Synthesis and Self-Assembly of Core-Shell Gold Nanorod-PNIPAM Nanoparticles

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Abstract

An essential requirement for the use of nanoparticles in self assembly applications is ensuring their colloidal stability is maintained, as well as being able to tailor their properties for enhanced functionality. One way of doing so is through the incorporation of nanoparticles in responsive microgels, leading to the formation of inorganic/organic hybrid nanocomposites.

The aim of this research was to develop a generic protocol for the preparation of hybrid core-shell microgels composed of nanoparticle cores and responsive polymer shells. Specifically, core-shell gold nanorod - poly-N-isopropylacrylamide (PNIPAM) particles with high yield and monodispersity were synthesised. Due to the high sensitivity of the longitudinal plasmon band to its local environment, the change in refractive index caused by the temperature-induced collapse of the PNIPAM shell led to a red-shift on the order of tens of nanometres in the plasmon band. This shift was reversible for multiple heating/cooling cycles, and no aggregation of the gold nanorod cores was observed.

Concentrating the gold nanorod-PNIPAM solutions at high volume fractions enabled them to crystallise, thereby exhibiting strong diffraction peaks. The formed colloidal crystals could be melted upon annealing, and re-formed upon cooling due to the responsive behaviour of the PNIPAM shell. These crystals exhibited fascinating optical behaviour which opens a pathway to a new class of hybrid materials with potential use in a wide array of applications.
Declaration

This is to certify that:

i  The thesis comprises only original work undertaken by the author in the School of Chemistry, The University of Melbourne towards the PhD except where indicated

ii  Due acknowledgement has been made in the text to all other material used

iii  The thesis is less than 100,000 words in length, exclusive of table, diagrams, bibliographies, appendices and footnotes

Sarah Jaber
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Chapter 1

Introduction

1.1 Overview

The synthesis of nanoparticles with high control over size and shape has been the focus of much research in the last few decades. The reason for this is that nanoparticles exhibit fascinating size- and shape-dependent properties different from their bulk counterparts. While individual nanoparticles can exhibit size- and shape-dependent optical, catalytic and magnetic properties, there is now a growing interest in using nanoparticles as building blocks for the preparation of more complex, self-assembled functional materials. However, the various synthetic protocols developed lead to differences in the surface chemistry of the nanoparticles due to the stabilising ligands, as well as differences in their solubility in organic and aqueous media. As a result, the colloidal stability of nanoparticles is a topic of concern, especially for application purposes. Before one can change the environment surrounding the nanoparticles and use them as building blocks, their stability must first be maintained. Colloidal stability is generally established through ligand exchange procedures, or polymer encapsulation. These methods can in turn offer more functionality to the nanoparticles by providing their surface with varying reactive terminals as well as facilitating phase transfer.

One way of providing stability to the nanoparticles while also enhancing their functionality is preparing inorganic/organic hybrid systems. Inorganic nanoparticles can be incorporated into organic materials such as polymer microgels, imparting enhanced stability to the nanoparticles. Of particular interest is using responsive microgels, since these materials can respond to external stimuli such as temperature or pH. Incorporating nanoparticles into responsive microgels leads to the design of functional materials that possess the optical, catalytic or magnetic properties of the nanoparticles and can also react to their surroundings.
1.2 Optical properties of metal nanoparticles

Additionally, the thickness of the polymer shell can be controlled, leading to the development of a flexible spacer for nanoparticles, which plays an important role in 2D and 3D assembly.

The aim of this thesis was to combine nanoparticles, specifically gold nanorods, with a microgel composed of poly-N-isopropylacrylamide (PNIPAM), to create novel functional materials for the preparation of 3D colloidal crystals. To address that goal, first the synthesis of monodisperse gold nanorods was explored, followed by their encapsulation in PNIPAM microgel shells, and finally the crystallisation behaviour of these hybrid particles.

Chapter 1 presents a background on the optical properties of gold nanoparticles and the properties of microgels, as well as an overview of the relevant literature on gold nanorods and core-shell inorganic/organic hybrid nanoparticles. Chapter 2 details chemical materials and instrumentation used throughout this work. Chapter 3 provides a detailed investigation and comparison of a range of different synthetic protocols for the preparation of gold nanorods while Chapter 4 explores the encapsulation of the nanorods in PNIPAM microgels and characterises their optical behaviour. Chapter 5 then combines these particles to study their crystallisation behaviour and the formation of 3D colloidal crystals. Finally, Chapter 6 covers preliminary work done on extending the protocol to other nanoparticle cores, followed by conclusions and future work in Chapter 7.

1.2 Optical properties of metal nanoparticles

Metal nanoparticles have attracted much attention due to their size- and shape-dependent optical properties. For gold and silver nanoparticles, this is manifested through unique scattering and absorption properties in the visible and NIR spectrum that lead to the bright colours observed in Au and Ag colloids\cite{1-4}. When these metal nanoparticles are irradiated with light, a dipole is induced by the electric field of the incoming radiation. The dipole oscillates in phase with the electric field. The nanoparticles exhibit an absorption peak at the resonance frequency of the free electrons, called a localised surface plasmon resonance (LSPR)\cite{5}. The optical behaviour of gold nanoparticles can be described by Mie theory, which comprises Mie’s solutions to Maxwell’s equations for the absorption and scattering of electromagnetic radiation by spheres\cite{6}. The absorbance of a dilute colloidal solution with
N particles per unit volume is dependent on the ratio of incoming \( I_0 \) to outgoing \( I_d \) light intensity over a pathlength \( d \) as be given by\(^{[5,7]}\):

\[
A = \log \left( \frac{I_0}{I_d} \right) = \frac{N C_{\text{ext}} d}{2.303} \tag{1.1}
\]

where \( C_{\text{ext}} \) is the extinction cross-section.

For spherical particles that have a wavelength dependent dielectric function \( \epsilon = \epsilon' + i\epsilon'' \) and are embedded in a medium with a dielectric function \( \epsilon_m \), \( C_{\text{ext}} \) can be written as:

\[
C_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=0}^{\infty} (2n + 1) \text{Re} \{a_n + b_n\} \tag{1.2}
\]

where \( a_n \) and \( b_n \) are Mie scattering coefficients which are functions of the particle radius \( R \) and wavelength \( \lambda \) in terms of Ricatti-Bessel functions, and \( k = \frac{2\pi}{\lambda} \).

For small particles where \( kR \ll 1 \) the main contribution to the extinction comes from the dipole oscillation, and therefore only the first term of the series is important. Consequently, \( C_{\text{ext}} \) can be written as:

\[
C_{\text{ext}} = \frac{24\pi^2 R^3 \epsilon_m^{3/2}}{\lambda} \frac{\epsilon''}{(\epsilon' + 2\epsilon_m)^2 + \epsilon''^2} \tag{1.3}
\]

Metals exhibit strong optical effects as a result of the dynamic response of the electrons. For many metals, the region of absorption until the bulk plasma wavelength is dominated by the free electron behaviour, which can be accounted for by the Drude model. The dielectric function can be written in terms of its real and imaginary parts:

\[
\epsilon' (\lambda) = \epsilon(0) - \frac{\lambda^2}{\lambda_p^2} \tag{1.4}
\]

\[
\epsilon'' (\lambda) = \frac{\lambda(\lambda^2 + \lambda_d^2)}{\lambda_p^2 \lambda_d} \tag{1.5}
\]

where \( \epsilon(0) \) is the short wavelength dielectric constant which accounts for all UV absorption bands, and \( \lambda_d \) is the damping constant of the conduction electrons. \( \lambda_p \) is the bulk plasma wavelength, which is characteristic for each metal, and can be defined as:

\[
\lambda_p = \frac{2\pi e}{\omega_p} = \sqrt{\frac{4\pi^2 c^2 m \epsilon_0}{Ne^2}} \tag{1.6}
\]

where \( m \) is the effective electron mass, \( \epsilon_0 \) the permittivity in vacuum, \( N \) the electron density and \( e \) the charge of the electron.
Looking at the denominator in equation 1.3 we can see that a surface plasmon band will appear when

$$\epsilon' = -2\epsilon_m$$  \hspace{1cm} (1.7)

provided $\epsilon''$ is small. These equations thus help show the dependence of the absorption peak on the inherent properties of the metal, the radius of the particle and the dielectric constant of the surrounding medium.

Optical spectra of spherical gold nanoparticles show a maximum at the LSPR, as can be seen in Figure 1.1. For a 15 nm Au sphere, a plasmon band is observed at around 520 nm. For non-spherical Au nanoparticles multiple LSPR modes can be detected, as can be seen in Figure 1.1 for Au nanorods.

---

Figure 1.1: Representative absorbance spectrum for colloidal aqueous solutions of 15 nm diameter Au nanospheres (black) and Au nanorods with an aspect ratio of 4 (red). The spheres exhibit a localised surface plasmon resonance around 520 nm, while the rods show two surface plasmon resonances - a transverse band around 520 nm and a longitudinal plasmon band around 800 nm.

Gans predicted that the surface plasmon mode would split into two distinct bands for very small ellipsoids\textsuperscript{[7,8]}. The two plasmon resonances, known as transverse and longitudinal
1.3 Synthesis of gold nanorods

modes, arise due to oscillations along the width and length of the rod respectively. The transverse band is in a similar position as for Au spheres, whereas the position of the longitudinal plasmon band depends on the aspect ratio (AR), which is the ratio of length to width of the Au rod. Treating the rod as an ellipsoid, the polarisability $\alpha$ can be described as:

$$\alpha = \frac{4\pi abc(\epsilon_{Au} - \epsilon_m)}{3\epsilon_m + 3L_{xyz}(\epsilon_{Au} - \epsilon_m)}$$

(1.8)

In equation 1.8, a, b, and c correspond to the length of the ellipse along the x, y and z axes, with $(a > b = c)$. $L_{xyz}$ denotes the depolarisation factor along the respective axis with

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

(1.9)

$$L_{y,z} = \frac{(1 - L_x)}{2}$$

(1.10)

In the above equations, $e$ is the ellipticity of the rod, determined by $e^2 = 1 - (b/a)^2$. From the Gans-Drude theory, the position of the longitudinal plasmon band of gold nanorods can be determined$^7$:

$$\lambda^2 = \lambda_p^2(\epsilon_0 + \epsilon_m\frac{1}{L} - 1))$$

(1.11)

Equation 1.11 highlights the dependence of the position of the longitudinal plasmon band on the dielectric constant of the surrounding medium, $\epsilon_m$ and the depolarisation factor $L$, indicating the high sensitivity to changes in refractive index and shape.

1.3 Synthesis of gold nanorods

While metal nanoparticles spheres have been synthesised for hundreds of years, it was not until the last 15 years that significant progress was made towards the wet-chemical synthesis of gold nanorods. In order to achieve shape control, additives such as surfactants, ligands and passivants have been used that can bind to the surface of the nanoparticles$^7,9,10$. Early syntheses of gold nanorods involved the electrochemical reduction of gold chloride, HAuCl₄,
using hard templates such as porous alumina\textsuperscript{[11]}, or soft templates, like cetyltrimethylammonium bromide (CTAB), a cationic surfactant\textsuperscript{[12,13]}. These methods had quite low yields and reproducibility, and limited size control.

1.3.1 Seed-mediated synthesis

The use of CTAB as a soft template, however, inspired the seed-mediated method, which was first developed by Jana and Murphy in 2001\textsuperscript{[14]}. Seed-mediated growth is generally used to synthesise nanoparticles with shape control, and involves two stages. The first is a nucleation step that involves preparing spherical seed particles, of around 1 - 4 nm by reducing gold chloride, HAuCl\textsubscript{4}, with a strong reducing agent, such as sodium borohydride (NaBH\textsubscript{4}). The growth step is then performed by adding more Au\textsuperscript{3+} ions with a surfactant that can aid with the shape templating, in the presence of a second reducing agent, and the seed particles. The growth step is much slower than the nucleation step and occurs under milder reducing conditions.

In the protocol by Jana and Murphy, the prepared seed particles were around 3.5 nm in diameter and capped with citrate. At the room temperature reaction conditions, citrate cannot reduce the gold and thereby serves as a capping agent. They found that they could control the aspect ratio of the gold nanorods by varying the ratio of seeds to metal salt. This work highlighted the importance of CTAB as a rodlike micellar template and the presence of seed particles. No rods were obtained in the absence of either CTAB or seeds, since ascorbic acid is too weak to reduce Au(III) to Au(0) without the seed particles. The yield of rods was still quite low and shape separation had to be performed via centrifugation to separate the rods from spheres. The same authors then extended their protocol by introducing silver ions into the growth solution\textsuperscript{[14]}. Prior electrochemical syntheses had made use of silver to aid with aspect ratio control, and the use of silver was also demonstrated by Kim et al who prepared gold nanorods via photochemical reduction of the gold salt in the presence of CTAB\textsuperscript{[15]}. However, Murphy’s results showed that for a constant concentration of AgNO\textsubscript{3}, the aspect ratio could be controlled by varying the amount of added seeds. Adding a higher amount of silver led to the formation of spheroid shaped particles.

The use of silver to control aspect ratio was then pioneered by Nikoobakht and El-
Sayed\textsuperscript{[16]} who found that by varying the amount of added AgNO\textsubscript{3}, rods with aspect ratios from 1.5 to 4.5 could be prepared. The key to this improvement was replacing citrate with CTAB as the capping agent in the seed formation step. The aspect ratio could now be controlled by varying the amount of silver added to the growth solution. To identical growth solutions, 50 - 300 \(\mu\)l 0.004 M AgNO\textsubscript{3} solution were added, and the change in longitudinal plasmon band monitored. Their results are given in Figure 1.2, where the top panel clearly showed a red-shift in the longitudinal plasmon band as the silver content was increased (samples 1 - 5). The bottom panel in Figure 1.2 also highlighted the relationship between the position of the longitudinal plasmon band and aspect ratio for the different prepared gold nanorod solutions, which followed a linear trend as expected.
Figure 1.2: Top: Plot of optical density versus wavelength showing how the position of the longitudinal plasmon band of gold nanorods can be shifted by adding different amounts of 0.004 M AgNO₃, increasing for samples 1 - 5 from 50 - 300 µl. Bottom: Plot of the position of the longitudinal plasmon band versus aspect ratio, highlighting the increasing aspect ratio with blue-shifts of the longitudinal plasmon band. Reproduced from reference [16].

A comparison of the seeds used by Murphy and El-Sayed was presented by Liu and Guiyot-Sionnest who showed that the seeds prepared with either CTAB or citrate had different crystal structure [17]. CTAB-capped seeds were around 1.5 nm in diameter and appeared single crystalline under high resolution transmission electron microscopy (HRTEM). The citrate-capped seeds were slightly larger, around 3 nm in diameter, and HRTEM showed twinned crystals. As a result of the difference in crystal structure, in the presence of Ag, sin-
1.3 Synthesis of gold nanorods

gle crystalline CTAB-capped seeds led to the growth of single crystalline nanorods having a [100] axis as the growth direction with \{110\} and \{100\} side facets. Twinned citrate-capped seeds, on the other hand, predominantly gave an elongated bipyramid shape, which were penta-fold twinned around the \{100\} axis and the \{100\} side facets tilted toward the \{111\} plane. These results explained the differences that were obtained in the work by Jana and Murphy compared to Nikoobakht and El-Sayed\cite{14,16}.

1.3.2 Influence of various parameters

The synthesis of gold nanorods is sensitive to several factors, and adjusting the growth conditions affects the final product. The composition and concentration of the surfactant, temperature, pH, the amounts of the reagents, and the structure of the seeds all play a role in the synthesis\cite{7,18,19}. CTAB is a crucial parameter in the synthesis of gold nanorods\cite{20}. CTAB serves as a stabilising agent to prevent the aggregation of the formed nanorods, and it also forms micelles that act as soft templates to direct the growth along the longitudinal axis. CTAB produced from different manufacturers or different batches can also affect the final product of the gold nanorods. If the CTAB has a high enough iodide content, the synthesis will yield spheres or byproducts over rods\cite{21}.

Silver also plays an important role, although the details of the mechanism are still not properly understood\cite{22}. The presence of Ag$^+$ increases the yield of the nanorods and can control the aspect ratio. Without Ag, the products tend to contain a range of different shapes including rods, spheres, and plates\cite{23}. Ag(I) ions are believed to selectively bind to the higher energy \{110\} facets of Au and slow down the growth rate at these sites. This ensures predominant deposition of Au on the \{100\} facets, leading to longitudinal growth.

The surface of the Au is thought to be negatively charged due to the adsorption of Br$^-$ ions. As a result, the positively charged ammonium headgroup of the CTAB electrostatically binds to the Au. Since the hydrophobic hydrocarbon tail does not like to be in water, a second layer of CTAB is formed with the hydrophobic tail pointing inside and interacting with the inner layer, forming a partially interdigitated bilayer on the surface of the Au nanorods\cite{24,25}. The bilayer provides the particles with a positive charge and stabilises them in water. CTAB molecules tend to stabilise the \{100\} facets of gold, and thereby preferentially bind to the middle of the nanorods. The heads of the nanorods are enclosed with \{110\}, \{111\} and \{001\} facets, meaning that less CTAB can be found on the ends
of the nanorods. Adding more Au therefore leads to deposition of the atoms on the ends, leading to a dogbone shape.

The quality of the final product is also highly sensitive to the amount of reducing agent, generally ascorbic acid. The reduction of Au$^{3+}$ to Au$^{1+}$ occurs as follows$^{[26]}$:

$$\text{CTA}^+-\text{AuBr}_4^- + \text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{CTA}^+-\text{AuBr}_2^- + \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2\text{Br}^-$$

After addition of the seeds, the second reduction from Au$^{1+}$ to Au$^0$ occurs:

$$2 \text{CTA}^+-\text{AuBr}_2^- + \text{C}_6\text{H}_8\text{O}_6 \rightarrow 2 \text{Au} + \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 4\text{Br}^-$$

Considering the pKa of ascorbic acid (4.17) and the pH of the growth solution ($\sim 3$), the stoichiometry of the reaction can be calculated, which reveals that a molar ratio of AA:Au of 1.6 is required for complete reduction of Au$^{[26]}$. The minimum AA:Au molar ratio needed is 1.1 and a ratio greater than 1.6 generally leads to dog-bone and more spherical shapes.

The sensitivity of the gold nanorod synthesis to the different parameters can lead to variations in the results, making the protocol not easily reproducible. In addition, the conversion of gold ions to metallic gold is quite low. Consequently, the last few years have witnessed a rapid increase in the number of synthetic protocols developed for the synthesis of gold nanorods$^{[27–36]}$. Many are based on the original protocols, with either the introduction of new species into the reaction or replacement of ascorbic acid as a reducing agent, in an attempt at enhancing the purity of the prepared rods and improving the reproducibility of the synthesis. In Chapter 3, four of these methods will be studied in detail, and a comparison of the methods will be provided.

1.3.3 Mechanism of gold nanorod growth

The last several years have seen significant progress being made in the synthesis of gold nanorods. While different aspect ratios and high monodispersity can now be achieved through the use of different additives, the growth mechanism of gold nanorods is still not fully understood$^{[37]}$. Most mechanisms describe preferential adsorption of the CTAB on the side crystal facets, thereby allowing the reaction medium more access to the ends for further growth. AgNO$_3$ assists in selective binding and packing of the CTAB. It is actually difficult to study the growth of the gold nanorods, because isolating particles at different stages of the growth is hard unless the growth can be stopped. Walsh et al. studied the
symmetry breaking process that leads to anisotropic particles from spherical seeds by characterising the atomic structure of the formed particles at different stages of the reaction\textsuperscript{[38]}. They found that silver was essential in breaking the symmetry for the formation of single-crystal gold nanorods. Park et al. recently used strongly binding ligands such as thiolated polystyrene to arrest the growth of the nanorods and transfer them into a non growth solution (toluene)\textsuperscript{[39]}. This allowed them to observe with TEM the structure of the particles at different stages throughout the reaction, to obtain an idea on the growth mechanism. The authors proposed that the rod goes through a range of shapes as it is growing, and that the different shapes reported by people in the literature actually correspond to different stages of the growth process. TEM images taken at different times during the reaction are shown in Figure 1.3. Based on these results, they classified the gold nanorod growth into five stages. Stage 1 (0 - 2 min) consisted of rapid isotropic growth from the 1.2 nm seed particles (a) to \(~\)6 nm spheres. Stage 2 (2 - 5 min, b - c) involved rapid anisotropic growth, where the diameter of the particles almost remained the same, but the length increased forming a spherocylinder. Stage 3 (5 - 20 min, d - e) consisted of fast non-uniform rod growth, where around the end of the rods, the growth rate of the diameter became faster than that of the length, leading to the formation of a dumbbell shape. In stage 4 (20 - 45 min, f - g) side facet reconstruction occurred, where the growth rate of both the length and diameter decreased. The hemispherical ends of the rods were flattened, and this led to stage 5 (h), relaxation, where a thermodynamically stable shape was reached.
1.3 Synthesis of gold nanorods

These observations allowed them to formulate a mechanism for the growth of gold nanorods. They found that seeds with \{100\}, \{110\} and \{111\} facets were needed for directional growth. The smaller seeds with predominantly \{100\} and \{111\} facets led to the rods shown in stage 2. The size of a CTAB micelle is \(\sim 2.9\) nm, and when the area of a facet became close to that, the micelles adsorbed more strongly on the \{100\} as opposed
1.3 Synthesis of gold nanorods

to \{111\}. Therefore the rods grew mainly in length. At this stage, CTAB adsorption along the rods continued and formed a dense bilayer. This was then followed by further growth along the \{111\} facets which led to an increase in width and the dumbbell shape observed in stage 3. Moving from stage 3 to 4 showed a slowing down in the overall growth rate due to consumption of the gold and ascorbic acid, and the rearrangement of CTAB on the surface of the Au nanorods to form flat bilayers. The anisotropic particles formed through kinetic control slowly transformed into the more thermodynamically favourable shape through the ageing process (stage 5). The shape and quality of the seeds determined the fraction of byproducts formed.

1.3.4 Functionalisation and surface chemistry

The CTAB bilayer stabilising the gold nanorods can be easily disrupted. For example, if the CTAB concentration drops below the critical micelle concentration (cmc), organic solvents are added, or the salt concentration is increased, the bilayer can be destroyed and the rods become unstable\cite{40}. As a result, for the use of nanorods in potential applications, the surface chemistry must be manipulated to ensure the stability of the rods under a wide range of conditions\cite{41}. The strong affinity of thiols to Au has been used to functionalise nanorods with thiol molecules. Small molecules do not provide enough steric effect to overcome the strong attractive forces among Au nanorods, and therefore larger molecules such as thiolated polymers or long-chain alkanethiols or polyethylene glycol(PEG) are used\cite{42–44}. Thiols tend to preferentially bind on the ends of the nanorods, possibly due to the lower amount of CTAB, making these sites more accessible. Gold nanorods functionalised with thiolated-PEG, disulfides and dithiocarbamates exhibit a high degree of stability and can be dispersed in a wide range of solvents and made biocompatible\cite{45–47}. The group of Hamad-Schifferli systematically investigated the stability of gold nanorods after passivating their surface with a range of amphiphilic ligands\cite{48}.

The positive charge of gold nanorods has been exploited to add charged polyelectrolytes via layer by layer assembly\cite{49}. This allows the charge of the gold nanorods to be tuned and they can be made negatively charged through the electrostatic addition of a negative polyelectrolyte. Examples include polyacrylic acid (PAC), polystyrene sulfonate (PSS), both being negatively charged, and poly(diallyldimethylammonium chloride) (PDADMAC) and poly(allylamine hydrochloride) (PAH) as positively charged polyelectrolytes.
1.3.5 Effect of coating gold nanorods

The plasmon resonance of nanoparticles is affected by changes in their size and shape, as well as changes in surrounding refractive index and interparticle distance. Therefore different coating materials, which induce changes in the local refractive index around the nanoparticles, can be detected via spectral changes\cite{50,51}. Gold nanorods have been coated with different shells, such as dielectric materials (silica), semiconductors (such as metal oxides, TiO$_2$), or other metals such as Ag, or Pt\cite{23}.

One of the biggest challenges in nanoscience is the controlled assembly of particles\cite{52}. As-synthesised nanoparticles stabilised with ligands can form superlattices upon evaporation for example, where the spacing is determined by the length of the ligand\cite{53–55}, usually giving around 1-3 nm spacing. Precise spacer control between nanoparticles can be achieved by changing the capping material of the nanoparticles through ligand exchange. To further increase the spacing, DNA functionalisation can be used. In the case of Au nanoparticles, thiolated DNA strands can bind to the nanoparticles due to the high affinity of thiols to Au, and different structures can be obtained, such as linear chains with controlled interparticle distance whose scattering behaviour depends strongly on the number of particles in the chain\cite{56}. While this can give spacings up to 10 nm, DNA functionalisation is an expensive technique and not easily scalable. A way to increase spacing even further is by silica coating\cite{57,58}. This protocol has been developed for several years now, and can coat different nanoparticles and shapes. The shell thickness can be precisely tuned\cite{59,60}, but when it comes to assembly, it is difficult to obtain high enough volume fractions while maintaining the low polydispersity\cite{61}. However, to create spacers with >10 nm lengths, a new type of coating material is necessary. This coating should be tuneable in size, colourless and chemically stable. It should provide the nanoparticles with good colloidal stability and be relatively inexpensive since large volume fractions are needed. These criteria preclude proteins and DNA as practical shell materials. The material proposed in this thesis to satisfy these requirements are microgels. In the following section, the properties and recent literature on microgels and nanoparticles coated with microgels will be presented.
1.4 Responsive microgels

Microgels are colloidal internally cross-linked particles with sub-micrometer diameters that have an internal gel structure and are swollen by a suitable solvent\cite{62}. Gels that are swollen with water are called hydrogels. The most widely studied microgel is composed of poly-N-isopropylacrylamide (PNIPAM). PNIPAM is a microgel made of the monomer NIPAM that is held together by cross-link points and swollen in water. Microgels can undergo transformations due to changes in external stimuli such as temperature, pH, ionic strength or electric field, and when that occurs, they are referred to as smart or intelligent microgels\cite{63-66}.

PNIPAM undergoes an endothermic entropy-driven volume phase transition (VPT) in water. The first report of a hydrogel undergoing a VPT was in 1977 by Tanaka\cite{67}. The driving force for the swelling process and phase transition are interactions between the network components and the solvent. Through the amide groups of the NIPAM, hydrogen bonds form with water. The isopropyl groups however, induce hydrophobic interactions, referred to as polymer-polymer interactions. If the solvent-polymer interactions are stronger than the polymer-polymer, the PNIPAM exists in a random coil structure. It is in a swollen state and water is a good solvent for swelling. If the hydrogen bonds with water break, from an increase in temperature for instance, the polymer-polymer interactions become dominant, and as a result this leads to a coil to globule transition. Water becomes a poor solvent for the PNIPAM and the network collapses, expelling out the water. This volume phase transition (VPT) occurs at the lower critical solution temperature (LCST) of PNIPAM. PNIPAM hydrogels have a lower critical solution temperature (LCST) of around 32-33°C. This coil to globule transition is accompanied by a dramatic change in the volume of the microgel\cite{62,68-71}.

The VPT can be described through the classical Flory-Rehner theory\cite{72}, which is based on the assumption that the free energy of the gel, $F_{gel}$, is the sum of the free mixing energy of the gel $F_{mix}$, the free energy of the network elasticity $F_{el}$, and the free energy of charged microgels $F_{ion}$. A change in volume leads to a change in free energy, which can be described in terms of osmotic pressure, $\Pi$:

$$\Pi_{gel} = -\left(\frac{\partial F}{\partial V}\right)_T = \Pi_{mix} + \Pi_{el} + \Pi_{ion}$$ (1.12)
The osmotic pressure terms in equation 1.12 can be further expressed as:

\[
\Pi_{\text{mix}} = -\frac{N_A k_B T}{\nu} (\phi + \ln(1 - \phi) + \chi \phi^2)
\]  

(1.13)

\[
\Pi_{\text{el}} = -\frac{N_c k_B T}{V_0} \left( \frac{\phi}{2\phi_0} - \left( \frac{\phi}{\phi_0} \right)^\frac{1}{3} \right)
\]  

(1.14)

\[
\Pi_{\text{ion}} = -\frac{f N_c k_B T}{V_0} \frac{\phi}{\phi_0}
\]  

(1.15)

In the above equations, \(N_A\) is Avogadro’s number, \(k_B\) the Boltzmann constant, \(T\) the absolute temperature, \(\nu\) the molar volume of the solvent, \(\phi\) the polymer volume fraction, with \(\phi_0\) the polymer volume fraction in the initial state. \(N_c\) is the number of chains in the gel network, \(V_0\) the volume of the relaxed gel network, \(f\) the number of counterions per chain, and \(\chi\) is the polymer-solvent interaction parameter, known as the Flory-Huggins parameter. The interaction of the solvent molecules with the polymer particles leads to a change in the free energy, which is related to the Flory-Huggins parameter by:

\[
\chi = \frac{\Delta F}{k_B T} = \frac{\Delta H - T \Delta S}{k_B T}
\]  

(1.16)

where \(\Delta H\) and \(\Delta S\) are the changes in enthalpy and entropy, respectively, for the interaction of a monomer in the chain with the solvent. Microgels with a LCST, such as PNIPAM, have negative values of \(\Delta H\) and \(\Delta S\)\(^{[62]}\).

There are two ways the microgels can be cross-linked; chemically or physically. Physical cross-links involve cross-linking through forces such as hydrogen bonding or ionic interactions\(^{[63,73]}\). Chemical cross-linking involves actual chemical bonds between the polymer and the cross-linker. A suitable cross-linker molecule must possess two terminal double bonds; these are then sites that can be attacked by the radicals formed by the initiator during the polymerisation and the cross-linking can occur. For example, a commonly used cross-linker is N,N-Methylenebisacrylamide (BIS). The role of the cross-linker is two-fold. First, it helps hold the polymer together and prevents it from dissolving into solution or falling apart. The second role is that the amount of cross-linker points, also referred to as the connectivity or cross-linker density, controls how much the polymer changes upon exposure to external stimuli. A high cross-linker density means a high number of connection points between the polymer chains, and that yields a more solid-like structure. As a result the temperature
induced collapse is not very strong. For lower cross-linker densities, the polymer is more liquid-like and consequently can undergo more dramatic changes in volume upon surpassing the VPT temperature (VPTT). The cross-linker density can be controlled during the synthesis and can also affect the size of the microgel. The cross-linker density is expressed as a nominal molar ratio to the NIPAM concentration.

**Synthesis of PNIPAM microgels** PNIPAM particles were first prepared using surfactant-free precipitation polymerisation by Pelton and Chibante\[^{[74]}\]. In precipitation polymerisation, all the ingredients are mixed together in a solvent, water in the case of NIPAM. The polymerisation takes place under nitrogen and at temperatures higher than the VPTT, usually at 70°C. This temperature is used because the initiator undergoes thermal decomposition to produce free radicals. The most commonly used water-soluble initiators are either peroxide or azo based compounds. The nitrogen atmosphere is necessary because otherwise oxygen would quench the free radicals formed by the initiator and the polymerisation would not occur. A schematic depiction is given in Figure 1.4. The free radicals formed from the initiator attack the monomer, creating oligoradicals which lead to radical propagation and chain growth. The growing polymer chains collapse if they reach a critical length and form precursor particles that are colloidally unstable. The precursor particles can then grow through different ways. They can either aggregate together until a colloidal stable polymer forms, deposit onto the surface of existing polymer particles, or grow through adding more monomers. Once the microgels reach a critical size, they become stabilised through electrostatic interactions. The charge of the microgels arises from fragments of the initiator molecule that get incorporated into the polymer chains during the nucleation and growth phases\[^{[73]}\].
Since the polymerisation is taking place at temperatures above the VPTT, the formed particles are in a collapsed state. They still contain a lot of water however. When the polymerisation has finished, the mixture is left to cool to room temperature and the particles swell. The solution has to then be cleaned of unreacted monomers or uncross-linked polymer chains through methods such as dialysis or centrifugation.

The advantage of precipitation polymerisation is that the size of the particles can be well controlled (above a certain diameter) with narrow size distributions\cite{75}. Co-monomers can be incorporated into the polymer network to add more functional groups. Hybrid particles can also be prepared through the incorporation of inorganic nanoparticles. The formation of smaller microgels is difficult however below around 100 nm. In order to access smaller diameters, more stabilising agents have to be added.

The cross-linker BIS has been shown to polymerise much faster than NIPAM. As a result, the cross-linker density varies throughout the microgel. The inner microgel core is more highly cross-linked, and the extent of cross-linking decreases as we go more towards the periphery of the microgel\cite{62,76-78}.

### 1.5 Hybrid inorganic/organic nanoparticles

Introducing nanoparticles with optical, catalytic, and magnetic properties into microgel networks yields multifunctional nanoparticles that retain the inherent properties of the nanoparticles, as well as the responsive behaviour of the microgel\cite{63,64,68,79,80}. A major advantage
of the efficient encapsulation of nanoparticles with microgels is the introduced high colloidal stability which allows the use of the core without aggregation.

Karg et al. classified the different methods of incorporating nanoparticles into the microgel network into 3 main types: microgels with nanoparticles dispersed within the network, microgels covered with nanoparticles, and core-shell microgels[63]. A schematic description of the three different types is shown in Figure 1.5. Microgels can act as templates for the in-situ synthesis of nanoparticles, and as such give way to a system where the nanoparticles are randomly distributed throughout the microgel network[81–83]. Otherwise, nanoparticles can be incubated with microgels and incorporated into the network through electrostatic interactions, hydrogen bonding or covalent bonding[84–87]. Furthermore, the hybrid particles can serve as nanoreactors for catalytic reactions when loaded with catalytic nanoparticles[64,88]. PNIPAM microgels have also been coated with nanoparticles such as Au nanorods[89,90] or semiconductor quantum dots[91], either by making use of electrostatic interactions or through covalent bonding.

The main focus of this work will be on core-shell hybrid microgels. These consist of particles having a well-defined structure, with a single nanoparticle core and the polymer shell grown around the core. The effective particle volume increases due to the polymer shell, and thus provides a spacer between the nanoparticles cores which allows us to control the interparticle spacing[92,93]. This becomes important in the self-assembly of these particles where the nanoparticle neighbouring distance can thus be controlled.

The selective incorporation of functional groups into the microgel core is a big challenge[92]. For the preparation of core-shell microgels with an inorganic nanoparticle core, the nanoparticles have to be functionalised with a ligand having terminal double bonds. The double bonds ensure that the nanoparticles are covalently fixed in the microgel. These double bonds then form radicals from the initiator radicals. The reactive nanoparticles participate in the polymerisation by being incorporated into the growing polymer chains during the early stages of the process. They form the nuclei that then grow to form the hybrid particles. Having reactive centres on the surface of the nanoparticles ensures that they are in the interior of the microgel.
Figure 1.5: Hybrid microgels are classified into three main types: core-shell microgels (top), which have one nanoparticle core for each shell, microgels filled with nanoparticles (middle) and microgels covered with nanoparticles, such as gold nanorods (bottom). The sketch depicts the collapse of the microgel network upon the change in temperature, $\Delta T$. For microgels covered with nanoparticles, the distance ($d$) between the particles decreases from the swollen state to the collapsed. Reproduced from reference \cite{63}.
1.5 Hybrid inorganic/organic nanoparticles

1.5.1 Core-shell microgels

In general, the synthesis of core-shell microgels involves three main steps: synthesis of the nanoparticles, functionalisation of the nanoparticles, and polymerisation of the monomer and cross-linker. To form core-shell structures, the surface of the nanoparticles has to be functionalised to provide free double bonds for the polymerisation to initiate from. The nanoparticles are then incorporated into the polymerisation medium, thereby allowing the shell to grow around the core in a well-defined manner\textsuperscript{[63]}. The main polymerisation methods generally employed are surfactant-free emulsion polymerisations and living polymerisations, such as atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer (RAFT)\textsuperscript{[94,95]}.

One of the main challenges in the synthesis of core-shell microgels is the functionalisation of the nanoparticles surface. The main requirement for a suitable ligand is providing a double bond terminus, through which the polymerisation can occur. A first approach involved coating the nanoparticles with a silica shell, which could easily be functionalised with agents such as methacryloxypropyltrimethoxysilane (MPS)\textsuperscript{[89]}. The Liz-Marzán group\textsuperscript{[96]} then developed a method that involved polymerising the Au nanoparticles with styrene and divinylbenzene. They found this combination useful especially for CTAB-coated Au nanoparticles since CTAB forms a surfactant bilayer on the nanoparticles surface, where both these compounds could be dissolved and then polymerised into a thin polystyrene (PS) layer that possessed terminal double bonds. A PNIPAM shell was then further grown onto the nanoparticles. While this method led to core-shell microgels, it involved a two-step polymerisation and was quite limited in its application to non-CTAB coated nanoparticles.

Different approaches were then developed that led to direct polymerisation of NIPAM on the nanoparticle surface without the use of an intermediate shell. Karg et al.\textsuperscript{[97]} introduced the use of butenylamine, which easily replaced citrate molecules from the surface of 15 nm Au nanoparticles, binding to the nanoparticles surface through the amine and providing terminal vinyl groups. However, butenylamine is hydrophobic and so sodium dodecylsulfate (SDS) was also added prior to butenylamine to ensure stability of the nanoparticles, especially in the centrifugation steps used to concentrate the nanoparticles. Liz-Marzán et al. employed butenoic acid, which is similar to butenylamine, except it has a carboxyl group instead of an amine, through which it attaches to the nanoparticles. They demonstrated
butenoic acid as suitable for CTAB-coated Au spheres and rods of different sizes. Another group also made use of butenoic acid for the polymerisation of magnetic nanoparticles. However, this consisted of magnetic nanoparticles clusters surrounded by a PNIPAM shell.

More recently, Liz-Marzán et al. developed a new ligand system consisting of polyelectrolytes which worked for a variety of differently sized and shaped Au nanoparticles such as rods, stars and decahedra. Using carbodiimide chemistry they grafted allylamine onto polyacrylic acid (PAA), a negatively charged polyelectrolyte, forming a PAA-N-allyl modified polyelectrolyte. Then, using a layer by layer assembly approach, the PAA-N-allyl was adsorbed onto CTAB-coated Au nanoparticles which are positively charged, or onto PVP-capped Au nanoparticles by first coating those with positively charged poly(allylaminehydrochloride) (PAH). This method preserved the native ligands on the nanoparticles and the ligands were bound through electrostatic interactions.

Core-shell hybrid particles have been prepared using silica nanoparticles, silica coated gold nanoparticles, gold nanoparticles, silver nanoparticles and magnetic nanoparticles. The developed functionalisation strategies so far are still limited to specific nanoparticles and surface ligands. As of yet, no generic ligand or method exists for the coating of different nanoparticles with PNIPAM.

**Gold-PNIPAM core-shell particles** The most studied system has been Au nanoparticles in PNIPAM. Contreras-Cáceres et al. polymerised a polystyrene (PS) shell around 50 nm Au nanoparticles to obtain a thin layer of double bond terminated nanoparticles. Following that, a PNIPAM shell was grown onto the PS coated gold nanoparticles. The porous network of PNIPAM allowed the diffusion of molecules through to the core, and the Au core could be overgrown through a seeded growth mechanism. Others have further shown that Ag could also be overgrown on the gold core, with almost no secondary nucleation. Our group previously prepared Au-PNIPAM core-shell microgels in a way that allowed precise control over the shell thickness and the responsive behaviour by changing the monomer concentration and cross-linker density during the synthesis. The first step involved radical polymerisation of NIPAM and BIS with potassium peroxodisulfate as initiator in the presence of butenylamine-functionalised 15 nm Au nanoparticles. Typical results are given in Figure 1.6. The resulting Au-PNIPAM were highly monodisperse and possessed a single Au nanoparticles core as can be seen in the TEM images. Through spin coating or convex-
tive assembly, these monodisperse particles were assembled into hexagonally close-packed 2D monolayers\cite{108}, as shown in the tapping mode atomic force microscopy (AFM) height profile in Figure 1.6.

![Figure 1.6: TEM image (left) of a Au-PNIPAM core-shell particles with butenylamine-functionalised 15 nm Au nanoparticle cores. The particles could be assembled into 2D monolayers, as shown in the tapping mode AFM height profile (right) of 2D assembled Au-PNIPAM particles.](image)

Carregal-Romero et al.\cite{109} studied gold core-shell systems as catalysts for the reduction of ferricyanide ions by borohydride in aqueous solution. They observed that PNIPAM acted as a protective agent for the gold nanoparticles, making them stable and preventing them from aggregating. The effect of the cross-linker density on the catalytic activity was studied and they observed that the catalytic activity was higher at lower cross-linker densities. This is due to both the cross-linker effect on the swelling behaviour of the microgel, and the effect of the cross-linker density on the porosity of the microgel. Different nanoparticles could also be introduced into the same microgel system, resulting in microgels with various properties. For example, Sánchez-Iglesias et al.\cite{110} synthesised gold cores surrounded by a thin layer of nickel, which was in turn surrounded by a PNIPAM shell. This produced a hybrid microgel with optical and magnetic properties, and thermoresponsive behaviour.

In addition to direct heating of the solvent, indirect heating via the metal nanoparticles can trigger the VPT. Noble metal nanoparticles such as Au and Ag can undergo localised heating through laser excitation at the wavelength of their LSPR, which can be transferred
into their surrounding medium, thereby acting as a heat source\textsuperscript{111}. Consequently, for core-shell Au-PNIPAM microgels this photothermal behaviour can be used to induce the VPT, which is especially useful due to the fact that this transition occurs at a \( \mu \text{s} \) time scale. A recent study by Rodríguez-Fernández et al.\textsuperscript{112} used core-shell Au-nanorod-PNIPAM core-shell microgels, which were prepared using the PS precoating method of Contreras-Cacerás et al.\textsuperscript{96} The Au nanorods encapsulated in PNIPAM were irradiated in the NIR with laser light at 800 nm. They observed an instantaneous increase in absorbance at lower wavelengths attributed to the increased scattering, and a red-shift of the LSPR due to the change in refractive index. This change remained as long as the sample was illuminated, and was reversible. However, these particles were of poor quality. Many empty PNIPAM spheres could be seen, with some appearing on the outside of the PNIPAM shell, as well as some aggregated rods. For self assembly applications, monodispersity is extremely important.

1.6 Assembly

Currently, there is a growing demand for functional materials with properties that can be controlled via external stimuli\textsuperscript{113–115}. Responsive photonic crystals for example, can have applications as colour displays, chemical sensors, inks and paints\textsuperscript{116}. A way to prepare self-assembled colloidal crystals is necessary, because microfabricated crystals require quite a lot of time and cost. Stimuli-responsive photonic crystals are designed in a way whereby external stimuli can induces changes in the refractive index of the particles or a change in the lattice constant in the crystalline arrays. For example, in colloidal crystals composed from hydrogels, the lattice spacing can be tuned by the swelling and deswelling of the hydrogel.\textsuperscript{116}

In the swollen state, the refractive index of the particle is almost equal to that of the solvent. When it collapses, the refractive index increases and approaches that of a dehydrated polymer network. This change in refractive index can be seen visually. When a dilute microgel solution is in a swollen state it is almost transparent but becomes turbid and opaque upon the network collapse. Concentrated dispersions of microgels have even more complex optical properties. Microgels are able to crystallise into ordered arrays, and thus Bragg diffraction of the incident lights occurs, leading to opalescence. The particles are in a swollen state and tightly compressed together. This crystallinity can be destroyed.
by heating, which causes the particle deswelling, going back to the liquid phase with randomly scattered light. This behaviour is important because the diffracted wavelength can be tuned, and this is useful for optical sensors.\textsuperscript{[117]}

Colloidal crystals can be fabricated by two main methods: top down or bottom up techniques\textsuperscript{[52]}. The top-down approach makes use of microfabrication techniques, such as electron beam lithography, to create patterned substrates having cavities of desired shapes and sizes at specific positions along the substrate. Particles can then be assembled into these holes, such as with capillary force assembly, yielding 2D arrays of assembled particles with controlled distance. The advantage of top down methods is the spacing between the particles can be very well-controlled. However, it is quite a costly and time-consuming technique and becomes more complicated with 3D assemblies. Bottom-up assembly makes use of interparticle forces and particle-substrate interactions to assemble nanoparticles from the colloidal solutions. Monodisperse colloidal particles are typically assembled at the air-liquid interface or in a thin liquid layer on a solid substrate using techniques such as spin coating or convective assembly. Large area high quality 2D monolayers of Au-PNIPAM have been prepared with these techniques\textsuperscript{[107,108,118–120]}.

Methods used for 2D assembly can also be used to prepare 3D crystals. Techniques for 3D assembly include sedimentation, solvent evaporation, electrostatic interactions, and physical confinement. The most common example of a 3D colloidal crystal is the opal, which is made of close-packed silica spheres. The stacking of the silica spheres leads to a crystalline structure having spacings on the order of the wavelength of visible light, which is the reason for the iridescent colours we observe. While the silica spheres can stack in either a face-centred cubic (fcc) or hexagonal close-packed (hcp) structure, the fcc structure is the predominant packing structure upon sedimentation\textsuperscript{[121]}. While bottom up assembly is quite scalable and versatile, it offers little control over the interparticle spacing. The polymer nature of the microgels, however, allows external control over the size of the particles and the volume fraction. Therefore, this allows tuning of the volume fraction without changing the particle number concentration.

**Assembly of organic PNIPAM microgels**  Colloidal crystals have been prepared from pure hydrogel particles, such as PNIPAM. It was shown by several groups that PNIPAM colloidal crystals showed a significant intensity response to changes in temperature\textsuperscript{[23,122–130]}. 
Heating the crystalline array above the LCST causes the particles to collapse, thereby shrinking and melting the crystalline structure\textsuperscript{[131,132]}. The lattice spacing is thus increased and the system becomes a disordered liquid again. This process is entirely reversible, because cooling the particles will cause them to swell again, and as a result the iridescence will reappear. Hellweg et al. found that at high volume fractions, PNIPAM microgels crystallised into face centred cubic (fcc) structures. This was consistent with what is expected for hard spheres. The lattice constants obtained from small angle neutron scattering matched well with the size of the particles in the dilute microgels showing that assemblies of the particles did not undergo much deformation\textsuperscript{[122]}. The assembly of PNIPAM was taken further by Hu et al., who modified the PNIPAM particles with a molecule that could under photo-induced cross-linking. As a result, the polymer particles were covalently bound to each other while packed in high volume fractions, and increases in temperature led to changes in interparticle spacing while maintaining the crystallinity. This led to changes in the wavelength of the diffraction peak. This created a temperature stable responsive colloidal crystal with fast response rate that could be used in sensors and displays\textsuperscript{[130]}.

**Assembly of core-shell particles**  The main advantage of coating nanoparticles with PNIPAM compared to other shelling materials is the fact that PNIPAM can be used as a flexible spacer between the nanoparticles. The polymer shell increases the effective particle volume, and therefore interparticle distance. As a result PNIPAM can be used as a spacer where the distance is controlled either through shell thickness, or through temperature. This becomes important in self assembly and leads to a vast array of possibilities. Inorganic nanoparticles also have a higher refractive index than organic polymers, which leads to stronger optical bandgaps, and the cores can potentially act as a local reporter on transitions occurring within the structure\textsuperscript{[93]}. A further advantage of assembled inorganic nanoparticles incorporated in microgels is the photothermal behaviour of the metal core can be exploited for inducing the VPT.

We previously showed that hexagonally close-packed 2D monolayers of Au-PNIPAM having different shell thicknesses could be prepared using different assembly methods and by varying the substrate charge\textsuperscript{[108]}. By using core-shell microgels with two different shell thicknesses, the surface coverage and interparticle spacing could be controlled. We further showed that the PNIPAM shell could be removed by heat treatment, retaining a mono-
layer of well-separated Au nanoparticles on the surface. This concept was then applied by Vogel et al.\textsuperscript{[118]} who assembled Au-PNIPAM at the air/water interface of a Langmuir trough with transfer to solid substrates, followed by removal of the PNIPAM shell by heat treatment. Another group demonstrated removal of the PNIPAM shell via oxygen plasma treatment leaving well-ordered Au nanoparticle arrays.\textsuperscript{[119]} Volk et al. recently assembled Ag@Au-PNIPAM core-shell particles at the air/water interface, into highly ordered monolayers which showed long range dipolar plasmon coupling and precise control over the interparticle distance.\textsuperscript{[120]} These works highlighted how coating nanocrystals with PNIPAM shells provides a generic pathway to ordered 2D arrays of nanocrystals with tuneable lattice spacings.

For 3D assembly, Suzuki et al. demonstrated the formation of PNIPAM colloidal crystals containing localised Au nanoparticles throughout the microgel. They observed Bragg diffraction peaks and the 111 plane of their crystalline arrays confirming fcc lattice structure.\textsuperscript{[133]} The same group later prepared assemblies from a mixture of PNIPAM microgels and Au nanoparticles, and studied the crystallisation dynamics after photothermally annealing the crystal.\textsuperscript{[134]} Karg et al. used Au-PNIPAM microgels for the preparation of nanocrystal superlattices, where interparticle spacings and crystallisation of the particles could be controlled through volume fraction and temperature.\textsuperscript{[111]} This work highlighted the potential of PNIPAM-coated nanoparticles for large scale photonic crystals.

1.7 Applications of hybrid microgels

Microgels, in particular hybrid inorganic/organic microgels have many potential applications in sensing, drug delivery, and catalysis.\textsuperscript{[98,109,135–139]} Furthermore, these composites can be used as temperature sensors due to the changes induced on the nanoparticles core by the VPT. Hydrogels are of interest in drug delivery because of their water solubility, biocompatibility, and their porous structure which allows particles to be loaded into the interior of the microgel network and then released upon temperature- or pH-induced collapse.\textsuperscript{[140,141]}

Ballauf’s group\textsuperscript{[88,142]} studied the catalytic activity of Pd and Ag nanoparticles generated within PS-PNIPAM core-shell systems. They demonstrated that these systems can be used as “nanoreactors” whereby the microgel acts as a medium for the catalytic reaction. The thermoresponsive nature of PNIPAM renders the system a smart nanoreactor. At
temperatures below the VPT, the open structure allows reactants to diffuse into the network, allowing the catalytic nanoparticles to be fully accessible to the reactants. Above the VPT, the collapse of the network makes the diffusion of reactants into the microgel network slower, and therefore this allows the catalytic behaviour to be controlled by temperature to a certain extent. Carregal-Romero et al.\textsuperscript{[109]} further studied Au core-shell systems as catalysts for the reduction of ferricyanide ions by borohydride in aqueous solution. They observed that PNIPAM acted as a protective agent for the Au nanoparticles, making them stable and preventing them from aggregating. The catalytic activity was shown to be higher at lower cross-linker densities. This is due to both the cross-linker effect on the swelling behaviour of the microgel, and the effect of the cross-linker density on the porosity of the microgel.

The group of Liz-Marzán have used Au-PNIPAM core-shell microgels for surface enhanced Raman scattering (SERS) sensing\textsuperscript{[98,135]}. In order to obtain a good SERS signal and use this technique for the detection of a wide range of analytes, the molecule to be detected must be close to the metal nanoparticles. This is generally difficult for molecules with a low metal affinity. Au-PNIPAM, and even more so Ag-overgrown Au-PNIPAM microgels are being used to trap molecules in their network, which are then brought into close contact with the metal nanoparticle core through temperature.

1.8 Research questions

Coating nanoparticles with polymer microgels has recently become a research area of great interest. First of all, microgels provide the nanoparticles with excellent colloidal stability. In addition, coating nanoparticles with responsive microgels leads to hybrid materials with various functionalities. Hybrid inorganic/organic microgels composed of a nanoparticle core and a responsive polymer shell can lead to functional materials with fluorescent, plasmonic, magnetic and catalytic properties, as well as responsive behaviour to external stimuli such as temperature. This allows one to tailor the properties of nanoparticles, either through the type of nanoparticle used as core or through the choice of shell material. Nanoparticles are highly sensitive to their environment, and their properties can also be tuned through the shell thickness and temperature. Despite the versatility of these particles, their widespread use is still at early stages, and much potential exists for their application in sensing and
1.8 Research questions

optical displays and devices. In terms of assembly, microgels shells provide a soft and flexible spacer for controlling the interparticle separation.

In this thesis, the aim was to explore the PNIPAM coating of anisotropic nanoparticles, specifically gold nanorods, and their 3D assembly. In order to do so, monodisperse gold nanorods first had to be synthesised in a reproducible way and on a large scale, followed by exploring the PNIPAM coating and crystallisation. The key research questions which will be addressed throughout this thesis are:

1. Can we develop a protocol for coating monodisperse gold nanorods with a PNIPAM shell with a high yield, and characterise their optical properties and swelling behaviour?

2. Can we assemble these particles in 3D and explore their crystallisation and melting behaviour?

3. Can a generic protocol be developed that can be used for the coating of different nanoparticles with PNIPAM?
Chapter 2

Materials and Instruments

This chapter lists the Materials and Instruments used throughout this thesis. Experimental details are provided within the relevant chapters.

2.1 Materials

Gold(III) chloride trihydrate (Aldrich, ≥ 99.9%), cetyltrimethylammonium bromide (CTAB; Sigma ≥ 98% H5882 Lot SLBHO222V), sodium borohydride (NaBH₄; Aldrich, ≥ 98.0%), silver nitrate (AgNO₃; Sigma), ascorbic acid (AA; Aldrich), hydrochloric acid (HCl; Thermo Fisher, 32%), 5-Bromosalicylic acid (BrSA; Aldrich technical grade, 90%), sodium oleate (NaOl; TCI chemicals, 97%), hydroquinone (HQ; Sigma-Aldrich, ≥ 99%), hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆; Sigma-Aldrich), and citric acid (Sigma-Aldrich) were used as received for the synthesis of nanoparticles. For the functionalisation the following chemicals were used: sodium dodecylsulfate (SDS; Ajax Laboratory Chemicals, Techn.), poly(sodium-4-styrenesulfonate) (PSS; Aldrich, average M₉₉ 70,000), 11-mercaptoundecanoic acid (MUA; Aldrich), 3-butenolic acid (butenoic acid; Aldrich, 97%), and butenylamine hydrochloride (butenylamine; Aldrich, 97%). N-isopropylacrylamide (NIPAM; Aldrich, 97%), N,N’-methylenebisacrylamide (BIS; Fluka, ≥ 99.5%), potassium peroxodisulfate (KPS; Fluka, ≥ 99.0%) and 2,2’-azobis(2-methylpropionamidine) dihydrochloride (AAPH; Aldrich, granular, 97%) were used for the polymerisation without further purification. Water was purified using a MilliQ-system (Millipore). The final resistivity was 18 MΩcm.
2.2 Instrumentation

2.2.1 Centrifugation

All samples were centrifuged using a Beckman-Coulter CS-15 centrifuge equipped with a CO650 fixed-angle rotor.

2.2.2 UV-vis Spectrometry

UV-vis spectra were recorded with an Agilent 8453 spectrophotometer. The temperature of the sample cell was controlled by a circulating waterbath (Lauda, Germany) and measured with a mercury thermometer in a cell filled with water before the actual measurement was done. This provided a precision in temperature of ±0.25 K. Before each measurement, the samples were equilibrated for 10 minutes at the respective temperature. Spectra were taken at temperatures between 10 and 52°C. Spectra were measured using 1 cm pathlength quartz cuvettes for solutions and 1 mm pathlength quartz cuvettes for the crystals.

2.2.3 Zeta Potential

Zeta potential measurements were taken using the Brookhaven Instruments Corporation ZetaPALS (using a 35 mW red diode laser $\lambda = 660$ nm) which determines zeta potential using phase analysis light scattering. Measurements were carried out for highly diluted solutions in water at a temperature of 20°C.

2.2.4 Transmission Electron Microscopy

TEM images were recorded on an FEI TF 20 TEM operated with an acceleration voltage of 200 kV. Samples were prepared by drop-casting around 10 µl of dilute dispersions on carbon-coated copper grids (400 mesh) and left to dry in air. For the gold nanorods, the solutions were centrifuged twice (8000 rpm, 20 min) before measurements to remove excess CTAB and redispersed in water. This allowed better quality TEM images to be obtained. Size analysis of the images was performed using ImageJ image processing software.
2.2.5 Dynamic Light Scattering

Dynamic Light Scattering (DLS) measurements and analysis were performed on a Brookhaven BI-200SM goniometer with BI-9000AT autocorrelator system with a 633 nm laser at an angle of 90°. Very dilute samples were measured at 25 and 50 ± 0.1 °C.
Chapter 3

Synthesis and Functionalisation of Gold nanorods

A major goal of this thesis was to explore the coating of nanocrystals with PNIPAM. In particular, a key objective was to be able to uniformly coat monodisperse gold nanorods of different aspect ratios. In order to achieve that goal, first the synthesis of monodisperse gold nanorods with different aspect ratios had to be realised. In this chapter, four different protocols were tried and compared for the preparation of gold nanorods. The aim was to access a variety of aspect ratios (AR) and hence longitudinal surface plasmon resonances, as well as finding a protocol that produced the highest yield of gold nanorods with little or no shape impurities. The first protocol studied was based on the initial silver-assisted seed-mediated method developed by El-Sayed\cite{16} and Liu\cite{17}, which used ascorbic acid as a reducing agent as discussed in Chapter 1. These rods will be referred to as ‘AA-rods’. The second protocol makes use of an aromatic additive, 5-Bromo-salicylic acid (Br-SA), which is employed as a pre-reducing agent, ensuring that there is a mixture of Au(III) and Au(I) prior to the final reduction with ascorbic acid. Consequently, these rods will be referred to as ‘BrSA rods’. The idea of using aromatic additives was introduced by Murray, and his work used sodium oleate (NaOl) in conjunction with CTAB as a binary surfactant. That was the third protocol tried, and those rods will be referred to as ‘NaOl’ rods. Finally, the fourth method makes use of hydroquinone HQ as a reducing agent, rather than ascorbic acid, and these rods will be called ‘HQ rods’. Each synthetic protocol offers a different level of control over the aspect ratio, and hence longitudinal plasmon band, as well as final shape, yield, and impurities. The detailed procedure and results of each will be presented
3.1 Synthesis of gold nanorods

All glassware was thoroughly cleaned with fresh aqua regia, rinsed at least three times with MilliQ water followed by ethanol, then dried in the oven. Due to the low concentrations of Au$^{3+}$ needed, stock solutions were prepared by dissolving the entire contents of a 1 g or 5 g bottle of HAuCl$_4$·3H$_2$O (Sigma Aldrich) in a specific volume and then the mass of HAuCl$_4$·3H$_2$O determined by the difference in weight of the full bottle and the empty bottle. This way eliminated contamination of the gold salt by spatulas and provided an accurate gold ion concentration that was reproducible throughout the various syntheses. In this thesis, 2 stocks solutions of Au$^{3+}$ were prepared with concentrations of 0.105 69 M and 0.155 107 M, and the amounts of gold needed for each synthesis were calculated accordingly. All solutions were prepared in MilliQ water unless stated otherwise.

3.1.1 Seeds

The seeds were prepared for all corresponding rod syntheses as follows. A 5 mM Au$^{3+}$ solution was prepared by dissolving 16.1 µl of 0.155 107 M HAuCl$_4$·3H$_2$O in 5 ml water. This was then added to 5 ml of 0.2 M CTAB solution, which had been dissolved by heating. The mixture was placed in a water bath at 32°C and kept stirring for 10 min to allow complexation of the Au(III) and CTAB. Then, under vigorous stirring (~1200 rpm), 300 µl of freshly prepared 0.02 M NaBH$_4$ was added quickly and stirring was continued for 2 min, after which the seeds were stored at 32°C for 30 min.
3.1 Synthesis of gold nanorods

Figure 3.1: Photograph of an aqueous 5 mM Au\(^{3+}\) solution in 0.1 M CTAB at 32°C (left). Upon the rapid addition of 300 µl of freshly prepared 0.02 M NaBH\(_4\) under vigorous stirring (∼1200 rpm), reduction of the Au\(^{3+}\) occurred, indicated by an instant colour change (right).

Figure 3.1 shows the colour of the seed solution before and after addition of NaBH\(_4\). The change in colour from yellow to golden brown was instantaneous, indicating reduction of the Au. After several hours (>3), the colour started to change to red indicating that the seeds had grown in size (larger than 5 - 6 nm) and could no longer be used. In the literature, different groups slightly vary the stirring time, temperature, ageing time of the seeds and scale of preparation, but the overall premise and concentrations used are always the same.

A few factors were found that affected the quality of the seeds and therefore the quality of the rods. The rate of stirring was important, especially ensuring that the stirring was homogeneous. Sufficient time (5 - 10 min) should be allowed for the Au-CTAB complex to form and equilibrate at the temperature before reduction with sodium borohydride. Due to the low volume and concentration of NaBH\(_4\), it was preferable to prepare a larger volume than needed to reduce errors. Consequently, the 0.01 M NaBH\(_4\) was prepared by dissolving 37 mg in 50 ml water. The NaBH\(_4\) bottle was stored in a glove box.

3.1.2 Conventional ascorbic acid reduction

The silver-assisted seed-mediated method involves the addition of the seed solution to a reduced mixture of Au, Ag, and CTAB. The aspect ratio can be controlled by the amount of added AgNO\(_3\), and the pH of the solution. The following protocol is based on the method reported in the paper by Liu et al.\cite{17} In this work, the highest amount of silver was used, which should lead to an aspect ratio of around 4. For our purpose, we scaled up the synthesis from 10 ml to 250 ml. The temperature of the growth solution was set at 30°C using a
3.1 Synthesis of gold nanorods

water bath. 250 ml of 0.1 M CTAB were prepared in a 500 ml conical flask. Upon complete
dissolution of the CTAB, 1.08 ml 0.1155 M HAuCl₄ was added. After around 5 min of gen-
tle stirring, 4.65 ml of 1 M HCl was added. Under vigorous stirring, 300 µl 0.1 M AgNO₃,
2 ml 0.1 M ascorbic acid, and 600 µl of seeds were sequentially added with 30 s between each
addition. Stirring was stopped 30 s after the final seed addition and the solution was left
undisturbed at 30 °C overnight. The gold nanorods were then centrifuged once at 7000 rpm
for 1 hr, and redispersed in water.

Figure 3.2: Sketch of the different steps in the formation of gold nanorods using the AA
protocol. 300 µl 0.1 M AgNO₃ was added to a mixture of 1.08 ml 0.1155 M HAuCl₄ and
4.65 ml of 1 M HCl in 250 ml of 0.1 M CTAB under stirring at 30 °C. After 30 s, the reduction
step occurred through the addition 2 ml 0.1 M ascorbic acid, followed by growth initiated
by the addition of 600 µl of seeds after another 30 s.

The results are shown in Figure 3.3, with UV-vis absorbance spectra, TEM micrographs,
and size histograms from analysis of the TEM. An average of 150 particles were counted
for each sample. The rods in the top panel were prepared as described above. For the rods
in the bottom panel, the synthesis was scaled up even further to 500 ml, instead of 250 ml.
In addition, no stirring was used; instead, the bottle in which the reaction was performed
was shaken vigorously after each addition. The concentrations of all species were the same
for both rods. These slight variations in the way the synthesis was performed led to quite a
significant change in the final shape and aspect ratio of the gold nanorods. The rods the top
panel exhibited a longitudinal plasmon band at 847 nm, while the rods in the bottom panel
were red-shifted to 913 nm. This red-shift was manifested by an increase in size: the rods in
the top panel had dimensions of 51.8 ± 6.3 x 12.6 ± 1.9 nm, with an aspect ratio of 4.2 ± 0.8,
while those in panel B were $55.2 \pm 8.9 \times 10.8 \pm 2.1$ nm, with an aspect ratio of $5.2 \pm 1.3$. To distinguish between the two, they will be referred to by their aspect ratios. For AA-rods-5.2, the size distribution was broader, as indicated by the greater standard deviations in size, as well as the broader plasmon resonance band. Gaussian fits of the longitudinal plasmon band gave full width at half maxima (FWHM) of 241 for AA-5.2 and 181 for AA-4.2, which further indicated the larger population for AA-5.2. However, in addition to the variation in size between the two rods, a difference in the final shape was also observed. AA-4.2 had a dogbone shape, while AA-5.2 were more cylindrical. The TEM images of both rods also revealed the presence of spherical impurities, which is a typical byproduct of the synthesis of gold nanorods due to the fact that spheres are the more thermodynamically stable shape.
3.1 Synthesis of gold nanorods

Figure 3.3: UV-vis, TEM and size histograms of typical results from the ascorbic acid reduction protocol. TOP: AA-4.2 rods with UV-vis spectrum (left) showing a longitudinal plasmon band at 847 nm. Analysis of the TEM images (middle) and corresponding size histograms (right) gave dimensions of 51.8 x 12.6 nm, with an aspect ratio of 4.2. Bottom: AA-5.2 rods with UV-vis spectrum (left) showing a longitudinal plasmon band at 913 nm. Analysis of the TEM images (middle) and corresponding size histograms (right) gave dimensions of 55.2 x 10.8 nm, with an aspect ratio of 5.2.

A minimum ratio of AA to Au of 1.1 is necessary for conversion of the Au\(^{3+}\) to Au\(^{1+}\). However, as discussed earlier, a molar ratio of 1.6 is required for complete reduction of all the gold, which is what is used in the typical AA seed-mediated synthesis. Reports in the literature have shown that one of the reasons for the formation of a dogbone shape could be due to excess AA\(^{143}\). In order to try to improve the shape of the rods prepared with the AA method, two parameters were varied: the ageing time of the seeds, and the amount of ascorbic acid added. We tried ageing of the seeds for 30 min and 5 min prior to addition to the growth solution, and AA:Au ratios of 1.3, 1.5 and 1.6. A ratio of 1.1 was also tried, but the resulting solution remained clear, indicating that either no or very few gold nanorods
UV-vis absorbance spectra of the six nanorod samples are shown in Figure 3.4 and the corresponding TEM images given in Figure 3.5. The spectra for the molar ratio of 1.6 were almost identical regardless of 5 min to 30 min seed ageing time. For the 5 min ageing, the position of the plasmon band did not change much with changes in AA molar ratio. Additionally, the TEM images of the 5 min aged seeds at AA molar ratios of 1.6, 1.5, and even as low as molar ratio of 1.3 all revealed a dog-bone shape. This indicated the ageing time of 5 min probably meant there was still a larger concentration of residual NaBH$_4$ in the seeds, and so the gold was reduced even further, which could explain the constant dog-bone shape. A dog-bone shape appears when the rate of growth along the diameter is greater than along the length of the rod. For the 30 min aged seeds, the longitudinal plasmon band was most red-shifted for the 1.3 ratio, and blue-shifted for the 1.5 and 1.6 ratios. This was in agreement with results by Sharma$^{[143]}$ who observed an initial red-shift upon going from 1.1 to 1.3 ratio, followed by a blue-shift upon increasing the ratio to 1.6. They attributed the initial red-shift to an increase in the length of the rods, followed by growth along the diameter of the rods. This could then explain the reason for the formation of a dogbone shape upon reaching a ratio of 1.6, due to the deposition of more Au atoms on the ends of the rods. Contrary to the 5 min aged seeds, the rods formed with the 30 min aged seeds showed a change in the shape of the rods upon changing the AA molar ratio. From the TEM images in Figure 3.5, it was apparent that the dogbone shape only arose for the 1.6 ratio. For both 1.5 and 1.3 ratios, the rods were more uniform in diameter.
3.1 Synthesis of gold nanorods

Figure 3.4: UV-vis spectra of AA rods prepared with seeds aged for either 5 min (solid lines) or 30 min (dashed lines) for AA to Au of 1.6, 1.5 and 1.3.

Figure 3.5: TEM images of the rods prepared with 30 min (top) and 5 min (bottom) aged seeds with AA:Au ratios varying from 1.6 (left) to 1.5 (middle) and 1.3 (right).

The results highlighted the sensitivity of the final shape of the formed nanorods to the
3.1 Synthesis of gold nanorods

molar ratio of ascorbic acid, and showed that even small changes had quite a large effect. Even though utilising a lower amount of AA can improve the shape of the gold rods, it affects the yield, because less Au gets reduced during the synthesis. This sensitivity can lead to inconsistencies and low reproducibility within this technique from batch to batch, and that is one of the main reasons why newer protocols have been developed that employ either a second reducing agent in addition to AA, or a completely different reducing agent, as will be discussed in the following sections.

3.1.3 Using aromatic additives

The addition of aromatic compounds can affect the micellisation behaviour of CTAB. As a result, new work arose that exploited these additives to try and improve the synthesis of gold nanorods and better understand the mechanism for rod formation\[28,29,35\]. The Murray group\[28\] investigated the use of salicylate salts, and found that they could reduce the CTAB concentration from 0.1 M (used in the conventional syntheses) to 0.05 M. They also introduced the use of 5-Bromosalicylic acid as an additive, which was then further developed in the paper by Scarabelli et al.\[35\]

3.1.3.1 Bromosalicylic acid Pre-Reduction

This protocol based on the work of Scarabelli et al.\[35\] involved the addition of a second reducing agent, 5-Bromo-Salicylic acid (Br-SA), which was allowed to mix with the Au(III)-CTAB complex, leading to the pre-reduction of Au\(^{3+}\) to Au\(^{1+}\). Since this reaction took place at room temperature, the reduction proceeded quite slowly, and thus allowed precise tuning of the gold nanorods. The final aspect ratio of the rods depends on the pre-reduction time, with the AR becoming shorter for longer pre-reduction times. A pre-reduction time of 60 min was chosen for our experiments with the aim of obtaining rods exhibiting a longitudinal plasmon band around 800 nm.

The main steps of the synthesis can be seen in Figure 3.6. Initially, 250 ml of 0.1 M CTAB solution was prepared, and upon complete dissolution of the CTAB, 0.5 g Br-SA was added. The solution was kept for 15 min under stirring to ensure all the Br-SA had dissolved. After that, 4.8 ml 0.01 M AgNO\(_3\) solution was added, and kept stirring at 400 rpm for 15 min. 250 ml of 0.001 M Au\(^{3+}\) was then added (1.612 ml of 0.155 107 M H\(_{2}\)AuCl\(_4\).3H\(_2\)O stock solution). The dark orange colour indicated the formation of the Au(III)-CTAB complex. After
60 min pre-reduction time while stirring at 400 rpm, a change in the colour of the solution to light orange was observed, which indicated that the solution now contained a mixture of Au$^{3+}$ and Au$^{1+}$. Complete reduction was then performed by the addition of 1.3 ml of 0.1 M AA solution under vigorous stirring (1000 rpm). All gold species had now been reduced to Au$^{1+}$ and the solution immediately turned colourless, which can be seen in Figure 3.6. After 30s, 800 µl of seeds which had been aged for 30 min were injected. Stirring was stopped after 30s and the solution was left to stand at room temperature overnight. The final gold nanorod solution had a dark red colour. The prepared rods were then removed from their growth solution by one centrifugation step at 7500 rpm for 1 hr, and redispersed in MilliQ water.

Figure 3.6: Top: Sketch of the different steps in the formation of gold nanorods using the BrSA protocol. 0.5 g Br-SA was added to 250 ml of 0.1 M CTAB, followed by 4.8 ml 0.01 M AgNO$_3$ and 250 ml of 0.001 M Au$^{3+}$. After 60 min pre-reduction time, the final reduction step occurred through the addition of 1.3 ml of 0.1 Mascorbic acid, followed by growth initiated by the addition of 800 µl of seeds after 30 s. The bottom panel shows corresponding photographs of the solutions at the different stages of the synthesis.

The results of this method are shown in Figure 3.7, with the UV-vis spectrum showing a
narrow longitudinal plasmon band at around 805 nm. TEM images of the particles showed highly monodisperse rods, with almost no shape impurities. No shape separation step was performed. The solution was only centrifuged once at 7500 rpm for 1 hr to remove excess CTAB. Size analysis from TEM gave dimensions of 45.6 ± 4.0 nm x 12.3 ± 1.2 nm, with an average aspect ratio of 3.7 ± 0.5. This was in good agreement with the results reported in Scarabelli et al. [35], which gave an AR of 3.8 from a pre-reduction time of 60 min.

BrSA-3.7

Figure 3.7: UV-vis, TEM and histograms of typical results from the Bromo-salicylic acid protocol. BrSA-3.7 rods with UV-vis spectrum (left) showing a longitudinal plasmon band at 805 nm. Analysis of the TEM images (middle) and corresponding size histograms (right) gave dimensions of 45.6 x 12.3 nm, with an aspect ratio of 3.7.

3.1.3.2 Sodium Oleate

The Murray group later introduced an enhanced protocol that used sodium oleate (NaOl) as a co-surfactant with CTAB. Sodium oleate is composed of a long chain unsaturated fatty acid and is a water-soluble anionic surfactant. This allowed them to reduce the CTAB concentration even further, down to 0.037 M, which should reduce the cleaning step of the rods post-synthesis. Additionally, using a co-surfactant opened the doors for further tunability in terms of dimensions, especially the diameter of the nanorods. Due to the double bonds in NaOl, it could also slowly reduce the Au\(^{3+}\), similarly to the Bromo-salicylic acid. Therefore, the molar ratio between AA and Au was 1:3, which is much lower than that reported for the conventional AA synthesis.

Rods with an aspect ratio of 3 were prepared as follows. In 250 ml water, 9 g CTAB were dissolved to a concentration of 0.047 M, with 1.543 g sodium oleate, under stirring in a water
3.1 Synthesis of gold nanorods

bath at 50 °C. Upon dissolution, the temperature was brought down to 30 °C, and 18 ml of 4 mM AgNO₃ were added. The solution was kept undisturbed for 15 min, after which 250 ml of 1 mM Au³⁺ (1.612 ml of 0.155 107 M) were added under stirring at 700 rpm. Stirring was continued for 90 min to allow the reduction of Au³⁺ to Au¹⁺, as indicated by the gradual change in colour from golden brown to colourless. 2.5 ml 32 % HCl was added and stirred at 400 rpm for 15 min. The stirring speed was then increased to 1200 rpm and 1.25 ml 0.064 M ascorbic acid was quickly added, followed by 0.4 ml seeds 30 s later. The solution was left stirring for 30 s, after which the stirring was stopped and it was left overnight at 30 °C. The aspect ratio could be varied by changing the amounts of sodium oleate, AgNO₃, HCl, and seeds. For an aspect ratio of 2.5, the amounts used were: 1.234 g sodium oleate, 24 ml 4 mM AgNO₃, 1.8 ml 32 % HCl, and 0.1 ml seeds.

Figure 3.8: Sketch of the different steps in the formation of gold nanorods using the sodium oleate protocol. A certain amount of NaOl was added to 250 ml of 0.047 M CTAB, followed by 18 ml of 4 mM AgNO₃ and 250 ml of 1 mM Au³⁺ at 30 °C. After 90 min pre-reduction time, 2.5 ml 32 % HCl was added and stirred at 400 rpm for 15 min, followed by the final reduction step through the addition of 1.25 ml 0.064 M ascorbic acid, and finally the growth initiated by the addition of 0.4 ml of seeds after 30 s.
3.1 Synthesis of gold nanorods

Figure 3.9: UV-vis, TEM and histograms of typical results from the sodium oleate protocol. Top: NaOl-3.1 rods with UV-vis spectrum (left) showing a longitudinal plasmon band at 755 nm. Analysis of the TEM images (middle) and corresponding size histograms (right) gave dimensions of 93.7 ± 7.3 by 30.5 ± 2.5 nm, with an aspect ratio of 3.1 ± 0.4. The bottom panel shows rods having a longitudinal plasmon band at 712 nm, and dimensions of 107.5 ± 8.2 by 44.8 ± 2.4 nm, with an aspect ratio of 2.4 ± 0.2. As mentioned earlier, this protocol allowed the preparation of rods with larger diameters. NaOl-2.4 had a larger amount of impurities than NaOl-3.1. Based on the amounts of reagents used from the Murray paper, our rods should have had dimensions of 90 x 30 nm and 125 x 40 nm, respectively. Our results deviated from this slightly, especially the length of the NaOl-2.4. One of the problems associated with this synthesis was that although it is versatile in terms of accessing different nanorod dimensions, it was not found to be very reproducible. Our results varied
from the expected dimensions, and repeating the reaction with the same parameters led to discrepancies in the size.

3.1.4 Hydroquinone reduction

As described in section 3.1.2, the synthesis of gold nanorods is highly sensitive to the experimental parameters, particularly the ascorbic acid concentration. In a study by Murphy\textsuperscript{[144]}, they found that a typical synthesis of gold nanorods only resulted in a 15\% conversion of the Au ions to metallic gold. In section 3.1.3.2, we showed that aromatic additives could be added to CTAB, to improve the monodispersity and shape of the rods, and also to access lower concentrations of CTAB and AA. However, other groups also chose to investigate reducing agents other than ascorbic acid. Vigderman et al.\textsuperscript{[31]} introduced hydroquinone as an alternative reducing agent to ascorbic acid. At concentrations $\sim 10$ times higher than the gold concentration in the growth solution, it was found to lead to a slow rate of growth of the gold nanorods with aspect ratios around 6 - 8. Since hydroquinone is a weaker reducing agent than ascorbic acid, the window of allowed concentrations is much wider. While for AA the molar ratio of AA:Au had to be in the range of 1.1 - 1.6, with 1.1 barely forming any rods, and 1.6 or greater leading to dog-bone and more spherical shapes, it was found for HQ that a large excess could be used without affecting the final shape of the rods. In addition, the large excess of reducing agent means that the reaction can proceed until all the Au(III) is reduced to Au(0). As a result, the yield of gold nanorods is much higher than the 15\% shown for rods reduced with ascorbic acid.

The HQ-rods were prepared as follows. A 250 ml solution of 0.1 M CTAB was prepared, and 1183 $\mu$l 0.10569 M Au$^{3+}$ was added to yield a gold concentration of 0.5 mM. The CTAB and gold solution was shaken for a few seconds, and left to stand for around 5 min. Then 1000 $\mu$l 0.1 M AgNO$_3$ was added, and shaken again. For the reduction, 12.5 ml of 0.1 M aqueous hydroquinone solution were added. The solution turned clear after shaking for $\sim 30$ s. Once clear, under vigorous stirring, 4 ml of seeds were injected, followed by quick shaking. The solution was then left to sit overnight in a water bath at 32 $^\circ$C.
3.1 Synthesis of gold nanorods

1183 µl 0.105 69 M Au\(^{3+}\) was added to 250 ml 0.1 M CTAB. 1000 µl 0.1 M AgNO\(_3\) was then added, and the mixture was shaken. After 30 s, the reduction step occurred through the addition of 12.5 ml of 0.1 M aqueous hydroquinone solution, followed by growth initiated by the addition of 4 ml of seeds.

Figure 3.10: Sketch of the formation of gold nanorods using hydroquinone as reducing agent.

Figure 3.11: UV-vis, TEM and histograms of results from the hydroquinone reduction protocol. HQ-7.2 rods with UV-vis spectrum (left) showing a longitudinal plasmon band at 1063 nm. Analysis of the TEM images (middle) and corresponding size histograms (right) gave dimensions of 88x 12.3 nm, with an aspect ratio of 7.2.

The prepared rods are displayed in Figure 3.11. The rod solution had a dark brown colour due to the longitudinal plasmon band in the NIR region, at 1063 nm, with length and width of 88.0 ± 13.4 and 12.3 ± 1.0 nm, respectively. This corresponded to an aspect ratio of 7.2 ± 1.2. The TEM showed highly monodisperse rods with no spheres or other shape impurities. This could also be seen from the very low absorbance of the transverse band, as
compared to the rods prepared by the other methods. The lack of shape impurities was one of the biggest advantages of this method, which was likely attributed to the lower reducing capability of hydroquinone as compared to ascorbic acid.

Due to the high quality of the rods, we wanted to check the tunability of the synthesis, and whether shorter aspect ratios could be accessed. This was tried by reducing the amount of seeds and silver. A 100 ml synthesis of HQ-7.2 involved the addition 400 µl of 0.1 M AgNO₃, which corresponded to a final concentration of 0.4 mM, and 1.6 ml of seeds. The amount of seeds was reduced to 1.2 ml, and 2 different silver concentrations: 200 µl and 160 µl were tried. This corresponded to 0.2 and 0.16 mM final Ag concentration, respectively. The obtained absorbance spectra and TEM images are given in Figure 3.12. Indeed shorter aspect ratios could be accessed, as evidenced by the blue-shift in the longitudinal plasmon band to shorter wavelengths. However, the quality of the rods was compromised. The rods with 200 µl Ag had a broad plasmon resonance band, indicating a larger population distribution. Both samples had a higher amount of shape impurities, especially spheres, as seen in the TEM images. This increase in impurities was also manifested in the transverse band, which showed a much higher absorbance at the plasmon band as compared to Figure 3.11, indicating a higher amount of spheres.

Figure 3.12: UV-vis spectra for the rods prepared with constant seed volume of 1.2 ml and varying volume of 0.1 M AgNO₃: 200 µl (purple) and 160 µl (blue) and their respective TEM images.

Reduction with hydroquinone was found to provide a way of synthesising rods with large aspect ratios and extremely high quality. However, using the same protocol for obtaining
3.2 Discussion - Comparison of the different methods

The preceding section introduced four different protocols for the synthesis of gold nanorods. The first represents the first wet chemistry seed-mediated synthesis, and has been widely used for the last 20 years. Despite its widespread use, there are several issues with the synthesis, mainly the formation of byproducts, low yield, and the high sensitivity of the quality of the final product to several parameters, especially the ascorbic acid concentration. In an attempt to circumvent these issues and develop more robust and reproducible procedures, many new protocols have been developed in the last few years. Table 3.1 compares the reaction conditions and reagent concentrations for the four methods. The concentrations represent the final concentration of each reagent in a 250 ml synthesis. We can see for the AA rods, a molar ratio of AA:Au of 1.6 was used, as discussed in section 3.1.2. For the BrSA and NaOl protocols, due to the fact that the Bromosalicylic acid and sodium oleate can reduce Au(III) to Au(I), a lower amount of AA was required to reduce the remaining Au(III). This led to molar ratios of 0.52 and 0.32 respectively, which could explain the cylindrical shape of these rods as compared to the dog-bone shape formed by the AA method alone. For the HQ method, replacement of AA with HQ, a weaker reducing agent, enabled a large excess of reducing agent to be used, a molar ratio of 10 compared to 1.6 for AA, while maintaining the rod-like shape and quality of the final product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[CTAB]</th>
<th>Additive</th>
<th>[Au³⁺]</th>
<th>[AgNO₃]</th>
<th>V(HCl)</th>
<th>RA</th>
<th>RA:Au ratio</th>
<th>V(seeds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-4.2</td>
<td>0.1 M</td>
<td>None</td>
<td>0.5 mM</td>
<td>0.12 mM</td>
<td>4.65 ml</td>
<td>AA, 0.8 mM</td>
<td>1.6</td>
<td>600 µl</td>
</tr>
<tr>
<td>BrSA-3.7</td>
<td>0.05 M</td>
<td>BrSA, 4.6 mM</td>
<td>0.5 mM</td>
<td>0.096 mM</td>
<td>None</td>
<td>AA, 0.26 mM</td>
<td>0.52</td>
<td>400 µl</td>
</tr>
<tr>
<td>NaOl-3.1</td>
<td>0.047M</td>
<td>NaOl, 5.0 mM</td>
<td>0.5 mM</td>
<td>0.14 mM</td>
<td>2.5 ml</td>
<td>AA, 0.16 mM</td>
<td>0.32</td>
<td>200 µl</td>
</tr>
<tr>
<td>HQ-7.2</td>
<td>0.1 M</td>
<td>None</td>
<td>0.5 mM</td>
<td>0.4 mM</td>
<td>None</td>
<td>HQ, 5 mM</td>
<td>10</td>
<td>4000 µl</td>
</tr>
</tbody>
</table>

Table 3.1: The reaction conditions for the different syntheses, comparing the concentrations needed for each reagent. The concentrations represent the final concentration of each reagent in a 250 ml synthesis. RA = reducing agent.

Table 3.2 presents lengths, widths, aspect ratios, LSPR peak positions, and FWHM for the different methods from analysis of the TEM images and UV-vis absorbance spectra.
3.2 Discussion - Comparison of the different methods

From size analysis from TEM, we can see that the BrSA-3.7 rods had the narrowest size distribution. The HQ rods had quite a broad distribution in terms of length, but a very narrow distribution in width. The NaOl-2.4 had the sharpest longitudinal plasmon band, with FWHM of 133 nm, followed by HQ rods with a FWHM of 139, NaOl 3.1 with FWHM of 151. The Br-SA rods had a FWHM of 163, and lastly the AA rods had the widest plasmon resonance with a FWHM of 181 for AA-4.2 and 240 for AA-5.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length(nm)</th>
<th>Width(nm)</th>
<th>Aspect Ratio</th>
<th>$\lambda_{max}$ (nm)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-5.2</td>
<td>55.2 ± 8.9</td>
<td>10.8 ± 2.1</td>
<td>5.2 ± 1.3</td>
<td>913</td>
<td>240</td>
</tr>
<tr>
<td>AA-4.2</td>
<td>51.8 ± 6.3</td>
<td>12.6 ± 1.9</td>
<td>4.2 ± 0.8</td>
<td>847</td>
<td>181</td>
</tr>
<tr>
<td>BrSA-3.7</td>
<td>45.6 ± 4.0</td>
<td>12.3 ± 1.2</td>
<td>3.7 ± 0.5</td>
<td>805</td>
<td>163</td>
</tr>
<tr>
<td>NaOl-3.1</td>
<td>93.7 ± 7.3</td>
<td>30.5 ± 2.5</td>
<td>3.1 ± 0.4</td>
<td>755</td>
<td>151</td>
</tr>
<tr>
<td>NaOl-2.4</td>
<td>107.5 ± 8.2</td>
<td>44.8 ± 2.4</td>
<td>2.4 ± 0.2</td>
<td>712</td>
<td>133</td>
</tr>
<tr>
<td>HQ-7.2</td>
<td>88.0 ± 13.4</td>
<td>12.3 ± 1.0</td>
<td>7.2 ± 1.2</td>
<td>1063</td>
<td>139</td>
</tr>
</tbody>
</table>

Table 3.2: Table summarising the length, width and aspect ratio of all the rod samples, as determined from TEM analysis. The position of the longitudinal plasmon band is also shown, as well as the FWHM maximum determined from a Gaussian fit of the plasmon band.
Figure 3.13: A plot showing the LSPR peak position (right axis) and aspect ratio (left axis) for all the prepared rods. The samples were arranged in decreasing aspect ratio to clearly show the trend between aspect ratio and LSPR.

The determined longitudinal plasmon band positions and AR are also shown in Figure 3.13 to better compare the different rods. For the various samples the AR is plotted on the left-hand axis (closed circles) and the LSPR positions on the right-hand axis (triangles). The trend between AR and LSPR could be observed where the LSPR blue-shifted with decreasing AR. It has been shown in the literature that the LSPR wavelength is linearly dependent on the aspect ratio\(^{[31]}\), and is generally represented by the following equation:

\[
\lambda_{max} = 95 \times AR + 420
\]  

(3.1)

Equation 3.1, however, holds best for cylindrically shaped gold nanorods. Any deviations in that shape, whether dog-bone shapes or slight changes in the nanorod tip, tend to result in significant shifts in the longitudinal plasmon band, and hence deviations from the equation. Figure 3.14 compares the calculated LSPR for each AR based on equation 3.1 (theoretical) shown in orange and the actual LSPR obtained from UV-vis (experimental), shown in blue. A linear fit of the experimental data gave the following equation:
3.2 Discussion - Comparison of the different methods

\[ \lambda_{max} = 73.6 \times AR + 532.6 \]  

(3.2)

Figure 3.14: Linear plots of AR of the different rods and the corresponding calculated (blue line) and theoretical (red line) \( \lambda_{max} \) values.

Despite the fact that the rods were made with different protocols and therefore had varying amounts of CTAB, different surface chemistry and dimensions, a linear relationship between the AR and LSPR could still be found with a very good fit \( (r^2 = 0.99) \).

Since the conventional ascorbic acid reduction method with only CTAB as surfactant has been around for the longest time, it is still the most widely used. However, in this chapter, we have shown the problems associated with that synthesis, mainly in terms of the resulting dog-bone shape of the rods and the high amount of sphere byproducts. The shape of the rods could be somewhat improved by tuning the molar ratio of AA to Au. This did not help with the shape impurities though, and this method was still quite limited in terms of versatility. Using Bromosalicylic acid as a co-reducing agent to AA was found to greatly improve the quality of the prepared nanorods as indicated by the TEM images, size distributions, and narrowness of the longitudinal plasmon band. Additionally, the
3.3 Functionalisation of gold nanorods

BrSA method was the most reproducible. The use of sodium oleate as a co-surfactant and co-reducing agent allowed us to access rods with thicker diameters than any of the other methods, as well as narrow size distributions. However, our results deviated from the expected results based on the published work, and the method was not found to be reproducible from batch to batch. Replacing ascorbic acid with hydroquinone allowed the synthesis of high aspect ratio gold nanorods with little or no spherical impurities. The large excess of HQ meant that slight deviations in concentration or volume due to experimental errors hardly affect the final product, ensuring a high degree of reproducibility from batch to batch. This method produced the best results for high aspect ratios - attempts to reduce the aspect ratio negatively affected the quality of the rods and introduced more shape impurities.

3.3 Functionalisation of gold nanorods

Synthesised rods are stabilised with cetyltrimethylammonium bromide, CTAB. CTAB is a cationic surfactant composed of a trimethylamine which binds to the Au and a hydrophobic tail that can self-assemble into a bilayer on the NP surface\[7\]. CTAB is crucial for the synthesis and stabilisation of gold nanorods, but since a high concentration of CTAB is generally employed during the syntheses, the rods need to be cleaned of excess CTAB after the synthesis through centrifugation. However, there is a fine balance between having too much or too little CTAB. There is a continuous exchange between the CTAB bilayer and surfactant molecules in the solution. Therefore enough CTAB needs to remain in the gold nanorod solution to ensure dynamic equilibrium between the bound and unbound surfactant. In general, the gold nanorods can only be centrifuged twice and redispersed in water. One further centrifugation step leads to irreversible aggregation because too much CTAB has been removed and the nanorods are no longer stable in solution. This sensitivity to the amount of CTAB presents a challenge for the functionalisation of rods. Enough CTAB has to be removed from the nanorod surface in order to reduce steric hindrance and allow a new ligand access to the surface without compromising the stability of the rods. Another issue with CTAB is its toxicity, which becomes a problem for biological applications.
3.3 Functionalisation of gold nanorods

3.3.1 Ligand exchange for further functionalisation

Gold nanorods coated with CTAB are positively charged, which limits some of their use especially when used in the presence of negatively charged species. In the following, CTAB was exchanged for sodium dodecyl sulfate (SDS), a negatively charged surfactant; Polystyrene sulfonate (PSS), an anionic polymer; and mercaptoundecanoic acid (MUA), a thiolated long chain carboxylic acid.

3.3.1.1 Sodium dodecyl sulfate

The transfer of rods from positively charged CTAB to negatively charged SDS was studied as follows. HQ-rods that had already been cleaned once from excess CTAB were divided into 1.5 ml aliquots and centrifuged at 7700 rpm for 10 min. The supernatant was removed and the rods were suspended in different concentrations of CTAB: 0.5, 1, 5, 10, and 100 mM. The critical micelle concentration (cmc) of CTAB is 1 mM at 25°C \cite{145}. UV-vis spectra and zeta potential measurements of the rods in different CTAB concentrations were collected. The rods were then added dropwise into 10 ml 0.1 M SDS solutions under stirring. After 1 hr, the rods were centrifuged again and redispersed in 1.5 ml water. Rods dispersed in 1 mM
3.3 Functionalisation of gold nanorods

CTAB were also transferred into different concentrations of SDS: 4, 8 (cmc), and 10 mM. The spectra of the rods in CTAB and SDS are compared in Figure 3.16. The plot on the left shows absorbance spectra for the rods dispersed in different concentrations of CTAB (solid lines). The spectra all overlap with a longitudinal plasmon resonance at 863 nm. Upon transfer to 0.1 M SDS, all the samples blue-shifted to around 846 nm, an overall shift of 17 nm. The right side of Figure 3.16 shows spectra for the rods in 1 mM CTAB transferred to SDS solutions at 4, 8 and 10 mM. The plasmon band shifted from 863 nm to 850 nm for all solutions, with a 13 nm blue-shift, which is smaller than for the 0.1 M SDS. For all concentrations of SDS, no peak broadening was observed, indicating that no aggregation occurred during the process.

Figure 3.16: UV-vis for the rods in different concentrations of CTAB and SDS. The plot on the left compares as-prepared HQ-rods after centrifugations and redispersion in different CTAB concentrations (solid lines): 0.5 mM, 1 mM, 5 mM and 10 mM CTAB. These solutions were then added dropwise into 0.1 M SDS and then centrifuged and redispersed in water. The dashed lines show spectra of the rods initially in different CTAB concentrations now in SDS. The plot on the right shows spectra for the rods in 1 mM CTAB transferred into different SDS concentrations: 4 mM, 8.2 mM, 10 mM, and 0.1 M.

The shift in plasmon band meant the local refractive index surrounding the gold nanorod had changed, which was a good indication that the rods were in SDS. The reason for such a large shift considering SDS and CTAB have relatively similar chain lengths could be due to the fact that CTAB forms a bilayer on the gold nanorod surface while SDS most likely forms a monolayer. Zeta potential measurements were done to check if the charge of the
solutions has changed and the results are presented in Figure 3.17. The rods in different concentrations of CTAB had zeta potential values between +20 - 30 mV, which shifted to negative values between -40 and -70 mV after transfer to 0.1 M SDS (left) and different SDS concentrations (right). The charge reversal suggests successful transfer of the rods to SDS.

![Figure 3.17: Zeta potential of the rods in different concentrations of CTAB and SDS. The plot on the left compares the zeta potential for the above rods in different CTAB concentrations (black triangles): 0.5 mM, 1 mM, 5 mM and 10 mM CTAB then transferred into 0.1 M SDS (purple circles). The plot on the right shows values of zero potential for rods in 1 mM CTAB (black triangle) transferred to the different SDS concentrations (purple circles).]

3.3.1.2 Polystyrene Sulfonate

PSS functionalisation was performed based on the protocol by Mehtala et al.\cite{146}. 50 ml NaO1-rods (previously centrifuged once and redispersed in water) were centrifuged at 8000 rpm for 1 hr at 25 °C. The supernatant was then removed. The concentrated residue was added dropwise to a stirred solution of 50 ml 0.15 wt % PSS (70kDa molecular weight). The rods appeared to go well into the PSS with no signs of aggregation or colour change. The solution was then centrifuged at 8500 rpm for 30 min. After centrifugation, the supernatant (which was faintly coloured) was removed and the same process repeated as above. Another 8500 rpm centrifugation for 30 min was done, then the supernatant was removed and the residue was redispersed in 10 ml PSS.
3.3 Functionalisation of gold nanorods

Figure 3.18: UV-vis monitoring the exchange of NaOl rods initially in CTAB added dropwise into an aqueous solution 0.15 wt % PSS (70kDa molecular weight). The left figure shows the change in plasmon band and absorbance after the successive washes upon PSS addition. The spectrum on the right compares the normalised spectra of the rods before and after PSS exchange.

The progress of the exchange was monitored by taking spectra of the solution after each centrifugation step, which are shown in Figure 3.18 (left). The longitudinal plasmon band blue-shifted with each new addition of PSS, and the absorbance decreased due to some loss of material after centrifugation. The peak remained narrow, and Figure 3.18 (right) compares the spectrum of the rods in CTAB and after the final redispersion in PSS. The longitudinal plasmon underwent a blue-shift of 19 nm from 759 to 738 nm.

3.3.1.3 Mercaptoundecanoic Acid

Thiolated ligands are highly attractive for functionalisation of gold nanorods due to the strong affinity of thiols to gold. Long chain carboxylic acids, such as mercaptoundecanoic acid (MUA), are thus suitable candidates. These compounds are composed of a long chain hydrophobic hydrocarbon backbone with a thiol on one end and a carboxylic acid on the other, which aids its solubility in water. MUA tends to have a low solubility in water, and so solutions are usually prepared in other solvents, such as isopropanol or toluene. Wijaya\textsuperscript{[44]} proposed a ‘round-trip’ phase transfer method, where the gold nanorods were first transferred into organic solvents using dodecanethiol (DDT). The gold nanorods were
then extracted back into the aqueous phase by refluxing in an MUA solution, which caused the rods to aggregate out of the organic solution, and they could then be redispersed in aqueous solutions.

Attempts to reproduce this functionalisation protocol led to the irreversible aggregation of the gold nanorods following the transfer to organic solvent with DDT. A much more straightforward method was then found which involved adding MUA directly to a gold nanorod solution. A 20 mM MUA solution was prepared in water by sonication and dropwise addition of 0.2 M NaOH, until the initial cloudy white suspension completely dissolved into a clear solution. Addition of the base leads to the deprotonation of the carboxyl groups of the MUA, thereby facilitating stabilisation in water. Under vigorous stirring, 4 ml of this solution was then added to 10 ml of BrSA-rods that had been centrifuged once and redispersed in water. The solution was left stirring overnight, followed by centrifugation twice at 8000 rpm for 20 min, and redispersion in basic water (pH \sim 10). The supernatant was clear and the gold easily redispersed in the water.

Successful functionalisation was confirmed by a change in the longitudinal plasmon band. Figure 3.19 compares spectra of the gold nanorod solution before and after functionalisation.

Figure 3.19: UV-vis spectrum comparing the normalised spectra before and after MUA exchange. 4 ml of a basic 20 mM MUA solution in water was added to 10 ml Br-SA rods which had been cleaned once from CTAB by centrifugation. The figure compares the spectra of the BrSA rods in CTAB (black) versus the rods in MUA (pink) after they had been washed from excess MUA and redispersed in basic water.

Successful functionalisation was confirmed by a change in the longitudinal plasmon band. Figure 3.19 compares spectra of the gold nanorod solution before and after functionalisa-
tion with MUA. A 10 nm red-shift was observed going from a longitudinal plasmon band of 806 nm for the rods @ CTAB to 816 nm for the rods @ MUA. Additionally, the zeta potential of the gold nanorods changed from 12.80 ± 0.94 mV to -25.11 ± 1.97 mV. Zeta potential measurements were conducted on the washed solutions, indicating that excess CTAB and MUA had been removed.

The presented results demonstrated the gold nanorods stabilised in CTAB could be successfully functionalised with different surfactants and molecules. The advantage of the discussed functionalisation strategies was they provided gold nanorods in different surfactant environments and with a negative surface charge. This is useful for reactions involving the gold rods where charge plays a role. In addition, the rods can then be further functionalised through additions of other various molecules. The gold nanorods in SDS were found to be stable, even several weeks after the transfer. Rods at MUA and PSS however, were only found to be stable for a few days after the functionalisation, as indicated by some sedimentation and slight change in colour after a few days. The disadvantage of MUA functionalisation was that it only works in a basic environment. However, despite the limitations, this study showed that the gold nanorod surface could be manipulated, opening up their use for further chemistry.

### 3.3.2 Ligand exchange for polymer coating

One of the best methods for the stabilisation of gold nanorods is polymer coating. Coating nanorods with responsive polymers also introduces new properties to the nanoparticles, making them functional materials. One of the aims of this work was to coat gold nanorods with thermoresponsive poly-N-isopropylacrylamide (PNIPAM). The growth of a stable polymer shell around the nanoparticles is significantly enhanced by the presence of hydrophobic ligands with free double bonds on the surface of the gold nanorods. The presence of the ligand provides a hydrophobic seed surface for the polymerising PNIPAM to adsorb to. The ligand participates in the polymerisation and becomes cross-linked into the microgel, thereby containing the nanorod inside the polymer network.
3.3 Functionalisation of gold nanorods

3.3.2.1 Butenoic acid

Gold nanorods were functionalised with butenoic acid based on the protocol by Contreras-Caceres et al.\cite{98} They introduced the use of butenoic acid as a ligand to functionalise the surface of gold nanorods for growing a PNIPAM shell around the rods, proposing that butenoic acid replaces the CTAB on the surface of the rods. We used a modified protocol of that used by Contreras-Caceres et al. whereby the amount of butenoic acid used was doubled. A 100 ml solution of AA-rods that had been cleaned once of excess CTAB and redispersed in the same volume of water was heated to 70 °C under stirring. Then, 600 µl of butenoic acid were added and left at 70 °C for 1 hr. Once cooled, the dispersion was centrifuged at 6000 rpm for 1 hr, and the concentrated gold solution was redispersed in the desired volume of water (either 10 or 100 ml); this will be discussed further in the next chapter. A typical spectrum of rods functionalised with butenoic acid is given in Figure 3.20.

3.3.2.2 Butenylamine

Butenylamine (BA) was shown to be a good ligand for growing a PNIPAM shell on the surface of citrate-functionalised gold nanospheres\cite{97}. It binds to the gold nanoparticle through the amine, while providing double bonds on the surface for polymerisation to initiate from. The presence of CTAB on gold nanorods, however, complicates the surface functionalisation. 250 µl of 3.7 M of BA solution in ethanol was added to 100 ml AA-rods at 70 °C under stirring. The reaction was left for 1 hr after which the rods were centrifuged at 6577 ref for 1 hr and redispersed in water. Although the particles appeared stable (no change in colour), the spectra shown in Figure 3.20 indicate aggregation due to the peak broadening and increased absorbance to the red of the longitudinal plasmon band. As a result, we added Tween-20, a nonionic polysorbate surfactant, to act as a stabilising agent, especially during the centrifugation step. To do this, 1 ml of 0.1 M Tween-20 aqueous solution was added to the gold nanorod solution prior to the BA addition. This helped the stability of the gold rods, as can be seen in Figure 3.20 where the Rods @ BA with Tween-20 showed no peak broadening or aggregation.

Functionalisation with both butenoic acid and butenylamine led to strong blue-shifts of
the longitudinal plasmon band. In order to check that this was due to changes in refractive index as a result of the presence of a new ligand, and not just from stripping off CTAB during the centrifugation steps, spectra of gold nanorods at CTAB were compared after centrifugation. Prior to any centrifugation, the rods exhibited $\lambda_{\text{max}}$ at 850 nm which shifted to 846 nm after the first centrifugation round and 844 nm after the second. Since the rods had already been centrifuged once before functionalisation, they had $\lambda_{\text{max}}$ at 846 nm. The position of $\lambda_{\text{max}}$ shifted to 827 nm after functionalisation with butenoic acid and 826 nm for butenylamine. This is a much stronger shift than that caused by centrifugation, and thereby indicated the rods had been successfully functionalised.

Figure 3.20: UV-vis spectra for AA rods cleaned once from CTAB functionalised with butenoic acid (top left) and butenylamine (top right). For the butenylamine, functionalisation without a stabilising agent (dotted green line) showed aggregation depicted through peak broadening which was not observed when using Tween-20 (solid green line). The bottom panel shows spectra for the same AA rods at CTAB, undergoing one and two centrifugation cycles, to compare the observed blue-shift to that upon functionalisation.
3.4 Conclusion

The widespread use of gold nanorods has led to the development of several synthetic procedures, where the aspect ratio of the nanorods can be controlled by varying different parameters. With the aim of trying to make monodisperse rods with a narrow size distribution and low yield of impurities, four procedures were trialled. This was a necessary step for realising the aims of this thesis. It was found that the BrSA method produced the most reproducible rods with the position of the longitudinal plasmon band at almost the same wavelength between different batches. In addition, these rods were found to be very monodisperse with little to no shape impurities. Rods produced with HQ as a reducing agent instead of AA were also of extremely high quality, however the aspect ratios were above 7, meaning longitudinal plasmon bands in the NIR, which made optical characterisation difficult with the spectrometers used in this study. Attempts to blue-shift the plasmon peak towards the visible region were successful, however at the expense of the monodispersity and purity of the rods. Due to its high reproducibility and quality, BrSA was thus the method of choice for most experiments presented in this thesis. It was then shown that the as-prepared rods could be further functionalised, either to change the charge or allow the addition of different species to the gold rods. Even though gold nanorods are generally considered difficult to functionalise, we successfully showed that the surface chemistry could be manipulated through changing the charge via SDS or MUA, or simply adding a neutral surfactant. These protocols pave the way for further chemistry to be done on the rods. Additionally, we showed that ligands possessing terminal double bonds could be attached to the surface of the nanorods. This chapter was highly significant in forming the necessary foundation for addressing the main aims of this thesis. In order to be able to answer the research questions, specifically coating rods with PNIPAM, monodisperse gold nanorods had to first be synthesised and characterised in detail. The next chapter will present a study on the growth of a PNIPAM shell around the gold nanorods and the effect of the shell on the optical properties of the rods.
Chapter 4

Core-Shell Rods-PNIPAM: Synthesis and Characterisation

As discussed in Chapter 1, one of the most widely studied hydrogel systems is based on the monomer N-isopropylacrylamide (NIPAM). Poly-NIPAM (PNIPAM) hydrogels have a lower critical solution temperature (LCST) of around 32 - 33 °C at which stage the gel undergoes a volume phase transition (VPT) and the previously swollen gel network collapses.

This chapter focuses on the coating of PNIPAM on the surface of gold nanorods to form core-shell hybrid particles. Combining gold nanorods with PNIPAM leads to functional materials that possess the optical properties of the gold nanorods and the thermoresponsive nature of the polymer shell. It was previously shown that 15 nm gold nanospheres could be successfully coated with PNIPAM\textsuperscript{[97]}\textsuperscript{[97]}. Having a thick polymer shell around the gold nanoparticle changes its local refractive index. For gold nanospheres, this change in refractive index is displayed by a red-shift in the surface plasmon resonance of around 3-4 nm. For gold nanorods, the longitudinal plasmon band is much more sensitive to refractive index changes than the transverse band as given in the Gans-Drude theory described in Equation 1.11. Consequently, coating gold nanorods with PNIPAM and the corresponding temperature-induced shell collapse are expected to lead to dramatic optical effects. The detailed synthesis of core-shell rod-PNIPAM particles will be discussed in the following sections, with a focus on the effect of different parameters on the particles, as well as variations for optimisation of the synthetic protocol. The characterisation of the particles, in particular the optical properties, will be presented, followed by a detailed explanation of the obtained results.
4.1 Synthesis via radical polymerisation

PNIPAM microgels were prepared by a surfactant-free emulsion polymerisation method, where the monomer NIPAM was polymerised in a solution containing the nanorods, cross-linker N,N’-Methylenebisacrylamide (BIS) and a radical initiator to start the polymerisation at 70 °C. Since the gold nanorods are positively charged, a cationic radical initiator 2,2’-Azobis(2-amidinopropane) dihydrochloride (AAPH) was used as opposed to the usual negatively charged potassium peroxodisulfate (KPS). For the preparation of core-shell particles, the core nanoparticles had to first be functionalised with a ligand that can bind to their surface, while providing double bonds to the exterior of the nanoparticle surface for the polymerisation to initiate from.

A modified version of the protocol developed by Contreras-Caceres et al. was used. The rods were functionalised as described in Chapter 3 section 3.3. The highly concentrated aqueous rod solution served as the reaction medium for the polymerisation. 0.1924 g NIPAM and 0.0265 g BIS (10% cross-linker density) were weighed into a 2-neck round bottom flask, and the 10 ml rod dispersion was added in. The flask was attached to a reflux condenser, and heated to 70 °C in an oil bath, under stirring and a nitrogen atmosphere. After 15 min of equilibration time at 70 °C, 100 µl of 0.1 M AAPH was injected into the mixture. The reaction was left to proceed for 1 h, after which it was removed from the heat and diluted to 50 ml with Milli-Q water. Considering the reaction volume is 10 ml, the amount of NIPAM and BIS used corresponds to a NIPAM concentration of 0.17 M and a cross-linker density of 10%. In order to better control the concentration of NIPAM, the protocol was modified by redispersing the rods in the same volume of water as before functionalisation. For example, if 100 ml of rods were functionalised with butenoic acid, then after centrifugation, they were redispersed back into 100 ml of water. This 50 ml of rods was then added to 0.1924 g NIPAM and 0.0265 g BIS, which then corresponds to 0.017 M NIPAM concentration. This allowed more flexibility with changing reaction volume and reagent concentrations.
Figure 4.1: UV-vis absorbance spectra of Br-SA rods functionalised with butenoic acid (black) and the same rods coated with PNIPAM (blue). The spectra were normalised to the absorbance at the longitudinal plasmon band to allow for easier comparison.

Figure 4.1 compares absorbance spectra of the rods before and after coating with PNIPAM. Two main effects are observed upon PNIPAM encapsulation. The first is increased absorbance at low wavelengths (around 300 nm), due to enhanced Rayleigh scattering from the polymer shell. Particles with a radius \( R \) smaller than the wavelength of irradiated light, \( \lambda \), exhibit Rayleigh scattering after illumination\(^{[97]}\). The scattering intensity, \( I_{sc} \), depends on the wavelength as follows:

\[
I_{sc} \propto \frac{1}{\lambda^4} \tag{4.1}
\]

Scattering of particles having a wavelength larger than or comparable to \( \lambda \) can be treated as Rayleigh-Debye-Gans scattering provided the following Rayleigh-Debye-Gans approximation is fulfilled

\[
1 < \alpha < |m - 1|^{-1} \tag{4.2}
\]

Here,
4.1 Synthesis via radical polymerisation

\[ \alpha = \frac{2\pi n_m R}{\lambda} \]  \hspace{1cm} (4.3)

where \( m \) is the ratio of the refractive index of the scattering objects, \( n_s \), to the refractive index from the surrounding medium, \( n_m \). Due to the low refractive index of PNIPAM, the scattering of microgels with dimensions even up to several hundreds of nm can be considered as Rayleigh-Debye-Gans scattering. The second observation is a small red-shift in the longitudinal plasmon resonance of the gold nanorod core, due to the change in the local refractive index due to the introduction of the PNIPAM shell. In Chapter 3, rods were prepared by four different synthetic methods, each one providing different aspect ratios and LSPR peak positions. In this experiment, the goal was to see whether the rods prepared by various methods, and therefore having different surface chemistries and sizes could be successfully encapsulated with PNIPAM. To do this, rods from the four methods were functionalised with butenoic acid and polymerised with 0.017 M NIPAM and 10 \% BIS. TEM micrographs are presented in Figure 4.2.
4.1 Synthesis via radical polymerisation

Figure 4.2: Representative TEM images of the core-shell structure obtained by coating rods of various aspect ratios prepared by four different methods with PNIPAM. Top left: AA-5.2 rods; top right: BrSA-3.7 rods; bottom left: NaOl-2.4 rods; bottom right: HQ-7.2 rods. Polymerisation conditions were 50 ml functionalised rods in the presence of 0.017 M NIPAM and 10% BIS at 70 °C, initiated with 100 µl AAPH. The same protocol used in Chapter 3 for naming rods is used here, with the aspect ratio following the rods type.

All four types of rods were successfully coated with PNIPAM leading to core-shell par-
ticles with a single gold nanorod core per PNIPAM shell. Organic polymers generally have a low contrast in TEM and as a result, a large difference in contrast is seen between the darker inorganic core and the organic PNIPAM shell. This was a major result since it answered the part of the first research question of this thesis - can we develop a protocol for coating monodisperse gold nanorods with a PNIPAM shell with a high yield? However to completely answer the question, optimisation of the protocol had to be explored followed by characterisation of the optical properties and swelling behaviour.

In order to obtain the best quality core-shell particles for self-assembly and potential alignment of the gold nanorod cores, high monodispersity is required. For that reason, the AA-rods were disregarded due to their dogbone shape and low batch to batch reproducibility, as was discussed in Chapter 3. The same reproducibility issue was found for the NaOl-rods. In addition, NaOl-rods coated with PNIPAM had the highest amount of empty polymer shells. The reason for this can be attributed to the fact that a lower yield of nanorods is formed due to the lower reagent concentrations used in the synthesis. As a result, the two types of rods that were predominantly used for PNIPAM coating and further experiments are the BrSA- and HQ-rods. Both methods consistently produced rods of similar size and quality, while the longer aspect ratio offered by the HQ-rods is advantageous for the potential alignment of the nanorods.

### 4.1.1 Effect of monomer concentration and cross-linker density

The first studies into coating rods with PNIPAM showed that a uniform shell with a single nanorod core could be obtained. The next step was to see how versatile the coating method was in terms of varying the shell thickness and optical response to temperature. The thickness of the PNIPAM shell is dependent on the concentration of the NIPAM during the synthesis. While the cross-linker density dictates how thermoresponsive the shell is, it also affects the overall size of the PNIPAM. The highest NIPAM concentration used in this study was 0.017 M because NIPAM concentrations higher than 0.017 M led to the presence of more empty shells for the same gold nanorod concentration. This section presents results from varying the cross-linker density for two different NIPAM concentrations. The synthesis conditions are detailed in Table 4.1. The mol% of BIS is the nominal molar ratio of cross-linker feed, which corresponds to the cross-linker feed relative to the amount of NIPAM. For all the syntheses, BrSA-rods with an aspect ratio of ~ 4 were used, with the amount of
4.1 Synthesis via radical polymerisation

gold nanorods and initiator used kept constant.

<table>
<thead>
<tr>
<th>[NIPAM]</th>
<th>m(NIPAM)</th>
<th>Cross-linker density</th>
<th>m(BIS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.017 M</td>
<td>192.4 mg</td>
<td>25 % BIS</td>
<td>65.5 mg</td>
</tr>
<tr>
<td>0.017 M</td>
<td>192.4 mg</td>
<td>15 % BIS</td>
<td>39.3 mg</td>
</tr>
<tr>
<td>0.017 M</td>
<td>192.4 mg</td>
<td>10 % BIS</td>
<td>26.2 mg</td>
</tr>
<tr>
<td>0.017 M</td>
<td>192.4 mg</td>
<td>5 % BIS</td>
<td>13.1 mg</td>
</tr>
<tr>
<td>0.01 M</td>
<td>113.2 mg</td>
<td>25 % BIS</td>
<td>38.5 mg</td>
</tr>
<tr>
<td>0.01 M</td>
<td>113.2 mg</td>
<td>15 % BIS</td>
<td>23.1 mg</td>
</tr>
<tr>
<td>0.01 M</td>
<td>113.2 mg</td>
<td>10 % BIS</td>
<td>15.4 mg</td>
</tr>
<tr>
<td>0.01 M</td>
<td>113.2 mg</td>
<td>5 % BIS</td>
<td>7.7 mg</td>
</tr>
</tbody>
</table>

Table 4.1: This table provides details on the amounts of NIPAM and BIS used in each 50 ml synthesis. The cross-linker density was varied from 5 to 25 mol% for two different NIPAM concentrations 0.017 M and 0.01 M. Reaction volume, time, temperature, initiator and amount of gold nanorods were kept constant.

Photographs of the prepared microgel solutions are shown in Figure 4.3 for 0.017 M NIPAM (left) and 0.01 M NIPAM (right), with cross-linker densities from 25 to 5% for each concentration. Figure 4.3 reveals that the particles prepared with 0.017 M NIPAM, i.e. thicker PNIPAM shells, were more turbid. As the PNIPAM shell increased in thickness, the scattering from the microgel also increased since the scattering intensity ($I_{sc}$) scales to the power of 6 of the radius $R$ of the shell ($R^6$). A higher degree of turbidity was also observed for the 25% cross-linker densities, with the solutions becoming less turbid as the cross-linker density decreased. This could be attributed to the increasing refractive index as more BIS was added. The particles with the lowest amount of BIS appeared to be very clear in colour and almost resembled the pure gold nanorod solution.
4.1 Synthesis via radical polymerisation

Figure 4.3: Photographs of the different solutions prepared with 0.017 M NIPAM (left) and 0.01 M NIPAM (right) with the corresponding different cross-linker densities.

Figure 4.4: TEM images of core-shell rods-PNIPAM synthesised with 0.017 M NIPAM with varying cross-linker densities from 25 to 5 %.

TEM images of the particles prepared with 0.017 M NIPAM are presented in Figure 4.4. A core-shell structure was clearly seen for the particles having 25, 15 and 10 % cross-
linker densities, with the thinnest shell for the 10% cross-linker. For the 5% cross-linker density, no shell was observed, either indicating that no PNIPAM shell grew around the gold nanorods, or the shell was too thin and the polymer lacked enough electron density to be seen under the TEM. Looking at the TEM images for the 0.01 M NIPAM concentration in Figure 4.5, a similar trend was depicted. Thick shells were apparent for the 25 and 15% cross-linker, but no shell was visible for the 10 and 5%. In addition, the TEM of the 0.01 M 5% sample appeared 'dirty', with polymer agglomerates around the gold nanorods, indicating random polymerisation of the NIPAM. An interesting difference between the two NIPAM concentrations was that for the 0.01 M samples, the shell stopped forming at a higher cross-linker density than for the 0.017 M. This could be attributed to the higher concentration of NIPAM, which enabled a stable shell to form even at lower cross-linker densities. Most reports on the synthesis of PNIPAM in the literature use much higher concentrations of NIPAM (∼ 0.1 M), and consequently lower cross-linker densities\textsuperscript{[78]}.

![TEM images of rods-PNIPAM with varying cross-linker densities](image)

Figure 4.5: TEM of rods-PNIPAM synthesised with 0.01 M NIPAM with varying cross-linker densities from 25 to 5%.

The sizes of the particles were measured by DLS and the results are presented in Table
4.1 Synthesis via radical polymerisation

4.2, with hydrodynamic radii $R_h$ given at 25 and 50 °C. As expected, it can be seen that the overall sizes for the particles prepared with 0.017 M were larger than the 0.01 M for each cross-linker density. The polymer collapse above the volume phase transition temperature (VPTT) as characterised by the change in radius was most pronounced for the 0.017 M 10% sample. Minimal changes in radius were observed for the 0.017 M 5% and 0.01 M 10%, in line with the TEM observations that little or no shell was present around the gold nanorod cores. For the 0.017 M 5% no size could be measured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_h$ (nm)(25°C)</th>
<th>$R_h$ (nm)(50°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.017 M, 25%</td>
<td>185</td>
<td>141</td>
</tr>
<tr>
<td>0.017 M, 15%</td>
<td>178</td>
<td>123</td>
</tr>
<tr>
<td>0.017 M, 10%</td>
<td>183</td>
<td>101</td>
</tr>
<tr>
<td>0.017 M, 5%</td>
<td>68</td>
<td>54</td>
</tr>
<tr>
<td>0.01 M, 25%</td>
<td>144</td>
<td>113</td>
</tr>
<tr>
<td>0.01 M, 15%</td>
<td>155</td>
<td>121</td>
</tr>
<tr>
<td>0.01 M, 10%</td>
<td>79</td>
<td>69</td>
</tr>
<tr>
<td>0.01 M, 5%</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4.2: Hydrodynamic radii $R_h$ were obtained by DLS measurements at a 90° angle for the different particles. Samples were measured at 25 °C and 50 °C to determine the sizes in the swollen and collapsed states.

To further try to understand how the NIPAM concentration and cross-linker density were affecting the formation of the shell, the optical properties of the 8 samples were looked at. Absorbance spectra are plotted in Figure 4.6, illustrating the effect of cross-linker density on the spectra of the hybrid microgels. The spectra of the microgels with 0.017 M NIPAM concentration (overall thicker shell) for BIS amounts from 5 mol% to 25 mol% are shown in the graph on the left, while the spectra of the hybrids with 0.01 M NIPAM concentration (overall thinner shell) on the right. The graphs were normalised to the absorbance at the longitudinal plasmon resonance of the gold nanorods (~ 790 nm), which enabled us to observe the effect of changing the BIS concentration on the absorbance at low wavelengths. The samples with higher cross-linker density scattered more strongly, as indicated by the increasing absorbance moving from 5% to 25%. The same trend was observed for both
4.1 Synthesis via radical polymerisation

NIPAM concentrations. However, the absorbance values for the 0.017 M were higher than the 0.01 M samples, which was expected due to the fact that the 0.017 M particles were thicker and hence scattered more strongly. For the 0.017 M 5%, 0.01 M 5%, and 0.01 M 10% samples, almost no scattering was observed in the spectra shown in Figure 4.6. The spectra very closely resembled that of a pure gold nanorod solution. This correlated well with the TEM images which indicated no shell was present around the gold nanorods for these samples. The change in cross-linker density also affected the longitudinal plasmon resonance of the particles. The plasmon resonance became less pronounced as the connectivity of the hybrid particles increased, and the spectra became dominated by the scattering of the PNIPAM shell.

![UV-vis absorbance spectra](image-url)

Figure 4.6: UV-vis absorbance spectra normalised to the absorbance at the longitudinal plasmon resonance of the gold nanorod cores for samples with different cross-linker densities prepared with 0.017 M NIPAM (left) and 0.01 M NIPAM (right).

A ratio \( \gamma \) has been previously used to quantify the effect of scattering on the optical properties of gold cores\(^{[97]}\). \( \gamma \) is a ratio of the maximum absorbance of the hybrid to the absorbance at 300 nm, compared to the ratio of maximum absorbance of the pure gold nanorods to the absorbance at 300 nm. Since our spectra were normalised to the absorbance at \( \lambda_{\text{max}} \), the expression could therefore be simplified to give:

\[
\gamma = \frac{\text{Abs}(300\,\text{nm})}{\text{Abs}_{\text{Au}}(300\,\text{nm})}
\]  

(4.4)
Based on equation 4.4, if the absorbance of the hybrid is similar to that of the pure Au nanorod, $\gamma$ will be close to 1. $\gamma$ serves as a useful parameter to characterise the plasmonic properties of the hybrid systems. As the scattering contribution from the PNIPAM shell increases, the plasmonic character of the particles will be reduced, and therefore $\gamma$ will be significantly less than 1. Calculated values of $\gamma$ for the samples with different NIPAM concentration and cross-linker density are given in Table 4.3 and are plotted in Figure 4.7 for both concentrations for easier comparison. Overall, the change in $\gamma$ was highest for the 0.017 M samples, going from a value of 0.08 for the 25% cross-linked, indicating very little plasmonic contribution, to 0.99 for the 5% cross-linked sample, which indicated that the spectrum of the hybrid was almost identical to that of the pure Au nanorod. This was consistent with the observations from TEM and UV-vis that showed this sample had almost no PNIPAM shell. In addition, the higher monomer concentration led to thicker shells, and therefore a higher degree of scattering at lower wavelengths, which explained the big change in $\gamma$ as we moved from 25 to 5% cross-linking. For the 0.01 M particles, the values of $\gamma$ lay closer together. Although a similar trend of higher $\gamma$ value for lower cross-linker was observed, the value for the 5% cross-linker was actually lower than the 10% one, with 0.94 and 0.88 respectively. This could be due to the fact that both these samples appeared to have no shell in the TEM and were thus more difficult to characterise than the samples with a well-defined shell.
The results presented so far have shown the effect of varying the NIPAM concentration and cross-linker density on the formation of a shell around the gold nanorods. It was established that the higher NIPAM concentration led to thicker shells, as predicted, but it appeared as though the samples prepared with lower NIPAM/BIS amounts had no shell. Their spectra corresponded well with that of pure gold nanorods, i.e. almost no scattering could be detected. One way to further elucidate the presence or absence of a shell was to check if the core-shell particles experienced any optical response to a change in temperature. Since PNIPAM is thermoresponsive, increasing the temperature above the VPTT should lead to a change in the optical behaviour. Consequently, absorbance spectra were measured for all the solutions at temperatures higher than the VPTT and the results are given below.
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Figure 4.8: UV-vis absorbance spectra of the particles prepared with 0.017 M NIPAM (left) and 0.01 M NIPAM (right) for cross-linker densities from 5 to 25 % at 25 °C (solid line) and 45 °C (dashed line).
Figure 4.8 compares spectra of all eight samples at 25°C and 45°C, i.e. swollen and collapsed states. All solutions underwent a red-shift in the longitudinal plasmon band and increase in absorbance at low wavelengths as a result of the change in refractive index and increased scattering caused by the collapse of the PNIPAM shell. Surprisingly, even the particles that appeared to have no shell in the TEM images showed a slight change after heating. For the 0.01 M 5% sample, the red-shift in the plasmon band was accompanied by a slight decrease in absorbance, and after cooling, the peak did not fully recover. This indicated that this sample was the least stable and some aggregation occurred after heating, which could be due to the lack of a complete shell stabilising the rods. For the other two samples that did not seem to have a shell in the TEM, a likely scenario could be that the NIPAM did polymerise and was lightly cross-linked with gold nanorods just dispersed throughout the polymer network, as opposed to centred in individual PNIPAM spheres. The other samples showed a slight increase in absorbance of the plasmon band accompanied with the red-shift, which was also attributed to increased scattering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max}}$ (25°C), nm</th>
<th>$\lambda_{\text{max}}$ (45°C), nm</th>
<th>$\Delta\lambda_{\text{max}}$, nm</th>
<th>$\gamma$</th>
<th>$\Delta\text{Abs}_{45\degree C-25\degree C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.017 M, 25%</td>
<td>795</td>
<td>812</td>
<td>17</td>
<td>0.08</td>
<td>1.56</td>
</tr>
<tr>
<td>0.017 M, 15%</td>
<td>793</td>
<td>815</td>
<td>22</td>
<td>0.12</td>
<td>1.01</td>
</tr>
<tr>
<td>0.017 M, 10%</td>
<td>797</td>
<td>819</td>
<td>22</td>
<td>0.33</td>
<td>0.67</td>
</tr>
<tr>
<td>0.017 M, 5%</td>
<td>795</td>
<td>818</td>
<td>23</td>
<td>0.99</td>
<td>0.23</td>
</tr>
<tr>
<td>0.01 M, 25 %</td>
<td>796</td>
<td>811</td>
<td>15</td>
<td>0.20</td>
<td>0.28</td>
</tr>
<tr>
<td>0.01 M, 15 %</td>
<td>795</td>
<td>819</td>
<td>24</td>
<td>0.48</td>
<td>0.32</td>
</tr>
<tr>
<td>0.01 M, 10 %</td>
<td>791</td>
<td>814</td>
<td>23</td>
<td>0.94</td>
<td>0.05</td>
</tr>
<tr>
<td>0.01 M, 5 %</td>
<td>791</td>
<td>810</td>
<td>19</td>
<td>0.88</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4.3: The table presents $\lambda_{\text{max}}$ (25°C) and $\lambda_{\text{max}}$ (45°C) values determined from the spectra shown in Figure 4.8, the change in wavelength $\Delta\lambda_{\text{max}}$, $\gamma$ values, and the change in absorbance $\Delta\text{Abs}_{45\degree C-25\degree C}$ at 300 nm.

Table 4.3 summarises the optical behaviour as determined from Figure 4.8. The positions of the longitudinal band at 25°C and 45°C for all samples are given. All samples exhibited a temperature-induced red-shift as a result of the refractive index change, which was calculated and shown in Table 4.3 as $\Delta \lambda_{\text{max}}$. The largest change in plasmon band should be expected
for the lowest cross-linker density since the lower the cross-linker density, the more responsive the system. Microgels with higher cross-linker density are more solid-like, and hence their volume change is not as dramatic. This trend was seen in the samples, with the smallest change in $\lambda_{\text{max}}$ observed for the 25% cross-linked samples for both 0.017 and 0.01 M NIPAM concentrations. The changes for the other cross-linker densities were quite comparable, between 22 and 24 nm. The lower change in 0.01 M 5% was likely due to the lack of a proper shell surrounding the gold nanorods.

The change in absorbance at 300 nm was determined from the spectra in Figure 4.8 and the values are given in Table 4.3 to highlight the effect of monomer concentration and cross-linker density on the scattering. It was expected that the increase in absorbance at 300 nm should be higher for thicker shells, and indeed, the values confirmed this. Figure 4.9 presents a visual summary of the temperature-induced change in the longitudinal plasmon band wavelength, and the absorbance at 300 nm, i.e. the effects on the optical properties of the gold nanorod and the scattering contribution from the PNIPAM shell. The values of $\Delta \lambda_{\text{max}}$ are plotted on the left axis with $\Delta$ Abs plotted on the right axis against the cross-linker density for the 0.017 M than 0.01 M concentrations. The overall trend of $\Delta$ Abs being higher for the thicker shells is clearly seen, with generally increasing scattering for higher cross-linker densities. Figure 4.9 also shows how the $\Delta \lambda_{\text{max}}$ was smallest for the highest cross-linker density, and most pronounced for the 5% cross-linker. The results are plotted on the left axis in Figure 4.9 for each cross-linker density and NIPAM concentration.
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Figure 4.9: Values of $\Delta \lambda_{\text{max}}$ (left axis) and $\Delta \text{Abs}_{45^\circ \text{C}-25^\circ \text{C}}$ at 300 nm (right axis) for 0.017 M NIPAM and 0.01 M NIPAM plotted against the cross-linker densities from 5 to 25 %. The values were obtained from Table 4.3.

Overall expected trends for the different NIPAM concentrations and cross-linker densities used to prepare core-shell gold nanorod-PNIPAM particles were observed. The samples prepared with the higher NIPAM concentration of 0.017 M NIPAM led to thicker shells, as could be seen in the TEM and DLS measurements. These samples showed more pronounced scattering in the UV-vis spectra. Surprisingly, a threshold NIPAM/BIS ratio was found below which no PNIPAM shell appeared to form. The particles however were stable, as determined by the fact that no aggregation was observed in the TEM and UV-vis spectra (even after they had been cleaned by centrifugation). The only particles that exhibited signs of aggregation were the 0.01 M 5% ones, which showed a decrease in absorbance at the longitudinal plasmon band upon heating, and the plasmon band did not completely recover upon cooling. Reasons for the existence of this threshold concentration for shell formation are discussed in Section 4.3.
4.1 Synthesis via radical polymerisation

4.1.2 Changing various parameters

The effects of changing various parameters involved in the synthesis of core-shell gold nanorod-PNIPAM hybrid particles were studied. The aim of this work was to determine the best conditions under which monodisperse particles could be prepared, as well as identify the most crucial parameters for the formation of a shell.

4.1.2.1 Functionalisation of rods

The importance of the functionalisation of the gold nanorod surface was studied by comparing rods that were dispersed in 1 mM CTAB (unfunctionalised) and rods that had been functionalised with butenoic acid. Both were polymerised with 0.01 M NIPAM and 10 % BIS, and initiated with 100 µl AAPH. The reaction was left for 1 hr and after cooling, the solutions were centrifuged at 9000 rpm for 45 min at 27°C. A difference could already be seen in the way the particles deposited in the vial after centrifugation. Generally core-shell rods-PNIPAM deposited as a pellet on the side of the Falcon tube and needed sonication and shaking to redisperse in water. For the unfunctionalised rods, the particles sedimented to the bottom of the vial, and quickly redispersed with gently swirling in a similar behaviour as pure gold nanorods. UV-vis spectra and TEM images are given in Figure 4.10 for the unfunctionalised (left) and functionalised (right) rods with PNIPAM. The UV-vis spectra are given at 20 and 40°C. For the unfunctionalised rods, the spectrum did not change much upon heating. A slight increase in absorbance was observed at 300 nm, as well as a red-shift of 9 nm in the longitudinal plasmon band. This was significantly less than the 22 nm red-shift observed for the core-shell particles prepared with the functionalised rods. The increase in absorbance at 300 nm for the functionalised rods also doubled, indicating more scattering and hence more contribution from the shell. TEM showed that the unfunctionalised rods were clumped together, surrounding random agglomerates of polymer. The functionalised rods, on the other hand, were well-separated and dispersed throughout the PNIPAM network.
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4.1.2.2 Effect of surface chemistry: Butenoic acid vs. Butenylamine

Prior to deciding on butenoic acid as a ligand for nanorod functionalisation, butenylamine was also tried. The reason for this was that in previous work, butenylamine had been utilised to functionalise 15 nm citrate-coated gold nanoparticles. Butenylamine is a short chain amine with a terminal double bond on one end. Butenylamine is a solid in powder form, and due to its hydrophobic nature solutions are prepared in ethanol. In the case of the citrate-coated particles, SDS was added as a surfactant to help maintain the stability of the nanoparticles after the extra hydrophobicity introduced by butenylamine, and it was
found to aid during the centrifugation steps after the functionalisation. In Chapter 3, it was shown that butenylamine could successfully functionalise gold nanorods. However, the addition of a surfactant was crucial since lack of a surfactant led to direct aggregation of the rods. Using SDS led to the rods irreversibly aggregating upon centrifugation after functionalisation or radical initiation during polymerisation. SDS could not be used since it is negatively charged, which leads to charge instabilities due to the positively charged CTAB. A neutral surfactant was then tried, Tween-20, which is a polysorbate surfactant. This provided the stability needed without any charge issues, and indeed, the rods remained stable after centrifugation and during polymerisation.

Butenylamine coated rods were polymerised in the same way as described in Section 4.1. 50 ml were polymerised with 0.017 M NIPAM and 25 mol% BIS. Once the polymerisation was complete, the solution looked turbid and the particles were still stable - no visible aggregation was seen. The TEM images however, as given in Figure 4.11, showed empty shells and several rods attached to the exterior of the PNIPAM microgels as well as some core-shell shell structures. Additionally, the particles were not as monodisperse as those obtained when butenoic acid was used to functionalise the gold nanorods.

Figure 4.11: TEM images showing the hybrid microgels obtained when butenylamine was used as a ligand for surface functionalisation of the rods. These particles were prepared with 0.017 M NIPAM and 25 mol% BIS and initiated with AAPH.

In summary, these results highlighted the importance of having initiation sites on the surface of the gold nanorods for obtaining a well-defined core-shell structure. Additionally,
the ligand used for functionalising the nanorods also played a role, whereby using butenoic acid over butenylamine was found to give a much higher yield of core-shell particles.

### 4.1.2.3 Reducing shell thickness

The prepared core-shell Au-nanorod-PNIPAM particles have diameters on the order of 300 - 400 nm. In the 3D assembly of these core-shell particles, in order for alignment of the gold nanorod cores to occur, thinner shells are needed. One way of tuning the shell thickness is by reducing the monomer concentration. It was shown above that the shell thickness decreased when going from 0.017 M to 0.01 M NIPAM as indicated by the lower absorbance, i.e. scattering at low wavelengths. However, a certain cross-linker density was needed to obtain a well-defined shell. Here, the NIPAM concentration was then varied for a constant cross-linker density of 25 %, which was the highest cross-linker density used. Particles were prepared with 0.02, 0.01, 0.005 and 0.0025 M NIPAM concentrations, and corresponding TEM images and UV-vis spectra are presented in Figure 4.12.

![TEM images and UV-vis spectra of particles with a constant cross-linker density of 25 %, and varying monomer concentrations of 0.02, 0.01, 0.005, and 0.0025 M NIPAM.](image)

Figure 4.12: TEM images and UV-vis spectra of particles with a constant cross-linker density of 25 %, and varying monomer concentrations of 0.02, 0.01, 0.005, and 0.0025 M NIPAM.

Less scattering was observed for decreasing concentrations of NIPAM, indicating the
formation of thinner shells. The longitudinal plasmon resonance was also least prominent for the 0.02 M shell, highlighting the dominant scattering contribution from the shell. Although a shell could be seen for the 0.005 M, the particles were not as monodisperse as those prepared with higher concentrations. This showed that the concentration limit for shell formation was being approached. That was further proven by observing the 0.0025 M sample which had no visible shell.

Another attempt at reducing shell thickness was to double the amount of gold rods used as cores while keeping the NIPAM and BIS concentrations constant, instead of trying to reduce the NIPAM concentration (since very low masses were already being used). 100 ml of rods were functionalised with butenoic acid and then redispersed in 50 ml water. This 50 ml rod solution was then used as reaction medium for the polymerisation, thereby having double the number of rods as usual. Two polymerisations were tried, one with 0.01 M NIPAM and 10 % BIS and the other with 0.01 M NIPAM and 25 % BIS. The results for the 0.01 M 10 % BIS sample are shown in Figure 4.13. During the synthesis, the sample looked slightly turbid, but upon centrifugation, the sedimented particles were very hard to redisperse and some aggregates could not be dispersed. Heating the solution caused a small red-shift with slight peak broadening and a decrease in absorbance at the longitudinal plasmon band. After cooling back to 20 °C, the plasmon band returned to its original position but the absorbance did not fully recover, indicating some irreversible aggregation or sedimentation of the particles. The TEM images revealed a random array of gold nanorods that appeared to have no shell, and were more aggregated rather than well-separated. Some polymer could be seen but instead of having a core-shell structure, the rods appeared stuck to the polymer. The particles prepared with 0.01 M NIPAM and 25 % BIS showed very similar behaviour, and therefore the results are not presented here.
4.1 Synthesis via radical polymerisation

4.1.3 Polymerisation Quenching

Now that various parameters had been studied and their effects determined, the next step was to study the actual core-shell formation to gain an understanding on how the shell grew around the cores. In order to try to understand the polymerisation process, aliquots were removed from the reaction mixture at specific times following the injection of the radical initiator AAPH. If the shell is gradually increasing, this should also allow us to isolate samples with thinner shells by stopping the polymerisation at certain times after initiation. For this study, polymerisation reaction was performed with 0.01 M NIPAM and 25 mol% BIS. After addition of 0.1 ml of 0.1 M AAPH, 1 ml aliquots were withdrawn every minute for the first 10 min, then every 5 min until 30 min had passed, and finally at 45 min and 60 min. The aliquots were directly quenched in liquid N\textsubscript{2} in air, followed by centrifugation and redispersion in water in order to remove any remaining initiator and inhibit further growth. Absorbance spectra were taken at the different times and are shown in Figure 4.14. The spectra were normalised to the absorbance at $\lambda_{\text{max}}$. 

Figure 4.13: UV-vis spectra and TEM images of the resulting particles when doubling the concentration of the gold nanorod cores for a 0.01 M NIPAM, 10% BIS polymerisation. The left side compares the spectra at 20°C heated to 40°C and then cooled back to 20°C to see if any aggregation could be observed.

The effect of reducing the NIPAM concentration for a set cross-linker density complements the results determined by varying the cross-linker density for constant NIPAM concentrations. Both experiments led to the conclusion that below certain concentrations a well-formed PNIPAM shell could be not detected around the nanorod cores.
4.1 Synthesis via radical polymerisation

Figure 4.14: Absorbance spectra of Br-SA rods polymerised with 0.01 M NIPAM and 25 mol% BIS. 1 ml aliquots were withdrawn every minute for the first 10 min, then every 5 min until 30 min had passed, and also at 45 min and 60 min. The aliquots were directly quenched in liquid $N_2$ in air, followed by centrifugation and redispersion in water in order to remove any remaining initiator and inhibit further growth.

An increase in absorbance at lower wavelengths was observed as time increased. This indicated a gradual increase in shell thickness as time progressed, due to scattering from thicker shells. The absorbance at 300 nm was then plotted as a function of time in Figure 4.15. The increase in absorbance was fastest during the first 10 mins, following an almost linear trend. As time progressed, the absorbance change became less pronounced, reaching a plateau after 30 min. The change in absorbance could be fit with a single exponential function, indicating exponential growth with the growth rate decaying with time.
4.1 Synthesis via radical polymerisation

Figure 4.15: Absorbance values at 300 nm for the different reaction times from Figure 4.14 plotted vs time, and fitted with a single exponential function.

TEM images were also taken at different times of the polymerisation to observe the structure of the particles at different times. Figure 4.16 presents TEM images at 3, 6, 10 and 15 min after addition of the radical initiator. A very faint shell could already be seen after 3 min, indicating that the reaction occurs quite fast. Although the shell was not too visible, the rods seemed well-separated in the 6 min sample. By 10 min, a relatively thick shell could be clearly seen, and by 15 min the reaction appeared almost complete with the formation of a well-defined PNIPAM shell. Hydrodynamic radii ($R_h$) obtained by dynamic light scattering (DLS) are given for the 5 min sample and 15 min sample. By 5 min, a shell with radius of 106.4 nm at 20°C had already formed, and exhibited thermoresponsive behaviour as indicated by the collapse in size to 61.3 nm at 50°C. By 15 min, the shell had grown to a radius of 135.2 nm at 20°C, which showed a collapse to 108.4 nm at 50°C.
4.2 Characterisation of Optical Properties

Table 4.4: Table showing values of the hydrodynamic radius, $R_h$ obtained by DLS for the aliquots taken at 5 and 15 min after polymerisation initiation.

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_h$(20°C)</th>
<th>$R_h$(50°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>106 nm</td>
<td>61 nm</td>
</tr>
<tr>
<td>15 min</td>
<td>135 nm</td>
<td>108 nm</td>
</tr>
</tbody>
</table>

Figure 4.16: TEM images of core-shell particles formed at 3 min, 6 min, 10 min and 15 min post polymerisation initiation.

The polymerisation quenching experiment shed light on the growth rate of core-shell gold-PNIPAM. Shell growth around the nanorod core could already be observed within the first few minutes, indicating that polymerisation was being initiated from the surface of the nanorods. While the quenching method could lead to core-shell particles with thinner shells, it was found to not be scalable and the thinner shelled particles lacked monodispersity.

4.2 Characterisation of Optical Properties

While the previous section focused more on the shape and size of the prepared particles, the following section presents a more detailed look at the optical properties of the gold nanorod-PNIPAM hybrid particles. The effect of changing the temperature on the optical behaviour of the nanorods is shown in Figure 4.17 for BrSA-3.7 rods polymerised with 0.01 M NIPAM and 25% BIS. The top panel of Figure 4.17 shows spectra taken at increasing temperatures from 10 to 55°C. The sample was kept at each temperature for at least 10 min to equilibrate before spectra were acquired. With increasing temperature, a red-shift in the longitudinal plasmon band was observed due to the change in refractive index induced by the collapse
of the polymer network. A plot of the position of the longitudinal plasmon band versus temperature plotted on the bottom of Figure 4.17 revealed an overall red-shift of 24 nm in the longitudinal plasmon band. This large red-shift highlights the sensitivity of the gold nanorods to their surrounding environment and presents a novel method of tuning the position of the longitudinal plasmon band of the gold nanorods through the PNIPAM shell.
4.2 Characterisation of Optical Properties

Figure 4.17: Top: Plot of absorbance versus wavelength at temperatures ranging from 10 to 55 °C for core-shell particles prepared from BrSA-3.7-rods with 0.01 M NIPAM and 25% BIS, taken Bottom: The wavelength at the longitudinal surface plasmon resonance (LSPR) plotted at various temperatures in the range of 10 to 55 °C, crossing through the VPTT.

To check if the temperature induced red-shift would return to the original wavelength upon cooling, the temperature was cycled between 20 and 45 °C, and spectra were taken at each temperature. The results are given in Figure 4.18. The red-shift in the longitudinal
plasmon band was found to be highly reproducible, with the plasmon band shifting to almost the same position each time the solution was heated to 45 °C, and then completely recovering to the same wavelength upon cooling to 20 °C. This indicated the stability of the shell surrounding the gold nanorods. No aggregation was observed even after at least four heating/cooling cycles.

Figure 4.18: Plot of the position of $\lambda_{\text{max}}$ upon alternating the temperature between 20 and 45 °C for a core-shell rods-PNIPAM solution prepared with NaOl-4.1-rods polymerised with 0.01 M NIPAM and 25% BIS. The fact that the longitudinal plasmon band returns to its original position even after several heating/cooling cycles highlights the reversibility of the volume phase transition on the position of the longitudinal plasmon band of the gold nanorod cores.

The higher polymer density due to the change in particle dimensions during the volume phase transition (VPT) is manifested by the increased absorbances at the lower wavelength regime. By monitoring the change in absorbance in the low wavelength regime as a function of temperature, the VPT can be followed using UV-vis spectroscopy. Spectra were collected at temperatures ranging from 10 - 55 °C and the absorbance at $\lambda = 300$ nm was plotted versus temperature for samples prepared with different NIPAM/BIS ratios. Figure 4.19 shows swelling curves for 0.01 M NIPAM 25% BIS (top), 0.01 M NIPAM, 10 % BIS (middle) and 0.017 M NIPAM, 10 % BIS (bottom). The spectra were normalised to the absorbance
4.2 Characterisation of Optical Properties

at 55°C for comparison.

The swelling curves in Figure 4.19 portray the increased scattering as the microgel collapses. For the higher amount of BIS, the temperature induced change was not as dramatic as for the 10%. This was due to the decreased swelling behaviour as a result of increasing BIS amounts. The VPT temperature (VPTT) could be determined by taking first derivatives of the spectra and the obtained values are given in table 4.5.
4.2 Characterisation of Optical Properties

Figure 4.19: Swelling curves for 0.01 M NIPAM, 25 % BIS (top); 0.01 M NIPAM, 10 % BIS (middle); and 0.017 M, 10% BIS (bottom). The swelling curves were obtained by plotting the absorbance at 300 nm (which corresponds to scattering from the PNIPAM shell) at different temperatures from 10 to 55°C.
### 4.3 Discussion

#### Reducing shell thickness

In the preceding sections results from the optimisation of PNIPAM coating of gold nanorods were presented. It was demonstrated that varying the monomer concentration and cross-linker density influenced the size and optical properties of the core-shell particles. Particles prepared with higher monomer concentrations and cross-linker densities have thicker shells and this can be seen by the higher absorbances at lower wavelengths due to a larger scattering contribution from the PNIPAM. A very interesting trend was observed when the cross-linker density was decreased past a certain limit. Below a specific point, no PNIPAM shell appeared to form. This leads to the conclusion that there is a threshold NIPAM/BIS ratio below which the monomer does not polymerise in a well-defined way around the core. For higher NIPAM concentrations, lower cross-linker densities can be accessed. A possible explanation for this could be the mechanism by which the polymerisation occurs. For core-shell microgels, it is believed that the radical initiator forms radicals on the gold core, which is why the gold has to be functionalised with a ligand that possesses double bonds on its surface. NIPAM radicals then deposit on the gold core and the cross-linker holds them together and the shell gradually grows as more NIPAM deposits. Surfactant-free precipitation polymerisation provides limitation in terms

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_h$(20°C)</th>
<th>$R_h$(50°C)</th>
<th>VPTT(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M, 25%</td>
<td>280 nm</td>
<td>131 nm</td>
<td>37</td>
</tr>
<tr>
<td>0.01 M, 10%</td>
<td>152 nm</td>
<td>102 nm</td>
<td>36</td>
</tr>
<tr>
<td>0.017 M, 10%</td>
<td>225 nm</td>
<td>85 nm</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 4.5: Table showing values of the hydrodynamic radius, $R_h$ obtained by DLS for different connectivities, as well as the VPTT determined from the swelling curves.

The obtained VPTT values are a few degrees higher than those reported for pure PNIPAM microgels. The cross-linker values used here are higher and the NIPAM concentrations lower than typical emulsion polymerisations. Furthermore, the VPTTs were determined from UV-vis spectra which give us an estimation related to how the local refractive index is changing rather than how the particle dimensions are changing. Table 4.5 also shows typical $R_h$ values obtained from DLS at 20 and 50°C.
of particle size variation. Microgels prepared this way are on the order of hundreds of nm to micron size diameters. In order to prepare particles with a smaller diameter, which was one of our aims, the growing precursor particles in the early stages of the polymerisation need to be stabilised. The small precursor particles have a very large surface area, and the charge provided by the initiator is not sufficient to stabilise them. Other groups have shown that adding a surfactant to the synthesis can stabilise the precursor particles and consequently smaller diameters can be accessed. Pelton and coworkers found that by adding SDS as a surfactant, the size was decreased by a factor of 10. In our case, adding SDS was not an option due to the charge issues from the CTAB, as discussed in section 4.1.2.2 for the functionalisation. Most reports in the literature are for purely organic microgels, where colloidal stability of the inorganic core is not an issue. This gives more room for variation, whereas our work had more limitations. Based on the above, a possible reason why we failed to obtain thinner PNIPAM shells on the gold nanorods is due to the instability of the formed precursor particles. Microgels become stabilised through electrostatic stabilisation once they reach a critical size. In the case of higher NIPAM concentrations such as 0.017 M, the produced particles keep growing by oligomers depositing on them until a stable size is reached. This explains why the shells are thick, because the particles keep growing due to the large amount of NIPAM present. Theoretically, reducing the amount of NIPAM should lead to thinner shells. However, we found that this was the case until a certain concentration limit. When we reduced the NIPAM concentration past the ”threshold” concentration, there was not enough NIPAM to keep forming oligomers and depositing on the precursor particles, and the precursor particles were not stable enough to stay in solution and form microgels. As a result, we observed no shell growth around the nanorods. However, our results showed that the gold nanorods were still stable and did not undergo aggregation even after centrifugation, which indicated that the PNIPAM had been adsorbed onto the gold nanorods but the structure could not be visualised with the TEM.

**Charge of the microgels** Most PNIPAM polymerisation reactions use potassium per-oxidisulfate as the initiator, whereby the $S_2O_8^{2-}$ ions are embedded into the PNIPAM and thus provide a negative surface charge. The zeta potential of these microgels is then around -10 mV, not highly charged but still slightly negative. The azo-based initiator we are using here, AAPH, is normally referred to as a cationic surfactant. AAPH undergoes thermal
decomposition to form a cationic carbon radical as shown in the reaction scheme in Figure 4.20\textsuperscript{[147]}. Since the initiator molecules determine the final charge of the microgels, it is expected that the formed microgels should be slightly positively charged. The zeta potential of the hybrid particles was measured and surprisingly, the particles were found to have a negative zeta potential of $-14.4 \pm 0.6$ mV at pH 6. At more basic pH (12) the zeta potential was also negative ($-22.4 \pm 0.5$ mV). However, at a pH of 2 a slightly positive zeta potential of $+2.2 \pm 0.6$ mV was measured. A possible reason for this change in zeta potential is due to the fact that butenoic acid is used for functionalisation. Butenoic acid, also known as vinylacetic acid, has been shown before to be a co-monomer with PNIPAM. This means that during the polymerisation reaction the butenoic acid can react with the NIPAM and BIS and thus be part of the polymer network. However, for that to happen there must be some excess butenoic acid that is not attached to the gold nanorods. This is a very likely scenario considering the functionalisation process used. After the functionalisation the rods are centrifuged and concentrated. The rods are only centrifuged and redispersed once because any further centrifugation steps were found to lead to aggregation. This could therefore mean that there is butenoic acid remaining in the solution.

![Figure 4.20: Scheme showing the thermal decomposition of the radical initiator AAPH.](image)

If the butenoic acid is acting as a co-monomer, then carboxyl groups are presented on the surface of the microgel. Microgels are made of a highly cross-linked core which gradually decreases, leaving loose dangling bonds at the ends. The confirmation for the presence of carboxyl groups on the exterior of the microgel is that the zeta potential changed with pH. In highly acidic conditions, at a pH of 2, the zeta potential changed from negative to positive $+2.2$ mV, which is consistent with the fact that the carboxylic acid is protonated in an acidic environment, explaining the slight positive charge. In highly basic conditions, at a pH of 12, the butenoic acid is deprotonated, and therefore negatively charged due
4.3 Discussion

to the carboxylate ions, leading to a negative zeta potential. The zeta potential values are consistent with the explanation that the butenoic acid has exposed carboxyl groups on the surface of the microgel. This was quite an interesting observation, because the rods themselves are positively charged due to the CTAB, and because a cationic initiator was used, the surface charge of the microgels was expected to be positive. In fact, when a negatively charged initiator such as KPS was tried, the rods immediately aggregated due to charge instability. This further showed that the negative charge must arise from the butenoic acid after initiation and once a polymer shell has already formed. Previous studies in the literature have shown that copolymer microgels composed of NIPAM and butenoic acid have been prepared. Their structure consists of microgels containing carboxylic acid functional groups that are localised on the surface but are relatively isolated from each other.\textsuperscript{[148]} Allylic monomers such as butenoic acid can behave as chain transfer agents instead of propagating monomers in the presence of free radicals. To understand why or how the carboxylic groups can be localised on the microgel surface, the degradation pathways of the butenoic acid, or the way in which the butenoic acid reacts with free radicals must be considered. There are two ways that the butenoic acid can react in a free radical environment, as depicted in the reaction pathway in Figure 4.21. The first is free radical propagation through the double bond, which is what is expected to occur for the butenoic acid that is bound to the gold nanorods. Since the gold nanorods are thought to act as nucleation sites for the growth of the PNIPAM shell, this is a likely mechanism where the butenoic acid forms a free radical that can induce PNIPAM chain propagation as well and growth can initiate from the surface of the nanorods.
Figure 4.21: Reaction pathway of butenoic acid upon radical initiation. Two possible pathways exist: Propagation or chain transfer. Chain transfer produces a resonance stabilised radical which can undergo effect chain transfer to the monomer (left), polymer chain end-capping whereby a free radical attacks the allylic radical, terminating the polymerisation (middle) or degradative chain transfer which quenches the polymerisation (right). Adapted from reference [148].

The second pathway is chain transfer with abstraction of the methylene protons. This forms the corresponding radical shown in Figure 4.21. Very few reports exist of homopolymers made from butenoic acid because the chain transfer mechanism plays an important role and is likely a competing pathway for the chain propagation. It has been hypothesised that this pathway is in fact dominant in cases where the butenoic acid is diluted and several radical centres are present, which is the situation during microgel syntheses. In the chain transfer process, the formed radical is a resonance stabilised allylic radical. As a result of the resonance stability, it usually remains a free radical until it is terminated or quenched at the end of the polymerisation, in what is known as degradative chain transfer. The likelihood of degradative chain transfer occurring in our synthesis is suppressed. The reason for this is
that the carboxylic acid group at the end of the butenoic acid is electronegative and thereby
electron-withdrawing, meaning that it strengthens the C-H bond at the methylene position
and inductively destabilises the resonance structure which is electron deficient. As a result,
the probability of degradative chain transfer occurring is reduced, and instead, alternative
processes such as polymer chain end-capping Figure 4.21 (middle) and chain transfer to
the monomer Figure 4.21(left) are more likely to occur. In polymer chain end capping, a
free radical attacks the allylic radical, thereby terminating the polymerisation. In the chain
transfer to the monomer, the allylic radical is now grafted on to the monomer. In both of
these scenarios, the butenoic acid attaches to the ends of the NIPAM polymer chains\cite{148}.

The amount of cross-linker and initiator also affect the kinetics and end structure of
the microgels. The amount of cross-linker used in our study varied between 5 to 25 mol
%. These are relatively high proportions of cross-linker density, meaning that the microgels
and the growing oligomers will likely contain vinyl groups due to unreacted ends of the
BIS molecule. The high initiator concentrations used indicate there is a high amount of free
radicals throughout the synthesis. This in turn means that these unreacted vinyl groups can
be initiated by these free radicals, thereby cross-linking the carboxy-terminated oligomers
formed in the polymer chain end capping and monomer chain transfer pathways. The above
discussion helps explain the incorporation of the carboxyl groups of the butenoic acid into
the microgel.

4.4 Conclusion

This chapter aimed at answering the first research question of this thesis: Can we develop
a protocol for coating monodisperse gold nanorods with a PNIPAM shell with a high yield,
and characterise their optical properties and swelling behaviour? Indeed, core-shell gold
nanorod-PNIPAM particles having a single gold nanorod core were successfully prepared
using surfactant-free emulsion polymerisation. The effect of varying the monomer concen-
tration and cross-linker density on the size of the core-shell particles was studied. Attempts
at reducing the shell thickness led to the observation that a threshold NIPAM/BIS ratio
existed below which no shell would form. The influence of the functionalisation of the rods
and the ligand used was also shown to have a strong effect on the quality of the core-shell
structure. Quenching the polymerisation at different times after the addition of the radi-
4.4 Conclusion

calc initiator indicated that the kinetics of the reaction are quite fast; a shell had already formed within the first few minutes. The optical behaviour of the gold nanorod cores could be manipulated through the PNIPAM shell collapse, causing a strong reversible red-shift in the longitudinal plasmon band. The swelling behaviour of the core-shell particles could be monitored through UV-vis spectroscopy and the VPTT determined from the obtained swelling curves. A closer look into the polymerisation mechanism revealed that at the low concentrations of NIPAM utilised in this study, the formed precursor could not be stabilised without a surfactant and hence kept growing to give thick shells. Additionally, the butenoic acid used to functionalise the nanorods likely acts as a co-monomer, leading to negatively charged carboxy-terminated microgels. The next chapter presents the self assembly of the core-shell particles to form 3D colloidal crystals.
Chapter 5

3D Assembly of Rods-PNIPAM: Crystallisation and Melting Behaviour

The main advantage of coating nanoparticles with PNIPAM compared to other shelling materials is the fact that PNIPAM can be used as a flexible spacer between the nanoparticles with interparticle spacings up to hundreds of nanometres. The polymer shell increases the effective particle volume, and therefore interparticle distance. As a result PNIPAM can be used as a spacer where the distance is controlled either through shell thickness, or through temperature. This is extremely important in self assembly as it provides a way to control nanoparticle distances. The synthetic protocol developed in Chapter 4 opened the pathway toward exploring the crystallisation of core-shell rods-PNIPAM because it allowed the preparation of highly monodisperse particles at high volumes. This was the crucial step necessary to access high enough volume fractions for particle crystallisation to occur. As discussed in Chapter 1, most nanocrystal superlattices have generally been prepared using surfactant capped nanocrystals, leading to interparticle spacings of only several nanometres. DNA and silica coating have also been exploited for assemblies, but they are limited techniques in terms of spacing control, scalability and tunability. While the controlled 3D assembly of purely organic PNIPAM has been previously studied, very little work has been presented on the optical behaviour of 3D assemblies of core-shell metal nanoparticle-PNIPAM particles.
5.1 Preparation of 3D colloidal crystals

Gold nanorod-PNIPAM solutions were synthesised as described in Chapter 4. For the 3D colloidal crystals study, BrSA-3.8 rods were used as cores. After the solutions were cleaned via centrifugation and redispersion, they were passed through a 0.45 µm filter (Millipore) to remove any potential aggregated particles and freeze-dried to obtain a solid polymer material. This allowed us to weigh out the polymer and prepare different weight percent concentrations to determine the volume fraction at which the particles would crystallise.

Core-shell gold rod-PNIPAM particles already displayed iridescent behaviour upon centrifugation, as can be seen in Figure 5.1. The photograph on the left shows the pellet that sedimented on the side of the Falcon tube when a 50 ml 0.01 M 25 % rod-PNIPAM solution was centrifuged. While the concentration and hence volume fraction of the sample was unknown, the sediment appeared crystalline and iridescent due to the particles being forced into a close-packed structure through centrifugation. The photograph on the right shows how the crystallinity could be destroyed through redispersing the crystalline assembly into the solution upon slight shaking. The crystallinity apparent after centrifugation was the first sign that 3D assemblies of these particles could be prepared.

Figure 5.1: Photographs of the iridescent sediment formed upon centrifugation of 50 ml 0.01 M 25 % rod-PNIPAM solution. The iridescence highlighted the crystalline assemblies that form upon packing the rod-PNIPAM particles close together.

Once the solutions were prepared, 30 µl of the solution were placed in a quartz cuvette with 0.1 mm spacing. The cuvette is composed of two separate quartz slides, one with a smooth surface and one with 0.1 mm deep groove. The solution was deposited on the side with the groove, and the other side with the smooth surface was placed on top to seal
the cuvette through capillary forces. Care was taken to ensure no air bubbles were formed. Generally crystallisation could be seen either directly upon sealing cuvette, or after one cycle of heating and cooling. Heating caused the particles to collapse and hence rearrange inside the cuvette. Upon cooling, they swelled back and locked into position. Highly concentrated samples tended to be very viscous and hence needed to be heated to make them liquid prior to filling the cuvettes. The filled cuvette was then placed in a UV-vis spectrometer and spectra were recorded. Figure 5.2 shows the optical properties of the prepared 3D crystals from a 5 wt% solution of 0.017 M 10% rod-PNIPAM particles. The spectrum of the crystalline sample (purple line) was compared to the pure Au-nanorod-PNIPAM solution (black solid line). Upon crystallisation, three new peaks appeared, in addition to the transverse and longitudinal plasmon bands, at 1021 nm, 513 nm and 349 nm.
Figure 5.2: Absorbance spectra of 0.017 M 10% rod-PNIPAM solution (solid black line), the crystal that formed from a concentrated 5 wt% solution at 20 °C (solid pink line) and the melting of the crystal upon heating above VPTT (dashed black line). Upon crystallisation three Bragg diffraction peaks appear at different wavelengths, which completely disappear upon melting of the crystal.

The new peaks corresponded to Bragg diffraction peaks, where the lattice spacing could be determined using Bragg’s law:

\[ m\lambda_{\text{max}} = 2d_{hkl}\sqrt{n_{\text{crystal}}^2 - \sin^2\theta} \]  \hspace{1cm} (5.1)

where \( m \) is an integer, corresponding to the order of diffraction, \( d_{hkl} \) the distance between adjacent (hkl) lattice planes, \( n_{\text{crystal}} \) the refractive index of the crystal, and \( \theta \) the angle of incidence. Bragg diffraction peaks are caused by the diffraction and constructive interference of the waves of incident light, with wavelengths comparable to the lattice spacings. In constructive interference, the scattered waves remain in phase since the path length of each wave equals an integer multiple of the wavelength of the incident light. This integer
5.1 Preparation of 3D colloidal crystals

 corresponds to the order of diffraction. The first peak to the red of the longitudinal plasmon band appeared at 1021 nm, and for \( m = 1 \) corresponded to the first order diffraction peak.

Using Bragg’s law and the wavelength at which diffraction occurred, the lattice spacing could be determined. For our measurements, \( \theta = 0 \), and so equation 5.1 was rearranged to:

\[
m\lambda_{\text{max}} = 2d_{hkl}n_{\text{crystal}}
\]

The volume fraction was determined from the weight percent using the density of PNIPAM of 1.1 g/cm\(^3\) and assuming a 10\% water content. Therefore for a 5 wt\% solution the volume fraction was found to be 0.04. The refractive index of the crystal was determined from the volume fraction of the crystal, and the refractive indices of PNIPAM and water, assuming the effective refractive index scaled linearly with the two components:

\[
n_{\text{crystal}} = \phi 1.389 + (1 - \phi) 1.332
\]

which gave \( n_{\text{crystal}} = 1.334 \)

It has been shown previously that PNIPAM crystallises into face-centred cubic (fcc) structures\(^{[122]}\). For face-centred cubic packing:

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

As a result, for crystallisation along the 111 plane, equation 5.3 could be substituted into 5.2 to determine the lattice spacing \( a \):

\[
a = \frac{\sqrt{3}m\lambda_{\text{max}}}{2n_{\text{crystal}}}
\]

From the diffraction peak at 1021 nm, a lattice spacing of 662 nm was therefore determined.

\[
a \approx 2\sqrt{2}R_g
\]

Substituting the calculated value of \( a \) into equation 5.5 a radius of 234 nm was determined, which corresponded very well to the hydrodynamic radius of 225 nm determined for these particles a 0.017 M 10\% gold nanorod-PNIPAM hybrid (Chapter 4 Figure 4.19).

The appearance of three peaks was an unexpected feature. The two peaks to the blue of the longitudinal plasmon band in Figure 5.2 appeared at wavelengths of \( \sim 510 \) and 340 nm, which was equivalent to \( \frac{1}{2} \) and \( \frac{1}{3} \) of the first order diffraction peak, respectively.
Consequently, these two peaks corresponded to second and third order diffraction peaks. The first, second and third order diffraction peaks had full width at half maxima (FWHM) of 20, 32 and 62 nm respectively. The presence of sharp diffraction peaks of several orders indicated long-range ordering in the crystal. In summary, these results showed that highly ordered 3D colloidal crystals exhibiting three Bragg peaks spanning from the NIR through to the visible and UV regions of the electromagnetic spectrum were successfully prepared.

In Figure 5.2, the spectrum of the crystalline sample was measured at 20°C, which was in the swollen state. Once the temperature was raised above the VPTT of the rods-PNIPAM (\(\sim\) 37°C), the particles collapsed and the interparticle spacing therefore increased. As a result, the crystal structure melted and transitioned to the liquid state. This can be seen as the ‘melted’ spectrum (black dashed line) in Figure 5.2. The three Bragg peaks completely disappeared, and the same red-shift in longitudinal plasmon band and increase in absorbance at lower wavelengths usually seen in solution was also observed here. A visual depiction of the melting of the crystal is given in Figure 5.3, which shows photographs of the crystalline sample from Figure 5.2. The left photograph shows the highly crystalline sample exhibiting green-blue iridescence. Upon heating above the VPTT, the iridescent colour completely disappeared and gave a reddish turbid colour shown in Figure 5.3 (right), which was similar to the colour of a rod-PNIPAM solution in the collapsed state.

![Figure 5.3](image)

Figure 5.3: Photograph of the crystal measured in Figure 5.2 loaded in a cuvette with 0.1 mm pathlength before (left) and after (right) heating above the VPTT (\(\sim\) 37°C). The iridescent colour completely disappeared and gave a reddish turbid colour, similar to that of the rod-PNIPAM solution.
5.2 Melting and recrystallisation

5.2.1 Effect of temperature on the crystals

Heating the crystals above the VPTT caused the particles to collapse and hence changed the spacing between the particles, which led to the loss of the local ordering and consequent melting of the crystals. In Figure 5.2 the final result of melting was seen, which was the complete disappearance of the Bragg peaks. However, we were interested in seeing how the peaks changed with incremental heating. Figure 5.4 portrays spectra of a crystalline sample prepared from 0.017 M NIPAM, 10% BIS at temperatures ranging from 21 to 38°C. The Bragg peak became more intense as the temperature was raised, as indicated by the increased absorbance, due to changes in refractive index. The change in Bragg peak was monitored in Figure 5.5, where wavelength at the first order Bragg peak was plotted on the left axis along with the absorbance at the wavelength (right axis). The Bragg peak at 21°C appeared at 1022 nm with an absorbance of 0.26. Upon sequential heating it slightly blue-shifted to 1019 nm and the absorbance increased to 0.33 at 37°C. In chapter 4 the VPTT for a 0.017 M NIPAM, 10% BIS core-shell microgel was found to be 37°C, which indicated the particles would undergo collapse at that temperature and therefore the crystal should melt above that temperature. After reaching the VPTT, the crystal melted, as indicated by the disappearance of the peak at 1020 nm and drop in absorbance at that wavelength to 0.12 at 38°C.
5.2 Melting and recrystallisation

Figure 5.4: Absorbance spectra for a 5 wt% crystalline sample prepared from 0.017 M NI-
PAM, 10% BIS rod-PNIPAM solution taken at temperatures ranging from 21 to 38 °C, highlighting the change in Bragg peak upon incremental heating.

Figure 5.5: Plot of the wavelength of the first order Bragg diffraction peak (left axis) and the absorbance at that peak (right axis) versus temperature for the crystal depicted in Figure 5.4.

As the temperature was increased, the particles began to undergo a change in size and
shift in the crystal lattice, whereby slight changes in interparticle separation led to small shifts in the Bragg peak wavelength. While the overall crystal was beginning to melt, small crystallites still existed which caused the increase in intensity. Once the VPTT was reached, no more crystallinity could be maintained due to the larger interparticle distances, and the particles were in the liquid phase again.

5.2.2 Effect of light on the crystals

Hybrid nanomaterials whose colloidal and optical properties can be controlled by external stimuli such as temperature or light are gaining more attention. For core-shell particles, the presence of an absorbing core particle means that the phase transition can also be triggered by light. Gold nanoparticles can undergo photothermal heating upon exposure to light at or close to the surface plasmon band. For instance, Rodriguez-Fernandez et al. used a cw 800 nm laser to excite the longitudinal surface plasmon resonance (LSPR) of the Au nanorods resulting in collapse of the PNIPAM shell\cite{112}. In such composite systems, the thinner, charge stabilised PNIPAM shells should respond much faster and reversibly to temperature changes. Furthermore, the particles can be selectively heated by absorption of light within the core. A handheld 532 nm 40 mW laser was used to attempt photothermal induced melting of a rod-PNIPAM crystal structure. We found that due to the low power and small illumination area of the laser used, it was necessary to have the crystal close to the VPTT of the solution. The results are given in Figure 5.6 which shows absorbance spectra for a 0.017 M NIPAM, 10% BIS rod-PNIPAM crystal placed in a holder set at 37 °C. From Figure 5.4, it was apparent that the crystal underwent complete melting at 38 °C. Spectra were collected after shining the laser on the crystal for certain lengths of time. In Figure 5.6, it can be seen that after 60 s laser illumination, the 1st order Bragg peak slightly blue-shifted and decreased in intensity, similar to the trend observed after heating the solution. Further illumination times led to similar behaviour, but not enough heat was generated to completely melt the crystal. As a result, the temperature of the holder was raised to 38 °C, which showed no change in the spectrum compared to that at 37 °C with 360 s laser illumination. Once the temperature was stabilised at 38 °C, 60 s of illumination were enough to lead to complete melting of the crystal as indicated by the disappearance of all Bragg peaks.
5.3 Conclusion

Core-shell Au nanorod-PNIPAM particles could be concentrated into high volume fractions which led to the formation of 3D colloidal crystallis. This was detected by the iridescence of the concentrated solutions, and the appearance of Bragg diffraction peaks in the absorbance spectra. For low volume fractions, the first diffraction peak lay to the red of the longitudinal

![Graph showing absorbance vs wavelength for different temperatures and laser irradiation times.](image)

Figure 5.6: Melting of the 0.017 M NIPAM, 10% BIS rod-PNIPAM crystal through a combination of temperature and light using a 532 nm 40 mW laser at different illumination times for the crystal set at a temperature of 37 °C.

While a laser with a wavelength closer to the longitudinal plasmon band would be more suited for this study, this was a preliminary experiment aimed at seeing whether crystal melting was possible using a laser. The initial results, even with a green low power laser, were promising, and future work will be aimed at targeting the longitudinal plasmon band for studying laser-induced melting dynamics.
plasmon band, and higher order Bragg peaks were exhibited at lower wavelengths. This led to a crystalline material that exhibited diffraction behaviour in the NIR, visible, and UV regions. Incremental heating of the crystals caused slight shifts in the position of the diffraction peak and its intensity. As the temperature was increasing, the particles began moving around and rearranging, and different crystallite sites formed which explained the increase in intensity at higher temperatures. Once the temperature reached the VPTT of the microgel, the particles collapsed, leading to an increase in particle spacing that destroyed the crystalline phase and reformed the liquid phase. As a result, the Bragg peaks completely disappeared. Although interesting diffraction behaviour could be seen from these materials, future work will be aimed at investigating thinner PNIPAM shells for the alignment of the nanorod cores.
Chapter 6

Extending to Other Nanoparticles - Preliminary Results

The focus of this thesis has been on the coating and assembly of gold nanorods with PNIPAM. One of the aims, however, was to see whether a generic protocol could be developed that could be extended to other nanoparticles, such as different metal nanoparticles, magnetic nanoparticles or semiconductor quantum dots. The main challenge in doing so is finding a ligand that can successfully bind to the nanoparticle surface and also provide the terminal double bonds required for polymerisation initiation in order to form a core-shell structure. The key difference between the various nanoparticles lies in their surface chemistry, and finding one ligand that can bind to different nanoparticle surfaces is very difficult. Magnetic nanoparticles and quantum dots for example are generally synthesised in organic solvents, which presents an additional obstacle since the synthesis of PNIPAM is performed in aqueous conditions. Therefore, these particles would first have to be transferred into water before functionalisation, or must be functionalised with a ligand that can also act as a phase-transfer agent. As a result, finding a generic protocol that can be applied to nanoparticles with different surface chemistry remains a challenge. However, for particles with similar surface chemistry, the developed protocols can be extended. While it has been shown that different sized and shaped Au nanoparticles can be coated with PNIPAM, this chapter presents preliminary results on extending the protocol to metal nanoparticles other than gold. The incorporation of individual quantum dots and magnetic nanoparticles in a core-shell structure remains a challenge, and potential solutions will be discussed under ‘Future work’ in the next chapter.
6.1 Silver nanoparticles

6.1.1 Synthesis and functionalisation of Ag

Silver nanoparticles were synthesised as follows. To 500 ml boiling water under stirring, 1 ml 0.27 M AgNO$_3$ was added, followed by 11 ml of a mixture of 1 wt% sodium citrate and 0.05 wt% citric acid 1 min later. After 30 s, 5.5 ml of a mixture of 0.08 wt% NaBH$_4$, 1 wt% sodium citrate and 0.05 wt% citric acid was added. At this point the solution turned from colourless to brown. The solution was left stirring for 30 min before it was removed off the hot plate.

Functionalisation of the nanoparticles with SDS and butenylamine (BA) was carried out similar to the method reported in Karg et al.\cite{Karg97}. The amount of SDS was calculated to yield $\approx 0.5$ monolayer, assuming a surface coverage of 1 molecule per 0.4 nm$^2$. For example, 3.278 ml of a 0.624 mM aqueous SDS solution were added dropwise to 300 ml of the previously prepared Ag nanoparticle dispersion. After 20 min of stirring following the SDS addition, 0.392 mL of a 2.88 mM butenylamine hydrochloride solution in ethanol were added dropwise and stirring was continued for 20 min. The amount of BA was calculated to account for $3/4$ of a monolayer. The functionalised Ag nanoparticles were then concentrated by three centrifugation steps for 90 minutes at 5500 rpm. The brown concentrated residues were collected and stored in the dark at room temperature, and the slightly yellow supernatant was discarded.

6.1.2 Core-shell Ag-PNIPAM

Core-shell microgels were prepared by a surfactant-free radical polymerisation. A reflux setup was assembled with a three-neck round bottom flask connected to a condenser. For Ag-PNIPAM, 100 ml of water containing the 0.01 M NIPAM and 25 mol% BIS were heated to 70 $^\circ$C and the solution degassed with nitrogen for 30 minutes under stirring. Then, 1 ml of the concentrated functionalised Ag nanoparticles in water was added dropwise. The solution turned from colourless to a yellow brown colour. After 15 min equilibration time, the polymerisation was initiated by the rapid addition of 2 mg KPS dissolved in 1 ml water (freshly prepared). The particle dispersion became slightly turbid within the first 15 minutes of reaction time. The reaction was stopped 2 hours after the addition of the initiator,
the dispersion was left to cool down to room temperature under stirring. The prepared Ag-PNIPAM core-shell particles were then cleaned twice by centrifugation for 60 min at 8000 rpm and redispersion in water.

6.1.3 Results

The advantage of preparing nanoparticles through the presented protocols was their surface chemistry was similar to 15 nm citrate-capped Au nanoparticles, and so similar functionalisation and polymerisation strategies could be tried. The synthesised Ag nanoparticles can be seen in Figure 6.1. The nanoparticles had an average diameter of $14.9 \pm 2.6$ nm, as determined by TEM size analysis. As can be seen in the TEM image of the Ag nanoparticles in Figure 6.1 (left) and from the relatively large standard deviation in diameter, the particles did not have a high degree of monodispersity. Generally the synthesis of monodisperse Ag nanoparticles is quite difficult, especially with citrate as the capping agent. However new protocols have been developed recently that provide much better size control and monodispersity and can be used in future work\cite{149}. Even though the Ag nanoparticles did not have the best quality, the formation of core-shell Ag-PNIPAM was successful, as shown in Figure 6.1 (middle), which showed one Ag nanoparticle per PNIPAM shell.

![Figure 6.1: Left: TEM image of the Ag nanoparticles. Size analysis revealed an average diameter of $14.9 \pm 2.6$ nm. Middle: Ag-PNIPAM particles prepared with 0.01 M NIPAM and 25 % BIS, clearly showing the core-shell structure. Right: Optical spectra of the citrate-coated 14.9 nm Ag nanoparticles (blue line) and the corresponding Ag-PNIPAM solution (black line).](image)

Optical spectra before and after PNIPAM coating are shown in Figure 6.1 (right).
Ag nanoparticles (blue line) showed a strong plasmon resonance peak at 390 nm, which is typical for Ag nanoparticles of this size. After PNIPAM coating, the surface plasmon band red-shifted by 14 nm to 404 nm due to the change in local refractive index. The characteristic increase in scattering at lower wavelengths was also observed.

### 6.2 Platinum nanoparticles

#### 6.2.1 Synthesis and functionalisation of Pt

Platinum nanoparticles were prepared via a seeded protocol. For a 100 ml aqueous seed synthesis, 135 µl of 0.4 M $\text{H}_2\text{PtCl}_6$ stock solution was added to the boiling water under stirring. After 1 min, 3.3 ml of a mixture of 1 wt% sodium citrate and 0.05 wt% citric acid were added, followed by 1.1 ml of a mixture of 0.08 wt% $\text{NaBH}_4$, 1 wt% sodium citrate and 0.05 wt% citric acid 30 s later. The solution was left to boil for 30 min.

Once the formed seeds had cooled, the shelling was performed. For a 300 ml synthesis, 10 ml of the formed seeds were mixed with 290 ml water. To this was added 450 µl of 0.4 M $\text{H}_2\text{PtCl}_6$ stock solution, immediately followed by a 5 ml of a mixture of 1 wt% sodium citrate and 1.25 wt% ascorbic acid. The solution was then heated until boiling, and left boiling for 30 min. The solution had a dark golden brown colour.

Functionalisation of the Pt nanoparticles was done similarly to the method described above in Section 6.1. To 300 ml synthesis of the prepared Pt nanoparticles, 1.66 ml of 0.624 mM aqueous SDS solution were added dropwise, followed by 532 µl 2.88 mM butenylamine hydrochloride solution in ethanol 20 min later. The functionalised Pt nanoparticles were then concentrated by three centrifugation steps for 90 minutes at 6000 rpm, and the dark concentrated residues collected and stored.

#### 6.2.2 Core-shell Pt-PNIPAM

For Pt-PNIPAM, 100 ml of water containing 0.01 M NIPAM and 25 mol% BIS were heated to 70 °C and the solution degassed with nitrogen for 30 minutes under stirring. Then, 1 ml of the concentrated functionalised Pt nanoparticles in water was added dropwise. The solution turned from colourless to a dark brown colour. After 15 min equilibration time, the polymerisation was initiated by the rapid addition of 2 mg KPS dissolved in 1 ml water...
6.2 Platinum nanoparticles

(freshly prepared). The particle dispersion became slightly turbid within the first 15 minutes of reaction time. The reaction was stopped 2 hours after the addition of the initiator, the dispersion was left to cool down to room temperature under stirring. The prepared Pt-PNIPAM core-shell particles were then cleaned twice by centrifugation for 60 min at 8000 rpm and redispersion in water.

6.2.3 Results

Results from the synthesis and polymerisation of Pt are presented in Figure 6.2, which shows TEM images of the Pt nanoparticles (left) and core-shell Pt-PNIPAM (right). The Pt nanoparticles appeared quite monodisperse and TEM size analysis gave an overall diameter of 20.7 ± 3.0 nm. The TEM image of the Pt-PNIPAM shows that all the Pt nanoparticles were coated - however, some particles had multiple cores. This is probably due to the fact that citrate is not the best ligand for the particles and some agglomeration occurred. Another explanation could be the induced hydrophobicity upon functionalisation drove the particles to aggregate slightly.

Figure 6.2: Left: TEM image of the Pt nanoparticles. Size analysis revealed an average diameter of 20.7 ± 3.0 nm. Right: Pt-PNIPAM particles prepared with 0.01 M NIPAM and 25 % BIS, clearly showing the core-shell structure.

Since Pt nanoparticles do not have a surface plasmon resonance in the visible region, the optical spectra only shows Rayleigh scattering. As such the optical spectra are not included here. To the best of our knowledge this is the first report of core-shell Pt nanoparticles. The advantage of having Pt nanoparticles coated PNIPAM is the porous network of the
6.3 Conclusion

This chapter presented preliminary results on extending the protocol to silver and platinum nanoparticles. It was shown that core-shell Ag-PNPAM and Pt-PNIPAM could be prepared, as indicated by the structure in the TEM images. PNIPAM can act as a stabiliser for further experiments to be done on the core particles. This is a first step in showing the versatility of coating nanoparticles with PNIPAM. Further work aims to examine the incorporation of individual quantum dots and magnetic nanoparticles in a core-shell structure remains a challenge. Having hybrid nanomaterials with a variety of optical, catalytic and magnetic properties will open up a variety of applications in sensors and optical displays.
Chapter 7

Conclusions and Future Work

7.1 Conclusions

The aim of this thesis was to explore the PNIPAM coating of anisotropic nanoparticles, specifically gold nanorods. Due to their soft nature and optical properties, microgels are promising candidates for the large scale fabrication of colloidal crystals. The key research questions posed throughout the thesis were:

1. Can we develop a protocol for coating monodisperse gold nanorods with a PNIPAM shell with a high yield, and characterise their optical properties and swelling behaviour?

2. Can we assemble these particles in 3D and explore their crystallisation and melting behaviour?

3. Can a generic protocol be developed that can be used for the coating of different nanoparticles with PNIPAM?

To answer the first question, with the aim of synthesising monodisperse gold nanorods with a narrow size distribution and low yield of impurities, four procedures were trialled. It was found that the BrSA method produced the most reproducible rods with the position of the longitudinal plasmon band at almost the same wavelength between different batches. In addition, these rods were found to be very monodisperse with little to no shape impurities. Rods produced with HQ as a reducing agent instead of AA were also of extremely high quality, however the aspect ratios were above 7, meaning longitudinal plasmon bands in the NIR, which made optical characterisation difficult with the spectrometers used in this study.
Attempts to blue-shift the plasmon peak towards the visible region were successful, however at the expense of the monodispersity and purity of the rods. Due to its high reproducibility and quality, BrSA was thus the method of choice for most experiments presented in this thesis. It was then shown that the as-prepared rods could be further functionalised, either to change the charge or allow the addition of different species to the gold rods. Even though gold nanorods are generally considered difficult to functionalise, we successfully showed that the surface chemistry could be manipulated through changing the charge via SDS or MUA, or simply adding a neutral surfactant. These protocols pave the way for further chemistry to be done on the rods. The most important functionalisation strategy for the purpose of coating nanorods with PNIPAM was showing that ligands possessing terminal double bonds could be attached to the surface of the nanorods. As a result, Chapter 3 was highly significant in forming the necessary foundation for addressing the research questions.

Chapter 4 answered the research question on whether gold nanorods could be coated with a uniform PNIPAM shell, and the optical behaviour of the formed core-shell particles studied. Indeed, core-shell gold nanorod-PNIPAM particles having a single gold nanorod core were successfully prepared using surfactant-free emulsion polymerisation. TEM images revealed the high quality of the core-shell particles, with almost 100% of the PNIPAM shells having one gold nanorod core. Optimisation of the procedures was done by studying the effect of varying the monomer concentration and cross-linker density on the size of the core-shell particles. Attempts at reducing the shell thickness led to the observation that a threshold NIPAM/BIS ratio existed below which no shell would form. The influence of the functionalisation of the rods and the ligand used was also shown to have a strong effect on the quality of the core-shell structure. Quenching the polymerisation at different times after the addition of the radical initiator indicated that the kinetics of the reaction are quite fast; a shell had already formed within the first few minutes. The optical behaviour of the gold nanorod cores could be manipulated through the PNIPAM shell collapse, causing a strong reversible red-shift in the longitudinal plasmon band. The swelling behaviour of the core-shell particles could be monitored through UV-vis spectroscopy and the VPTT determined from the obtained swelling curves. The results led to a closer look into the polymerisation mechanism, which revealed that at the low concentrations of NIPAM utilised in this study, the formed precursor particles could not be stabilised without a surfactant and hence kept growing to give thick shells. Additionally, the butenoic acid used to functionalise
the nanorods appeared to behave like a co-monomer, leading to negatively-charged carboxy-terminated microgels.

Once the successful synthesis of the core-shell rod-PNIPAM particles was achieved, their 3D assembly could be examined and therefore the third research question was answered in Chapter 5. Upon concentrating the core-shell particles into high volume fractions, they underwent crystallisation. This was first detected by the iridescence of the concentrated solutions, and the appearance of intense Bragg diffraction peaks in the optical spectra. For low volume fractions, the first diffraction peak appeared to the red of the longitudinal plasmon band, and higher order Bragg peaks were exhibited at lower wavelengths. This led to the formation of a crystalline material that displayed diffraction behaviour in the NIR, visible, and UV regions. Once the crystal was heated above the VPTT of the microgel, the particles collapsed, leading to an increase in particle spacing that destroyed the crystalline phase and reformed the liquid phase. As a result, the Bragg peaks completely disappeared. Preliminary studies also found that the crystal could be melted by making use of laser-induced photothermal heating of the gold core.

The third research question was highly ambitious in wondering whether a generic protocol could be developed that could be extended to a variety of nanoparticles, including magnetic and semiconductor nanoparticles. The surface chemistry and colloidal stability of different nanoparticles presents a challenge, especially when attempting to find a ligand that can functionalise a range of nanoparticle surfaces. As such, this question still remain a challenge. Nevertheless, we did show that other metal nanoparticles, such as Ag and Pt, could be successful incorporated in PNIPAM in a core-shell structure.

In conclusion, this thesis presented a detailed study on the synthesis of monodisperse gold nanorods with different aspect ratios, and the encapsulation of the nanorods in PNIPAM microgels. PNIPAM provided the nanorods with enhanced colloidal stability, as opposed to their native CTAB bilayer, which could easily be destroyed, rendering the nanorods unstable. In addition, the PNIPAM microgel added further functionality to the nanorods, where their optical behaviour could be modulated through the temperature responsive behaviour of the PNIPAM shell. Finally, the presence of the PNIPAM shell allowed the concentration of the core-shell particles at high enough volume fractions to induce colloidal crystallisation. The formed 3D rod-PNIPAM colloidal crystals exhibited strong Bragg diffraction peaks of
different orders ranging from the NIR, through to the visible and UV regions of the spectrum. This indicated the high quality of the crystal and long range-ordering. This work therefore opens a pathway to plasmonic hybrid crystalline materials with flexible interparticle spacer control.

7.2 Future Work

Since the third research question on extending the protocol to other nanoparticles is still relatively unanswered, future work will be aimed at optimising the protocol to be able to incorporate magnetic nanoparticles and semiconductor quantum dots. This will allow a library of functional materials with tuneable properties to be created. The incorporation of quantum dots is especially interesting, since for thin enough shells, energy transfer can be studied between the core and a dye molecule or gold nanoparticle attached to the exterior of the PNIPAM shell or embedded within it. The distance can be controlled through temperature and as a result temperature-dependent quenching can be examined for a range of molecules.

One of the issues faced in this work was that the formed core-shell particles had thick shells. As a result, the overall shape of the particles was spherical, and the anisotropic nature of the core material was not evident. In order for these hybrid particles to be anisotropic in shape, thinner PNIPAM shells are needed. Additionally, preparing 3D crystals with rods encapsulated in thin PNIPAM shells will lead to the potential alignment of the rods and formation of nematic liquid crystals with polarisation-dependent optical behaviour. One way of doing this is through using linear PNIPAM molecules prepared by living polymerisation methods such as RAFT. These techniques allow precise control over the length of the PNIPAM, which can be synthesised with different end-groups such as thiols, allowing them to be grafted onto nanoparticle surfaces. However, while this seems like a viable solution to obtaining thin shells, achieving large enough volume fractions of these small nanoparticles to induce crystallisation would require syntheses on the litre scale. This provides a further challenge in terms of monodispersity, cost of materials and time, which will be tackled in the future.
Bibliography


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