\). For simplicity, we only consider the condition of rods that are much smaller than the wavelength of the incident light. In this case, the gold nanorod can be approximated as an ideal dipole (quasistatic approximation), and the field outside the rod can be treated as a superposition of the incoming electromagnetic wave and the field of a dipole. Supposing the gold ellipsoid has two different semi-axes lengths \( a > b = c \), the polarizability in the field parallel to one of its axes can be written as\(^{[11]}\)

\[ \alpha_p = 4\pi abc \frac{\epsilon_l - \epsilon_m}{3\epsilon_m + 3L_p(\epsilon_l - \epsilon_m)}, \]  

(1.6)

where \( p = 1, 2, 3 \) indicates the different polarizations of light with respect to one of the three axes, and \( L_p \) is the geometrical depolarization factor. For prolate spheroids, \( L_p \) can be written as\(^{[11]}\)

\[ L_1 = \frac{1 - e^2}{e^2} (-1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e}), \]  

and

\[ L_2 = L_3 = \frac{1 - L_1}{2}, \]  

(1.7)  

(1.8)
where $e^2 = 1 - b^2/a^2$. The extinction and scattering cross-sections can then be expressed as

\[ \sigma_{\text{ext}} = k \cdot \text{Im}(\alpha), \text{ and} \]

\[ \sigma_{\text{sca}} = \frac{k^4}{6\pi} |\alpha|^2, \]

and the absorption cross-section of a gold nanorod can be calculated according to Eq. (1.5).

When the polarization of the incident light is parallel to different axes of the rod (ellipsoid), the absorption cross-sections are different. As a result, the surface plasmon resonance is split into two parts, namely the longitudinal surface plasmon (when $L_1$ is used) and the transverse surface plasmon (when $L_2 = L_3$ is used). According to Eq. (1.6), the wavelength where the longitudinal plasmon occurs depends strongly on the eccentricity $e$ of the ellipsoid (or aspect ratio of the rod) and there is an almost linear relation between them in the quasistatic approximation (see Fig. 1.2 from P. Zijlstra\textsuperscript{[13]}). On the other hand, the wavelength where the transverse plasmon occurs does not change with increasing aspect ratio, and occurs always around 530 nm.

![Figure 1.2: (a). Calculated absorption cross-sections with different aspect ratios. The semi-major axis length $a$ was chosen from 15 to 35 nm, while the semi-minor axis length was kept at 7.5 nm. (b), Aspect ratio dependence of the longitudinal and transverse surface plasmon resonance for spheroids. The longitudinal one shows a linear dependence and shifts strongly with aspect ratio, while the transverse plasmon stays almost the same. The dielectric constant of the surrounding medium was chosen as 2.25 for all the calculations. This figure is copied from the PhD thesis by P. Zijlstra\textsuperscript{[13]}.](image)

Another feature of nanorods that was used in my project is the relation between their absorption cross-section and the relative orientation with respect to the polarization of the incident light. As the name indicates, when the long axis of the rod is perpendicular to the polarization of light, it only absorbs the light around 530 nm, and that is the transverse plasmon resonance. On contrast, when the long axis is parallel to the polarization of light, it only absorbs the wavelength which depends on its aspect ratio, that is, the longitudinal plasmon resonance. The complete dependence of the angle absorption between the major axis of rod and polarization of light was calculated and plotted in Fig. 1.3. The absolute value of the absorption cross-section of the longitudinal surface plasmon resonance follows a cosine squared dependence on this angle. For 0 or 180 degree (parallel) it reaches the maximum value and for 90 or 270 degree (perpendicular), it goes to 0. According to this figure, even if the rod is not completely parallel to the polarization, it still absorbs some light at the longitudinal plasmon band.

The orientation dependent cross-section can only be exploited when the nanorods possess same degree of alignment with respect to the polarization of the light. Such alignment would enable one to fabricate optical devices such as filter which exhibit a strong wavelength and polarization dependent optical response.
1.3 This thesis

The structure of this thesis is as follows.

Ch 2: The chemical synthesis of gold nanorods using seed-mediated growth is described. I will show that the aspect ratio of gold nanorods can be controlled from 2 to 4.7 corresponding to a longitudinal plasmon from 600 to 870 nm, while the volume can be controlled from 1,300 to 36,000 nm$^3$ (30x).

Ch 3: The alignment of gold nanorods in an electric field in aqueous solution is studied. The torque exerted on an induced dipole is shown to be proportional to the volume of the rod and to the electric field squared. I will show the volume and $E^2$ dependence I got from experiment in this chapter.

Ch 4: The alignment of gold nanorods in a magnetic field in aqueous solution is described. The basic theory of the alignment in a magnetic field is the same as that in an electric field. This part of the experiment resulted from a collaboration with Dr. P.C.M. Christianen from Radboud University Nijmegen using birefringence of gold nanorod solution. Even though it was only a test experiment, a good result was obtained. Further research needs to be done systematically.

Ch 5: The conclusions are drawn and suggestions for further experiments are given.
Chapter 2

Synthesis of Gold Nanorods

2.1 Introduction

There are two approaches to make metal nano particles (NP). The "top-down" approach, which has been developed for several tens of years in the semiconductor industry, uses Electron Beam Lithography (EBL) or Focused Ion Beam Etching (FIB) to fabricate the metal nano particle. The biggest advantage of "top-down" approach is that, it allows a good control of a large number of different structures and patterns. However, it can only make 2-D particles, such as cuboid and cubes. Rod shape or sphere shape can not be fabricated by this method. Furthermore, because of the resolution of the EBL and FIB, sharp corners cannot be obtained neither, and the roughness of the metal surface, the variation of the particle size are also problems. The "bottom-up" approach, on the other hand, uses capping agents or surfactant to control the growth of metal nano particles. The advantages of the "bottom-up" approach are: the smooth surface in atom scale produced; the cheaper and easier way to produce NP; a full control of 3-D shape of NP. The biggest drawback of this approach is that, although complex configuration such as star-shaped NPs are reported to be made\footnote{15}, it is still difficult to make arbitrary configurations.

Seed-mediated synthesis or seed-mediated growth method, which is one of the "bottom-up" approaches, is proved to be very suitable for making metal nanoparticles. Using this method, the aspect ratio of the gold nanorods can be varied from 1.5 to 10, according to B. Nikoobakht and M. A. El-Sayed\footnote{16}. In their study, hexadecyltrimethylammonium bromide (CTAB) was used as surfactant to make aspect ratio from 1.5 to 4.5, while for larger aspect ratio, a binary surfactant mixture of benzyldimethylhexadecylammonium chloride (BDAC) and CTAB was used. To date, there was no report discussing the control of length and width of gold nanorods respectively. By systematically varying the concentration of chemical compounds on the reaction mixture, I will show that tuning length and width respectively is achieved, and as a result, the volume and shape of the gold nanorods are controlled.

2.1.1 Theory of Synthesis

Though it can be dated back to 1989 that Wiesner and Wokaun\footnote{17} produced anisometric gold colloids, the current concept of seed-mediated growth method started in 2001, as reported by Jana et al\footnote{18}. They succeeded in producing rod-like gold nanoparticles by adding citrate-capped small gold spheres (seeds) to a mixture of \( Au^+ (H Au Cl_2) \), which was reduced from \( Au^{3+} (H Au Cl_4) \) by ascorbic acid in the presence of CTAB and silver ions. In 2003, Nikoobakht and El-Sayed\footnote{16} replaced the citrate seeds with CTAB stabilized particles, and they demonstrated the control of aspect ratio by adjusting the silver concentration in the growth solution.
Although, there is no clear theory that can exactly explain the growth process of gold nanorods until now, Orendorff and Murphy\cite{19} proposed a silver underpotential deposition (UPD) mechanism by combining the UPD\cite{20}, electric-field-directed growth\cite{21} and a surfactant preferential binding growth mechanism\cite{22},\cite{23}. According to Fig. 2.1, \( \text{AuCl}_2^- \)-CTAB micelles, which are reduced from \( \text{AuCl}_4^- \)-CTAB by ascorbic acid, collide with CTAB-capped gold seeds, leading to sphere symmetry breakdown and different facets with preferential binding of CTAB. The reduction of silver ions on the side face, \{110\} for example, is faster than that on the end face (\{100\}) because of a greater positive shift in potential for silver UPD on \{110\}\cite{24}. The deposition of silver inhibits the gold growth on the sides of the rods, resulting in the growth of a rod shape. The relatively slow deposition of \( \text{Ag}^- \) on the two end faces of rods finally stops the growth procedure.

![Silver underpotential deposition (UPD) mechanism proposed by Orendorff and Murphy.](image)

\footnotesize Figure 2.1: Silver underpotential deposition (UPD) mechanism proposed by Orendorff and Murphy. The red color represents the gold (\( \text{Au}^0 \)) while the green color represents the silver \( \text{Ag}^0 \). This figure is copied from \cite{19}

### 2.2 Experimental

Hexadecyltrimethylammonium bromide (99%), sodium borohydride (\( \geq 98\% \)), gold(III) chloride hydrate (99.999%), L-ascorbic acid (\( \geq 98\% \)) and silver nitrate (99.99%) for producing gold nanorods were all brought from Sigma-Aldrich. PharmaSpec UV-1700, a UV-Visible spectrophotometer from SHIMADZU, was used for measuring the absorption spectrum of the solution of gold nanorods between 500 and 1000 nm.

To measure the length and width of gold nanorods, a scanning electron microscope (SEM), FEI NanoSEM 200 owned by the Condensed Matter Physics group of Leiden Institute of Physics, was
used. The resolution of this SEM is $\sim 1 \text{ nm}$. For imaging in the SEM, samples should be conductive and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Nonconductive samples tend to be charged when scanned by the electron beam, which affects the quality of the images. Therefore, the gold nanorods were separated from CTAB by centrifugation (Eppendorf 5424).

To keep the AuNRs from aggregating, 14000 rpm of centrifugation speed and 6 to 10 min of time duration were set for large and small gold nanorods respectively. Supernatant containing CTAB and excess chemicals was discarded, and the pellet containing the nanorods was redispersed in milliQ water. This procedure was repeated once again. 1 $\mu$L of this solution was cast onto a silicon substrate. After keeping the sample in air at room temperature for about 10 hours, all the water evaporated and only gold nanorods as well as a little CTAB were on the silicon substrate. Sample then was gently rinsed by milliQ water, and the rest of CTAB was washed away, but gold nanorods stayed because of the van der Waals force between them and the silicon substrate. Drying the sample with $N_2$, clean samples for SEM were obtained.

2.3 Results

2.3.1 Tuning the Width by Varying Silver Concentration

The Preparation of Seed Solution

6.4 mg sodium borohydride ($NaBH_4$) powder was mixed with 10 mL ice-cold water. 25 $\mu$L of 100 mM $HAuCl_4$ was added into 10 mL 0.1 M CTAB solution. While vigorously stirring the mixture, 0.6 mL ice-cold $NaBH_4$ solution was added, resulting in the color of the mixture changing from golden to brownish yellow. Continuing vigorous stirring for 2 mins, I kept the solution at 25°C for 2 hours. Note that the 6.4 mg sodium borohydride is a large excess to make sure all the $Au^{3+}$ ions are reduced to $Au$ atoms.

The Preparation of Growth Solution

25 $\mu$L of 100 mM $HAuCl_4$ was added into 5 mL 0.1 M CTAB solution. To 8 flasks of this solution, 3.1, 6.3, 9.4, 12.5, 21.9, 31.3, 37.5, 46.9 $\mu$L of 16 mM $AgNO_3$ were added, so the concentration of the silver ions was 0.01, 0.02, 0.03, 0.04, 0.07, 0.1, 0.12, 0.15 mM respectively. 27.5 $\mu$L of 100 mM ascorbic acid was added into each flask, changing the color of all the solutions from golden to colorless. Hence, 8 growth solutions with different silver concentration were obtained.

The final step was to add 30 $\mu$L of the seed solution into each of the growth solutions, and keep them at 25°C. The color of these solutions gradually changed within 60 minutes. For different amount of $AgNO_3$ added into the growth solution, the color of the final solutions is different, indicating a different plasmon band for each reaction.

UV-VIS Absorption Spectrum

Spectra of different solutions of gold nanorods measured are shown in Fig. 2.2(a). From this figure we can see that for different silver concentration, the transverse plasmon band always occurs around 520 nm, while the longitudinal band shifts. The wavelength where the peak of longitudinal plasmon bands occur is plotted in Fig. 2.2(b). It is clearly seen that the longitudinal band redshifts with the increase of $AgNO_3$ concentration up to 0.12 mM, after which it experiences a blueshift again, indicating an
increase of aspect ratio for low silver concentration followed by a decrease of aspect ratio for higher [Ag⁺]. This matches the result obtained by B. Nikoobakht, M. A.El-Sayed\[^{16}\].

![Figure 2.2:](image)

*Figure 2.2: (a). The absorption spectra of gold nanorod solutions with silver concentrations varying from 0.01 mM to 0.15 mM. Different color indicates different concentration of silver ions in the solution; (b) The wavelength where the peak of the longitudinal band occurs.*

**SEM Imaging**

![Figure 2.3:](image)

*Figure 2.3: The AuNRs made by using (a) 0.01 mM, (b) 0.07 mM of silver ions.*

The SEM images of gold nanorods with both low (0.01 mM) and medium (0.07 mM) silver concentration are shown in Fig. 2.3. We can immediately see that for low silver concentration (Fig. 2.3 (a)), gold nanorods are fat while for high silver concentration (Fig. 2.3 (b)) they are narrow. Also, we can conclude that the length of gold nanorods are similar for both silver concentration. For very low silver concentration, the size distribution of AuNRs is large, but if more Ag⁺ were used, the AuNRs were almost identical. This means silver also has an effect on the size distribution as well as the averaged size of gold nanorods.
Based on these SEM images, the length and width of about 100 nanorods for each silver concentration was measured manually, and hence the aspect ratio of them was calculated. The statistical results are shown in Fig. 2.4. From this figure we can see that, as the concentration of $AgNO_3$ increases, the length of the nanorods stays constant, whilst the width (or diameter) decreases. As a result the aspect ratio of the gold nanorods increases with the silver concentration up to 0.12 mM, which agrees with the spectra in Fig 2.2.

![Figure 2.4: (a) Length, (b) Width, (c) Aspect ratio of Nanorods v.s. silver concentration. The error bars represent the standard deviation of each sample. Dashed lines are a guide to the eye.](image)

2.3.2 Tuning the Volume by Varying the Seed Concentration

After knowing how silver ions influence the size of gold nanorods, the next step was to put different amount of seeds into the growth solution with the same concentration of silver ions. Another 8 reactions were performed following exactly the same procedure as that in section 2.3.1. Only at this time, the concentration of $AgNO_3$ was kept at 0.12 mM for all these 8 reactions, but 0.5 µL, 1 µL, 2 µL, 4 µL, 8 µL, 15 µL, 30 µL and 60 µL of seed solution was used for each reaction. Absorption spectra of these rods are shown in Fig. 2.5. From this figure, we can see that the longitudinal band also red shifts with the the volume of seed solution up to 30 µL, and there was a little blueshift after that, showing the aspect ratio of gold nanorods decreased a little. The amplitude
of the longitudinal plasmon bands are almost the same indicating the amount of the seeds does not affect the total amount of Au\(^{3+}\) ions that are reduced to gold atoms.

Figure 2.5: (a) Absorption spectra of Gold Nanorods made by adding 0.5 µL, 1 µL, 2 µL, 4 µL, 8 µL, 15 µL, 30 µL and 60 µL of seed solution. The silver ions in all these solutions were kept at 0.12 mM. (b) Wavelength where the longitudinal plasmon occurs for each volume of seed solution. The dashed line is a guide to the eye.

2.3.3 Varying the Silver Ions and Seeds Together

Figure 2.6: The wavelength of longitudinal band v.s. silver ions concentration. The legend shows the volume of seed solution used in the synthesis procedure.

6 sets of gold nanorods were produced, with the volume of seed solution being 0.5 µL, 3 µL, 10 µL, 15 µL, 30 µL, and 60 µL. For each set the concentration of Ag\(^+\) was tuned from 0.01 mM to 0.15 mM. The wavelength, at which the longitudinal plasmon of all these 6 sets occurs, always increases with the concentration of silver ions. For clarity I just show two sample sets (with the volume of
seed solution being 0.5 µL and 60 µL) in Fig. 2.6. There are two points that can be deduced according to this figure. Firstly, for the same volume of seed solution, the wavelength where the longitudinal band occurs always increases with the concentration of Ag⁺ up to 0.12 mM. Secondly, at every concentration of silver ions, the wavelength of longitudinal band also always increases with the volume of seed solution, indicating that the seeds have an effect on the longitudinal plasmon and hence the aspect ratio of gold nanorods. These two points are two of the key results of my synthesis experiment. They represent the dependence of the longitudinal band, or aspect ratio in an other word, on both the silver concentration and seed population. This is an important experimental example for understanding the unclear mechanism of seed-mediated growth method.

Measuring the Nanorods by SEM

![SEM images of Gold Nanorods](image)

Figure 2.7: The SEM images of Gold Nanorods produced by using (a) 0.5 µL seed and 0.04 mM Ag⁺, (b) 3 µL seed and 0.05 mM Ag⁺, (c) 10 µL seed and 0.12 mM Ag⁺, (d) 60 µL seed and 0.04 mM Ag⁺.

Four sample sets (with 0.5, 3, 10, 60 µL of seed solution) were chosen for SEM observation. Fig. 2.7 includes one SEM image from each sample set with the same scale. According to these images, not only the width (compare (a) and (c)), but also the length (compare (b) and (d)) of gold nanorods is different. Also, these images are good proof that homogeneous AuNRs of different size can be made by using seed-mediated method. The image in Fig. 2.7 is not as clear as the other three, because the nanorods made by using 60 µL of seed were so small that they almost reach the limitation of Scanning
The length, width and the aspect ratio of gold nanorods were plotted in Fig. 2.8. There are several results that can be concluded from this figure. Firstly, with the same amount of seeds (same color in the figure), the length always stays constant, and the width shows a decreasing trend as the silver concentration goes up to 0.12 mM. As a result the aspect ratio always increases for each amount of seeds. Secondly, both length and width drop down when the volume of seed solution is increased, hence the volume of the individual nanorod decreases. Thirdly, even though the volume decreases with the seeds, the aspect ratio of nanorods increases at the same silver concentration, which matches the absorption spectra I got before (Fig. 2.6).

![Figure 2.8: (a) Length, (b) Width, (c) Aspect ratio of Nanorods of different silver concentrations and seeds amounts (in µL). The error bars represent the standard deviation of each sample. The dashed lines are guides to the eye.](image)

In conclusion, I can synthesize gold nanorods in the triangle in Fig. 2.9, with the aspect ratio between 2 and 4.7, which means the wavelength of longitudinal plasmon being 600 to 870 nm, and the volume between 1,300 to 36,000 nm³ (about 30 times difference in volume!). In principle, even smaller gold nanorods can be produced by simply using more than 60 µL of seed solution.
Figure 2.9: The volume and aspect ratio of gold nanorods I can tune. The space between the colored points can be easily filled by using the proper amounts of seeds and silver ions.

Figure 2.10: (a) Absorption spectra for different concentrations of ascorbic acid (indicated in the insert) in the growth solution. (b) The wavelength where the longitudinal plasmon occurs at different [AA]. The absorbance of the peak of longitudinal plasmon for different concentration of ascorbic acid.
2.3.4 The Critical Effect of L-Ascorbic Acid

While keeping the concentration of $\text{AgNO}_3$ at 0.12 $mM$ and the volume of seed solution at 30 $\mu L$, the concentration of ascorbic acid (AA) was tuned from 0.45 $mM$ to 0.6 $mM$ in the growth solution. The absorption spectra of the gold nanorods are shown in Fig. 2.10 (a). At first, the longitudinal band red shifted to a maximum wavelength with the increase of the ascorbic acid, and afterwards blue shifts to shorter wavelength (see Fig. 2.10 (b)), indicating the ascorbic acid also has an effect on the shape of gold nanorods. The absorbance of the longitudinal plasmon as well as the total absorption, on the other hand, show an increasing trend when more and more ascorbic acid is added into the growth solution, indicating that more and more $\text{Au}^{3+}$ ions are reduced to $\text{Au}^0$. Therefore we can conclude that the $\text{HAuCl}_4$ I usually added in the solution is in excess for the normal amount of ascorbic acid, and in all the gold nanorod solutions I mentioned in previous sections, $\text{Au}^{3+}$ or/and $\text{Au}^+$ ions still exist. When the ascorbic acid is less than 0.45 $mM$, there is no longitudinal plasmon detected by the UV-Visible spectrophotometer (see Fig. 2.10 (a)), indicating that no gold nanorods are synthesized. This is believed to be a good proof for the mechanism of seed-mediated method. Ascorbic acid, which is a mild reducing agent, is said to reduce $\text{Au}^{3+}$ in two steps: It first reduces the $\text{Au}^{3+}$ ions to $\text{Au}^+$ producing $\text{AuCl}_2^-$ $- \text{CTAB}$ micelles; then the excess of ascorbic acid in the presence of $\text{Au}$ atoms (seeds) can reduce the $\text{Au}^+$ ions to $\text{Au}^0$. As a result, no longitudinal plasmon for less than 0.45 $mM$ indicating that the ascorbic acid can only reduce $\text{Au}^{3+}$ ions to $\text{Au}^+$ but not further. It is noticeable that changing the concentration of AA by only approximately 6% around the optimal (from 0.47 $mM$ to 0.50 $mM$ or from 0.50 $mM$ to 0.53 $mM$), the spectra of the gold nanorods change a lot, which means the ascorbic acid is very critical for the quality of gold nanorods.

2.4 Conclusion

1. A good control of seed-mediated synthesis method for a big range of seed and silver concentration is achieved, and a nice series of spectra of the synthesized nanorods are obtained. The wavelength of the longitudinal plasmon band can be tuned from 600 nm to 870 nm (aspect ratio from 2 to 4.7) by adjusting the amount of silver ions and seeds. Gold nanorods with even longer plasmon wavelength (or larger aspect ratio) can be produced by using a binary surfactant mixture of BDAC and CTAB, and that would be the objective of further research.

2. High resolution scanning electron microscopic images of gold nanorods were obtained for different silver and seed concentration. According to these images, homogeneous gold nanorods with only few byproducts were produced. The measured length, width and the calculated aspect ratio give a clear picture of how silver ions and seed affect the size and shape of gold nanorods. The volume of the gold nanorods can be controlled is from 1,300 to 36,000 $nm^3$ approximately, which is about 30 times difference. Even smaller gold nanorods are expected to be produced by simply using more than 60 $\mu L$ of seed solution.

3. A critical effect of L-ascorbic acid on the synthesis of gold nanorods, which has not been reported before, was discovered. This effect is believed to be a good proof and support to the growth mechanism of seed mediated method. The relation between the absorption spectrum and the concentration of ascorbic acid is interesting and is suggested to be investigated in further research. The concentration of ascorbic acid is believed to be another factor for controlling the volume and aspect ratio of gold nanorods.
Chapter 3

Alignment in Electric Field

The alignment of gold nanorods in aqueous solution in an electric field was studied by van der Zande et al[25] more than ten years ago. After that, surprisingly, there was no other published study about this. In their experiment, van der Zande et al studied nanorods with a width of 15 nm and length ranging from 39 to 729 nm (aspect ratios from 2.6 to 49). In this range, the longitudinal plasmon fell outside the range of the laser wavelength. So they measured the transverse plasmon, which is fixed at around 520 nm for all the rods. They found full alignment for an aspect ratio larger than 12, with a surprisingly large polarizability of $\sim 10^{10}$ Å ($\sim 10^4 \times V$). In this chapter I will describe the alignment of rods with small aspect ratio rods and different volumes probed on resonance with the longitudinal plasmon.

3.1 Theory of Alignment in Electric Field

In the presence of an electric field, although the whole gold nanorod is electrically neutral, the free electrons are pushed to one part of the rod by the field, making that part negative. The other part, because of the loss of electrons, shows a positive charge. As a result, a gold nanorod has an induced dipole moment $\vec{p}$, given by[26]

$$\vec{p} = \tilde{\alpha} \vec{E}$$

where $\tilde{\alpha}$ is the polarizability of the gold nanorod, which is a second rank tensor in our case. Choosing the coordinate system properly, the polarizability of a gold nanorod can be written as:

$$\tilde{\alpha} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{pmatrix}$$

with $\alpha_\perp$ being the polarizability of a gold nanorod perpendicular the rod and $\alpha_\parallel$ the polarizability along the rod. These two parameters can be calculated according to Eq. (1.6). So we can split the electric field $\vec{E}$ into two components, one being along the rod $\vec{E}_\parallel$ and one perpendicular $\vec{E}_\perp$ (See Fig. 3.1). Therefore, we have two induced dipole moments $\vec{p}_\parallel$ and $\vec{p}_\perp$, with the amplitudes:

$$p_\parallel = \alpha_\parallel E \cos\beta,$$  \hspace{1cm} (3.3)

$$p_\perp = \alpha_\perp E \sin\beta.$$  \hspace{1cm} (3.4)
Figure 3.1: Induced dipole moments of gold nanorod in electric field.

Accordingly, the torque that the gold nanorod experiences in the electric field can be written as\(^{(26)}\)

\[
\tau = \vec{p} \times \vec{E}, \quad \text{so}
\]

\[
\tau_\parallel = E^2 \alpha_\parallel \cos \beta \sin \beta \tag{3.5}
\]

\[
\tau_\perp = E^2 \alpha_\perp \sin \beta \cos \beta \tag{3.6}
\]

Since these two torques are in opposite directions, the magnitude of the total torque is

\[
\tau = E^2 \Delta \alpha \sin \beta \cos \beta \tag{3.7}
\]

where \(\Delta \alpha = \alpha_\parallel - \alpha_\perp\).

Thus, the energy of alignment can be written as:

\[
U = -\int \tau d\beta = -\frac{1}{2} E^2 \Delta \alpha \cos^2 \beta \tag{3.8}
\]

The probability of angle \(\beta\) is proportional to \(\exp(-\frac{U(\beta)}{k_B T})\). The degree of alignment \(F\), which is the average over the angular distribution of the particles in the electric field \(E\), can be written as\(^{(27)}\)

\[
F(E) = \frac{3}{2} <\cos^2 \beta> E - \frac{1}{2} \tag{3.9}
\]

For induced dipole moment orientation this equation can be reduced to\(^{(27)}\)

\[
F = \frac{3}{4} \left[ \frac{e^\gamma}{\sqrt{\gamma} D(\gamma)} - 1 \right] - \frac{1}{2} \tag{3.10}
\]

with

\[
\gamma = \frac{\Delta \alpha E^2}{2 k_B T} \quad \text{and} \quad D(\gamma) = \int_0^\gamma e^{t^2} \, dt \tag{3.11}
\]

For low degree of alignment are find\(^{(27)}\):

\[
F \approx \frac{\Delta \alpha E^2}{15 k_B T} \tag{3.12}
\]
So the degree of alignment is proportional to the applied electric field squared. And because $\Delta \alpha \propto \frac{1}{3} \pi abc$ (see Eq. (1.6)), the alignment is also proportional to the volume of the nanorod for a fixed aspect ratio.

3.2 Experiment

3.2.1 Setup

![Figure 3.2: The setup of alignment in electric field. FG=function generator.](image)

The experimental setup for alignment in an electric field is drawn in Fig. 3.2. The waveform is generated by the function generator (FG) and amplified 30 times by the amplifier. The amplifier is linked to two transparent ITO coated coverslips that are parallel and spaced by 100 $\mu$m. The laser beam with $\lambda = 671$ nm goes through two ITO coverslips (with the ITO inside) and the solution, and reaches the detector, which detects the transmitted intensity of the laser beam. To resolve the very small signal, a lock-in amplifier is employed, which detects the signal change at the modulation frequency of the applied field only.

![Figure 3.3: (a) The potential applied to the transparent ITO by a function generator coupled to an amplifier; (b) The laser intensity detected by the detector.](image)
Signals from the function generator are shown in Fig. 3.3 (a). There are two frequencies. The high
frequency is fixed at 300 kHz, and is used to align the gold nanorods. The reason for choosing so high
a frequency was that we wanted to avoid conduction by ions that existed in the sample solution. (The
ions came from the procedure of seed-mediated growth). The other frequency \( f \), which is considerably
lower than the high one, is varied from 27 Hz to 20 kHz. This frequency is to switch on and off the
electric field in the solution. So when the field is on, gold nanorods will be more likely parallel to
the E-field, which is perpendicular to the polarization of the laser beam. So the transmission of the
sample goes up at laser wavelength when the field is on. When the field is switched off, the Brownian
motion causes the rods to orientate in random directions, so gold nanorods in solution absorb more
light at 671 nm. As a result, the total intensity of the laser that is detected by the detector should be
similar to the wave shown in 3.3 (b). (I sketched a square wave here, but the real signal should not
be so perfect because there is always some response time for the rods to be aligned.) The frequency
of this intensity change is \( f \). The lock-in amplifier removes all the noise at the frequency other than
\( f \), and a \( 10^{-5} \) relative change in intensity can be detected.

3.2.2 Gold Nanorods in Water

To obtain an optimum signal, I synthesized the nanorods with a longitudinal plasmon close to the
wavelength of the laser (using the method in Chapter 2). The nanorods have a relatively large volume
\((62 \times 25 \times 25 \text{ nm}^3)\). Measuring the absorption spectrum, the absorbance of gold nanorods solution was
found to be 1.13 at 671 nm (see Fig. 3.4 (a)). In order to get rid of CTAB as much as possible, the
nanorods were washed once and subsequently concentrated by centrifugation. In the end, the CTAB
remaining in the solution was estimated to be 1 mM and the concentration of the nanorods was 42
times as much as before (the absorbance at 671 nm was 1.13\( \times 42 \approx 47.5 \)).

The voltage on the ITOs was varied from 3 V to 33 V (electric field from 30,000 to 330,000 V/m),
and the linear dependence of the signal on \( E^2 \) (starting from the origin point of the coordinates) is
detected for different value of \( f \) varying from 27 Hz to 20 kHz (see Fig. 3.4 (b)).

![Absorption spectrum of the gold nanorod solution in a cuvette with a 10 mm path length.](image1)

![Linear dependence of alignment on electric field squared for f varying from 27 Hz to 20 kHz.](image2)

Figure 3.4: (a) Absorption spectrum of the gold nanorod solution in a cuvette with a 10 mm path
length. (b) Linear dependence of alignment on electric field squared for \( f \) varying from 27 Hz to 20
kHz. For clarity, I selected three typical frequencies, which are 77, 8237 and 19237 Hz. The vertical
coordinate represents the ratio of intensity change to the total intensity of the laser beam that reaches
the detector.

Fig. 3.4 (b) also shows that for different values of \( f \) but the same value of the electric field, the
signal is different. This can be understood as follows. At low frequencies, gold nanorods in solution
have time to follow the slowly changed field so the intensity change of the laser beam is large. When
the frequency is increased, gold nanorods may not follow the field, so they oscillate slightly, and the intensity change is less. This is similar to the spring system with damping under an oscillating driving force: The Brownian motion is the restoring force acting as an entropic spring, and the viscosity of the solvent being the damping. The inertial form (second order derivative) is negligible. The solution of this equation of dynamics for the complex amplitude can be written as

\[
\frac{1}{1 + i\frac{\omega}{\omega_c}}
\]

(3.13)

where \(\omega_c\) is the cutoff frequency of the system. The amplitude varies as:

\[
\frac{1}{\sqrt{1 + \left(\frac{\omega}{\omega_c}\right)^2}}
\]

(3.14)

and the phase varies as:

\[
\arctan\left(\frac{\omega}{\omega_c}\right)
\]

(3.15)

Figure 3.5: (a) The signal vs. driving frequency at the same electric field strength. Both the coordinates are in log scale. (b) Phase difference (in degree) between the driving electric field and the signal v.s. driving frequency at the same electric field strength. The initial non-zero phase difference results is because of the phase shift of the lock-in amplifier. The red curves in these two figures are fits to the theory.

The relation between the signal from the lock-in amplifier (vertical coordinate) and the frequency of the driving field (horizontal coordinate) is shown in Fig. 3.5 (a). From 27 Hz to 2237 Hz the signal stays constant, which means the rods can follow the field, and after that it shows a rapid decrease, which means the field variation is too fast for the rods to follow. The red curve is a fit to the data obtained using Eq. (3.14). It is clear that they match very well with \(\omega_c\) being \(4 \times 10^4\). Fig. 3.5 (b) shows the change of phase difference between the driving electric field and the signal with respect to the driving frequency. At very low field, the phase fits Eq. (3.15) (red curve) nicely with \(\omega_c\) being \(1.1 \times 10^4\), which is the same order but 4 times smaller than that obtained from the amplitude. When the frequency increases, the phase change is different from what is expected, and the last three points do not fit the red line. The reason for this difference maybe due to the high order harmonic frequency generated by the function generator, and the detect limit of the lock-in amplifier (because the amplitude of the signal is very low according to Fig. 3.5 (a)). The initial non-zero difference arises from the phase shift of the lock-in amplifier.
3.2.3 Gold Nanorods in THF

When a field higher than 330,000 V/m was applied to the sample, \( dV/V \) increased less linearly with respect to \( E^2 \). This maybe because of the output limit of the amplifier. Even though the sample was washed with milliQ water, there are still ions, \( Br^- \), \( Cl^- \) and excess \( Au^{3+} \) for example, in the solution. The ions move along the electric field lines so the solution turns to be conductive. At high electric field (high voltage), the amplifier cannot supply enough power to the system. To test how gold nanorods are aligned at high field, I employed a less polar solvent, tetrahydrofuran (THF) with the same gold nanorods I used in Fig. 3.4. The work of putting AuNRs in THF was done by one of my supervisors Peter Zijlstra according to the paper by I. Pastoriza-Santos et al\(^{[28]}\). Since the refractive index of THF is different from that of water, the absorption spectrum red shifts by 13 nm. Hence the absorbance at 671 nm is 1.48 instead of 1.13 (See Fig. 3.6 (a)). A linear dependence up to the potential of 105 V (1,050,000 V/m) for \( f \) varying from 27 Hz to 20 kHz, and from 105 V to 120 V (1,050,000 to 1,200,000 V/m) the less linear increase appears (see Fig. 3.6 (b)). A strange thing in THF is that, I got considerably smaller signal than in water at the same applied potential. The concentrations of these two samples were almost the same because the absorbance is the same at the peak of spectrum. Neither of them was aggregated because there was no strange feature in their spectra in Fig. 3.4 (a) and 3.6 (a). This phenomenon maybe because of the unproper control of the width of the sample cell.

![Figure 3.6: (a) Absorption spectrum of the gold nanorods in THF in a 10 mm path length cuvette. (b) Linear dependence of alignment of gold nanorods in THF on electric field squared for \( f \) varying from 27 Hz to 20 kHz up to 105 V. For clarity, I choose three typical frequencies, which are 77, 8237 and 19237 Hz. All the other conditions and parameters, including the nanorods I used, are the same as Fig. 3.4.](image)

3.2.4 Effect of the volume

According to Eq. (3.7), the alignment depends not only on the applied electric field, but also on the volume of the gold nanorods. The volume dependency was also investigated during my project. Both \( 62 \times 24 \times 24 \) and \( 52 \times 21 \times 21 \ nm^3 \) were investigated respectively, the former being 1.5 times larger than the latter. Their signal v.s. \( E^2 \) curves for two different values of \( f \) are shown in Fig. 3.7. I got linear dependence for both large and small nanorods up to 120,000 V/m. For both 77 and 9237 Hz, the signal of the large nanorods is always larger than that of the small ones (normalized to the absorbance at 671 nm). At 77 Hz, the signal of large nanorods is 3 times as much as that of the small ones, while at 9237 Hz, it is 2 times larger. That is because the relaxation time for large gold nanorods is longer than for the small ones, so when the frequency of the driving field increases, the signal of large rods decreases quicker than that of the small ones.
3.3 Conclusion

1. Linear dependence of alignment of gold nanorods on electric field squared is perfectly achieved both in water and THF, which matches the theory at low degree of alignment.

2. Amplitude and phase of the signal at different driving frequencies from 27 Hz up to 20 kHz is measured. At low frequency of electric field, gold nanorods in solution have time to follow the slowly changed field, so the signal detected is large and phase difference between the signal and applied field is small. At high frequency, gold nanorods cannot follow the field, so the signal is smaller and the phase difference is larger. The amplitude change of the signal with respect to the driving frequency also fits the theory nicely. In terms of the phase difference between the signal and the driving field, it is strange at high frequency, which may be ascribed to the detection limit of the setup.

3. The volume effect of gold nanorods is investigated, and the experimental result qualitatively agrees with the theory but not very well. The deviation of the experiment from the theory maybe because of the uncertainly in the concentration after centrifugation.
Chapter 4

Alignment in Magnetic Field

As we got nice alignment result in an electric field, we were also interested in the alignment of gold nanorods in a magnetic field. A short test experiment was done in collaboration with Dr. Peter C.M. Christianen from Radboud University Nijmegen. The experiment was done in Radboud University Nijmegen because it occupies a strong magnetic field setup, up to 34 T. Instead of the intensity of the transmitted laser beam, we detected the birefringence of the sample this time. Although that was a very short experiment, I will show that we also got a linear dependence on the square of the magnetic field, which matches the theory I will explain in Sec. 4.1, with the signal significantly larger than we expected from the diamagnetic gold nanorods.

4.1 Theory

4.1.1 Linear dependence on $B^2$

The basic idea of the alignment in a magnetic field is very similar to that in an electric field. In a magnetic field, since gold nanorods are much smaller than the wavelength of the light, we can treat them as induced magnetic dipoles. The induced dipole moment is

$$\vec{m} = \frac{1}{\mu_0} \tilde{\chi} \cdot \vec{B}$$

(4.1)

where $\mu_0$ is the permeability of free space, and $\tilde{\chi}$ is the magnetic susceptibility of gold nanorod. By choosing the proper coordinates, it can be written as

$$\tilde{\chi} = \begin{pmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{pmatrix}$$

(4.2)

Due to the shape of a gold nanorod, the magnetic susceptibility in our case is

$$\tilde{\chi} = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix}$$

(4.3)

where $\chi_\perp$ and $\chi_\parallel$ are the susceptibility perpendicular and parallel to the gold nanorod, respectively.

They can be written as:

$$\chi_\perp = \frac{\chi_H}{1 + D_\perp \chi_H} \quad \text{and} \quad \chi_\parallel = \frac{\chi_H}{1 + D_\parallel \chi_H}$$

(4.4)
with \(D_\parallel\) and \(D_\perp\) being the dimensionless demagnetizing factor\(^\text{30}\) along and perpendicular to the rod.

So the magnitude of the torque that the gold nanorod experienced in the magnetic field is

\[
\tau = \frac{B^2}{\mu_0} \Delta \chi \sin \beta \cos \beta, \quad \text{(4.5)}
\]

with \(\Delta \chi = \chi_\parallel - \chi_\perp\). So the torque is proportional to \(B^2\) which is similar to Eq. (3.7).

\[
U = \int \tau d\beta = -\frac{B^2}{2\mu_0} \Delta \chi \cos^2 \beta
\]

The degree of alignment can again be obtained from the Boltzmann distribution, which for low degree of alignment is given by

\[
F = \frac{\Delta \chi B^2}{30\mu_0 k_B T}
\]

Therefore the degree of alignment also linearly depends on the square of the applied magnetic field. However, since for gold, the magnetic susceptibility \(\chi_H\) is \(-3.6 \times 10^{-5}\), and \(\Delta \chi = \frac{\chi_H}{1 + D_\parallel \chi_H} - \frac{\chi_H}{1 + D_\perp \chi_H}\) which is proportional to \(\chi_H^2\), the orientational magnetic energy \(\Delta \chi B^2\) is much small with respect to the thermal energy \(k_B T\). Weak signal was expected to be detected.

### 4.1.2 Birefringence

According to the Ph.D thesis by I. Shklyarevskiy\(^\text{31}\), the refractive index of a solution of small particles in a nonmagnetic medium can be written as

\[
n^2 = n_1^2(1 + N <\alpha>)
\]

where, \(<\alpha>\) is the polarizability averaged over \(N\) particles (in our case is the polarizability of gold nanorods that can be calculated according to Eq. (1.6)), and \(n_1\) is the refractive index of the surrounding medium, in our case water.

Supposing the external magnetic field is homogeneous and in the positive z direction, the three components of \(n\) can be written as\(^\text{31}\):

\[
n_x^2 = n_1^2 \{1 + N[\alpha_\perp + (\alpha_\parallel - \alpha_\perp) <\sin^2\theta\cos^2\phi>]\}
\]

\[
n_y^2 = n_1^2 \{1 + N[\alpha_\perp + (\alpha_\parallel - \alpha_\perp) <\sin^2\theta\sin^2\phi>]\}
\]

\[
n_z^2 = n_1^2 \{1 + N[\alpha_\perp + (\alpha_\parallel - \alpha_\perp) <\cos^2\theta>]\}
\]

where \(\theta\) is the angle between the long axes of gold nanorod and the z-axis, and \(\phi\) is the angle that the projection of the long axis on to the \(xy\)-plane makes with the \(x\)-axis; \(\alpha_\parallel\) and \(\alpha_\perp\) are the polarizability along the long axis and short axis of gold nanorod respectively. In absence of the magnetic field, the gold nanorods are oriented in random direction in the suspending medium, thus \(n_x = n_y = n_z\). When there is an external magnetic field, the gold nanorods will be aligned in the field, and the average \(<\cos^2\theta>\) is different from \(<\sin^2\theta\sin^2\phi>\). Therefore, \(\Delta n = n_z - n_y\) is non-zero. This phenomena is called magnetic field induced birefringence.
4.2 Experimental

Figure 4.1: The sketch of the setup to measure magnetic field induced birefringence in a magnetic field. The arrow on the left indicates the direction of the magnetic field. The thickness of the cuvette is indicated by \( d \). This picture is copied from the thesis by J. Gielen\(^{30}\).

The setup used in Radboud University to measure the magnetic field induced birefringence is shown in Fig. 4.1. The cuvette with the solution to be measured is mounted between two polarizers perpendicular to each other and at 45 degree with respect to the magnetic field. A HeNe laser beam with \( \lambda = 632.8 \, nm \) is modulated by a photo-elastic modulator, PEM-90 from Hinds Instruments Inc., with a frequency \( f = 50 = \Omega / 2\pi \, kHz \) and a maximum retardation of \( A_0 = 0.383 \) waves\(^{31}\). The light transmitted through the second polarizer is coupled to an optical fiber and guided to a photodetector. The intensity of transmitted laser beam is\(^{30}\):

\[
I(t) \propto 1 - \cos(\delta) \cos(A_0 \cos(\Omega t)) + \sin(\delta) \sin(A_0 \cos(\Omega t)) \tag{4.12}
\]

where

\[
\delta = \frac{2\pi d \Delta n}{\lambda} \tag{4.13}
\]

is the retardation with \( d \) being the length of the sample.

A Fourier series expansion of this equation yields

\[
I(t) \approx 1 - \cos(\delta) J_0(A_0) + 2\sin(\delta) J_1(A_0) \cos(\Omega t) + 2\cos(\delta) J_2(A_0) \cos(2\Omega t) + ... \tag{4.14}
\]

with \( J_0, J_1, J_2 \ldots \) being Bessel functions, and the three terms on the right hand side being DC, first harmonic, and second harmonic terms, respectively. \( A_0 \) was chosen to be 0.383 waves to make \( J_0(A_0) = 0 \). So the DC term is independent of the birefringence. The retardation can then be obtained by dividing the second harmonic and the first harmonic amplitude with the proper scaling factors\(^{30}\):

\[
\delta = \arctan\left(\frac{J_2(A_0)V_{1f}}{J_1(A_0)V_{2f}}\right) \tag{4.15}
\]

Four samples of gold nanorods were tested in this setup. Two of them were \( 62 \times 25 \times 25 \, nm^3 \) coated with CTAB and thiol. The thiol coating was done by one of my supervisors Peter Zijlstra. The other two were much smaller, \( 36 \times 8 \times 8 \, nm^3 \) in volume, and coated with the same chemicals (CTAB and thiol respectively) as the large ones. The gold nanorods coated with CTAB are normal products by using seed-mediated growth. The reason for coating gold nanorods with thiol was that thiol coating could change the magnetic property of gold nanoparticles with the averaged size of 1.4 \( nm \) from diamagnetic to ferromagnetic according to P. Crespo et al\(^{32}\). I expected significantly larger signal for thiol coating if that also worked for gold nanorods with the size I used.

By measuring the retardation \( \delta \) of the solution of gold nanorods, the birefringence and hence the degree of alignment was measured.
4.3 Results

![Graph showing retardation measured on a solution of gold nanorods in a magnetic field with different coating for (a) low and (b) high concentration.]

The $\delta$ v.s. $B^2$ curves for all the four samples are shown in Fig. 4.2 (a). The linear dependence of the retardation on magnetic field squared is detected for all the samples up to $20 \, T$, which agrees with the theory very well. Compared to the CTAB coating samples, the thiol coating ones show smaller rather than larger retardation for both small and large size. This means the thiol coating really changes the magnetic property of our samples, but certainly not from diamagnetic to ferromagnetic. The disagreement with P. Crespo may arise from the significant size difference between their samples and ours. For the 1.4 $nm$ gold nanoparticles they used, the surface to volume ratio is much higher than for our samples. The thiol coating only interacts with the gold atoms on the surface. So in our case, the effect of thiol may be so small that it cannot fully change the magnetic property of gold nanorod but may cancel part of its diamagnetic property. That might be the reason why we got a smaller signal from thiol coated samples.

From Fig. 4.2(a) we can see that even though we obtained a signal, the retardation is very small. Therefore, I made higher concentration of gold nanorod solution by centrifugation. (Unfortunately, since it was only a test experiment, the exact concentration was not recorded.) During the centrifugation, gold nanorods with thiol aggregated so only the two samples with CTAB were measured again and the $\delta$ v.s. $B^2$ curves are shown in Fig. 4.2 (b). This time we also got the linear dependence of the retardation on magnetic field squared for both sizes up to $20 \, T$, and the retardation for both of them at $20 \, T$ was around 2.8 times ($7.15/2.58 \ & 1.43/0.51$ comparing (a) to (b)) as much as before.

4.4 Conclusion

1. Linear dependence of alignment of gold nanorods, with different size, coating and concentration, on the magnetic field squared is perfectly achieved up to $20 \, T$.

2. The result of thiol coating gold nanorods is different from the research by P. Crespo et al, but a possible explanation is proposed.

3. Systematic research (more samples with large variation of size, coating, and in even higher magnetic field ) needs to be done. The concentration of the gold nanorods in the sample is suggested to be recorded for quantitative analysis.
Chapter 5

Conclusions

A good control of seed-mediated synthesis by varying seed and silver concentrations was achieved. The wavelength of the longitudinal plasmon band could be tuned from 600 nm to 870 nm (aspect ratio from 2 to 4.7) by adjusting the amount of silver ions and seeds. Scanning electron microscopic images of gold nanorods were obtained for different silver and seed concentrations. According to these images, homogeneous gold nanorods with only few byproducts were produced. The measured length, width and the calculated aspect ratio gave a clear vision of how the silver and seed concentration affect the size and shape of gold nanorods. The volume of the synthesized gold nanorods ranged from 1,300 to 36,000 nm$^3$ approximately, which is a factor of 30. Even smaller gold nanorods are expected to be produced by simply using more than 60 µL of seed solution. A critical effect of L-ascorbic acid on the absorbance and wavelength of the longitudinal plasmon of synthesized gold nanorods, which has not been reported before, was discovered. This effect is associated with the growth mechanism of seed mediated method. The concentration of ascorbic acid is believed to be another factor for controlling the volume and aspect ratio of gold nanorods.

The alignment of gold nanorods in an external electric field was investigated. Linear dependence of the degree of alignment of gold nanorods on the electric field squared was achieved both in water and THF, which matches the theory. Amplitude and phase of the signal at different driving frequencies from 27 Hz up to 20 kHz were measured. At low frequency of electric field, gold nanorods in solution have time to follow the slowly changing field, so the signal detected was large and the phase difference between the signal and applied field was small. At high frequency, gold nanorods cannot follow the field, so the signal is smaller and the phase difference is larger. The volume effect on the alignment was also investigated, and the experimental result is in reasonable agreement with the theory.

A linear dependence of alignment of gold nanorods on the magnetic field squared was achieved up to 20 T. This measurement was done by means of birefringence, with different size, coating and concentration. The signal obtained from this experiment was significantly larger than what was expected according to the diamagnetic property of gold nanorods. The result of thiol coating gold nanorods was different from the research by P. Crespo et al, but a possible explanation is proposed. Systematic research needs to be done in the future to understand the magnetic properties of gold nanorods with different volumes and coatings.
Bibliography


