Evaporation induced self-assembly and characterization of gold nanorods

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Cover: Front cover is design with intension to elucidate a picture of droplet with nanoentities in suspension driven towards the three phase contact line. Back cover is the mimicry of convective flow of gold nanorods in suspension with a beam of light passing through.

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EVAPORATION INDUCED SELF-ASSEMBLY AND CHARACTERIZATION OF GOLD NANORODS

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1

Introduction

This chapter provides a brief introduction to the rapidly evolving field of nanoparticle self-assembly and the important nanoscale forces accountable for the self-assembly process. In the end, a short overview of this thesis is also presented.

1.1 Introduction

Nanoscale devices possess many unique optical, electrical and mechanical properties that are not found in their bulk counterparts. However, properties of nanomaterials consisting of nanoscale building blocks strongly depend on their assembly into superstructures. Various preferentially oriented crystalline arrays of the nanoparticles have the potential to modernize the large variety of technologies, including photovoltaics, sensing and magnetic data storage.^{1–5} In particular, anisotropic nanoparticles are important owing to the anisotropic shape and structure, which gives rise to anisotropic properties.⁶ On the other hand, assembly of anisotropic nanoparticles poses additional challenges as compared to the spherical ones. For example, applications such as plasmonics require control over the orientation of the particle relative to its neighbors and/or the substrate.⁷ Also, in applications like mechanically strengthened composites, the formation of interconnected assembled networks is essential.⁸ Generally, to harness their sole anisotropic properties, one should achieve control over the nanoparticle orientations within the assembled arrays as well as on their structure and spatial extent.

For practical applications it is important to develop tools enabling controlled assembly, which are rapid, scalable and compatible with existing technologies. A variety of mechanisms have been developed and optimized to achieve preferentially oriented assemblies of nanomaterials. One of the approaches is to manipulate the particle-particle or particle-scaffold interactions in order to facilitate the nanoscale formation of ordered superstructures. The usage of external fields, polymers, surface modification, DNA and templates are incorporated for assembling particles in a scalable manner.^{9–20}

The formation of nanoparticle assemblies by controlled liquid evaporation is a widely used technique, in which the assembly of nanoparticles in suspension is governed by a range of interactions, including depletion, capillary, electrostatic, steric, and Van der Waals interactions.^{21–25} Typically, these interactions give rise to a net attractive potential at longer length scales and a very short-ranged repulsion. Moreover, liquid flow near the three-phase contact line also affects the formation of nanoparticle structures; the ‘coffee-stain’ ring is a well-known phenomenon. In this thesis we focus on several aspects of evaporative assembly with the aim to better understand the role of fixed and moving contact lines on the assembly and deposition process.

1.2 Nanofabrication

Nanotechnology encompasses the discipline devoted to fabrication and application of devices with dimensions below 100 nm. Devices are often termed nanoelectromechanical systems (NEMS). Nanofabrication mainly uses two approaches; the first is referred to as top-down nanofabrication, while the second is designated as bottom-up.^{26,27} All self-assembly processes belong to the latter category.

Prior to the rapid development of nanofabrication, the field of microfabrication had an enormous technological impact. Batches of complex structures are typically built by micropatterning subsequent layers on a planar substrate.²⁶ Generally, lithographic micropatterning and pattern transfer is achieved by using ion or electron beams, as well as photon and atom beams to design matter from macroscopic to nanoscopic dimensions.²⁷

1.3 Self-assembly

Nature exhibits control over self-assembly on a broad range of length scales, ranging from astrophysical dimensions down to the subatomic length scales. The term self-assembly refers to assembly processes which take place without any external stimuli, building nano- and microstructures effectively by themselves, forming ordered arrays from a disordered random phase. Self-assembly is always driven by the interactions among the building blocks rather than the generally stronger bonding force within them.²⁷

To self-assemble building blocks into well-organized superstructures depends on the ability to control the size, shape and surface properties of the composing entities to a high level of perfection. Therefore a prime goal of self-assembly is to synthesize building blocks with specified dimensions and form, and through chemical control of their surface properties, such as for example surface charge, wetting properties (hydrophobic, hydrophilic) and/or chemical functionality. In addition, the aim in self-assembling systems is to obtain control over the attractive and repulsive forces between the building blocks to allow them to assemble spontaneously over multiple length scales creating integrated chemical, physical or biological systems with predesigned properties. In the absence of external influences, self-assembly is driven by free energy minimization to form static equilibrium structures. In the presence of external stimuli, a dynamically self-assembling system may prevail

that can adjust to its surrounding environment, by residing on an energetic minimum which is caused by the addition of energy to the system. Upon removing the external stimulus, the energetics of the system changes and the system will relax and may ultimately even disassemble. Any living organism is a perfect example of dynamic self-assembly. It reduces entropy by absorbing energy from the environment. This gradient in entropy between the organism and the environment can be maintained only as long as energy is driven from the environment into the organism in the form of food and heat. Once that flux ceases, the organism disassembles. Two main categories of self-assembly called static and dynamic are illustrated in Figure 1.1.²⁸

Figure 1.1: Schematic representation of static and dynamic self-assembly and their relation to co-assembly, hierarchical assembly and directed assembly.²⁸

1.4 Interaction between nanoentities in suspension

To ensure that particles have sufficient mobility to enable agglomeration into larger arrays, the solvent evaporation technique, i.e. controlled drying, is often used for the self-assembly of nanoparticles. The most important interactions that govern the self-assembly are briefly described in this section.

Capillary forces come into play as a solution containing particles is dried, exerting a strong force drawing parallel surfaces together as the solvent molecules between the neighboring particles evaporate.²³ Thus, as a solvent front moves through a collection of particles, it exerts forces that, when carefully controlled, can be used to align and pack particles.²⁹

Van der Waals forces originate from the electromagnetic fluctuations due to the incessant movements of positive and negative charges within all types of atoms, molecules, and bulk materials. They are therefore always present, usually acting in an attractive fashion to bring the entities together. The magnitude of these attractive interactions can be considerable; a few to hundreds of times greater than kT at short distances between nanoscale entities. As a consequence, Van der Waals forces are often considered to be a hindering interaction, which causes undesired precipitation of nanoparticles from solution. However, through the use of stabilizing ligands or appropriate solvents, such as index matching liquids, Van der Waals interactions can be controlled to provide a useful tool to guide self-assembly processes.³⁰

Electrostatic forces provide a means to form ionic, colloidal,³¹ and even macroparticle³² crystals. These interactions have recently been exploited at the nanoscale^{33,34} to create a variety of unique structures. Unlike Van der Waals interactions, which are primarily attractive in nature, electrostatic interactions can be either repulsive (between like-charged particles) or attractive (between oppositely charged particles) and even directional, as in the case of particles with asymmetric surface-charge distributions³⁵ or permanent electric polarization.³⁶ Furthermore, the magnitude and length scale of these electrostatic interactions can be tuned controllably through the choice of solvent (e.g. the dielectric constant) as well as the concentration and chemical nature (e.g. size and valence) of the surrounding counterions. Due to these unique attributes, electrostatic interactions are useful both for stabilizing particles in solution and for guiding their self-assembly into binary superstructures.

Steric interaction induced by surfactant or polymer layers around the

Figure 1.2: Total interparticle potential (black) between two 50 nm gold nanoparticles arising from the competition between Van der Waals attraction (blue) and steric repulsion (red) due to polyethylene glycol ligands of two different lengths.³⁷ Due to the compression of the ligands, the minimum energy separation is smaller than that of the extended ligands.

nanoparticles plays an important role when these particles come close enough for these molecular layers to interact. Such short range steric interaction not only induces phase separation of various curved surfaces, but can also modify the total effective potential that prevents precipitation of nanoparticles. As soon as the distance that separates the nanoparticles is reduced as a result of other interactions (i.e. Van der Waals or electrostatic), steric interaction between polymer/surfactant-coated nanoparticles will effectively keep them apart due to steric hindering, as is schematically depicted in Figure 1.2. Varying the spatial extent and conformation of the stabilizing layer enables tuning of this steric interaction.

Inter-particle dipole-dipole interactions, i.e. the forces arising from the interaction of dipoles in two neighboring particles, can be harnessed for assembly.³⁸ Some materials, such as cadmium chalcogenides, possess intrinsic dipole moments (in this case an electric dipole) that can facilitate particle

assembly through interaction with the dipole moments of nearby particles. These dipole moments arise from anisotropy in the crystal lattice of cadmium chalcogenides; the same crystal anisotropy and different growth rates of various crystal facets render the cadmium chalcogenides useful materials for nanorod synthesis.

The second law of thermodynamics fundamentally describes entropy in a similar way as the first law defines energy. The contribution of entropic interactions, often small and sometimes essential, on the structure and properties of soft matter is well-established. However, the complete picture of this phenomena is still not fully exposed. Also, energy is intuitively easy to design while entropy is not.³⁹ Entropy arises in nature from increased free volume that becomes accessible to entities in suspension, and consequently the system will expand. At low concentrations, the mixing entropy dominates while increase in concentration facilitates packing entropic effects. The entropic ordering considered in relation with the particle shape, size, and softness (in the light of previous works) by Anders and co-workers is summarized in Figure 1.3.⁴⁰

The most clear example of entropic effect in suspension is the depletion phenomena. This short range depletion attraction ($4\text{--}12\,kT$),⁴¹ in essence an entropic interaction, originates from the overlap of the excluded volume of the neighboring particles, therewith increasing the available volume for smaller molecules or additives dissolved in the solvent.^{21,22} This results in an osmotic pressure that forces the larger particles to cluster. Since the depletion attraction scales with the excluded volume overlap of the particles, particles with relatively low curvature, such as nanorods and nanocubes, experience this attraction strongly and thus assemble into well-defined structures in solution under the influence of this interaction. Furthermore, even with a different size and a similar shape; nanoparticles can self-separate and self-assemble in suspension. For example, the addition of a polymer to a dense colloidal dispersion increases the stability of colloidal aggregates because the polymer mediates an effective attractive force between the colloids. Feng and co-workers have shown that if the polymer partially adsorbs on the colloids, the colloid-polymer dispersion can solidify both when heated or cooled (see Figure 1.4).⁴²

Also, it is possible to tune the composition of the solution in which particles are suspended in order to control interparticle forces and therewith the assembly. For example, Weller et al. showed that optically anisotropic 3D

Figure 1.3: The general nature of entropic interactions applied to a broad class of known systems. Here it is represented in three orthogonal axes. One axis represents, schematically, the shape of the constituent particles, with spheres at the origin. The other two axes concern the sea of particles that are being integrated out and provide the effective interaction. On one axis is the inverse of the strength of the interaction between them (where 0 represents hard steric exclusion). On the other axis is the ratio of the characteristic size of the particles of interest to that of the particle being integrated out. Other axes, not shown, represent the shape of the particle being integrated out, mixtures of particle shapes and types, etc. Examples of known experimental and model systems are sketched to illustrate their location on these axes.⁴⁰

Figure 1.4: Schematic representation of a mixture of colloids (empty circles) and polymers (filled circles); the liquid can solidify both on increasing or decreasing temperature, forming a disordered aggregate or a crystal, respectively. Image courtesy of Mirjam Leunissen, Dutch Data Design (<http://dutchdatadesign.nl>).

superstructures can be formed from CdSe and CdS nanorods by allowing a non-solvent to diffuse into the nanocrystal solution,⁴³ causing the nanorods to cluster together into bundles of aligned rods in a manner reminiscent of the depletion attraction-driven assembly.

1.5 Why gold nanoparticles?

Gold has a fascinating natural beauty and shine that has attracted mankind for centuries. From Greek and Roman times gold has been used in coins, jewelry and ornaments. Nanomaterials made of bulk gold exhibit completely different properties than those made of nanocomponents of gold. Unlike bulk gold (always has a dark-yellow appearance), material made of nanoentities can have different colors depending on the particle size. Colored glass in the Roman civilization is one the oldest examples of this effect.

The interaction of electromagnetic radiation with gold nanoparticles gives rise to very interesting optical properties. A well-known surface plasmon resonance phenomenon will occur as soon as the frequency of incident radiation matches the collective oscillation frequency of the electrons.⁴⁴ Such interesting optical properties of gold nanoparticles at the nanoscale make them promising candidates for many useful applications.^{1,4,5}

For nanoparticles with a rod-like shape two distinct plasmon peaks are observed; a transverse peak appears due to the oscillation of free electron induced in the direction perpendicular to the long axis of the rod, while the longitudinal plasmon peak is due to free electron oscillations induced by the incident light polarized in the direction of the long axis of the rod. Control over the synthesis and assembly of nanorods with tunable aspect ratio paves the way for even more innovative uses of these particles in the future.

1.6 Why assembly of nanoparticles?

Self-assembled nanomaterials often exhibit unique properties that are distinct from the bulk material. During the past decade, significant progress has been made in the assembly of nanorods and understanding some of the self-assembly mechanisms, particularly related to gold nanorods. Nonetheless, methods that can be scaled up to large areas for device-scale applications are yet to be established. Solvent evaporation and drying can also strongly contribute to the assembly of nanostructures. Aligned nanostructures of rods often exhibit enhancement in electrical and thermal transport properties as compared to disordered nanostructures.⁴⁵

Large area assembly of nanorods requires an appropriate control of the interparticle interactions that can be altered by the chemical composition of the suspending medium. A better understanding of nanorod self-assembly mech-

anisms has enabled the development of strategies that can transform individual nanorods into well-defined two-dimensional (2D) or three-dimensional (3D) superstructures. Our aim in this work is to understand the effect of liquid dynamics on the suspended nanorods during solvent evaporation on various substrates.

1.7 Scope and outline of this thesis

As reviewed in the previous sections, the assembly of nanoparticles into superstructures in suspension and at interfaces exhibits many different and interesting features. In this thesis we present results of different studies into the assembly of gold nanorods. In chapter 2 we describe the synthesis of low aspect ratio gold nanorods as used in this thesis, and review their optical properties. The role of various chemicals used in the synthesis of nanoparticles is also addressed.

Nanoparticles and their assembled superstructures can be characterized by a range of different techniques. Imaging techniques such as scanning electron microscopy (SEM) are widely used, while more recently also other charged particle imaging have been developed, including helium ion microscopy (HIM). In chapter 3 we compare the aforementioned imaging tools as applied to our surfactant-coated gold nanorods. The surfactant, cetyltrimethylammonium bromide (CTAB) has a profound effect on the images in HIM, while in SEM this layer is much less visible. From a careful analysis of the HIM and SEM results, we determine the thickness of the surfactant layer and relate it to the CTAB molecule length.

In chapter 4 we study the deposition of CTAB stabilized gold nanorods on HOPG surfaces using SEM, STM and AFM techniques. The well-defined nature of the substrate, in terms of step edges and terraces gives rise to assembly of the nanorods specifically at the step edges. Moreover, the excess CTAB in solutions leads to self-assembled striped layers on the HOPG surface, which we also characterize in terms of periodicity and dynamic behaviour.

In chapter 5 we investigate the phase separation of gold nanospheres and nanorods on homogeneous unpatterned silicon surfaces during evaporative assembly. The phase separation occurring in the well-known coffee stain ring is discussed in terms of interparticle interactions related to the particle shape and size.

In the last two chapters, we focus on the evaporative assembly on chemi-

cally stripe-patterned surfaces consisting of alternating hydrophilic/hydrophobic stripes having widths in the micrometer range. More specifically, we focus on stripe-patterned surfaces with a wettability gradient, which allows to control the motion of evaporating droplets and their contact lines. In chapter 6 the deposition and assembly of nanoparticles (rods and spheres) preferentially on the hydrophilic regions are presented and discussed, also in relation to the results obtained on non-patterned surfaces. Finally, chapter 7 deals with the hydrodynamic confinement of gold nanorods and their alignment induced by the motion of a contact line on radial gradient patterned surfaces. The 2D order parameter within narrow deposits on the hydrophilic stripes is analyzed in relation to the dimensions of the single layer deposits.

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2

Synthesis of low aspect ratio gold nanorods

Design and synthesis of nanomaterials with tailored shape and size is one of the major challenges in nanoscience. In this chapter, we describe the basic aspects related to the synthesis of nanoparticles as used in the subsequent chapters of this thesis. After a brief summary of various synthesis approaches, we go into more detail pertaining to the seed mediated method. The reaction temperature, concentration of AgNO_3 , HCl and the presence of CTAB molecules in the growth solution are important for the formation of prolate rod-like nanoparticles with a tunable aspect ratio. On the basis of published literature, we briefly discuss the role of all constituents taking part in the synthesis reactions.

2.1 Introduction

The simple wet chemical synthesis method is one of the most frequently used and efficient ways to produce nanoparticles on a large scale. However, controlling the growth process of nanoparticles using wet chemical methods poses a challenging task. Until now remarkable progress has been made to control the size and shape of nanoparticles through confined growth by introducing surface capping, templates,¹ and other physical and chemical means.²

As a special class of materials, the synthesis of anisotropic metallic nanoparticles, and more specifically nanorods is challenging because most metals crystallize in a cubic crystal structure; additionally the surface energy favors the formation of isotropic compact shapes. Short aspect ratio gold nanorods are particularly appealing because these particles exhibit intense longitudinal as well as transverse plasmon bands. The longitudinal plasmon peak in the visible and infrared region of the spectrum makes them auspicious candidates for sensing, imaging as well as for gene delivery applications.³⁻⁶

To achieve control over their size and shape different methods have been employed by many scientists and groups around the world. Controlling their alignment in predefined orientations to produce close-packed assemblies of these nanorods and synthesizing them at very high yield and very limited size dispersion as well as with desired aspect ratios are still the major challenges. After a brief literature overview, in this chapter we present details on the synthesis of gold nanorods in terms of reactant concentration and post-synthesis treatment and we discuss the effect of the various reagents on the final product.

2.2 Synthesis

Synthesis is a Greek word used frequently in chemistry, biochemistry and chemical engineering. Generally, it refers to a combination of two or more entities that form something new by adopting artificial means.

2.3 Synthesis methods

There are quite a number of approaches described in literature which enable manufacture of gold nanoparticles in general and also more specifically fo-

cused on rod-shaped nanoparticles. All these methods were introduced and optimized to achieve a high yield of gold nanorods with well-defined size and shape.⁷ Here we briefly review some of them.

2.3.1 Template-assisted synthesis

Martin et al.^{8–10} introduced the template-assisted method for the synthesis of gold nanorods using electrodeposition of gold within the pores of alumina template membranes or nanoporous polycarbonate. The geometry of the template in combination with the reaction time and/or reactant concentration determines the final shape and dimensions of the nanorods. They showed the optical transparent nature of the gold alumina composites and also that the color of the composite membrane can be changed by changing the aspect ratio of the nanorods.^{10,11} Suspended nanorods can be produced by dissolving the matrix which releases the nanorods into the aqueous solution. In this way, it has also been possible to synthesize nanocomposites (nanorods embedded in cell membrane).¹² The gold nanorods can also be dispersed in organic solvents by polymer coating to stabilize the anisotropic nanoparticles after dissolution of the template membrane.¹³

Figure 2.1: Schematic representation of the two-compartment configuration enabling template-assisted synthesis of gold nanorods.¹⁴

In another approach, polycarbonate membranes are used in a two-compartment configuration, as schematically shown in Figure 2.1; the two compartments are separated from each other by a polycarbonate membrane. One compartment contains an aqueous solution of HAuCl_4 that will diffuse through the membrane; the other compartment contains a solution of NaBH_4 . The reducing agent NaBH_4 and the gold ions will move towards each other through

pores of the membrane, where these two chemical species will react to form gold nanorods. After the synthesis has finished, the membrane is dissolved into dichloromethane and the solution is sonicated in an ultrasonic bath for various times to release the gold nanorods.¹⁴

2.3.2 Electrochemical synthesis

Wang et al.^{15,16} demonstrated for the first time the electrochemical method for the synthesis of gold nanorods and also showed that the long nanorods prepared by this method are twinned crystals with $\{111\}$ and $\{110\}$ as dominant faces, while the short nanorods are single crystal with $\{110\}$ and $\{100\}$ as dominant faces. This is schematically summarized in Figure 2.2. They extended their electrochemical growth approach to transition metal clusters using reverse micelles in organic solvents.¹⁷ This method provides a markedly higher yield of gold nanorods as compared to the template-assisted method described in the previous section.

Figure 2.2: Orientation of the different facets of short (a) and long (b) crystalline nanorods as proposed by Wang et al.¹⁵

The synthesis is carried out using a simple two-electrode electrochemical cell as shown in Figure 2.3. The bulk gold metal anode is initially consumed during synthesis to form AuBr_4^- ; these anions together with cationic surfactants move towards the cathode where reduction takes place. It is still a matter of debate whether nucleation takes place within the micelles or occurs

on the cathode surface. Separation of the gold nanorods from the cathode surface is done by sonication. A silver plate is gradually immersed near the platinum electrode within the electrolyte solution to control the aspect ratio. The release rate of silver ions and therewith their concentration plays a crucial role in controlling the aspect ratio.

Figure 2.3: Schematic representation of the configuration used for the synthesis of gold nanorods via an electrochemical approach, consisting of a power supply (VA), anode (A), cathode (C), ultrasonic bath (U), electrode compartment (S), teflon spacer (T) and a glass electrochemical cell (G).¹⁶

The redox reaction takes place between silver ions generated from the silver metal and gold ions created in electrolyte solution from the anode surface. It was found that the concentration of silver ions and their release rate is responsible for the final length of the gold nanorods. However, the precise role of the silver ions as well as the complete mechanism still remains to be elucidated.¹⁶

2.3.3 Seed mediated growth

The concept of seed-mediated growth was first introduced by Jana et al. in 2001.¹⁸ This is the most popular and frequently used synthesis technique to

make colloidal gold nanorods, owing to the high yield and superb quality of nanorods. Moreover, the seed-mediated method can be easily used for controlling the particle size and to modify their shape. In the pioneering work of Jana et al.,¹⁸ they synthesized gold nanorods starting from citrate stabilized gold seed particles. The seeds were then added to the growth solution containing HAuCl_4 , which was reduced with ascorbic acid in the presence of silver ions and cetyltrimethylammonium bromide (CTAB) as surfactant. For the synthesis of long nanorods with aspect ratios up to 25, they improved this method using a three-step procedure without AgNO_3 .^{19–21} It was found that the addition of nitric acid in the third step expedites the formation of gold nanorods with high aspect ratio, large yield and very low polydispersity. The large number of spherical gold particles appearing as by-product was the main drawback of this technique.²²

Nikoobakht and El-Sayed in 2003²³ introduced a new method, in which they used CTAB-stabilized seeds instead of citrate seeds. It was a two-step mechanism, where in the first step CTAB-stabilized seeds are formed using HAuCl_4 , CTAB and ice cold NaBH_4 , while in the second step the seed solution was added to the growth solution containing HAuCl_4 , CTAB and ascorbic acid as reducing agent. Silver nitrate was introduced before the addition of the seed solution to assist in the rod formation and to control the aspect ratio. This method is capable of producing a very high yield of gold nanorods with aspect ratios below 6.²⁴

2.4 Experimental details

In the next section we provide details on the synthesis and characterization of nanorods used in this thesis. We briefly describe the general aspects and characterization tools.

2.4.1 Materials

Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%, Aldrich), silver nitrate (AgNO_3 , 99%, Acros), ascorbic acid (AA, 99%, Merck), cetyltrimethylammonium bromide (CTAB, Aldrich, 98%), sodium borohydride (NaBH_4 , 99%, Aldrich), hydrochloric acid (HCl , 37%, Merck), and sodium citrate (99%, Aldrich) were all used as received without further purification. All water that was used in the synthesis was of Milli-Q quality (18.2 $\text{M}\Omega\text{cm}$),

produced in a Simplicity 185 system (Millipore) or/and Milli-Q Reference ultrapure water purification system.

2.4.2 Ultra-violet and visible spectroscopy

Ultraviolet visible (UV-Vis) spectroscopy is the analytical technique used to determine the absorbance of ultra-violet and visible light when passing through a material, either a solid or a solution. Most measurements were carried out using a Varian Cary 300 Scan spectrometer; this system enables measurement of spectra in the range of 200-900 nm. For the measurement of spectra up to wavelengths of 1100 nm, we used an Ocean Optics HR2000+ spectrometer operated using the SpectraSuite software package, in combination with a Mikropack UV-Vis light source (model DH-2000-BAL).

Since only liquid samples are considered in this chapter, we used cuvettes (standard semi-micro UV) with outer dimensions 12.5 mm x 12.5 mm x 45 mm for the optical analysis; the optical path through the liquid amounts to 10.0 mm. These cuvettes can hold up to 1.5 ml liquid, enabling analysis of limited volumes of liquids. The absorbance is defined as the logarithm of the ratio of the incident intensity I_0 and the intensity I after passing through the sample i.e.

$$A = \log_{10} \left(\frac{I}{I_0} \right) \quad (2.1)$$

As an example, the absorbance amounts to $A = 2$ when 99% of the incident light is absorbed, i.e. $I/I_0=0.01$. According to the Equation 2.1, the value of the absorption is always larger than zero.

2.4.3 Helium ion microscopy

Helium ion microscopy (HIM) is an imaging technique, in which helium ions are used to determine the material properties. The important feature of the HIM is a helium ion source, which is long lasting and provides a beam of intense current originating from a volume not larger than a single atom. The ion source consists of a sharp needle which is maintained in ultrahigh vacuum (UHV) under cryogenic temperatures; applying a high voltage generates an extremely high electric field around the needle tip. This high electric field around the tip of the source increases the probability to ionize the helium atoms present near the source. The positive helium ions are accelerated towards the sample by passing through a series of focusing, alignment and

scanning elements. The secondary electrons are used for imaging of the sample. Due to a very thin collimated beam of helium ions, exceptionally high resolution is possible.

For this work we used a Zeiss Orion HIM, installed at the MESA+ Nanolab of the University of Twente. Further details pertaining to this technique are described in Chapter 3.

2.4.4 Scanning electron microscope

Scanning electron microscopy (SEM) imaging of our sample was performed on a Zeiss 1550 system. In scanning electron microscopy typically voltages in the range 0.1-30 kV are used to accelerate the bundle of electrons through electromagnetic lenses, which focus the beam onto the sample. The electrons will back-scatter from the sample and also produce secondary electrons. The detectors in the microscope enable detection of these electrons and convert the electrical signal into an image. The ultimate resolution of the SEM is of the order of 1 nm.

2.5 Gold nanorods

Gold nanoparticles having a rod-like morphology are of particular interest because of their anisotropic shape. These nanoparticles have been used as an additive for artistic purposes for centuries. However, only in the last decade scientists have begun to understand the fundamental concepts that explain the fascinating optical properties these particles possess.

2.5.1 Optical characterization

Collective oscillations of the free electron gas in metals arising from the interaction with light at optical frequencies gives rise to charge density fluctuations, which are generally referred to as plasmon polaritons. When plasmon polaritons are confined to metallic surfaces or, more generally to the interface between a metal and a dielectric, they are termed surface plasmon resonances (SPR). At the interface of bulk metals, SPR corresponds to propagating electron density waves, with characteristic frequencies given by the plasmon dispersion relations. For small metallic nanoparticles similar charge density waves give rise to so-called localized surface plasmon resonances (LSPR). In the lowest oscillation mode, the entire electron cloud is displaced from

the much heavier cores, as is depicted in Figure 2.4. Plasmonic nanoparticles comprising noble metals such as gold and silver typically exhibit strong optical extinction features in the visible range of the spectrum.

Figure 2.4: Schematic representation of the excitation of plasmon resonances through the polarization of metal nanoparticles, induced by electromagnetic radiation, i.e. polarized light.

The first quantitative description of the optical properties of spherical entities was provided by Mie.²⁵ Using the principles of electrodynamics, an exact solution of Maxwell equations was given in spherical coordinates. The resulting scattering and extinction efficiencies are given by

$$Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(a_n^2 + b_n^2) \quad (2.2)$$

$$Q_{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (2.3)$$

where a_n and b_n are the Mie coefficients in terms of spherical Bessel functions. The size parameter $x = ka$ is a function of the sphere radius a and the wave vector $k = 2\pi\sqrt{\epsilon_m}/\lambda$, with $\lambda/\sqrt{\epsilon_m}$ the wavelength in the medium surrounding the particles; ϵ_m represents the dielectric function of the medium in which the particles are suspended. The efficiencies Q are equal to the cross sections σ , normalized to the particle cross section πa^2 . Energy conservation provides the absorption efficiency through

$$Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{sca}} \quad (2.4)$$

or alternatively

$$\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{sca}}. \quad (2.5)$$

For particles much smaller than the wavelength of the light, the optical properties can be described within the quasi-static approximation. In fact, this dipole approximation is equal to the first order Mie calculation, obtained by only considering the $n = 1$ term in Equations 2.2 and 2.3. The absorption and scattering cross sections in the quasi-static regime are given by

$$\sigma_{\text{abs}} = k\text{Im}(\alpha) \quad (2.6)$$

$$\sigma_{\text{sca}} = \frac{k^4}{6\pi}\alpha^2 \quad (2.7)$$

where α is the polarisability of a single particle. For a gold sphere of radius a the polarisability is given by the Claussius-Mossotti equation²⁶ in the quasi-static approximation for the dipole contributions:

$$\sigma_{\text{sph}} = 4\pi a^3 \frac{\epsilon_{\text{gold}} - \epsilon_m}{\epsilon_{\text{gold}} + 2\epsilon_m} \quad (2.8)$$

with ϵ_{gold} the complex dielectric function of the particle, gold in this case. The quasi-static approximation only applies to spherical particles much smaller than the incident wavelength. For sphere dimensions in the order of the wavelength of the light or larger, the full Mie theory must be considered.

Mie theory can not be employed to calculate light scattering and absorption for non-spherical particles. However, within the quasi-static approximation, valid for small particles, introduction of a geometrical factor enables determination of optical properties of prolate and oblate ellipsoidal particles. Usually, metallic nanorods are treated as prolate ellipsoids, for which the polarisability can be described by introducing depolarisation factors L_x in the expression for the polarisability

$$\alpha_x = \frac{4\pi}{3}ab^2 \frac{\epsilon_{\text{gold}} - \epsilon_m}{\epsilon_m + L_x(\epsilon_{\text{gold}} - \epsilon_m)} \quad (2.9)$$

where a and b represents the long and short radii of the ellipsoid respectively. For $a = b$ in case of sphere gives $L_x = 1/3$, inserting this value in the above equation again yields Equation 2.8.

The depolarisation factor for a prolate ellipsoid along the long axis is given by

$$L_x = \frac{1 - e^2}{e^2} \left(\frac{1}{2e} \ln \left(\frac{1 + e}{1 - e} \right) - 1 \right) \quad (2.10)$$

Figure 2.5: Measured absorbance spectra of a gold nanorod solution. The insets schematically show the transverse and longitudinal SPR modes, which correspond to two absorption peaks, respectively. The peak near 600 nm is due to the presence of cubes and/or nanorods with $AR \sim 1.5 - 2$.

where $e = \sqrt{1 - \eta^2}$ and $\eta = a/b$ are the eccentricity and aspect ratio of the ellipsoid, respectively.

When a colloidal solution is exposed to electromagnetic radiation, the surface plasmon resonance absorption splits into two peaks when the shape of the particle changes from sphere to rod.²³ A typical spectrum for suspensions containing nanorods and nanospheres is shown in Figure 2.5. The pronounced peak at longer wavelengths in the near infra-red region is due to the longitudinal resonance, i.e. electrons collectively oscillating in the length of the nanorods. The weak short wavelength peak in the visible region (520 nm) is due to the electrons oscillating in transverse direction.²⁷⁻³⁰ The position of the longitudinal peak is very sensitive for the aspect ratio of the gold nanorods whereas the transverse peak is not. Moreover, the position of the longitudinal peak depends linearly on the mean aspect ratio of the gold nanorods.^{27,30} Figure 2.6 shows the optical extinction efficiency calculated using the quasi-static approximation as outlined above for ellipsoidal gold nanoparticles.³¹

2.5.2 Synthesis and deposition

For the nanorods used in our work, we use the two-step seed mediated synthesis protocol following the approach described by Nikoobakht and El-Sayed.²³

Figure 2.6: Optical extinction calculated using the quasi-static approximation for ellipsoidal gold nanoparticles corresponding to aspect ratios 1-9.³¹

Preparation of seeds

First CTAB coated seed particles were prepared by mixing 25 μ l of HAuCl_4 (0.1M) with 10 ml of CTAB (0.1M). Then 60 μ l of ice cold NaBH_4 (0.1M) was introduced while continuously stirring for a few minutes. The resulting solution quickly turns light brown, which indicates the formation of gold seeds. The solution was kept at room temperature for one hour to achieve saturation of the seed growth.

Preparation of growth solution

In all synthesis procedures, the growth solutions were prepared by adding HAuCl_4 in CTAB. This solution was heated to 33°C for 20 minutes while slowly stirring to dissolve CTAB, and then left to cool down to 25°C. While maintaining this temperature, AgNO_3 was added, followed by ascorbic acid with gentle stirring; the resulting solution becomes colorless. Next, HCl was added and finally the seed particle suspension was mixed into the growth solution. The final solution was left undisturbed overnight at room temperature. The precise amounts of the various chemicals are summarized in Table 2.1. After a number of synthesis experiments, the results seem to suggest that the aspect ratio may be controlled by varying the AgNO_3 and HCl

Table 2.1: Chemicals and their quantities used for the synthesis of low AR gold nanorods. The top panel summarizes the chemicals and quantities used in all syntheses. The middle panel lists the various amounts of AgNO_3 for a particular amount of HCl while the bottom panel shows the growth solutions with varying amount of HCl for a constant amount of AgNO_3 .

Material	Growth solution	Volume	Concentration	Final amount
CTAB	-	10 ml	0.1 M	1 mM
HAuCl_4	-	50 μl	0.1 M	5 μM
AA	-	70 μl	0.1 M	7 μM
Seeds	-	24 μl		
AgNO_3	A	05 μl	0.1 M	0.5 μM
	B	10 μl	0.1 M	1 μM
	C	15 μl	0.1 M	1.5 μM
	D	20 μl	0.1 M	2 μM
HCl	-	100 μl	1 M	100 μM
AgNO_3	-	15 μl	0.1 M	1.5 μM
HCl	E	40 μl	1 M	40 μM
	F	50 μl	1 M	50 μM
	G	80 μl	1 M	80 μM
	H	100 μl	1 M	100 μM

concentrations, as depicted in Figures 2.7 and 2.8 respectively. The chemical concentration for each spectrum in Figures 2.7 and 2.8 are shown in Table 2.1, where the top panel shows the chemicals which remain unchanged during all synthesis experiments. The middle and bottom panels summarize the chemicals used while varying the amount of AgNO_3 and HCl , respectively. As such, gold nanorods with AR values in the range 3-6 can be synthesis by playing with either silver nitrate or hydrochloric acid concentrations. However, for AR greater than 5, we observed that the number of spheres (large spheres with diameter $\sim 20 - 40$ nm) will increase significantly.

Drop casting

Drop casting experiments were carried out on various surfaces including oxide coated Si wafers, patterned substrates with alternating hydrophilic/hydrophobic stripes arranged in radial and linear arrays, and highly ordered pyrolytic

Figure 2.7: UV-vis spectrum of low AR gold nanorods as synthesized using the chemicals as listed in table 2.1. The curves A, B, C, and D clearly show that the longitudinal peak shifts towards longer wavelengths with increase in AgNO_3 . SEM images showing various low AR gold nanorods synthesized by varying AgNO_3 for $100\ \mu\text{l}$ HCl ; (A) $\text{AR} \sim 3$, (B) $\text{AR} \sim 3.5$, (C) $\text{AR} \sim 4$, (D) $\text{AR} \sim 5.5$. All scale bars are 100 nm.

graphite (HOPG) surfaces. Prior to use, these substrates were ultrasonically cleaned in distilled water and dried in a nitrogen flow. HOPG was freshly cleaved before each experiment. Droplets ($5 - 10\ \mu\text{l}$) of nanoparticle suspen-

Figure 2.8: UV-vis spectrum of low AR gold nanorods as synthesized using the chemicals as listed in table 2.1. The curves E, F, G, and H clearly show that the longitudinal peak shifts towards longer wavelengths with increase in HCl. SEM images showing various low AR gold nanorods synthesized by varying HCl; (E) AR $\sim$ 3.5, (F) AR $\sim$ 4, (G) AR $\sim$ 4.5, (H) AR $\sim$ 5.5. All scale bars are 100 nm.

sion were placed on the clean substrates and allowed to evaporate at room temperature. Typically, within two hours the solvent has completely evaporated, leaving deposits on these substrates. Details of all these deposits will

be the topic of subsequent chapters.

2.6 Centrifugation

Centrifugation is used to remove excess CTAB and to separate by-products present in the nanorod suspension after synthesis.

2.6.1 Removal of excess CTAB

For biological studies, applications in the medical sciences, and to visualize nanoparticles under the microscopes (SEM, HIM, STM etc.), it is important to remove the additional CTAB from the nanoparticle solutions. Layers of CTAB, and also large crystals (at room temperature) will hinder observing the embedded nanoparticles (see also chapter 3); moreover CTAB is toxic. Removal of excess CTAB molecules by centrifugation yields relatively ‘clean’ nanorod solutions for various analysis and applications.

2.6.2 Separating spheres and rods

Nanorods and nanospheres generally have different masses, hence centrifugation can be used for their separation in suspension.³² The theoretical sedimentation of spheres and rods is studied by Sharma et al.³³ A key aspect for the separation of different shapes are the diameters of the particles present in the growth solution. They derive the Svedberg coefficient for rods (S_0^{rod}) and spheres (S_0^{sph}) to describe the sedimentation behavior of sphere-rod mixture. The ratio of the Svedberg coefficients for single rod and single sphere is given by³³

$$\frac{S_0^{\text{sph}}}{S_0^{\text{rod}}} = \frac{3D^2}{2d^2} \left[2 \ln \frac{L}{D} - (v_{\text{perpendicular}} + v_{\text{parallel}}) \right] \quad (2.11)$$

where L , D , and L/D are the length, diameter, and the aspect ratio of the nanorods while d represents the diameter of the spheres and $v_{\text{perpendicular}}$, v_{parallel} are the sedimentation velocities correction factors perpendicular and parallel to the rod orientation, respectively. Clearly in Equation 2.11, the aspect ratio is not as important as the diameter of the particle, i.e. nanoparticles with larger diameters sediment faster than those with smaller diameters.

Furthermore, after centrifuging the gold nanorod solutions at 5600 rpm for 30 minutes, they also observed that the gold nanorods deposit on the side

Figure 2.9: Separation of gold nanoparticles by centrifugation. (a) The color of the resulting solutions and positions of the different particles in the tube after the centrifugation is schematically drawn. (b) Color display of the solutions taken from two different locations as depicted in (a).³⁴

wall of the centrifuge tube with high purity while nanospheres preferentially sediment at the bottom. The solution taken from the side wall and from the bottom of the centrifuged tube displays different colors as shown in the Figure 2.9.³³

In most cases, the general procedure in our experiments is as follows. The suspensions (as prepared) are centrifuged at 15000 rpm for 10 minutes to remove the excess CTAB. Also, the same growth solution is centrifuged again at 5600 rpm for 5 minutes to separate spherical nanoparticles from the nanorods. The supernatant containing primarily nanorods is carefully separated from the precipitate in the bottom of the centrifuge tube; the latter contains mostly spheres. The nanorod suspensions are stored in the refrigerator. The separation of nanorods and nanospheres is not perfectly selective; different suspensions have varying amounts of spheres.

2.7 Discussion

The formation of elongated gold nanoparticles has been a hot topic of discussion in the scientific community for quite some time now. Scientists from all over the world have different explanations of the mechanism that facilitates the anisotropic growth of the elongated nanoentities. However, still there is a need for further work to understand this effect at the nanoscale. The rod like shape most likely originates from a high unidirectional growth rate, which is

closely related to the reaction time, temperature and the chemicals used in the synthesis. In the following sections, the role of each chemical component taking part in the seed-mediated growth process will be discussed in relation to the previously published work.

2.7.1 Role of CTAB

The use of CTAB leads to single crystalline seed particles during sodium borohydride reduction of hydrogen tetrachloroaurate; CTAB stabilized seeds were used by Nikoobakht and El-Sayed for the first time to obtain gold nanorods in high yield.³⁵

The role of CTAB as surfactant during the synthesis of gold nanorods is very important because the adsorbed surfactant is assumed to form a bilayer on the surface of the nanorods³⁵ while the bromide ions form a complex with other reactants in the solution. This process alters the absorption of the surfactant on the gold surface and hence changes the growth mechanism.²³

Furthermore, CTAB develops a bilayer around the nanorod surface, with various facets exhibiting different affinities for CTAB. The CTAB preferentially assembles on the $\{110\}$ facets, forming a much denser layer as compared to the $\{111\}$ facets. Consequently, the $\{111\}$ facets are more accessible to the gold atoms, promoting anisotropic growth of the $\{111\}$ facets.³⁶ This is schematically shown in Figure 2.10.

Figure 2.10: Schematic representation of CTAB molecules on the different facets of gold nanorods.

2.7.2 Role of silver nitrate

It is well-known that silver ions (Ag^+) give rise to modification of the nanorod formation process and therewith enable controlling it. There are two possible explanations which have been described. A first hypothesis claims that silver

ions in the growth solution may adsorb in the form of silver bromide (AgBr) at the gold particle surface, where the bromide (Br) originates from CTAB in the growth solution. The presence of AgBr restricts the growth process on passivated facets of the crystal.¹⁸

Figure 2.11: Schematic representation of UPD of silver preferentially at $\{110\}$ facets of gold leading to breaking of the symmetry and nanorod formation.³⁷

The second explanation considers under potential deposition (UPD) of silver ions at the gold surface, i.e. the reduction of Ag^+ ions to (solid) Ag^0 at the metal surface at a potential smaller than the standard value of the Ag^+ reduction potential. Silver UPD is generally considered to hinder further gold growth and therewith reduced the growth speed of facets on which silver UPD is fast. Silver deposition is assumed to be faster on the $\{110\}$ side facets than on the $\{111\}$ and $\{100\}$ end facets, due to the lower reduction potential on the $\{110\}$ surface.³⁸ The different deposition rates of silver on various facets will lead to symmetry breaking (Figure 2.11) and consequently anisotropic growth, ultimately initiating the formation of nanorods.³⁷

The lower silver deposition rate on the end facets will favour preferential gold growth on these surfaces and therewith promote the formation of nanorods. Increasing the silver concentration in the growth solution will lead to more silver deposition on the side facets, enabling tuning of the aspect ratio. Ultimately, further addition of silver will halt the growth all together due to silver deposition on the entire surface of the rod.³⁸

The different silver UPD rates on various facets of gold is considered to be related to the number of nearest neighbours on the surface. For the different facets the coordination number, i.e. the number of gold atoms in the direct contact with the silver adatoms, varies. As is schematically shown in Figure 2.12, for the $\{110\}$, $\{100\}$ and $\{111\}$ facets the coordination numbers amount to 5 (one in the second layer right underneath the Ag atom), 4 and

Figure 2.12: Schematic pictures showing the coordination number, i.e. the number of nearest neighbour gold atoms relative to a silver adatom, on different crystal facets. It is assumed that the silver UPD rate is closely related to the coordination number. For clarity, the separation between the first and second layer is indicated by the red shading.³⁹

3, respectively.³⁹ In general, a larger coordination number is assumed to give rise to a higher silver UPD rate.

2.7.3 Role of ascorbic acid

Ascorbic acid (AA) acts as a weak reducing agent in the synthesis of gold nanorods and as such controls the overall reaction rate due to weak reduction of gold ions in the growth solution. The reduction of gold ions in the growth solution takes place in two steps. During the first step Au^{+3} is reduced by AA to Au^+ while the second step is initiated and catalyzed by the addition of the seed solution and gives rise to further reduction of Au^+ to Au^0 .³³

Upon increasing the AA concentration in the growth solution, the reduction of gold ions and therewith the nanorod growth becomes faster. As a result there is competition between (1) the nanorod growth and (2) passivation of the surface by the surfactant. At sufficiently high concentration this will affect the final shape of the nanorods, for example giving rise to taper-shaped particles as shown in the Figure 2.13.⁴⁰

2.7.4 Role of the size of seeds

Some researchers claim that the aspect ratio of gold nanorods could also be dependent on the size of seed particles used for the synthesis. For example, in case of smaller seeds, nanorods of longer aspect ratio will form, while larger seeds enable the synthesis of lower aspect ratio nanorods. It was concluded

Figure 2.13: Taper-shaped particles exhibiting an obvious deviation from the rod shape obtained for larger AA concentrations (the molar ratio of AA-Au was 1.6). Scale bar is 100 nm.⁴⁰

that the size of the seed is responsible for the thickness, length, and aspect ratio of the gold nanorod; a scheme summarizing the effect of small and large seed particles is shown in Figure 2.14.⁴¹

Figure 2.14: Schematic representation of different stages of gold nanorod growth for 8 nm and 5.5 nm seed particles.⁴¹

2.7.5 Role of HCl

The main role of HCl is to adjust the pH value of the growth solution. Okitsu et al.⁴² showed experimentally that the shape of the nanorods can be dramatically affected by varying the pH value of the solution. Using the seed mediated growth with much lower pH values (pH=1-2) Ni et al.⁴³ obtained gold nanorods with aspect ratio 6. Furthermore, the HCl concentration, i.e. the pH leads to a decrease of the reducing power of ascorbic acid, therewith decreasing the reduction rate of Au^{+3} to Au^{+1} . Also, some researchers stated that the increase of proton concentration (H^+) due to addition of HCl modifies the repulsion between growing nanorods in suspension and therewith facilitates the growth of nanorods with larger aspect ratios.⁴⁴ In some of our experiments we used pure as-received HCl (37% aqueous solution) without dilution, resulting in dog-bone like gold nanoparticles as shown in the Figure 2.15. Apparently, the competition between gold deposition and surface passivation (see previous section) is also affected by the pH.

Figure 2.15: Dog-bone like gold nanoparticles were synthesized by adding 15 μl of 37% concentrated HCl. The scale bar is 100 nm.

2.7.6 Role of gold salt

Oze et al.⁴⁵ investigated the role of the HAuCl_4 concentration on the efficiency of nanorod formation initiated by gold seed particles. In their experi-

ments they varied the concentration of gold salt in the range 0.125 to 0.001 M as shown in Figure 2.16. The optimum concentration of gold salt required for the effective transformation of gold seeds to nanorods was found to be 0.001 M. At the optimum ratio of Au^{+3} ions to CTAB molecules amounts to 1 : 200; in this case gold deposition on the different crystal facets is controlled by the CTAB zipping mechanism.⁴⁵ Larger CTAB concentrations far above the critical values (1 mM) leads to solubilisation of gold ions into CTAB making a strong micellar complex; this give rise to irregularly shaped particles.

Figure 2.16: UV-Vis spectrum of gold nanorods synthesized by varying the concentration of $\text{H[AuCl}_4\text{]}$.⁴⁵

2.8 Conclusions

The synthesis of low aspect ratio gold nanorods (AR=2-6) using a two-step seed mediated approach has been reviewed. Optical characterization combined with SEM image analysis indicates that the aspect ratio of the anisotropic nanoparticles is strongly dependent on the concentration of AgNO_3 and HCl . As such, these chemicals in principle enable controlling the final nanoparticle shape during the synthesis reaction. All other reagents do not appear to have a significant and systematic effect on the nanoparticle shape and therewith the aspect ratio. However, we did observe that for suspensions of nanorods with aspect ratio larger than 5, the number spheres (as

by-product) increases substantially. Finally, the role of each component participating in the growth of nanorods is highlighted in the light of previous literature reports.

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3

Imaging surfactant coated nanoparticles using HIM and SEM

Nanoparticles are of great interest in fundamental and applied research. However, their accurate visualization is often difficult and the interpretation of the obtained images can be complicated. We present a comparative scanning electron microscopy and helium ion microscopy study of cetyltrimethylammoniumbromide (CTAB) coated gold nanorods. Using both methods we show how the gold core as well as the surrounding thin CTAB shell can selectively be visualized. This allows for a quantitative determination of the dimensions of the gold core or the CTAB shell. The obtained CTAB shell thickness of 1.0–1.5 nm is in excellent agreement with earlier results using more demanding and reciprocal space techniques.

3.1 Introduction

Today, nanoparticles can be synthesized with a variety of shapes¹⁻⁴ and arrangements,^{5,6} allowing for different applications. To unveil the full potential of these nanoparticle based applications^{7,8} in general, it is imperative to understand and characterize the wide range of intriguing properties of these nanoscale entities. Important structural and compositional information can be obtained from high resolution imaging of these particles in their native form. It is crucial to realize that not only the shape but also the nearly always present surfactant layer influences the properties of the nanoparticles.⁹

Scanning Electron Microscopy (SEM) is routinely used to obtain information on the shape, size and arrangement of nanoparticles. This method is very successful in this research field as it is minimal invasive and can achieve the required resolution of a few nanometers down into the subnanometer range.¹⁰ With the advent of new detectors that allow energy filtering and separation of the different contributions to the signal as well as the possibility to use ultra low acceleration voltages, the surface sensitivity of the method has also increased substantially. Alternatively, a new charged particle scanning beam microscopy method has entered the market a few years ago. Helium Ion Microscopy (HIM) has an ultimate resolution as small as 0.29 nm and a very high surface sensitivity.¹⁰⁻¹³ It uses helium ions to generate a multitude of signals including secondary electrons (SE), backscattered helium (BSHe) and photons.

Despite their obvious advantages, both methods, SEM¹⁴ as well as HIM¹⁵ are plagued by carbon deposition in the scanned area. This carbon deposition reduces image quality and in particular hinders the detection of ultrathin carbon layers intentionally present on the sample. HIM is particularly sensitive to this effect for two reasons. Firstly, helium ions with a typical energy of 30 kV are very efficient in cracking hydrocarbons present on the sample surface. These hydrocarbons are either present on the sample and/or replenished from the vacuum during imaging. Secondly, due to the high surface sensitivity of HIM already very thin layers of carbon will be visible in the image. In particular the last point also applies for very low voltage SEM. However, applying appropriate cleaning procedures to the chamber as well as the sample prior to imaging this problem can be eliminated. Provided that deposition of carbon from the chamber vacuum can be excluded a very high sensitivity for intentionally deposited ultra thin carbon layers is possible in

HIM.¹¹

As a result of the surfactant assisted fabrication routes nanoparticles are usually covered by such a thin carbon based layer. In the case discussed here, gold nanorods are covered with an interdigitating double layer of cetyltrimethylammonium (CTA) which is formed during synthesis using CTA-bromide (CTAB). Comparison of Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM) measurements revealed that the thickness of this shell is between 1.0 nm and 1.5 nm,¹⁶ and thus less than the length of a single stretched CTA molecular ion of 2.2 nm.¹⁷

In this chapter we will present high resolution images of CTAB/gold core-shell nanoparticles obtained with SEM and HIM. In this context the underlying reasons for the visibility of either the gold core or CTAB shell in the different imaging modes will be discussed. By comparing core and shell we show that the thickness of the CTA-layer can be measured with sufficient accuracy reducing the necessity for more elaborate measurement strategies such as SAXS and TEM.

3.2 Materials and methods

3.2.1 Nanorod preparation

CTAB stablized gold nanorods of aspect ratios 4 and 5 were synthesized using a seed mediated synthesis.¹⁸ To remove excess CTAB from the suspensions, they were centrifuged at 15000 rpm for 10 minutes. The supernatant was carefully removed, leaving the sedimented nanorods in the bottom of the centrifuge tube. Finally, the nanoparticles were resuspended in the same amount of MilliQ water. This procedure was performed twice. In addition, the suspensions were centrifuged at 5600 rpm for 5 minutes to eliminate most spheres from the suspension. Ultraviolet-visible (UV-Vis) spectroscopy was used to identify typical resonances in the as prepared nanoparticles consisting of rods and some remaining spheres. The longitudinal peaks were situated at 800 nm and 860 nm for nanorods of aspect ratio 4 and 5, respectively. The corresponding rod lengths amount to 45 ± 5 nm for aspect ratio 4 and 55 ± 5 nm for aspect ratio 5. The width of all rods is between 10 nm and 12 nm. Samples were prepared for HIM and SEM analysis, by drop casting 30 μ l of each suspension onto a clean SiO₂ substrate. Within two hours the liquid has completely evaporated, leaving a coffee-stain ring of gold nanoparticles.

No further sample conditioning was necessary for the subsequent SEM and HIM imaging.

3.2.2 Charged particle beam microscopy

HIM measurements were performed using an ultra high vacuum (UHV) Orion Plus helium ion microscope from Zeiss.¹⁵ The microscope is equipped with an Everhardt-Thornley (ET) detector for Secondary Electron (SE) detection. A microchannel plate situated below the last lens just above the sample allows the qualitative analysis of Backscattered Helium (BSHe). This detector yields images in which dark corresponds to light elements, having a low backscatter probability, and bright areas, with a high backscatter yield, correspond to heavy elements in the specimen.

High Resolution Scanning Electron Microscopy (HRSEM) measurements were performed using a Merlin Field Emission SEM (FE-SEM) from Zeiss. The microscope is equipped with a on-axis in-lens secondary electron detector as well as a high efficiency off-axis secondary electron detector. The in-lens detector, which has been used in this study, is a high efficiency detector for SE1 and SE2 and owes its superb imaging results to the geometric position in the beam path and the combination with the electrostatic/electromagnetic lens. This detector is in particular powerful at low voltages provided a small working distance can be reached.

3.2.3 Simulation methods

In order to assess the yield and origin of secondary electrons as well as backscattered electrons in SEM, Monte Carlo simulations using CASINO¹⁹ have been utilized. The sample was modeled using a 2 nm thick carbon layer on a 10 nm thick gold slab on top of a silicon substrate. The density of the carbon layer has been manually set to 0.5 g/cm³. Secondary electron and backscattered electron yields were calculated as well as the $Z_{\max}$ distribution.

SRIM²⁰ calculations have been used to obtain insight into the contrast ratios for backscattered helium images. Backscatter yields for nanorods and CTA covered silicon were calculated using the Kinchin-Pease approximation. The same sample setup as above has been used with the exception that the carbon layer has been replaced with a layer of CTA stoichiometry and a density of 0.5 g/cm³.

3.3 Results

In Figure 3.1(A) a HIM image of gold nanorods is presented. The image has been obtained from an area covered by several layers of nanorods. An acceleration voltage of 34.9 keV and an ion dose of $1 \times 10^{17} \text{ cm}^{-2}$ were used. Although the alignment of the rods is visible, the blanket covering them makes the recognition of individual rods difficult. This blanket is formed from residues, mostly CTAB, of the nanorod synthesis. However, a SEM image of the same area is presented in Figure 3.1(B). An acceleration voltage of 0.7 keV and a probe current of 50 pA has been used to record the image. Here, the rods are clearly visible and the CTAB blanket is only visible where it is very thick (e.g. in the upper right corner of the hole). The effect of the blanket is best seen by comparing the area marked with an arrow. From the two crevices visible in the SEM image one is not visible at all while the other is barely visible in the HIM image.

Figure 3.1: Comparison of HIM and SEM images obtained from drop casted gold nanorods. (A) HIM SE image recorded with 35 keV at a working distance of 6.5 mm. (B) SEM image recorded at 0.7 keV using the in-lens detector and a working distance of 1.3 mm.

Figure 3.2 shows high resolution HIM images and cross sections obtained from an area with a low density of gold nanorods. The image has been recorded using an acceleration voltage of 20 kV and an ion dose of $1.6 \times 10^{17} \text{ cm}^{-2}$. This corresponds to 375 ions per pixel. A larger working distance

section	$\varnothing$ SE [nm]	$\varnothing$ BSHe [nm]
top	12.4	10.6
middle	12.8	10.4
bottom	11.9	10.0
average	12.4 $\pm$ 0.5	10.3 $\pm$ 0.3

Table 3.1: Nanorod diameter obtained from Gaussian profiles fitted to the cross sections (see Figure 3.2(D)) as marked in Figure 3.2(A)-(B).

had to be chosen to accommodate the BSHe detector.

A length of 45 ± 10 nm and a width 15 ± 4 nm has been obtained from the secondary electron image presented in Figure 3.2(A). This results in an aspect ratio of 3 for these CTA covered rods. In Figure 3.2(B) the simultaneously recorded BSHe image is presented. The images have been recorded with an intermediate primary energy of only 20 keV to ensure an enhanced BSHe signal from the nanorods. The energy of 20 keV has been specifically selected to increase the cross section for He scattering. Although lower energies would result in even higher BSHe yields, 20 keV is a good compromise between BSHe yield and SE as well as BSHe image resolution. Although the signal is still relatively weak the nanorods appear slightly smaller in the BSHe image. A composite image created using red and green for the SE and the BSHe signal respectively, is presented in Figure 3.2(C). Several rods are visible showing a yellow core (a result of the compositing process between red and green) surrounded by a thin green border. This is a result of the CTA shell surrounding the gold nanorods. The fact that the gold cores of the nanorods are smaller than the nano-entities in SE mode is also evident from the three selected cross sections shown in Figure 3.2(D). The nanorod diameters, obtained from Gaussian profiles, are listed in Table 3.1.

For comparison a similar area has been investigated using SEM at different voltages. In Figure 3.3 HRSEM images, colocalization analysis and cross sections are presented. The images have been recorded sequentially using 220 V and a current of 50 pA and 2000 V with a current of 200 pA for Figure 3.3(A) and (B), respectively.

The difference between the low voltage (LV) image obtained at 220 V and the higher voltage (HV) image obtained at 2000 V is evident by comparing Figure 3.3(A) and 3.3(B). While in the latter the rods show a good signal to noise ratio and are clearly separated from each other as well as the back-

Figure 3.2: HIM images and cross sectional analysis of gold nanorods. (A) HIM SE image. (B) HIM BSE image. (C) Composite image of (A) and (B). green: SE signal, red: BSE signal, yellow: both signals present. (D) marked sections showing SE (blue) and BSE (red) signals. The intensity profiles were fitted by Gaussians using a least square fit. Primary energy 20 keV; working distance 12.3 mm.

Figure 3.3: High resolution SEM images recorded at different primary energies. (A) SEM image of a low coverage area recorded at 220 eV. (B) SEM image of the same area as in (A) recorded at 2000 eV. (C) Composite image of the marked area in (A) and (B). Green: low voltage signal, red: higher voltage signal, yellow both signals present. (D) Cross sections sorted from top to bottom as marked in (A) and (B) showing the low voltage (blue) and high voltage (red) profiles. The Gaussian profiles are obtained from least square fits to the intensity data. Images acquired using the in-lens detector and a working distance of 1.6 mm.

section	$\varnothing$ LV [nm]	$\varnothing$ HV [nm]
top	13.5	10.4
middle	15.0	11.0
bottom	16.6	13.6
average	15 ± 1.5	11.7 ± 1.7

Table 3.2: Nanorod diameter obtained from Gaussian profiles fitted to the cross sections (see Figure 3.3(D)) as marked in Figures 3.3(A)-(B).

ground, this is not the case for the low voltage image. The thicker rods present in the composite image clearly show a yellow core surrounded by a green shell. This appearance is a consequence of the CTAB layer being visible only in the low voltage (green) channel but not in the higher voltage channel (red). The fact that some of the rods appear entirely red is due to the thresholding used when generating the composite image. The rods in question are in fact visible in the low voltage image but with a low signal to noise and consequently have been missed when creating the composite image. The fact that the rods are visualized to be thinner in the high energy image is also clear from the cross sections presented in Figure 3.3(D). For all cross sections the rod diameter is measured roughly 3 nm smaller in the 2000 V image (red in Figure 3.3(D)) as compared to the 220 V image (blue in Figure 3.3(D)). Table 3.2 summarizes the measured rod diameters for the selected cross sections.

3.4 Discussion

From the results presented above it is clear that both methods can selectively visualize the gold core as well as the surrounding CTAB shell. In the next paragraphs we want to shed light on the underlying reasons and discuss the benefits of the different methods.

Helium Ion Microscopy is characterized by a high surface sensitivity in particular for thin carbon layers.¹¹ The small escape depth of secondary electrons (SE) generated by swift ions²¹ results in the superior surface sensitivity and resolution¹³ of the HIM SE image. This fact allows the detailed imaging of even very thin carbon layers, such as the CTAB layer in the present study. However, the availability of the simultaneously recorded backscattered helium (BSHe) image allows to also visualize the heavy gold cores. The difference in

cross section and its Z^2 dependence yields a high contrast between the gold cores and the carbon layer or the surrounding silicon substrate. From SRIM calculations, backscatter efficiencies of 0.05 and 0.02 for the CTA covered gold rods and the CTA covered silicon, respectively, are calculated. Using a detector opening angle of $2 \times 45^\circ$ and the given dose per pixel results in 6 BSHe atoms per pixel on the gold nanorods and 2 BSHe atoms for the background. Despite the extremely small signal a contrast ratio of 3 is sufficient to confidently identify the gold rods. This contrast is enhanced further by utilizing the channeling into the underlying silicon substrate and so further suppressing the background signal.

Channeling is also observed in two different ways on some of the polycrystalline gold nanoparticles. Firstly, different crystallographic orientations of the gold rods with respect to the incoming beam will result in varying amounts of backscattered helium. This gives rise to the different intensities between the various gold nanorods in Figure 3.2(B). Secondly, channeling also reveals the polycrystalline nature of the nanoparticles themselves. The effect is in particular visible for the round nano-particles at the end of the top most two cross sections in Figure 3.2(B). Their coffee bean like appearance (brighter on the sides as compared to the darker middle) is most likely the result of twinning and thus different channeling conditions. Interestingly, the same contrast variation is observed in the SE image presented in Figure 3.2(B). Here, the contrast is a result of different CTA coverages for different crystallographic planes on the nanoparticles.²²

By carefully comparing the cross section of several nanorods, the CTAB shell thickness could be determined. From the values presented in Table 3.1 we calculate a minimum CTA shell thickness of ≈ 1.0 nm. This value is in excellent agreement with the expected thickness of 1.0–1.5 nm¹⁶ reported elsewhere. The shift between the SE (blue) and BSHe (red) signal is a result of the well known orientation dependence in SE images. This results in the pseudo topographic images also known from SEM. The detector is positioned in the top right corner relative to the image, resulting in an asymmetric rod profile. The BSHe detector, positioned in the beam path, does not suffer from this effect and yields a symmetric profile at the rod position. However, the actual shift is less than 10% of the rod diameter. It has to be pointed out that the shell thickness has to be taken into account when measuring the aspect ratio of such nanorods. The CTA shell reduces the aspect ratio from 4 to 3 due to the different relative contributions of the CTA shell to the length

signal	0.22 kV	2.0 kV
SE	3.87	1.4
BSE	0.11	0.48

Table 3.3: SE and BSE yields obtained from CASINO simulations using 1×10^4 primary electrons.

and width.

Modern scanning electron microscopes allow high resolution low voltage imaging in combination with a high surface sensitivity. By imaging the same area twice with different voltages one can selectively resolve the gold cores (HV) as well as the CTA shell (LV).

To better understand the difference between the two SEM imaging modes, Monte Carlo simulations using CASINO have been utilized. At least two effects can be identified which give rise to the difference between LV and HV SEM imaging. First, at low voltage the maximum penetration depth for electrons obtained from CASINO is 2.5 nm while at 2 kV the electrons easily pass through the rod into the underlying silicon substrate yielding a maximum penetration depth of up to 100 nm. However, back scattered electrons (BSE) are not only losing energy during the actual hard collision event but also on the way into the sample and when they return to the surface. At a primary energy of 220 eV the maximum escape depth of BSE, as calculated by CASINO, is 0.5 nm. As a consequence the gold core is completely invisible at 220 V, while at 2 kV a large portion of the signal stems from the embedded gold core. The effect is enhanced by a shift in the yields for SE and BSE as presented in Table 3.3. This shift results in the fact that at higher voltages the signal from the thin carbon layer diminishes in the huge contribution, composed of SE and BSE, from the gold core. The used in-lens detector allows for the efficient collection of these electrons at the small working distance used during measurement. It is the strong energy dependence of the SE as well as the BSE yields which is further enhanced by the choice of materials. Both contributions amplify the effect and allow the selective imaging of core and shell using different voltages.

From the diameter difference of roughly 3 nm (see Table 3.2) between LV and HV SEM images, we estimate a CTA shell thickness of 1.5 nm. Again this result is in excellent agreement with the expected CTA shell thickness of 1.0-1.5 nm.¹⁶

3.5 Conclusion

We present a comparative investigation of CTAB layer thickness on gold nanorods using HIM and SEM. Both methods can selectively image the gold core or the surrounding CTA shell. In HIM this is achieved by simultaneously recording the SE and BSHe signals. In SEM switching between ultra low voltage and higher voltage imaging achieves the same result. Although the detector efficiencies in BSHe mode are extremely high and less than 10 backscattered helium atoms are sufficient to obtain a decent signal, the quality of the BSHe images is inferior to the high resolution HIM-SE images obtained from the CTAB layer. This is at least partially due to the UHV HIM equipment used. The base pressure of less than 5×10^{-10} mbar ensures that thin carbon layers can be imaged over prolonged periods without adding new carbon as a result of cracking of hydrocarbons present in the sample chamber. In particular LV-SEM suffers from this problem and thin carbon layers are quickly deposited in the investigated area. On the other hand SEM has a faster sample turnover time and excels in the visualization of the gold cores. For the latter, carbon deposition is not an immediate problem and the definition of the rods is excellent allowing precision measurements of particle core length and width.

From both methods we estimated a CTAB layer thickness of 1.0 nm (HIM)-1.5 nm (SEM). Both values are in excellent agreement with the expected thickness of 1.0-1.5 nm. Both methods arrive independently at values smaller than the full length of the CTA molecule. Deviations from the ideal double layer CTA structure can easily explain this discrepancy. Curled up molecules or an incomplete double layer coverage will result in a thinner effective CTA shell.

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4

Assembly of CTAB-coated gold nanorods on HOPG

In this chapter, we present a detailed study of the deposition and assembly of CTAB-coated gold nanorods on HOPG surfaces. A droplet of nanorod suspension leaves behind interesting deposits of the constituents suspended in water at room temperature. These deposits were analyzed using SEM, STM and AFM in order to study the self-assembly behavior of the gold nanorods. Interestingly, self-assembly of CTAB molecules on the well-defined HOPG surface is observed as well.

4.1 Introduction

Murphy et al.¹ and El-Sayed et al.² introduced efficient approaches to synthesize gold nanorods, which are frequently used. These methods allow to synthesize nanorods with high yield and a very low degree of polydispersity. The availability of nanoparticles with high yield and uniform shape and size has enabled a wide range of studies focusing on the self-assembly of the prolate nanoentities. The self-assembly of colloidal nanocrystals into ordered superstructures has emerged as a powerful strategy for the bottom-up fabrication of novel nanostructured materials with pre-defined design, fascinating (collective) properties, and promising applications in functional devices.³⁻⁵ Considerable progress has been made in the spontaneous self-assembly of gold nanorods into 2D and 3D superstructures with long-range ordering.⁶⁻⁹ However, it remains a challenge to develop facile, controllable and reproducible self-assembly approaches toward discrete gold nanorod supercrystals with well-defined morphologies and characteristics.

Graphene is presently attracting a lot of attention owing to its potential for the next generation optics,¹⁰ electronics¹¹⁻¹⁴ and other future applications.^{15,16} An interesting aspect to be considered are functionalities introduced by the edges of graphene.¹⁷ It has been claimed that the areas of highest activity on graphite, i.e. highly ordered pyrolytic graphite (HOPG) substrates can be attributed to step edges on the surface.¹⁸ Furthermore, there are numerous reports in literature considering the interaction of metal atoms or metallic clusters with HOPG.¹⁹⁻²² Francis et al.²³ reported the formation of 3D clusters of silver and gold grown on the terraces and quasi-one-dimensional chains of clusters along the step edges. Also, a variety of shapes and sizes can be obtained depending on the pre-treatment and environment during the deposition. Penner and co-workers performed a systematic study aimed at finding appropriate conditions to obtain narrowly dispersed homogeneously distributed metal nanoparticles on HOPG,²⁴⁻²⁶ and also uniform nanowires at step-edges of HOPG.^{27,28} Metallic nanodeposits on HOPG can be prepared by several techniques, such as chemical vapor deposition,²⁹ physical vapor deposition,²⁸ open circuit potential deposition by immersing it in a solution comprised of metal ions,^{30,31} electrochemical deposition by applying potential pulses;^{24,32-34} deposition primarily at step-edges has been observed in a number of reports.^{23,27,28,35-40}

In relation to our system consisting of CTAB-coated gold nanoparticles,

it has also been observed that CTAB surfactant molecules can self-assemble on HOPG surface in the form of hemi-cylindrical micelles.^{41–43} The surface of HOPG is hydrophobic,^{44,45} while the CTAB molecules have a hydrophilic end group and a hydrophobic tail.⁴⁶ To shield their hydrophobic tail from the aqueous phase, these molecules form spherical and cylindrical micelles in suspension.^{47,48} Xu et al. were the first to observe adsorption of CTAB molecules on HOPG in head-to-head arranged layers; the characterisation was done using scanning tunneling microscopy (STM).⁴⁹

In this chapter, we present a preliminary study of gold nanorods deposited from a CTAB-containing aqueous environment onto HOPG substrates using electron microscopy (SEM), STM and atomic force microscopy (AFM). Droplets of nanorod suspension are deposited onto a freshly cleaved HOPG surface and the solvent is allowed to evaporate at room temperature. The deposits consisting of nanorods are imaged using the aforementioned imaging techniques, and analysed in relation to the contact line motion and the morphology of the substrate. Furthermore, the excess surfactant forms characteristic self-assembled islands over the entire HOPG surface, which are discussed in relation to previous literature reports. Finally, the role of the CTAB surfactant in the deposition and assembly of gold nanorods on HOPG terraces is discussed in terms of modified wettability.

4.2 Experimental

4.2.1 Synthesis and surface preparation

Gold nanorods (AR~3 and AR~5) used in this chapter were synthesized following the well-known seed mediated protocol described by Nikoobakht and El-Sayed²(see details in Chapter 2).

Highly ordered pyrolytic graphite (HOPG) is a very pure form of carbon that has a very smooth surface due to its layered structure. The forces within the lateral planes are much stronger than the forces between the planes, making it very suitable to cleave with ordinary tape to create a clean and smooth surface. These freshly cleaved surfaces are used as substrate material without any further treatment.

4.2.2 Analysis techniques

HOPG has a flat and smooth surface and is conductive. As such, it can be used in a number of different analysis techniques to investigate the deposits and assembly of entities on the surface. The techniques we used for this chapter are described below.

Scanning electron microscopy (SEM) imaging of our samples was performed on a Zeiss 1550 system with an optimum resolution of 1 nm at an accelerating voltage of 2 kV. In addition, a NaioSTM scanning tunneling microscope (Nanosurf, version 3.1) was used to analyze the CTAB-coated gold nanorods. The set point for the tip-current was 1 nA and tip-voltage was 1.5 V to visualize the deposits on the HOPG surface. Likewise, tapping mode atomic force microscope (AFM) imaging was performed on an Agilent 5100 atomic force microscope using HQ: NSC35/Al probes (Mikromasch) with a nominal spring constant of 5-16 N/m and resonance frequency 150-300 kHz.

4.3 Nanorods on HOPG

In all experiments a 5 μ l droplet of nanorod suspension is deposited on a freshly cleaved HOPG surface and the solvent is allowed to evaporate at room temperature. Typically after two hours the droplet has completely vanished leaving bright regions of deposits on the surface. For SEM and AFM analysis, nanorod suspensions of AR $\sim$ 5 were dried on the HOPG substrate, while two different nanorod suspensions (AR $\sim$ 3 and AR $\sim$ 5) are used for the STM analysis.

4.3.1 SEM results

It seems that the hydrophobicity of HOPG prohibits strong pinning of the three-phase contact line as observed on oxide-coated silicon substrates.⁶ As a result, stick-slip like movement^{50,51} was observed during drying and the corresponding patchy deposits are generally seen on the surface. Pinning generally occurs as soon as the nanoentities arrive at the three-phase contact line due to the convective flow induced by the evaporation of the solvent.^{6,52,53}

The suspended nanoentities close to the contact line will initially deposit on the surface as shown in Figure 4.1A. Such deposits are very often observed on hydrophilic surfaces, while on hydrophobic surfaces such as HOPG their occurrence is much less frequent. Due to the smaller contact area and larger

Figure 4.1: SEM image at various locations on the HOPG sample after drying. (A) First deposits of gold nanorods (arrows indicate the slip deposits of nanorods close to the step-edges). (B, C) Nanorods preferentially assembled at the step-edges. (D) Enlarged view of end-to-end aligned nanorods next to the step-edges, and (E, F) single layer arrays of nanorods on terraces.

contact angles, slip behaviour of the three-phase contact line is more likely on hydrophobic surfaces. Consequently, ‘coffee-stain’ like dense deposits are much less probable on non-wetting surfaces. However, as represented in Figure 4.1A on HOPG we do observe deposits which seem to arise from pinning; it appears as if the wettability of the surface is changed for some unexpected reason. In the subsequent sections, we will discuss potential features, which are responsible for ring-like deposits on HOPG.

The area, density and height (single layer and multilayer) of the deposits

Figure 4.2: (A) Angular histograms of gold nanorod orientation with respect to the step-edge direction on HOPG. (A) Orientation at the step-edges, and (B) on terraces.

depends on the concentration of the nanoentities in the vicinity of the contact line. The initial deposits appear dense and consists of many stacked layers with no preferential orientation. Also, at the positions where the contact line sticks, the deposits have different sizes; in some cases dense wide arrays of deposits are observed while elsewhere only thin dilute lines are observed. In addition, the deposited superstructures away from the initial deposits predominantly exhibit nanorods distributed in a single layer. Moreover, the regions where the three-phase contact line has moved are not completely depleted of nanorods, but exhibit clusters close to the HOPG step-edges; nanorods in these clusters show preferential orientation (as indicated by yellow arrows) in the direction of motion of the contact line.

Figure 4.1B and C represent zoomed images of deposits away from the initial deposits as discussed above. In most places nanorods have only been deposited near the step-edges with a strong preferential orientation as shown by the histogram in Figure 4.2A. Within these step-edge deposits nanorods are aligned in an end-to-end fashion, while they are completely aligned parallel to the step-edges (see Figures 4.1C and 4.1D). Away from the step-edges on the terraces of HOPG close-packed assemblies of side-by-side aligned nanorods are found, which do not exhibit a preferential orientation as shown in the Fig-

ures 4.1E and F. The random orientation is also obvious from the histogram in Figure 4.2B. Moreover, on the terraces the nanorods are distributed primarily in a single layer. Close examination of many images reveals that isolated nanorods do not occur.

4.3.2 STM results

As far as we are aware, scanning tunneling microscopy (STM) has not been employed to study deposits of CTAB-coated gold nanorods. As such we present the first STM images of nanorods with a CTAB coating. In Figure 4.3A the gold nanorods appear to be ‘buried’ under a thick layer of CTAB; surprisingly, despite this thick coating the structures are sufficiently conducting to be observed with STM. Also, clusters of nanorods stacked on top of each other and buried under a CTAB layer can be visualized using STM, as illustrated in Figure 4.3B. The striped features indicate that we are operating the STM at its limits; much thicker layers of CTAB and/or nanorods will not provide enough conductivity to enable current to pass through, thereby hindering STM measurements.

Nanorods placed side-by-side on the surface are shown in Figure 4.3C while Figures 4.3D and 4.3E reveal features which may be ascribed to traces of CTAB around the gold nanorods dried from suspension. Height profiles along three lines (3, 4 and 5) indicated in Figure 4.3E are plotted in the inset of the same figure showing the height of rods as well as the CTAB layers in the vicinity of the rods. Similarly, height profiles taken along the lines in Figures 4.3C and 4.3D are plotted in Figure 4.3F. A more quantitative analysis of these results reveals that the length (~ 50 nm) and width (~ 10 nm) of the nanorods are in good agreement with our observations in the SEM images, as ascribed in the previous section. However, the height of the nanorods in the profiles is considerably smaller and does not agree with the diameter of the gold nanorod used in this work.

Using the known step-edge height on HOPG surfaces, we carefully verified the calibration of the z-direction to eliminate this as a possible source for error. A possible explanation for the considerably smaller height of the nanorods in comparison to expectations based on their diameter is most likely related to the limited conductivity of the CTAB layer on the substrate and also on the nanorod surface. A CTAB layer on the HOPG substrate (see following section) will provide a barrier for tunneling. However, when the STM tip probes a coated gold nanorod, current has to pass through two layers of

Figure 4.3: STM images of (A) gold nanorods under a thick layer of CTAB. (B) Cluster of rods deposited on top of each other. (C) Rods placed side-by-side. (D, E) Rods with traces of CTAB; the inset in E shows line scans of line 3, 4, and 5, and (F) shows the plots of the line scan [black(a), green(1) and red (2)] in C and D respectively. Aspect ratios of the nanorods amounted to 3 (A,E) and 5 (B,C,D).

CTAB, on both sides of the nanorods. As a result of this much lower conductivity, the STM tip will move a much smaller distance in the z -direction to keep the tunneling current constant. As a consequence the apparent height is markedly smaller than the physical dimension of the nanorod.

4.3.3 AFM results

The SEM images in Figure 4.1 clearly show alignment of nanorods along the step-edges. However, these results do not conclusively indicate whether the nanorods are placed on the upper or lower side of the step edge. For this purpose, we use AFM to identify their position with respect to the step-edges. Figure 4.4A shows an overview of the nanorod deposits close to the step-edges. The white square region in Figure 4.4A is enlarged in Figure 4.4B, which shows that the nanorods are predominantly deposited at the lower side of the step-edge. Also, the step-edge height in this case is ~ 5 nm (corresponding to multiple HOPG steps) while the height of the nanorod is ~ 10 nm as depicted in the inset of Figure 4.4B. Similarly, Figure 4.4C illustrates another overview of the rod deposits, while Figure 4.4D is a magnified portion of Figure 4.4C, again confirming that the nanorods assemble at the lower side of the step-edge. Unlike the STM results, the height as determined in AFM is in agreement with the physical dimensions, i.e. the diameter of the nanorods used in this work. Close examination of many images reveals that besides the deposited nanorods other entities are adsorbed on the HOPG surface. These observation will be described in the next section.

4.4 CTAB assembly on HOPG

As outlined in Chapter 2 the concentration of CTAB in our growth solution amounts to 1 mM, while the concentration of all other chemicals only comprises approximately $13 \mu\text{M}$. In other words, the amount of these chemicals is negligible as compared to the CTAB density. Despite the fact that prior to deposition two centrifugation cycles are performed to remove CTAB, there will still be a surplus of CTAB in the solution.

CTAB is a cationic surfactant of which the molecules consist of a hydrophilic tail and a hydrophobic head. Consequently, CTAB molecules will preferentially adsorb on the hydrophobic HOPG substrate in such a way that they will hinder water from adsorption on the hydrophobic surface. As such

Figure 4.4: (A) Overview and (B) enlarged AFM images of gold nanorods deposited at the step-edges of HOPG. The inset in B depicts cross-sections as indicated by the green (1) and red (2) lines.

the effective wettability of the HOPG surface will be altered by establishing a hydrophilic layer underneath the gold nanorods. Here we present and describe observations of CTAB assembly on the HOPG surface; details as to possible mechanisms, also in relation to existing literature, will be discussed in the following section.

4.4.1 Morphology

Islands

As mentioned above, there is excess CTAB in the gold nanorod suspensions. Hence, it is to be expected that the large concentration within the droplet leads to adsorption of the surfactant molecules onto the hydrophobic surface, even prior to any nanorods being deposited on the substrate.

Figure 4.5: AFM images of CTAB islands formed on various terraces of HOPG. (A) Overview of the islands and (B) enlarged image of the white square region in A; the inset shows the line scans indicated by 1 (green) and 2 (red). (C) Another overview of the CTAB islands, and (D) enlarged view of the region enclosed by the white square in C.

The morphology as revealed by AFM images such as those in Figures 4.5A and 4.5C indeed confirm that the excess CTAB in the droplet of nanorod suspension gives rise to a different surface structure that is not observed on freshly cleaved HOPG surfaces. The brighter areas in the AFM images may be attributed to different graphite terraces, but they do not exhibit the characteristic 60° or 120° angles typically observed on freshly cleaved HOPG. As can be more clearly seen in the zoomed in images in Figures 4.5B and 4.5D the islands look more rounded, as if they were assembled onto the HOPG surface. We ascribed these islands to CTAB layers on the surface. Height profiles

as shown in the inset of Figure 4.5B reveal that the islands exhibit different heights; the smallest step size amounts to approximately 1 nm, while the larger step (red curve) is ~ 3 nm. This may be due to multiple layers of CTAB, or an HOPG step in combination with the CTAB layers.

Stripes and their periodicity

Zooming in on typical CTAB islands demonstrates the interesting arrangement of the self-assembled molecules on the terraces of the HOPG surface. Figure 4.6A shows an overview of the linear stripes arranged on the HOPG surface, while the white square region is enlarged in Figure 4.6B. As shown by the height profiles in Figure 4.6D, the stripes have different widths: the widest stripes are ~ 12 nm wide, the majority of stripes are ~ 8 nm in width, and some narrow stripes are ~ 2 nm wide. Notably, the height of the stripes in Figure 4.6B is 0.4 nm. This height does not reflect the true height of the CTAB structures on the surface; owing to the narrow gap between neighbouring stripes, the AFM tip is unable to reach all the way into these gaps to probe the actual height of the features.

A more accurate height of the CTAB stripes can be obtained from height profiles of isolated stripes next to regions where the bare substrate is exposed, such as shown in Figure 4.6C. From a profile as indicated (inset) we deduce that the actual height of the stripes amounts to approximately 0.8 nm. When we compare this to the physical length of CTAB molecules and the thickness in the range of 1.5–2 nm typically observed in experiments,^{54–56} the observation of a slightly smaller feature height suggests that the molecules do not adsorb in a conformation perpendicular to the substrate. The molecules may be compressed or, more likely, tilted with respect to surface normal.

Further zooming in on the self-assembled CTAB stripes as in Figure 4.7A reveals the periodically arranged stripes; a typical height profile is plotted in Figure 4.7B. Despite different widths, the distance separating the stripes appears to be identical everywhere and amounts to approximately 2.5 nm. Overview images such as those in Figure 4.6 seem to suggest that the general direction of the stripes is dictated by the underlying HOPG substrate; stripes on neighbouring terraces are oriented relative to each other at 60° or 120° angles. Surprisingly, despite the macroscopic preferred orientation of the stripes they are not perfectly straight at the nanoscale as indicated by the green dotted lines in Figure 4.7A.

Figure 4.6: Self-assembled CTAB molecules on the HOPG surface imaged using AFM. (A) Overview of CTAB self-assembled stripes. (B) Enlarged view of the white square region in A, revealing the characteristic stripes. (C) Stripes of CTAB with a height profile along the green line. (D) Stripe widths at various locations in B, indicated by the numbers 1-6.

Dynamics of the CTAB stripes

Close examination of sequentially obtained AFM images of the same area on the surface reveal interesting dynamics of the self-assembled striped features. A typical example is shown in Figures 4.8A-D. The time delay between each of the AFM images in Figures 4.8A-D amounts to approximately 4 minutes while 10 minutes for Figure 4.8E. Close examination reveals that the stripes on the terrace in the left part of the images appear stable for a long time, while the stripes on the terrace in the top of the image seem to disappear much faster. Moreover, the removal of the stripes seems to originate from defect sites, i.e. a vacancy in the stripe; one of these defects is indicated by

Figure 4.7: (A) Enlarged AFM image of CTAB stripes. (B) Periodicity of self-assembled arrays of CTAB on HOPG terraces. The green dotted lines indicate the deviation from the perfect linear arrangement.

the white arrow in Figures 4.8A-D.

When we look more closely at the stripes on the initially stable terrace in the left half of the image in Figure 4.8D we observed that also here the stripes slowly disappear, with vacancy lines nucleating at specific defect sites. The same is observed on the terrace near the right edge of the image. As indicated, the CTAB stripes seem to disappear with time in the regions where the surface morphology is probed using the AFM. However, from these and many other images we can not conclusively determine where the removed entities go. Zooming out does not reveal molecules piling up at the edges of the scan region. Moreover, protruding surface features represented by the brighter spots in the AFM images in Figure 4.8 do not seem to grow significantly in size. However, owing to the limited scan range we cannot unambiguously claim that the molecules desorb from the surface.

Further analysis of the AFM images after prolonged scanning of the surface leads to the intriguing observation that after complete removal of the aforementioned stripes, the exposed surface still exhibits a periodic structure. A typical example is shown in Figure 4.8E; the inset represents a line scan across the lower level of stripes. Surprisingly, this striped phase has an even more regular structure, with stripes of approximately 0.1 nm high and a mu-

Figure 4.8: (A-D) Sequential AFM images depicting the dynamics of self-assembled CTAB stripes on terraces; for reference, a defect which acts as a vacancy nucleation site is indicated by the white arrows. (E) After the large stripes have completely disappeared, a corrugation of the surface is still observed; the inset depicts the periodicity of the residual striped features.

tual spacing of 5.5 nm. As such, the periodicity is completely different from the previously described original striped phase. Nevertheless, the orientation seems to be the same.

4.5 Discussion

As described in the previous section, we deposited droplets containing CTAB-stabilized gold nanorods and an excess concentration of CTAB molecules on a freshly cleaved HOPG surface; in Figure 4.9 this is schematically shown. During the subsequent evaporation, the contact line remains pinned for some time, as is evident from the nanorod deposits as shown in Figure 4.1A. In this respect the behaviour is similar to that of nanoparticle droplets evaporating on hydrophilic surfaces.⁶ However, after the initial pinning the three-phase contact line moves inward in a stick-slip fashion,⁵⁰ leaving behind annular regions of relatively dilute deposits; the composition of these nanorod assemblies depend on the particle density and solution composition close to the contact line. Moreover, in the dried droplets we typically observe nanorods aligned along the step-edges and also close-packed single-layer self-assembled features on the terraces of the HOPG; the latter do not show any preferred orientation relative to the substrate.

Figure 4.9: Schematic representation of a droplet containing CTAB-coated nanorods and a surplus of CTAB on the HOPG surface; the arrows indicate the relative evaporation rate of the solvent.

From the alignment of the nanorods at the step-edges of the HOPG substrate, we can conclude that during solvent evaporation free energy minimization drives the orientation of the nanoparticles. As a first suggestion, one may assume that capillary interactions give rise to the orientation of the long axis along the step-edge direction, as shown in Figure 4.10. Also, attractive Van der Waals interactions or even depletion forces may be con-

Figure 4.10: Schematic drawing showing the alignment of nanorods at a step-edge and isotropically distributed nanoparticles on the terraces of HOPG.

sidered, since at a step-edge there is in principle more contact area between the nanorod and the different facets of the surface.

However, steps on the HOPG surface have a height ~ 0.3 nm or multiple shared while the nanorod radius of curvature is typically one order of magnitude larger. As such, the excluded volume potentially leading to depletion driven alignment or the larger Van der Waals forces will not be very significant. Nevertheless, we do observe (Figure 4.5) that nanorods specifically assemble at the lower side of the step-edge. There are possible explanations for this behaviour other than purely related to geometry of the step-edge. As outlined in the introduction of this chapter, the edge of graphene flakes and likewise the step edges of HOPG are the areas of considerable larger activity. This implies altered energetics at these places on the surface. Moreover, in the investigation of nanobubbles on HOPG substrate we observed that these nanoscopic gaseous domains preferentially assemble at the top of the steps.⁵⁷ Variations in hydrophobicity/hydrophilicity were attributed to variation of the atomic coordination at the top and the bottom of the steps. Such effects may also play a role here.

Although the density of deposited nanoparticles on the HOPG terraces is much lower, we do observe clusters of nanorods in these areas. The clusters generally consist of a single layer of a finite amount of mutually aligned nanorods. Despite the mutual alignment relative to each other, we did not observe any preferential orientation of the clusters with respect to the substrate surface features. The agglomeration is most likely driven by a similar

mechanism as described previously,⁶ aided by the capillary force due to the receding contact line.

We do not only observe the deposition of gold nanorods; also the surfactant molecules exhibit self-assembled layers over the entire surface, most prominent on the HOPG terraces. The molecules are arranged in the form of parallel stripes on the surface, primarily exhibiting a width of 8 nm, but in some cases narrower (2.5-3 nm) or wider (≈ 12 nm); the height amounts to approximately 0.8 nm. In solution the amphiphilic CTAB molecules form micelles to screen their hydrophobic tails from the aqueous phase. These spherical CTAB micelles have been reported to have a diameter of about 4.4 nm.⁵⁸

Moreover, on non-polar surfaces such as HOPG it has been reported that the CTAB molecules assemble in hemicylindrical micelles,^{41,42} as schematically shown in Figure 4.11. Manne et al.⁵⁹ proposed a model for deposition of surfactant on HOPG at various concentrations. At low concentration (approximately 10% of the critical micelle concentration) the molecules adsorb with their alkane chains extended on the substrate plane. Such a configuration of CTAB molecules oriented parallel to the HOPG surface has been observed experimentally,⁶⁰ where Van der Waals forces were considered as the predominant interaction between molecules and substrate. With increasing concentration, the chains of the adsorbate molecule gradually begin to desorb from the surface, and at concentrations near the critical micelle concentration, the adsorbates form the aforementioned hemicylindrical micelles, with the hydrophilic head-groups completely shielding the hydrophobic substrate from the solution.

As we know from different reports in literature,⁵⁴⁻⁵⁶ the CTAB molecules have a length of approximately 1.5-2 nm. This is in good agreement with the diameter of spherical CTAB micelles (4.4 nm), being equal to approximately twice the CTAB length. In principle, a molecule oriented perpendicular to the surface, and therewith the height of the hemicylindrical micelles (Figure 4.11) should be approximately 2 nm. However, the self-assembled CTAB stripes are markedly lower, typically 0.8 nm. We attribute this to the molecules being compressed upon evaporation of the solvent, giving rise to lower features as observed by AFM.

The widths as observed in our experiments in Figure 4.6 seems to reflect the formation of single, double or triple hemicylinders parallel to each other. Close examination of the height profiles in Figure 4.6D and specifically the

Figure 4.11: (A) Hydrophobic HOPG surface and amphiphilic CTAB molecule. (B) Initially adsorbed molecules will deposit flat on the surface to maximize the interaction between the hydrophobic tail and the non-polar substrate. (C) Subsequent adsorption of molecules will lead to the formation of hemicylindrical micelles. (D) Nanorods assemble on the exposed hydrophilic CTAB layer.

variation of the z -values on top of the stripes seems to be in agreement with this assumption. The width of the gaps separating adjacent stripes generally amount to 2.5 nm (Figure 4.7), very close to the length of a single CTAB molecule. The precise reason for the specific assembly of the micelles in striped arrays remains to be elucidated.

Finally, one of the interesting observations in our work is that deposition of assembled nanorods seems to occur preferentially on self-assembled CTAB layers, as shown in Figure 4.12. It appears as if the nanorods coated with the surfactant, with their hydrophilic end groups exposed, do not prefer to deposit on bare hydrophobic terraces of the HOPG. As such this supports our suggestion that prior to nanorod deposition, CTAB molecules first self-assemble on the surface due to their abundance in the solvent. Therewith

Figure 4.12: Gold nanorods on CTAB-coated HOPG. Height profiles in A and B are plotted on the right of the images. The dash rectangles indicate the CTAB layer height underneath the nanorod deposits.

the wettability of the HOPG surface is modified to be more hydrophilic and as a result will facilitate the deposition of surfactant-coated gold nanorods on these areas.

4.6 Conclusions

To summarize, in this chapter we have presented results of a study into the deposits of gold nanorods on freshly cleaved HOPG surface. An aqueous droplet containing gold nanorods stabilized with CTAB surfactant, and

in the solvent a surplus of CTAB molecules was left to evaporate. After complete evaporation of the fluid, the deposited nanoparticle deposits were analyzed using different imaging techniques, including electron microscopy (SEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

From the topographical analysis a number of conclusions can be drawn:

- On the hydrophobic HOPG surface, the three-phase contact line is not pinned during the entire evaporation process, as it is on hydrophilic substrates. The deposits reflect the stick-slip motion of the contact line with dense annular deposits (where the contact line ‘sticks’) separated by more diluted regions (where the three-phase line ‘slipped’).
- The dense deposits, corresponding to position where the contact line stopped moving, exhibit similar features as those on hydrophilic substrates, such as will be described in subsequent chapters. In the more dilute regions, nanorods preferentially arrange along the HOPG step edges, and more specifically on the lower side of the step. The majority of the terraces separating the steps were mostly depleted of nanorods. Where deposits were observed, they exhibit aligned side-by-side assembly, but not oriented along any specific directions of the substrate.
- To the best of our knowledge, we presented the first STM-based study of CTAB-coated gold nanoparticles. As most previous studies have been carried out on non-conducting substrates, this has not been an option. The conducting HOPG substrates enables STM imaging, and surprisingly the CTAB layers on the nanorod surface are sufficiently conductive to allow the tunneling current to pass through. We have been able to detect individual nanorods, but also multi-layers clusters of nanorods. Owing to the limited conductivity of the CTAB layers, the height features are not in agreement with the actual dimensions of the nanorods.
- Close examination of the AFM images revealed a striped phase on the HOPG surface, which we ascribed to self-assembled CTAB layers. In solution the surfactant molecules form spherical micelles. On hydrophobic surfaces it has been reported that they assemble into hemicylindrical micelles. The observed stripes seem to adapt to the orientation of the substrate on a micrometer length scale but exhibit undulations on the nanometer scale.

- Careful analysis of the stripe dimensions, i.e. width, height and spacing, seems to indicate that the stripes consist of multiple hemicylinders separated by a distance corresponding to the length of a single CTAB molecule.
- Finally, when analyzing subsequent AFM images the self-assembled CTAB stripes appear to be dynamic. With increasing scan time, defects develop and vacancy lines start to grow with varying speeds on the different terraces.

The results described in this chapter constitute only a preliminary study of the fascinating self-assembly of both gold nanorods and also CTAB molecules on the well-defined HOPG surface. To further substantiate possible mechanisms, which can account for these and related observations, considerably more work needs to be done.

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5

Shape-induced separation of nanospheres and aligned nanorods

We studied the phase separation and spatial arrangement of gold nanorods and nanospheres after evaporative self-assembly from aqueous suspension. Depending on the position relative to the contact line of the drying droplet, spheres and rods separate into various liquid crystalline phases. Nanorods exhibit a strong preference for side-by-side alignment, giving rise to smectic phases; spheres in solution are forced out of these regions and form close packed arrays. We discuss this self-separation into nanorod and sphere-rich phases in terms of various interactions, including electrostatic, van der Waals, and depletion interactions. The experimental results are compared to quantitative calculations of the colloidal interaction energies. We also describe and discuss the role of the surfactant on the different crystal facets of the nanorods on the assembly process.

5.1 Introduction

Phase separation of nanoparticles of different shapes and sizes has been and continues to be a topic of intense research. As an example, mixtures of rod-like and sphere-like particles have been shown to spontaneously phase-separate into rod-rich and sphere-rich phases.^{1–4} The physical origin of this separation of different phases is generally considered in terms of competing translational entropy and entropy of mixing. Similar phase separation mechanisms may also be relevant in protein crystallization,⁵ the manufacture of nanocomposite materials,³ assembly of block copolymers,⁶ but also in bio-separation and DNA partitioning methods.⁷

Obtaining a detailed understanding of the phase separation and assembly of nanoparticles, and therewith to achieve ultimate control over these processes in mixtures of particles of various shapes and sizes remains a major challenge. Since the middle of the 20th century, a considerable amount of theoretical work has been done on phase separation of various shapes and assemblies of nanoparticles.^{8–12} More specifically pertaining to the phase separation of rod-sphere mixtures, the theoretical work focussed on elucidating the formation of separate phases has been complemented by simulations as well as experimental work.^{13–19}

The formation of self-assembled superstructures of nanoparticles strongly depends on particle size,^{20,21} shape distribution,^{22–26} evaporation rate,^{27,28} and most importantly a range of interparticle interactions.^{12,20,21,27,29} The latter includes capillary forces,³⁰ depletion interaction,^{31–33} electrostatic forces³⁴ and surfactant-mediated interaction.¹² At sufficiently high concentrations, anisotropic particles such as rods and plates form various liquid crystalline assemblies, referred to as nematic, smectic, and columnar phase.^{3,11,35–41}

All the aforementioned interactions play a role in the self-assembly of nanoparticles. However, in the case of anisotropic micro- and nanoparticles extensive research has mainly been focussed on depletion interactions and initially this was considered to be the dominant interaction responsible for the phase separation of rod-sphere mixtures.⁴² The attractive interaction between spheres due to addition of rods was discussed by Auvray⁴³ and the interaction induced by thin rods was investigated using the Derjaguin approximation by Mao et al.⁴⁴ Moreover, it was shown that polydispersity in rod length considerably affects the result.³² In an experimental study, Koen-

derink *et al.*³³ concluded that already at very low concentration of high aspect ratio rods, phase separation of rod-sphere mixtures is found, demonstrating the high efficiency of rods as a depletion agent.

Although depletion interaction is important for phase-separation in microcolloidal systems, when going down toward the nanoscale DLVO forces also come into play and become more dominant. Especially the balance between Van der Waals forces and electrostatic interaction due to surface charge in nanoparticulate systems effectively competes with the entropic effects of depletion interaction. A number of studies have focussed on quantifying these interactions for suspensions containing only one single component with a narrow size distribution;^{12,29} examples include nanotriangles²⁵ and nanorods.^{45–47}

In this work we focus on the frequently observed phase separation upon drop-casting and subsequent evaporative self-assembly^{46,48–53} of differently shaped nanoparticles (nanorods and nanospheres) in mixed suspensions. As far as we are aware, a quantitative description of DLVO interactions for binary systems comprising nanorods and nanospheres have not been reported. We present results on the phase separation of aligned nanorod phases and nanosphere-rich domains. The observations are analyzed in terms of relevant nanocolloidal interactions. The novelty of this work lies in the fact that we apply the well-established DLVO formalism to estimate the interactions between differently shaped nanoparticles in relation to those between identical particles. Although many open questions remain, our findings expand the toolbox for controlling nanoparticle interactions at the nanoscale and therewith the assembly and phase separation.

5.2 Experimental

5.2.1 Materials

Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%, Aldrich), silver nitrate (AgNO_3 , 99%, Acros), ascorbic acid (AA, 99%, Merck), cetyltrimethylammonium bromide (CTAB, Aldrich, 98%), sodium borohydrate (NaBH_4 , 99%, Aldrich), hydrochloric acid (HCl , 37%, Merck), aminopropyltriethoxysilane (APTES, 99%, Acros), and sodium citrate (99%, Aldrich) were all used as received without further purification. All water that was used in the synthesis was of Milli-Q quality ($18.2\text{ M}\Omega\text{ cm}$), produced in a Simplicity 185

system (Millipore).

5.2.2 Synthesis and assembly

We adopted the two-step seed mediated protocol as described by Nikoobakht and El-Sayed⁵⁴ to synthesize the gold nanorods used for this study. First CTAB coated seed particles were prepared by mixing 25 μl of HAuCl_4 (0.1M) with 10 ml of CTAB (0.1M). Then 60 μl of ice cold NaBH_4 (0.1M) was introduced while continuously stirring for 3 minutes. The resulting solution quickly turns light brown, which indicates the formation of gold seeds. The solution was kept at 25°C for one hour without stirring to achieve saturation of the seed growth.

To synthesize aspect ratio (AR) 4 gold nanorods the growth solution was prepared by adding 50 μl of HAuCl_4 (0.1M) with 10 ml of CTAB (0.1M). This solution was heated to 35°C for 20 minutes while slowly stirring to dissolve CTAB, and then left to cool down to 25°C. While maintaining this temperature, 25 μl of AgNO_3 (0.1M) was added, followed by 70 μl of ascorbic acid (0.1M) with gentle stirring; the resulting solution become colorless. Next, 150 μl of HCl (1M) was introduced; the pH of the solution was maintained at 3. Finally, 24 μl of the seed particle suspension was added into the growth solution. The final solution was left undisturbed overnight at 25°C .

Similarly, for the synthesis of aspect ratio 6 nanorods, the growth solution was prepared by adding 50 μl of HAuCl_4 (0.1M) with 10 ml of CTAB (0.1M). This mixture was kept at 35°C for half an hour to completely dissolve the CTAB. Hereafter, while maintaining the solution at 25°C, 20 μl of AgNO_3 (0.1M) was added. Then 70 μl of ascorbic acid(0.1M) was added, followed by 100 μl of HCl (1M). Finally, 24 μl of seed solution was added into the growth solution. This solution was left undisturbed overnight at 25°C .

Before use, the nanorod suspensions were centrifuged at 15000 rpm for 10 minutes to remove the excess CTAB. Also, the same growth solution was centrifuged again at 5600 rpm for 5 minutes to separate spherical nanoparticles from the nanorods. The supernatant containing primarily nanorods was carefully separated from the precipitate in the bottom of the centrifuge tube; the latter contains mostly spheres. The nanorod suspensions were stored in the refrigerator. The separation of nanorods and nanospheres is not perfectly selective. Different suspensions have varying amounts of spheres; as such, the spheres are by-products.

For drop casting experiments, SiO_2 substrates were ultrasonically cleaned

in distilled water for 5 minutes at room temperature. Then the substrates were rinsed twice with distilled water and dried in a nitrogen flow. Droplets ($10\ \mu\text{l}$) of each solution were placed on the clean SiO_2 substrate and allowed to evaporate. Within two hours the solvent is completely evaporated, leaving a ‘coffee-stain’ like ring on the substrate.

5.2.3 Characterisation

Ultraviolet-visible (UV-Vis) spectroscopy measurements were carried out using two different systems: (i) a Varian Cary 300 Scan spectrometer; this system enables measurement of spectra in the range of $200 - 900\ \text{nm}$, and (ii) for the measurement of spectra up to wavelengths of $1100\ \text{nm}$ we used an Ocean Optics HR2000+ spectrometer operated using the SpectraSuite software package, in combination with a Mikropack UV-Vis light source (model DH-2000-BAL). We used standard semi-micro UV cuvettes with outer dimensions $12.5\ \text{mm} \times 12.5\ \text{mm} \times 45\ \text{mm}$ for the optical analysis; the optical path through the liquid amounts to $10\ \text{mm}$. These cuvettes can hold up to $1.5\ \text{ml}$ liquid, enabling analysis of limited volumes of liquid.

High resolution scanning electron microscopy (SEM; on a Merlin Zeiss 1550 system) was used for imaging of our samples; typical voltages in the range $0.1 - 30\ \text{kV}$ are accessible. All images in this manuscript were taken at an accelerating voltage of $2\ \text{kV}$.

5.3 Results

When a droplet is deposited on the substrate, the solvent evaporates slowly, typically within 1-2 hours. As soon as the droplet is in contact with the substrate, the contact line appears to be pinned. Due to convective processes a typical coffee stain-like ring is formed,^{55–59} with nearly all nanoparticles assembled into dense arrays near the three-phase contact line.

A typical image near the edge of the ring is shown in Figure 5.1(a). A UV-Vis absorbance spectrum of the suspension used in these drop-casting experiments is presented in Figure 5.1(b). At $520\ \text{nm}$ a characteristic peak is observed, which is partly due to the transverse resonance of the gold nanorods, but also expresses the relatively large number of spheres in the suspension. The wide peak centered near $980\ \text{nm}$ is only due to the longitudinal resonance of the nanorods with aspect ratio 6; the average length and width of

Figure 5.1: (a) Scanning electron microscopy image (SEM) showing the aligned phases of aspect ratio 6 nanorods together with nanospheres, near the edge of the contact line (visible in the upper left corner). The scale bar represents 400 nm. (b) A typical UV-Vis spectrum of the nanorod suspension prior to deposition on the surface.

Figure 5.2: SEM images at different positions of the coffee stain ring after drying a suspension of aspect ratio 6 nanorods; (a) Large scale overview of the edge; the scale bar represents $20\text{ }\mu\text{m}$. (b) Outer edge, where alternating rows of spheres and rods are observed; (c) Close-packed sphere arrays, bounded by aligned layered superstructures of rods; (d) Various phases of rods and spheres further away from the edge. The scale bar in (b), (c) and (d) correspond to 200 nm .

the nanorods amount to $60 \pm 5\text{ nm}$ and $9 \pm 1\text{ nm}$, respectively.

The nanoparticle assemblies exhibit various phases consisting of spheres and/or rods at different positions within the coffee stain ring. Clearly the rods and spheres self-separate into rod-rich and sphere-rich phases. To explore these various phases formed within the entire width ($9 - 10\text{ }\mu\text{m}$) of the coffee stain ring as shown in Figure 5.2(a), we identify three regions which we refer to as the outer, middle and inner areas.

At the very outer edge close to the three-phase contact line of the evaporating droplet, most of the rods are oriented parallel to this contact line. One to two nanorod lengths (approximately $100 - 200\text{ nm}$) away from the edge, rods are oriented perpendicular to the contact line, as shown in Figure 5.2(b). These perpendicularly oriented rows of nanorods are separated by a layer of spheres, effectively forming alternating rows of rods and spheres.

These alternating rods/spheres superstructures were observed up to a distance of approximately $3 - 4 \mu\text{m}$ from the contact line. Moreover, such phase separation was observed around the entire circumference of the droplet.

At a distance of $4 - 6 \mu\text{m}$ from the contact line, the middle portion of the coffee stain ring consists of completely different arrangements of superstructures, as shown in Figure 5.2(c). The nanorods form aligned mono- and multilayered ‘blankets’ of side-by-side assemblies. These three-dimensional superstructured nanorod layers appear to be oriented in arbitrary directions. Moreover, they enclose the close-packed arrays of spherical particles.

Close to the inner edge of the ring, approximately $6 - 10 \mu\text{m}$ from the contact line, the phase separation of rods and spheres becomes very pronounced as shown in Figure 5.2(d). Large three-dimensional superstructures are observed, with the nanorods assembled into smectic phases, i.e. the nanorods are aligned in distinct layers, with their long axis nearly perpendicular to that plane. These smectic phases are completely free of spheres. On the other hand, the spherical entities also aggregate but within the sphere-rich phases some nanorods can still be discerned.

To investigate the effect of nanorod shape on their assembly and phase-separation behaviour, we did a similar experiment using nanorods of aspect ratio 4 (length $55 \pm 5 \text{ nm}$, width $12 \pm 3 \text{ nm}$). The result is shown in Figure 5.3(a). From the UV-vis spectrum in Figure 5.3(b), we conclude that the much lower peak near 520 nm represents the markedly lower concentration of spherical particles in these suspensions. Also, the longitudinal peak for these suspensions is now at 810 nm , owing to the lower aspect ratio of the thicker but equally long nanorods.

The SEM image in Figure 5.3(a) reveals that the thick aspect ratio 4 nanorods also assemble into aligned smectic phases (top-left and bottom of the image), where the few spheres assemble at the boundary between various phases. In the middle and toward the right of the image, close-packed arrays of particles are observed. Judging by the diameter, these are nanorods aligned with their long axis perpendicular to the image plane, in literature referred to as the columnar phase; we cannot conclude whether this is a single layer, or a multi-layered structure. The results in Figures 5.1-5.3 suggest that during droplet evaporation the nanorods in suspension always assemble into highly ordered arrays with spheres forced out from these superstructures.

Finally, we also studied the behaviour of mixed suspensions, containing both thick and thin nanorods, with aspect ratios 4 and 6. The result is

Figure 5.3: (a) SEM image of aligned phases of aspect ratio 4 nanorods. The scale bar represents 100 nm. (b) UV-vis spectrum of a suspension of aspect ratio 4 nanorods (solid red line) prior to deposition on the surface. As a reference the spectrum of aspect ratio 6 nanorods from Figure 5.1(b) is included (dashed blue line).

Figure 5.4: (a) SEM image of nanorod assemblies after evaporative assembly of a mixture of thick (aspect ratio 4) and thin (aspect ratio 6) nanorods. The scale bar represents 200 nm. (b) UV-vis spectrum of the suspension containing thick and thin nanorods, mixed in a ratio of 3:10.

shown in Figure 5.4. For this purpose $1000\ \mu\text{l}$ of AR6 suspension was mixed with $300\ \mu\text{l}$ of AR4 suspension; the resulting UV-vis spectrum of the mixture (Figure 5.4(c)) clearly shows three features. One peak near 520 nm arises mainly from the spheres in the suspension and contains a minor contribution from the transverse plasmon resonance. The broad peak is due to the longitudinal plasmon resonance, and as such contains contributions from the aspect ratio 6 nanorods (the maximum at 970 nm) and the aspect ratio 4 nanorods (a shoulder around 900 nm).

Surprisingly, the SEM images in Figure 5.4 reveal that thick nanorods with aspect ratio 4 are assembled into layers of perpendicularly aligned layers,

Figure 5.5: Schematic representation of the various phase separations of spheres and rods at different positions of coffee stain ring as observed in the experiments. (1) Alternating layers of rods and spheres at the outer edge; (2) close-packed spheres fenced by aligned layers of rods; and (3) phase separated regions of rods and spheres close to the inner edge.

similar to the aforementioned results. These layers of close-packed nanorods (approximately in the center of the image) appear to be loosely stacked perpendicular to the contact line, most likely due to convective processes. The thin nanorods and the spheres do not appear to assemble into any notable structure. The agglomeration of the thick nanorods forces the thinner ones into more disordered structures further away from the contact line, in the left of Figure 5.4(a). Moreover, we do not observe mixed phases comprising both thick and thin nanorods.

5.4 Discussion

Prior to a quantitative discussion of the results in terms of colloidal interactions, we first summarize in Figure 5.5 the various superstructured phases we observe at different positions with respect to the contact line of the evaporat-

ing droplet. As indicated in the previous section, we deposit a liquid droplet of nanoparticle suspension which is left to dry. Initially, due to a finite contact angle and the relatively slow evaporation, convection is not very strong within the droplet in the first state of solvent evaporation. During this initial phase, the nanorod concentration gradually increases giving rise to formation of high density phases which eventually develop into aligned phases due to steric limitations. After some time, the volume within the droplets decreases substantially and the evaporation rate increases, which is most pronounced at the three-phase contact line. This will set up a flow profile which drives the liquid, where we assume assembled nanorod layers have already formed, toward the contact line where they assemble into superstructures.

Comparing the results in Figure 5.2(b) with those in Figure 5.4(a) reveals that the orientation of the layers of nanorods relative to the contact line differs in the two images. It is tempting to ascribe this to the different composition of the suspension, but close examination of many images indicates a more random process. In some images even mixed situations occur, with layers partly oriented perpendicular and partly parallel to the contact line. An example is shown in Figure 5.6. These observations support our claim that the nanorods assemble in suspension prior to being driven toward the contact line by convective flow. Although many reports in literature show similar layered ordering of the nanorods, to the best of our knowledge in none of these is there a focus on the interaction between the nanorods assemblies and the three-phase contact line.

5.4.1 Colloidal interactions in the self-assembly

As opposed to numerous previous studies, our suspensions consist of nanoscale rods and spheres, which clearly self-separate into nearly pure phases containing only nanorods or nanospheres (Figures 5.1 and 5.2).

The electron microscopy (SEM) images in the previous section reveal the close-packed structures with a relatively high degree of positional and rotational order, i.e. in smectic phases. Self-assembly in general arises from a balance of attractive and repulsive interactions between the nanoparticles in suspension, mediated by the solvent. To obtain a more quantitative understanding of the various interactions, below we briefly summarize the various interactions and compare their relative contributions to the overall nanoparticle interactions. Electrostatic, Van der Waals and depletion interactions are analyzed in line with previous work,^{12,25,29,46,47,60} specifically applied to

Figure 5.6: SEM image (aspect ratio 6 nanorods) revealing different orientations of the nanorod layers with respect to the three-phase contact line. In the lower left part, the layers are parallel to the contact line, while in the middle and top right, they are perpendicular.

our system of rods and spheres.

For the side-by-side electrostatic interaction for CTAB-coated gold nanorods, the interaction energy of curved particles is obtained using the Derjaguin approach; the curved nanrod surface is approximated as sets of infinitesimal parallel plates, which represent the nanorod cross-section. The exact expressions for a large range of particles and orientations have been summarized by Walker *et al.*²⁹ The plate-plate electrostatic interaction energy per unit area at constant potential is given by

$$U_{\text{es,plate}}(h) = \varepsilon_{\text{water}} \varepsilon_0 \kappa \phi_0 [1 - \tanh(\kappa h/2)] \quad (5.1)$$

with h the spacing between plates, $\varepsilon_{\text{water}} = 81$ the relative dielectric constant of water. For the effective screening length in our solution, taking into account the ionic strength, we assume $\lambda = 1/\kappa = 1.5$ nm.^{46,47} The surface potential of the CTAB-coated particles in 50 mM CTAB solution is estimated to amount to $\phi_0 = 60$ mV.⁴⁶

To estimate the rod-rod electrostatic interaction energy in the side-by-side

configuration, we assume a cylindrical shape of the nanorods:²⁹

$$U_{\text{es,ss}}(h) = L \cdot \sqrt{\frac{2r_1 r_2}{r_1 + r_2}} \left[\int_h^\infty \frac{U_{\text{es,plate}}(x)}{\sqrt{x-h}} dx \right] \quad (5.2)$$

where L is the total length and r_1 and r_2 are the radii of the two interacting rods; for identical rods $r_1 = r_2$. The distance of closest approach is given by h ; this is the separation of the outer surfaces of the CTAB layer coating on the nanoparticles.

To quantitatively estimate the Van der Waals interaction between two aligned nanorods spaced h apart, we use^{29,47}

$$U_{\text{vdW,ss}}(h) = -\frac{A_{\text{eff}} L}{24h^{3/2}} \sqrt{\frac{2r_1 r_2}{r_1 + r_2}} \quad (5.3)$$

where $A_{\text{eff}} \approx 10^{-19}$ J represents the Hamaker constant.

Finally, owing to the CTAB which remains in the solution, the nanorods will experience an attractive force due to depletion interaction. In principle, not only the CTAB micelles (diameter $d_{\text{micelle}} \approx 5.6$ nm) but also the spherical particles in solution may give rise to an effective osmotic pressure. However, considering their very small number density ($\sim 10^{21} \text{ m}^{-3}$), as compared to the micelle concentration (estimated to amount to $2 \times 10^{23} \text{ m}^{-3}$), the CTAB micelle concentration will dominate the effective depletion force. The attractive potential between side-by-side aligned nanorods, arising from the osmotic pressure P_0 is given by

$$U_{\text{depl,ss}}(h) = -\frac{L}{2} P_0 \left[-h \sqrt{(2r_{\text{rod}} + d_{\text{micelle}})^2 - h^2} + (2r_{\text{rod}} + d_{\text{micelle}})^2 \right] \quad (5.4)$$

with r_{rod} the radius of the nanorod.

Combining Equations 5.2-5.4 enables us to plot the overall interaction curve as a function of rod length and diameter. In the top panel of Figure 5.7 the separate contributions (electrostatic, Van der Waals and depletion) are compiled together with the overall interaction curve, for nanorods with length $L = 60$ nm and diameter $2r_{\text{rod}} = 10$ nm. The electrostatic interaction is positive, i.e. repulsive, while the Van der Waals interaction is attractive. The depletion interaction is also attractive but much smaller than the other two contributions, typically in the order of kT .^{46,47,61} Combination of these gives rise to a primary minimum $U_{\text{min}} = -6.24 \text{ kT}$ at an interparticle separation $h = 6.5$ nm. The strong decrease of the overall interaction curve below

Figure 5.7: (top) Theoretical curves for the electrostatic (red), Van der Waals (green) and depletion (blue) interactions for side-by-side aligned nanorods with length $L = 60$ nm and diameter $2r_{\text{rod}} = 10$ nm. The total interaction curve (black) is the sum of all individual contributions. (bottom) Minimum energy of the total interaction curve as a function of nanorod length L and diameter $2r_{\text{rod}}$.

$h = 2 \text{ nm}$ originates from the rapid drop of the Van der Waals interaction (Equation 5.3). In an actual colloidal system, repulsive steric interaction will dominate at such short distances; we have not taken this into account here and only focus on the primary minimum.

The various interactions contributing to the overall interaction curve depend on the length and diameter of the nanorods. This enables a straightforward calculation of the minimum interaction energy for various sizes and aspect ratios of the nanorods. The results are summarized in the bottom panel of Figure 5.7. As expected, with increasing length L of the nanorods, the mutual attractive interaction strength increases due to a larger overlap of the neighbouring particles. For larger diameter, i.e. a lower curvature, a similar effect occurs. For the largest nanorods ($L = 100 \text{ nm}$ and diameter $2r_{\text{rod}} = 26 \text{ nm}$) the minimum drops to large negative values. This is in line with experimental results which exhibit limited stability of such nanorod suspensions. The agglomeration is energetically much more favourable than their Brownian motion.

Considering that the minimum of the interaction curve for nanorods with moderate dimensions is markedly more negative than kT (the energy related to Brownian motion) implies that the assembly of nanorods is indeed favourable. However, their relatively low concentration (i.e. the number density of nanorods) provides a reasonable separation, therewith providing a fair stability of the solutions. During the drying of the suspension droplets, the concentration gradually increases, giving rise to spontaneous assembly of the nanorods in suspension.

5.4.2 Nanorod alignment and phase separation

The SEM images in Figures 5.1-5.3 clearly reveal that the nanorods have a strong preference to assembly into highly ordered arrays of side-by-side aligned nanorods. In addition, suspensions containing both nanorods and nanospheres exhibit a clear phase separation between the two types of particles. Similar phase separation has been observed previously in mixed suspension containing differently shaped particles.^{1,2,9,27}

As described in relation to Figure 5.2, the spheres seem to be surrounded by layers of perpendicularly aligned nanorods. This suggests that the nanorods first assemble in a side-by-side fashion, after which these layers move toward the edge of the drying droplet under the influence of convection. In that process the remaining spheres are trapped, giving rise to separate phases of rods

and spheres. To support the statement that nanorods have a (strong) preference to assemble side-by-side, as compared to their end-to-end alignment or in comparison to the sphere-sphere interaction, we compare the theoretically calculated overall interaction curves for the three cases in the top panel of Figure 5.8.

For the electrostatic interaction between two nanorods in a head-to-tail orientation, we use⁴⁶

$$U_{\text{es,ee}}(h) = 64kTN_A \frac{n_{\text{CTAB}}}{\kappa} \pi r_{\text{rod}}^2 \tanh\left(\frac{e\phi_0}{4kT}\right)^2 \exp(-\kappa h) \quad (5.5)$$

where $n_{\text{CTAB}} = 50 \text{ mM}$ represents the CTAB concentration in solution, $\lambda = 1/\kappa = 1.5 \text{ nm}$ is the electrostatic screening length and $\phi_0 = 60 \text{ mV}$ the surface potential of the CTAB-coated gold nanorods. We consider all suspensions to be at room temperature, i.e. $T = 298 \text{ K}$.

The Van der Waals interaction for end-to-end aligned nanorods is given by⁴⁶

$$U_{\text{VdW,ee}}(h) = -\frac{A_{\text{eff}} r_{\text{rod}}^2}{12} \left[\frac{1}{h^2} - \frac{1}{(h+L)^2} - \frac{2}{(h+2L)^2} \right] \quad (5.6)$$

with $A_{\text{eff}} \approx 10^{-19} \text{ J}$ the Hamaker constant.

Finally, the depletion interaction due to CTAB micelles in solution is given by⁴⁶

$$U_{\text{depl,ee}}(h) = -\pi r_{\text{rod}}^2 P_0 (d_{\text{micelle}} - h + 2\lambda) \quad (5.7)$$

where $d_{\text{micelle}} = 5.6 \text{ nm}$ is the diameter of the CTAB micelles. The osmotic pressure induced by the micelles is given by $P_0 \approx n_{\text{micelles}} \cdot R_c T$, with R_c the universal gas constant and $n_{\text{micelles}} = (n_{\text{CTAB}} - n_{\text{cmc}})/N_{\text{agg}}$ is the molar concentration of CTAB micelles. The concentration of CTAB in solution amounts to $n_{\text{CTAB}} = 50 \text{ mM}$, the critical micelle concentration to $n_{\text{cmc}} = 0.9 \text{ mM}$ and the aggregation number $N_{\text{agg}} = 140$.^{62,63}

In Figure 5.9 all the aforementioned contributions are plotted as a function of particle separation distance h for two nanorods with length $L = 60 \text{ nm}$ and diameter $2r_{\text{rod}} = 10 \text{ nm}$. The minimum is at a particle separation of approximately 8 nm , but most importantly the energy well in the primary minimum amounts to approximately $0.5 kT$. This implies that the end-to-end configuration is not a very favourable configuration, and will not be able to effectively compete with Brownian motion at room temperature.

Figure 5.8: (top) Theoretical curves for the overall interaction for nanorods (with length $L = 60$ nm and diameter $2r_{\text{rod}} = 10$ nm) aligned side-by-side (black) and end-to-end (blue), compared to the interaction energy of 20nm diameter spheres (red). (bottom) Effect of overlap length d on the overall interaction for nanorods (with length $L = 60$ nm and diameter $2r_{\text{rod}} = 10$ nm) aligned side-by-side. In the inset the dependence of the energy minimum $U_{\min}$ on the overlap d is shown.

Figure 5.9: Theoretical curves for the electrostatic (red), Van der Waals (green) and depletion (blue) interactions for end-to-end oriented nanorods with length $L = 60$ nm and diameter $2r_{\text{rod}} = 10$ nm. The total interaction curve (black) is the sum of all individual contributions.

A similar analysis can be performed for two interacting spheres with radii r_{sph} and coated with the same CTAB layer as the nanorods mentioned above

$$U_{\text{es,sph}}(h) = 2\pi\epsilon\epsilon_0\phi_0^2r_{\text{sph}} \ln [1 + \exp(-\kappa h)] \quad (5.8)$$

with the same parameters. The Van der Waals interaction as a function of particle separation is described by¹²

$$U_{\text{VdW,sph}}(h) = -\frac{A_{\text{eff}}r_{\text{sph}}}{24h} \quad (5.9)$$

and for the depletion interaction we use

$$U_{\text{depl,sph}}(h) = -\frac{\pi P_0}{12} \left[2(2r_{\text{sph}} + d_{\text{micelle}})^3 - 3(2r_{\text{sph}} + d_{\text{micelle}})h + h^3 \right] \quad (5.10)$$

The calculated curves for the different interactions for nanospheres with diameter $2r_{\text{sph}} = 20$ nm are plotted in Figure 5.10. The overall interaction curve exhibits a pronounced minimum near $h = 6.5$ nm at an energy $U_{\text{min}} = -2.2 kT$. As such, the sphere-sphere interaction is markedly stronger than that for end-to-end oriented nanorods in Figure 5.9.

Figure 5.10: Theoretical curves for the electrostatic (red), Van der Waals (green) and depletion (blue) interactions for two spheres with diameter $2r_{\text{sph}} = 20$ nm. The total interaction curve (black) is the sum of all individual contributions.

Now we turn back to the result in Figure 5.8. As is clear from this energy consideration, the side-by-side assembly of nanorods is the most preferential configuration. In comparison, the mutual interaction between nanospheres, which have a larger radius as that of the nanorods, is smaller but still amounts to $2kT$. As expected the end-to-end configuration is negligible and will, under normal ambient conditions, not be stable in relation to Brownian motion. The fact that curvature has a pronounced effect on the particle-particle interaction is clearly reflected in the top panel of Figure 5.8.

As revealed in Figures 5.1-5.3, after evaporative assembly the nanorod superstructures generally exhibit a smectic-like ordering. As opposed to a nematic ordering in which there is only orientation order, the nanorods also exhibit a strong positional ordering within the assemblies; layers of perpendicularly aligned prolate nanoparticles are stacked onto each other. Such smectic phases have been observed in a number of different micro- and nanocolloidal systems.^{2,4,9,26,27,38,40,41,47} This observation is in line with our assumption that these densely packed layers form in solution due to the decreasing volume within the droplet (and thus increasing nanoparticle concentration). Due to convective processes within the evaporating droplet, the particulate layers are then stacked on top of each other.

Figure 5.11: Theoretical curves depicting the effect of different nanorod diameters r_1 and r_2 on the overall interaction for nanorods (with length $L = 60$ nm). Interaction energies are given for two nanorods with radii $r_1 = r_2 = 5$ nm (black), with radii $r_1 = r_2 = 8$ nm (red) and the mixed case for $r_1 = 5$ nm and $r_2 = 8$ nm (blue).

To assess the favourable configuration of the side-by-side orientation, as observed in the layers of the smectic arrays, in the bottom panel of Figure 5.8 the overall interaction is plotted as a function of overlap distance d ; when $d = L$ the nanorods are completely parallel, while for $d \approx 0$ the rods are effectively in an end-to-end configuration. For decreasing overlap of the $L = 60$ nm nanorods the minimum interaction energy clearly decreases from $|U_{\min}| = 6.24 kT$ for 100% overlap, to $|U_{\min}| = 0$ for negligible overlap. As such, the sum of the colloidal interactions considered for our system confirms that the side-by-side configuration with nanorods ‘in registry’ is favourable and in combination with the temporal sequence of assembly contributes to the smectic phases observed.

Up to now we have only considered assemblies of identical nanorods, and also in combination with spheres. The theoretical expressions for electrostatic and Van der Waals interactions in Equations 5.2 and 5.3 also enable us to evaluate the effect of mixtures of nanorods (see Figure 5.4) with different diameters r_1 and r_2 . In Figure 5.11 the effect of varying diameters (and therefore different aspect ratios) is shown. As discussed in relation to Figure 5.8,

the curvature of the surface is relevant. Going back to the Derjaguin approximation, a relatively flat surface will give rise to larger overall interactions as compared to a surface with strong curvature. As such, we expect that the attractive interaction between nanorods with a larger radius will be stronger in comparison with thinner nanorods. The calculations in Figure 5.11 indeed support this and the experimental result in Figure 5.4 confirms that thicker nanorods assemble into superstructures more effectively. Convection of the assembled thick rods is more pronounced, therewith pushing out the spheres and the thinner nanorods. For the latter Brownian motion will be more pronounced owing to their smaller mass; this has not been taken into account in the calculation. A similar effect was reported by Ming and co-workers.⁹ In their study, they varied both the length and diameter of the nanorods, and concluded that only nanorods with different widths self-separate to form their own smectic superstructures; for nanorods with different lengths but with equal diameter such self-separation was not observed. Surprisingly, mismatched pairs of thick and thin rods have not been observed, nor do we find mixed phases comprising both types of nanorods, despite only a relatively small difference of $2kT$ between the energy minima in Figure 5.11. This may suggest that other processes may also be involved; in the next section we discuss the possible effect of the stabilizing CTAB layer on the assembly process.

5.4.3 Role of CTAB surfactant layer

In the previous section we have only considered long-range colloidal forces acting on the particles in suspension, and we discussed their relative contributions in the assembly process. Up to now, we have ignored the short-range steric interaction, as is evident from the strong drop in the overall interaction curve in Figure 5.7 (and also Figures 5.9, 5.10, and 5.11). However, the nanoparticles considered in this work are coated with a CTAB surfactant layer. In fact, this CTAB layer is considered to consist of a double layer of interpenetrating CTAB molecules.⁶⁴ Owing to this surfactant layer, there is a strong repulsive interaction at very short separation distances.

When nanoparticles in solution come so close to each other that the CTAB layers will interact, the configuration of the surfactant molecules on the different facets of the nanorod surface will determine the effective repulsive strength. This is schematically illustrated in Figure 5.12. The side facets of the nanorod are relatively little curved as compared to the outer ends. In fact,

Figure 5.12: Schematic drawing of the surfactant configuration at differently curved nanorod surfaces. The interaction between a flat and a curved surface (left), two flat surfaces (middle) and two curved surfaces are shown.

nanorod surfaces are generally considered not to be curved, but rather composed of multiple facets. Consequently, the approximately straight surfactant molecules form a dense layer. The dense packing is even enhanced by the fact that the CTAB-coating is more closely-packed on these side facets owing to their crystallographic orientation.⁶⁴ On the other hand, due to the strong curvature of spherical nanoparticles and also the approximately spherical ends of the nanorods, the CTAB molecules ‘radiate’ outwards. As a result, the angles of approach in flat-vs-sphere interactions are mismatched effectively giving rise to a repulsion. Now we turn back to the interacting nanoparticles. Two nanorods with dense layers of aligned CTAB molecules will enable a certain extent of interpenetration of layers of neighbouring particles (middle of Figure 5.12). In the case of two nanospheres (right of Figure 5.12), the outer region of the CTAB layers is relatively dilute therewith allowing the surfactant molecules to interact to a certain extent. Finally, the overlap between CTAB layers of two surfaces with markedly different curvature (left of Figure 5.12) will be hindered by the fact that one surfactant layer is densely packed, and the molecules on the two surfaces are not aligned.

Combining all the long-range and short-range forces in relation to the shape and size, a schematic summary is depicted in Figure 5.13. Depletion interaction was shown to be only a minor interaction, while Van der Waals attraction and electrostatic repulsion comprise the long-range interactions. We have shown that on the basis of the theoretical analysis the side-by-side oriented

Figure 5.13: Schematic summary of the assembly process in nanoparticle suspensions containing rods and spheres. Under the influence of long-range electrostatic and Van der Waals forces, combined with short-range surfactant interactions, similar particles will self-separate into sphere- and nanorod-rich phases; side-by-side alignment in the latter case is preferred.

alignment of nanorods is strongly favoured, with even a more pronounced energy minimum for larger nanorod diameters. Moreover, we discussed that the short-range interaction between surfactant layers on the nanoparticle surfaces also favour self-separation of the nanorods and -spheres into separated phases. Within the drying droplet the nanoparticle concentration in the suspension increases. As a result, the various superstructures are driven toward the three-phase contact line where they assemble into phase-separated superstructures, as shown in the experimental results in Figure 5.1-5.4.

5.5 Conclusions

In summary, we investigated the phase separation of aligned gold nanorods from nanospheres within the coffee-stain ring formed during evaporative self-assembly, using a combination of electron microscopy and a theoretical analysis. The orientation and density of the various crystalline phases at different positions of the coffee-stain ring is attributed to the convective flow, which

changes as the environment within the droplet become more dense owing to the continuous decreasing height of the droplet during evaporation. In the theoretical analysis, which provides a benchmark for interpretation of experimental results, all major interactions between the nanoparticles have been discussed for our specific system, which ultimately provides a net interaction energy depending on particle shape, size and orientation. Both the experimental results, as well as the theoretical analysis confirm that the side-by-side arrangement of the nanorods is the lowest energy state for our system. Furthermore, we also discuss variation of the energy minimum for different orientations, sizes, and shapes of the nanoparticles. Although the overall attractive interaction plays a major role in bringing the nanoparticles together in suspension, we also discuss the possibility that short-range steric interaction caused by the CTAB-coating on the nanoparticle surface could play a role in the self-separation of spheres and rods.

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6

Gold nanorod assembly on stripe-patterned gradient surfaces

Experimentally we explore the potential of using pre-defined motion of a receding contact line to control the deposition of nanoparticles from suspension. Stripe-patterned wettability gradients are employed, which consist of alternating hydrophilic and hydrophobic stripes with increasing macroscopic surface energy. Nanoparticle suspensions containing nanorods and nanospheres are deposited onto these substrates and left to dry. After moving over the pattern and evaporation of the solvent, characteristic nanoparticle deposits are found. The liquid dynamics has a pronounced effect on the spatial distribution. Nanoparticles do not deposit on the hydrophobic regions; there is high preference to deposit on the wetting stripes. Moreover, the fact that distributed nanoparticle islands are formed suggests that the receding of the contact line occurs in a stick-slip like fashion. Furthermore, the

formation of liquid bridges covering multiple stripes during motion of the droplet over the patterns is modeled. We discuss their origin and show that the residue after drying, containing both nanoparticles and the stabilizing surfactant, also resembles such dynamics. Finally, zooming into individual islands reveals that highly selective phase separation occurs based on size and shape of the nanoparticles.

6.1 Introduction

6.1.1 Nanoparticle assembly

A highly interdisciplinary field of research within materials science comprises that devoted to nanomaterials. Macroscopic materials built from nanoscale building blocks derive their properties from those of the individual composing elements.^{1–7} The bottom-up approach to design and manufacture novel nanoscale materials has rapidly matured over the past years. Impressive achievements in terms of well-accessible, reproducible synthesis procedures have led to the availability of a large diversity of monodisperse colloidal metallic, semiconducting and insulating particles with sizes ranging from micrometers to nanometers. Active and reproducible control over orientation and mutual alignment of nanoparticles in suspension as well as during adsorption at surfaces has mainly been limited to (controlled) drying experiments, in which hydrodynamic attractive forces compete with steric and/or electrostatic repulsive forces.^{7–16} Additionally, the application of external stimuli, such as electric, magnetic and optical fields have been explored.^{17–24}

One of the most frequently used methods to deposit nanoparticles on substrates, referred to as evaporative self-assembly,^{25–27} involves drying of a droplet containing nanoparticles on an isotropic homogeneously coated substrate. This generally gives rise to concentrated deposition within a dense ring near the three-phase contact line, the so-called coffee-stain effect.^{9,28–30} In a recent study on evaporative assembly (see chapter 5) of mixed suspensions containing nanorods and nanospheres, we focused on the phase-separation and alignment of the nanoparticles within this coffee strain ring. Depending on the position relative to the pinned contact line of the drying droplet, spheres and rods separate into various liquid-crystalline phases.³¹ Experimental observations were compared to quantitative calculations of the colloidal interaction energies, and the role of the surfactant on the different crystal facets of the nanorods was discussed.

6.1.2 Wettability gradients

Despite the vast amount of work in the field of nanoparticle self-assembly, reproducible control over the nanoparticles in suspension as well as during their assembly at interfaces still poses major challenges. The aforementioned pinning of the contact line during the evaporation, i.e. the coffee stain effect, hinders the homogeneous deposition of nanoentities over large surface areas. Consequently, exploring alternative approaches to isotropic nanoparticle deposition is a timely topic of research. As an example, recently it has been shown that the coffee stain effect can be suppressed using electrowetting.^{32,33}

Figure 6.1: Schematic representation of patterns used to create linear (left) and radial (right) wettability gradients; note that the stripe widths are not to scale. The gradient is created by the transition from the homogeneous PFDTS (gray) to the unpatterned SiO₂ (blue) via linear or radial striped regions with decreasing macroscopic hydrophobicity, with hydrophobic-to-hydrophilic ratios α typically varying from 0.9 to 0.25. The images in the bottom represent microscopy images of the patterned photoresist, before patterning; dark areas correspond to the photoresist, while light areas are the SiO₂ regions onto which a PFDTS self-assembled monolayer.

In that respect, assembly of nanoparticles by a moving contact line is particularly interesting since it enables deposition over much larger areas. A way to achieve controlled motion of the contact line is by using substrates with a coating that defines a gradient in the wetting properties.^{34–37} In recent work, we have shown that on morphologically flat but chemically patterned surfaces such wettability gradients can be created using striped patterns of alternating hydrophilic and hydrophobic stripes.^{38–40} Linear and radial striped patterns, such as schematically depicted in Figure 6.1, were shown to induce controlled motion of pure liquid droplets over distances up to a few millimeters. Typically, the pattern designs consist of an isotropic hydrophobic region, coated homogeneously with perfluorodecyltrichlorosilane (PFDTs), where the droplet is deposited (top of the linear pattern and center of the radial pattern in Figure 6.1). The gradient is formed by subsequent striped regions (indicated as linear and radial 1, 2 and 3 in Figure 6.1) consisting of alternating hydrophobic (PFDTs) and hydrophilic (SiO_2) stripes with an increasing macroscopic surface energy, which creates a preferential spreading direction for the droplets.³⁸

The fraction of hydrophilic surface area increases for radial sections further away from the center. We use a dimensionless parameter $\alpha = w/s$ to quantify the relative hydrophobicity of the pattern,⁴¹ where w and s represent the hydrophobic PFDTs and hydrophilic SiO_2 stripe widths, respectively. Areas with smaller values for α correspond to larger overall surface energy, and as such are more hydrophilic. The range of α values considered in this work amounts to $0.9 - 0.25$ for all patterns.

In this work, we use such stripe-patterned wetting gradients in an attempt to control the motion of the receding contact line of a droplet containing nanoparticles and with that the deposition of the nanoparticles at the trailing edge of the moving droplet. Moreover, inspired by the recent work of Ahmed and co-workers,⁴² who observed patterned deposition of gold nanorods on morphologically flat substrates with a linear pattern of hydrophilic stripes, we apply suspensions containing low aspect ratio gold nanorods (and a low concentration of nanospheres) on our gradient substrates. The choice for low aspect ratio nanorods derives from the fact that the shape anisotropy defines a preferential orientation with respect to the drying direction. Moreover, nanorods with an aspect ratio of approximately 6 are relatively easy to synthesize and have been shown to give rise to nicely packed, dense arrays. Considerably larger nanorods will lead to more disordered, randomly piled

arrays of the nanorods.⁴² After a summary of the experimental procedures, we first review the liquid behaviour on the different stripe-patterned surfaces. We discuss the residual liquid film on single stripes as well as the origin of liquid bridges covering several adjacent stripes at regular intervals. In the last section, we describe the deposition of the nanoparticles, which occurs primarily on the hydrophilic stripes. The shape of the deposits on the different patterns is discussed. We also zoom in on individual islands and show that within the micron-scale islands, phase-separation occurs based on size and shape of the different nanoparticle geometries in the suspensions.

6.2 Experimental details

6.2.1 Materials

Cetyltrimethylammonium bromide (CTAB, Aldrich, 98%), hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%, Aldrich), silver nitrate (AgNO_3 , 99%, Acros), ascorbic acid (AA, 99%, Merck), sodium borohydride (NaBH_4 , 99%, Aldrich), hydrochloric acid (HCl , 37%, Merck) and glycerol (ReagentPlus, Sigma, USA) were all used as received without further purification. All water that was used in the synthesis was of Milli-Q quality ($18.2\text{ M}\Omega\text{ cm}$), produced in a Milli-Q Reference A+ system.

6.2.2 Substrate preparation

The surface patterns of self-assembled monolayers (SAMs) of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTs, 97%, ABCR, Germany) on silicon wafers are created using standard clean room facilities. First, a positive photoresist is spincoated on freshly cleaned wafers with a natural oxide film, followed by soft-baking. Patterns are created via standard optical lithography, after which the exposed photoresist is washed-off. The remaining photoresist is hard-baked and provides surface protection during vapor deposition of PFDTs; the silane headgroup binds covalently to the native silicon oxide, exposing the fluorinated tail to the liquid. The assembly creates a densely packed layer of molecules with a height in the order of one nanometer, on which both glycerol and water have a stationary contact angle (CA) $\theta_{\text{st}} = 106^\circ$. Vapor deposition of PFDTs is done in a degassed chamber that is successively exposed to PFDTs and water reservoirs to introduce the respective vapors, initiating the reaction on the wafer surface. After formation

of the SAM, the photoresist is washed off, leaving a chemically patterned surface. The uncoated silicon oxide surface exposed after removing the photoresist exhibits typical static contact angles in the range of $30 - 40^\circ$, with receding angles of $10 - 15^\circ$.

6.2.3 Nanorod synthesis

We adopted the two-step seed mediated protocol as described by Nikoobakht and El Sayed⁴³ to synthesize the gold nanorods used for this study. First CTAB-coated seed particles were prepared by adding $25\ \mu\text{l}$ of HAuCl_4 (0.1M) to 10 ml of CTAB (0.1M). Next $60\ \mu\text{l}$ of ice cold NaBH_4 (0.1M) was introduced while continuously stirring for a few minutes. The resulting solution quickly turns light brown, indicating formation of gold seeds. The solution was kept at 25°C for approximately one hour without stirring.

As outlined in the Introduction section, we use gold nanorods with an aspect ratio (AR) of approximately 6. To synthesize gold nanorods (average length $56 \pm 12\ \text{nm}$ and diameter $10 \pm 1\ \text{nm}$; the size distributions have been determined from measuring 1000 nanorods in SEM images) the growth solution was prepared by adding $50\ \mu\text{l}$ of HAuCl_4 (0.1M) to 10 ml of CTAB (0.1M). At room temperature $20\ \mu\text{l}$ of AgNO_3 (0.1M) was added, followed by $70\ \mu\text{l}$ of ascorbic acid (0.1M) with gentle stirring; the resulting solution becomes colorless. Next, $100\ \mu\text{l}$ of HCl (1M) was added to maintain $\text{pH} \approx 3$. Finally, $24\ \mu\text{l}$ of the seed particle suspension was added to the growth solution. This solution was left undisturbed overnight at room temperature.

Before use, the nanorod suspensions were centrifuged at 15000 rpm for 10 minutes to remove the excess CTAB. Subsequently, the suspension was centrifuged again at 5600 rpm for 5 minutes to remove spheres from rods. The nanorod suspensions were stored in the refrigerator.

After centrifugation the nanoparticle suspensions contain predominantly nanorods, and a lower concentration of nanospheres. The latter are a residue of the synthesis, but provide interesting effects as to nanoparticle phase-separation.³¹ From careful analysis of the relative (transverse and longitudinal) peak heights in UV-Vis spectra, we deduce that the nanorod and nanosphere number densities amount to approximately $N_{\text{rods}} = 2.0 \times 10^{11}\ \text{cm}^{-3}$ and $N_{\text{spheres}} = 2.2 \times 10^{10}\ \text{cm}^{-3}$, respectively.

6.2.4 Liquid deposition and surface characterisation

Droplet deposition is done using an OCA 15+ goniometer (DataPhysics, Germany), employing a computer controlled syringe. Unless otherwise specified, for all droplets the volume is fixed to $1\text{ }\mu\text{l}$. The variation in droplet diameter just after being produced from the syringe was measured to be less than 5%. A ccd-camera is mounted within the OCA setup, which enables the capturing of a droplet profile. From this profile the dimensions and the contact angles can be extracted. This is done with the DataPhysics software, resulting in an accuracy of 0.5° for the contact angles. Deposition of the droplet is achieved by very slowly lowering the syringe with the suspended droplet toward the substrate until it contacts the patterned surface.⁴⁴ Droplets of nanorod suspension were placed on the patterned surfaces and allowed to evaporate at room temperature; typically within two hours the solvent was completely evaporated.

A color camera (1.2 MagePixel USB camera, model EO-1312C Edmund Optics, fitted with a close focus zoom lens with a 10x zoom in combination with 2x fixed focal length lens extender) is mounted above the deposition stage and is used to image the temporal evolution of the droplets over the patterned surface. The top-view camera has a frame rate of 10 fps, enabling a qualitative description of the slow movement of droplets. The color movies provide a means to monitor this residual liquid film.

For morphological characterization, an Asylum Research MFP-3D atomic force microscope (AFM) with an $80\text{ }\mu\text{m} \times 80\text{ }\mu\text{m} \times 15\text{ }\mu\text{m}$ closed loop scanner has been employed. Measurements were performed under ambient conditions in intermittent contact mode using Olympus AC240TS probes with a cantilever spring constant of approximately 2 N/m and a resonance frequency of 65 kHz . The tetrahedral tips have an opening angle of about 35° and a tip radius of 7 nm .

High-resolution scanning electron microscopy (SEM; on a Merlin Zeiss 1550 system) was used for imaging of our samples with nanoparticle deposits; typical voltages in the range $0.1 - 30\text{ kV}$ are accessible. Images used in this work were obtained at an accelerating voltage of 2 kV .

6.3 Liquids on chemically stripe-patterned gradients

6.3.1 Experimental results

We briefly review the gradient-induced droplet motion, as extensively reported in previous work.^{39,40} On the linear pattern, the droplet deposited onto the unpatterned PFDTs area initially spreads isotropically. Once the advancing three-phase contact line reaches the first striped pattern, the SiO₂ stripes give rise to a higher overall surface energy therewith inducing a preferential spreading direction for the liquid. Sequentially the droplet reaches the following patterns with decreasing α values, i.e. with increasing hydrophilicity (Figure 6.1). Droplet motion on radial patterns is also driven by the gradient defined by the ring-shaped striped regions with decreasing α values at larger distance from the center. Generally, the droplets on the radial patterns are markedly more circular as opposed to those on linear wettability gradient arrays. For the linear patterns, the confinement of the liquid between PFDTs stripes is stronger, forcing the liquid to move faster in the stripe direction as compared to the radial patterns considered in this work.

After the droplet has moved over the pattern, the receding side leaves behind a layer of residual liquid. In the case of water, this residual liquid layer evaporated relatively fast, but in the case of glycerol it is stationary. This happens both on the linear and the radial patterns.⁴⁰ Close examination of the liquid residue (Figure 6.2a) reveals that on the first striped region (radial 1 in Figure 6.1), only the hydrophilic SiO₂ stripes are covered with the polar liquid. However, on the subsequent striped areas of the pattern, liquid ‘bridges’ covering multiple stripes (both PFDTs and SiO₂) can be discerned.

In an attempt to understand the occurrence of bridges on the subsequent striped regions in Figure 6.2b,c we zoom in on a part of the radial pattern and the liquid on it. The similar size and regular position of liquid bridges suggests that their presence is probably related to a repeatedly occurring feature in the pattern. As outlined in our previous work³⁹ the bridges occur where the hydrophilic stripes in the neighbouring striped patterns are not connected, i.e. where the periodicity of both patterns is out of registry. Due to the different α values in the two regions the periodicity of the stripes is different, and as such the relative positions of the stripes shift with respect to each other. At positions where bridges are formed, the hydrophobic stripes of the second region originate where hydrophilic stripes of the preceding

Figure 6.2: (a) Image of glycerol remaining on the SiO₂ stripes after the droplet has moved outward; the image is obtained several minutes after initial deposition. On the first radial pattern, a homogeneous distribution of glycerol is observed on the hydrophilic stripes. On the second radial pattern, so-called ‘bridges’ occur, where the liquid covers several stripes. (b) Schematic representation of pinning of the receding contact line at the border between radial patterns (the shaded blue lines correspond to hydrophobic PFDTs, white represents the hydrophilic SiO₂). The gray rectangles represent the ‘bridges’, which originate from discontinuities in the PFDTs stripes. (c) Enlarged top-view image of an actual wetted surface, showing the bridges. Image adopted from reference.³⁹

Figure 6.3: Composed AFM image of the edge between two linear patterns with different α value, showing discontinuities (left) and connected PFDTs stripes. The dimension of the individual square images amounts to $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$.

region end. This perturbs the contact line structure, and as such gives rise to substantial pinning and thus bridge formation. Further enlargement of the border between the two regions (shown in Figure 6.2b) reveals a critical mismatch between the respective hydrophobic stripes that will lead to bridge formation.

To assess the actual connection between subsequent striped regions, we performed AFM measurements on the striped patterns. A typical result showing the border between two striped patterns with different α is depicted in Figure 6.3. In the composed AFM image, the PFDTs is visible as the ‘higher’ region (brighter). The top half of the image corresponds to the wider PFDTs stripes, i.e. a more hydrophobic pattern with a higher α values ($\alpha = 0.5$ in this case); the bottom half is more wetting, characterized by $\alpha = 0.3$.

6.3.2 Modelling liquid ‘bridges’

To verify our assumption that the bridges originate from a mismatch between two neighbouring patterns we developed a simple model. In this model the positions of bridges are calculated on the basis of the widths of wetting and non-wetting stripes, as schematically shown in the top panel of Figure 6.4. We define the width of the PFDTs and SiO_2 stripes on the first and second pattern as w_1 , s_1 , w_2 and s_2 , respectively. As indicated on the basis of our

Figure 6.4: (top) Schematic overview of the border between two adjacent patterns with dimensions of the PFDTs and SiO_2 stripes. (bottom) Snapshot of a droplet on a linear pattern leaving liquid bridges. Overlaid are the SiO_2 stripes (light blue) and the calculated positions of the bridges (dark blue); in this case, $s = 25 \mu\text{m}$, $w_1 = 22.5 \mu\text{m}$ and $w_2 = 12.5 \mu\text{m}$.

experimental results, to form a bridge the PFDTs stripe of pattern 2 needs to be connected with the SiO₂ stripe (in other words, w_2 needs to be smaller than s_1). If we start with two SiO₂ stripes of adjacent patterns aligned (left side in the top panel of Figure 6.4) and we label the number of stripes per pattern with n_i , where i indicates the number of the pattern, we obtain the following set of equations describing the position of the edges of neighbouring stripes

$$s_{1L} = n_1 (s_1 + w_1) \quad (6.1a)$$

$$s_{1R} = n_1 (s_1 + w_1) + s_1 \quad (6.1b)$$

$$w_{2L} = n_2 (s_2 + w_2) + s_2 \quad (6.1c)$$

$$w_{2R} = (n_2 + 1) (s_2 + w_2) + s_2 \quad (6.1d)$$

in which s_{1L} and s_{1R} denote the positions of the left and right edges of the SiO₂ stripes in pattern 1, and w_{2L} and w_{2R} being the positions of the left and right edges of the PFDTs stripes in pattern 2. As stated above, in order to form a bridge the position of a PFDTs stripe in pattern 2 needs to be within the position of a SiO₂ stripe of pattern 1. Thus

$$w_{2L} \geq s_{1L} \quad (6.2a)$$

$$w_{2R} \leq s_{1R}. \quad (6.2b)$$

After substituting $s_1 = s_2 = s$, which is the case for all our patterns, and rewriting, we obtain

$$n_1 \geq \frac{n_2 (s + w_2) + w_2}{s + w_1} \quad (6.3a)$$

$$n_2 \geq \frac{n_1 (s + w_1) - s}{s + w_2}. \quad (6.3b)$$

Alternatively, we can also use the relative widths of the stripes $\alpha_i = w_i/s$, i.e. the width w_i of the hydrophobic stripes divided by the width s of the hydrophilic stripes:

$$n_1 \geq \frac{n_2 (1 + \alpha_2) + \alpha_2}{1 + \alpha_1} \quad (6.4a)$$

$$n_2 \geq \frac{n_1 (1 + \alpha_1) - 1}{1 + \alpha_2}. \quad (6.4b)$$

Rewriting Equation 6.4 we obtain an expression for the limits of one integer (n_2) in terms of the other (n_1):

$$\frac{n_1(1 + \alpha_1) - 1}{1 + \alpha_2} \leq n_2 \leq \frac{n_1(1 + \alpha_1) - \alpha_2}{1 + \alpha_2}. \quad (6.5)$$

For any (positive) integer n_1 it is straightforward to determine whether there is an integer n_2 , which complies with the limits defined by Equation 6.5. If there is such an integer, this will give the position of a bridge.

We implemented this simple model and determined the bridge positions for a specific configuration (Figure 6.4), and superimposed it on an actual snapshot in which liquid bridges occur. The calculated liquid residues on the SiO_2 are marked in light blue, while the bridges are marked in dark blue (top part of the image). The calculated positions of the bridges align perfectly with the bridges in the snapshot, confirming the validity of our simple model and therewith the origin of the bridges.

6.4 Nanorod assembly on stripe-patterned gradients

6.4.1 Nanoparticle deposits

When a droplet of nanoparticle suspension is placed on a substrate, evaporative assembly generally leads to pinning of the contact line, and the formation of a coffee stain ring.^{9,28–30} Using linear or radial wettability gradients, the motion of the droplet and therewith the three-phase contact line can be controlled. Here we primarily focus on the trailing edge of the droplet, and the deposits left by the receding contact line. After the droplet has stopped moving and the solvent has been left to evaporate, typical overview images of the deposits on linear and radial stripe-patterned wettability gradients are shown in Figures 6.5 and 6.6, respectively. The gold nanoparticles show up as the brightest features in the SEM images.

Both the linear and radial wettability gradient have a hydrophobic region (consisting of pure PFOTS) on which the droplet is initially deposited (Figure 6.1). As soon as the droplet reaches the striped region consisting of alternating hydrophilic/hydrophobic surface, the liquid starts to move toward the other side of the pattern. When the advancing edge reaches the hydrophilic region (pure SiO_2), the receding edge becomes pinned and overall motion stops.

Figure 6.5: SEM image of deposits after placement and subsequent drying of a nanorod suspension on a linear striped wettability gradient. (A) General overview of the residual deposits after the droplet has moved (from left to right) and the solvent has evaporated. Bright parts represent the gold nanorods, while the deposits with a darker gray shade are most likely CTAB layers. (B,C) Zoomed in images of the regions at the border between different striped regions, as indicated in (A).

Figure 6.6: SEM image of deposits after placement and subsequent drying of a nanorod suspension on a radial striped wettability gradient. (A) General overview of the residual deposits after the droplet has moved (from right to left) and the solvent has evaporated. Bright parts represent the gold nanorods, while the deposits with a darker gray shade (on the left) are most likely CTAB layers. (B) Zoomed in image of the region at the border between different striped regions, as indicated. (C) Image obtained on the isotropic SiO_2 region outside the striped radial pattern.

Comparing the results in Figures 6.5 and 6.6, a number of similarities are observed on both types of patterns. On the advancing side of the droplet, which becomes pinned on the homogeneous SiO_2 surface, particle assemblies within the coffee stain ring are observed, very similar to previous work; an example is shown in Figure 6.6(C).³¹ Also, on both types of patterns the contact line on the trailing edge of the droplet initially moves a certain distance without leaving behind any deposits; both in the left of Figure 6.5(A) and the right of Figure 6.6(A), the striped pattern is completely free of deposited nanorods. Close inspection reveals that a few nanoparticles are left behind, but in a significantly lower concentration.

After traveling a certain distance, the receding contact line becomes pinned for the first time. At this position the deposits appear dense and multilayered owing to the pinned contact line and convective transport. The deposits further along the stripes, between the initial multilayered islands and the edge between the two striped regions, the deposits consist mainly of monolayers of nanorods. Furthermore, nanoparticles are only deposited on the hydrophilic stripes; the hydrophilic regions are completely depleted of nanoparticles. Apparently, the deposition is highly selective on the hydrophilic regions of the substrate, most likely due to convective flow during the drying.

At the edge where the different striped areas (with differing α values) meet, dense multilayer deposits are observed on the hydrophilic stripes. As can be seen in Figures 6.5(B) and 6.6(B), the deposits reflect the pinning of the contact line at this edge. Similar to the liquid ‘bridges’ described in the previous sections, wide deposits covering multiple stripes in the second region occur. Since the brightness is much lower, these are not gold nanoparticles, but most likely CTAB crystallite layers. Close examination of Figures 6.5(B) and 6.6(B) reveals that these CTAB residues originate on stripes where the hydrophilic stripes in two striped regions do not connect. This supports our conclusions of the previous section. Finally, at the edge between the last striped region and the homogeneous, isotropic hydrophilic region, there is complete wetting. The deposited nanoparticles at the edge and the CTAB on the wetting areas are depicted in Figure 6.5(C).

Moreover, on both types of gradient wetting patterns, the nanoparticle assemblies are centered on the hydrophilic stripes. Although it is difficult to follow the exact drying process, we assume that during the final stages hydrodynamic confinement of the liquid gives rise to a force directed toward the middle of the hydrophilic stripes. As a result, the hydrophobic stripes are

completely free of nanoparticles, and the nanoparticle islands are centered on the wetting stripes. Moreover, close examination of the deposits in Figures 6.5 and 6.6 indeed confirm this assumption in that there is a pronounced symmetry with respect to the middle of the stripes.

There are also differences when comparing the deposited nanoparticle islands on the two striped patterns. On radial patterns the connected deposited islands are relatively longer than the islands on the linear gradient surface. Most of the islands on radial patterned stripes are connected through a thin neck, while on the linear patterns the majority of the islands appear to be isolated, but also on these surfaces we find islands connected through a thin neck.

On linear stripe-patterned gradients the contact line moves in a stick-slip like motion. When the contact line is stuck, or pinned, nanoparticles are assembled at the three-phase contact line. The slippage of the contact line is seen in Figure 6.5 by the regions on the hydrophilic stripes between the deposited islands, which have a markedly lower density of nanoparticles. In contrast, on radial patterns the motion of the contact line does not exhibit such pronounced stick-slip like motion. On these surfaces, the deposited islands are often connected by a thin neck.

6.4.2 Shape- and size-induced phase separation of nanoparticles

Finally, in previous work we have shown that the deposition of nanoparticles from mixed suspensions containing nanorods and nanospheres gives rise to phase-separation.³¹ Colloidal interactions within the suspension give rise to shape-dependent clustering, followed by convection-driven assembly within the coffee-stain ring. Similarly, the hydrodynamic forces induced by the substrate design also appear to lead to the separation of differently shaped nanoparticles within the deposited islands.

As described earlier, the droplet on linear gradient patterned surface leaves behind trails of small patches of highly concentrated nanoparticle suspension. For instance some of the dried short nanoparticle deposits on linear gradient patterned surface are shown in Figure 6.7A. Such deposits display interesting and distinct phase separation of rods and spheres; especially in case of a moving contact that leaves behind dense suspension deposits on hydrophilic stripes. Within these deposits, the distinct phase separation of nanoparticles can be attributed to the increase in packing entropy of the system.^{45–56} In fact, the tendency of spheres to assemble with another nearby sphere will

Figure 6.7: (A) An overview of short nanoparticle deposits on hydrophilic stripes of linear gradient patterned surface. Grey stripes are SiO_2 , black stripes are PFDTs, and bright islands are nanoparticle deposits. (B, D, F) SEM images showing short islands of nanoparticle deposits with bright regions (spheres) in the middle surrounded by less bright deposits (rods). (C, E, G) Positioning, phase separation and the formation of neck-like connected regions of nanoparticles within the deposits.

Figure 6.8: (A) Schematic representation of nanoparticles in suspension showing depletion of thin rods from large spheres and hexagonally packed spheres will tend to increase the total volume available to rods. (B) Scheme showing excluded volume that depends on shape and orientation of nanoparticles.

finally assembled them in the middle of wider region of deposits. As a result, the total volume available to thin rods will increase, which will increase the entropy of rods and consequently, the system will decrease its free energy (see Figure 6.8). Furthermore, in computer simulation studies the only intrinsic nanoscale forces between nanoentities are steric interaction and the entropic effect of shape,^{57,58} which can collectively be termed as ‘shape entropy’.⁴⁸ The role of short-rang steric interaction in relation with phase separation is explained in chapter 5. Therefore, we highlighted merely the packing entropy effect in the aforementioned dense traces of nanoparticle suspension. Additionally in our system, nanoparticles are not only phase separated but found at specified location within the deposits. The packing entropy seems to have a pervasive effect on predominantly high concentration of nanoentities in suspension. Likewise, it appears that unstable contact line will help to increase the packing entropy of gold nanoentities to attain low energy in suspension. As a result, sphere-sphere and rod-rod population are separated within these islands. Moreover, close examination of the deposits reveals that nanorods appeared more loosely packed than the spheres as shown in Figure 6.7(C,E,G). This could possibly be the reason that spheres owing to their densely packed self-assembled arrays are always found in the middle of the wider regions. In contrast, rod-sphere combinations are less likely owing to both steric-interaction³¹ and packing entropy effects. In hydrodynamic fluctuating environment, the aforementioned effects will most likely become more effective and dominant. For instance, sphere-rich and rod-rich regions within some nanoparticle islands are clearly shown in Figures 6.7(B-G). The neck-like regions within the connected short deposits are always composed of nanorods while nanosphere regions are persistently observed in the middle of wider regions, which are completely depleted from rods. Furthermore, rods are always found at the periphery of the deposited islands. In this chapter, we merely focus on the deposited nanoparticle islands on linear patterned gradient surface whereas the structure of nanoparticle islands and their arrangement on radial patterned gradient surface will be discussed in chapter 7.

In Figure 6.9, a typical SEM image of a relatively large island is shown. The trailing part of the island, i.e. on the receding side in the top-right corner of the figure, contains a relatively high portion of nanorods. A monolayer of randomly oriented nanorods has been formed during the drying process. The nanorods within the dashed yellow box have been measured; a histogram of their length distribution is depicted in the top panel of Figure 6.9(B). Analysis

Figure 6.9: SEM image showing an overview of a large island as typically observed in the region where nanoparticles are deposited. On the outer edge (yellow dashed box) and within the interior (red dashed box) primarily nanorods are deposited; (B) Length distribution histograms within these nanorod-rich regions. In between these area (indicated by the blue dashed lines, only spheres are found; (C) Nanosphere diameter distribution histograms for the three regions indicated by 1, 2 and 3 in (A).

of the angular distribution reveals there is no preferential orientation.

Moving more toward the center of the deposited island, a ring-shaped region containing primarily nanospheres is observed. Within these sphere-rich regions, there appears to be separation of nanospheres with different diameters. To quantify this, a section of the ring has been subdivided into three regions, indicated by the vertical dashed blue lines and the numbers 1-3. The histograms in Figure 6.9(C) indeed confirm that with increasing distance from the edge, the average diameter of the spheres increases from approximately 17 ± 3 nm to 27 ± 5 nm.

Further toward the bottom-left in Figure 6.9 a multilayered superstructure containing both spheres and rods is found. Within the dashed red region, the nanorod lengths have been determined. The histogram in the bottom panel of Figure 6.9(B) indicates that the nanorods in this part of the droplet are markedly larger than those at the perimeter of the island. Although the phase-separation both in relation to size and shape of the different nanoparticles is obvious from these results, the exact origin remains to be elucidated. We hope that our present findings provide a motivation for further experimental and theoretical work into the evaporation-induced phase separation of nanoparticles.

6.5 Conclusions

We have presented experimental results of work focused on the use of wettability gradient surfaces to control the motion of liquid droplets and their three-phase contact line. Therewith we explored the potential to use the contact line dynamics as a tool to control nanoparticle deposition over large surface areas. In conventional evaporative self-assembly, nanoparticles generally deposit within the coffee stain ring near the pinned contact line. In this work, we studied the nanoparticle deposits created by the receding contact line at the trailing edge of the moving droplet.

The liquid dynamics on surfaces coated with striped wettability gradients in a linear or radial configuration have been reviewed. Some of the characteristic properties have been reviewed and the occurrence of so-called liquid ‘bridges’ was evaluated. In previous work it was assumed that these liquid bridges covering multiple stripes originated from pinning of the receding contact line at discontinuities between different striped regions of the pattern. A simple model was developed to test this assumption. Comparison of cal-

culated bridge positions with actual experiments has shown that indeed such a mechanism of pinning on discontinuities is highly probable.

In the second part of the work, we studied the deposits and their spatial distribution left by the receding contact line. SEM images after drying revealed that nanoparticle islands were deposited in the center of the hydrophilic stripes. The remarkably high selectivity gave rise to the hydrophobic areas being almost fully depleted of nanoparticles. A number of similarities between radial and linear stripe-patterned gradients were summarized, and also distinct differences have been addressed. Finally, we also zoomed in on individual islands. Surprisingly a highly selective phase separation was observed within the deposited islands. In large deposits, the outer rim consisted primarily of short nanorods while more inward a pure nanosphere phase was found. Analysis of the nanosphere diameters has shown that more toward the center of the islands larger spheres are assembled. Finally, the interior of the islands consisted of randomly oriented multilayered deposits with nanorods with a substantially larger length as compared to those in the outer rim. In case of short deposits, the outer rim is also composed of nanorods while spheres were primarily found in the middle of the wide region of deposits. In the light of many previous reports, we believe that as a result of moving contact line and preferential fluidic flow towards the hydrophilic stripes will facilitate the packing entropy effect and, will finally lead to such distinct phase separation. As a matter of fact, our present finding may well pave the way for further work on elucidating such effect.

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7

Dynamic nanorod alignment on radial stripe-patterned gradients

Controlling the alignment and orientation of nanorods on various surfaces poses major challenges. In this chapter, we investigate hydrodynamic confinement and capillary alignment of gold nanorod assembly on chemically stripe-patterned substrates. The surface patterns consist of alternating hydrophilic and hydrophobic micrometer wide stripes; a macroscopic wettability gradient enables controlling the dynamics of deposited suspension droplets. We show that drying of residual liquid on the hydrophilic stripes gives rise to spatially localized deposition and alignment of the nanorods. Moreover, a universal relation between the extent of order within the single layers of nanoparticles and the lateral dimension of the deposits is presented and discussed.

7.1 Introduction

Anisotropic nanoparticles are attracting considerable attention owing to their potential use in bio-sensing,¹ plasmonics,² catalysis,³ photovoltaics,⁴ surface-enhanced Raman spectroscopy,⁵ wave-guiding,⁶ and metamaterials.^{7,8} Many of these applications rely on aligned arrays of nanoparticles since the collective response of aligned arrays is much more pronounced than that of the individual nanorods. Additionally, the collective response also depends strongly on the number of nanorods within the aligned array. As a result, numerous groups around the world are working on the development of techniques to achieve aligned arrays of nanoparticles at various length scales.

A simple, inexpensive and often used approach to acquire aligned arrays of nanoparticles at relatively large scale is controlled drying of the droplet.^{9–13} Generally, drying of a droplet containing nanoparticles on an isotropic hydrophilic substrate leads to concentrated deposition within the dense coffee stain-like ring.^{14–19} In fact, the static pinned contact line during the evaporation even hinders the homogeneous deposition of nanoentities over a large surface area. Consequently, circumventing the coffee stain effect is a major goal. In that respect, deposition by a moving contact line is particularly interesting because in that case the deposition of micro- and nanoentities is dominated by physical processes on micrometer and nanometer length scales. In the case of a moving contact line, stick-slip motion gives rise to lines of deposited nanoparticles parallel to the drying boundary, which result from alternating pinning/depinning of the three-phase contact line.^{15,20–22} Likewise, spoke-like patterns and branch structures are thought to be the consequences of transverse instabilities of the receding contact line.^{9,23–28} Last year, Thiele published a comprehensive review on patterned deposition by a moving contact line.²⁹ More recently, the focus in evaporative assembly has moved to studying the effect of particle geometry on the assembly process.^{19,30–33} Obviously, the anisotropy of nano- and microparticles has a profound effect on the deposits and their superstructures. Specifically interesting for our work as presented here is the confinement by a three-phase contact line which leads to alignment of elongated nanoparticles parallel to this edge.^{32,33}

Recently, considerable work has been devoted to drying suspensions on morphologically patterned surfaces (with ditches, trenches or troughs).^{34–36} The alignment of nanoparticles in general and nanorods in particular on such substrates was achieved by effectively imposing a rigid constraint through

confinement by steric walls separated by a distance of the same order of magnitude as the length of the nanorods. In addition, capillary forces on the suspension during evaporation within the confined regions will give rise to further alignment of the nanoparticles. As an example, Lee *et al.*³⁷ have shown that patterned silver nanosphere arrays can be formed by a simple dip-coating process. They achieved confinement of nanoparticles using anisotropic buckling templates, while capillary forces were induced by a transferal process from the template to a substrate. These approaches applied to anisotropic nanoparticles have been shown to enable producing aligned arrays that consist of a limited number of nanorods, either oriented end-to-end or side-by-side depending on the width of the confined space. However, the inter-particle distance varied and the orientational order was limited owing to a lack of precise control in these studies. But most importantly, as far as we can judge, confining nanorod suspensions does not allow manufacturing of aligned arrays composed of a large number of nanoparticles in the selected regions.

The work reviewed in the previous sections pertains solely to inorganic particles, with a strong focus on noble metals owing to their plasmonic properties. However, the interactions governing the assembly and deposition are not specific to the type of nanoscale particle. Considerable research has also been devoted to biological systems comprising rod-shaped entities,^{38–41} where the work on virusses such as the Tobacco Mosaic Virus (TMV) is a prominent example. Results by Wargacki *et al.*³⁸ show that convective assembly under proper experimental conditions gives rise to well-order TMV monolayer with all virusses aligned over lengths up to 5 cm. Expanding on this, the use of patterned or wrinkled PDMS substrates was shown to give rise to predefined orientation of the TMV entities.^{39,40} Moreover, Balci and co-workers demonstrated the ability to transfer the aligned TMV using microcontact printing.³⁹ As an example of further work, Lettinga *et al.*⁴¹ considered the effects of hydrodynamic interactions on the orientational ordering, while Lewis and co-workers⁴² studied nematic liquid crystal equilibria of the filamentous *fd*-virus confined to rectangular wells.

Morphologically flat but chemically patterned surfaces have recently been employed in the investigation of nanoparticle deposition.^{43–47} For example, using patterns consisting of alternating hydrophilic and hydrophobic stripes Ahmed *et al.*⁴⁶ observed orientation and alignment of gold nanorods preferentially on top of the hydrophilic stripes on an otherwise morphologically flat

substrate. Aligned nanorods with low aspect ratio were primarily observed at the outer edges of the hydrophilic stripes owing to the capillary confinement. However, within these deposits away from the edge, the nanorods were isotropically distributed.

In this chapter, we focus on the combined use of a macroscopic wettability gradient to control contact line motion and a chemically defined pattern to direct the nanoparticles to specific areas on the surface. We study the effects of hydrodynamic confinement and capillary alignment on the formation of gold nanorod arrays, and clearly reveal the close relation between nanorod orientation and alignment to the capillary pressure induced by confining the liquid to narrow regions. We use morphologically flat, chemically stripe-patterned surfaces consisting of alternating radial hydrophilic/hydrophobic stripes, circularly arranged with a bare hydrophobic center and a bare hydrophilic region at the end of the stripes.^{48,49} The design of the surface pattern allows controlling the motion of the contact line and with that hydrodynamics and capillary interactions can be manipulated to align nanorods in the direction of the stripes. Results are analyzed in terms of a two-dimensional (2D) order parameter. We show that the degree of alignment exhibits a universal trend when relating the order parameter to the width of the nanoparticle deposits.

7.2 Experimental details

7.2.1 Materials

Cetyltrimethylammonium bromide (CTAB, Aldrich, 98%), hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%, Aldrich), silver nitrate (AgNO_3 , 99%, Acros), ascorbic acid (AA, 99%, Merck), sodium borohydride (NaBH_4 , 99%, Aldrich), and hydrochloric acid (HCl , 37%, Merck) were all used as received without further purification. All water that was used in the synthesis was of Milli-Q quality (18.2 M Ω cm), produced in a Simplicity 185 system (Millipore). All experiments were conducted under ambient conditions at room temperature (300 K). Air was not purified from any type of contaminant.

7.2.2 Synthesis

Over the past years, many efforts and successes have been reported pertaining to synthesis of well-defined nanoparticle suspensions with a very low degree

of polydispersity and ultimate control over shape and size. For a more elaborate overview we refer to chapter 2. In the realm of noble metal nanorods, the pioneering work by Murphy and co-workers has proven to be of great importance. In one of their earlier papers, they report excellent yields exceeding 97%.⁵⁰ More recently, a comprehensive review has appeared summarizing most research focused on gold nanoparticle synthesis.⁵¹ In their landmark paper, Lohse and Murphy not only provide a historical overview, but also treat all aspects related to controlling the shape of nanoparticles, including the formation of nanorods.

We adopted the two-step seed mediated protocol as described by Nikoobakht and El-Sayed⁵² to synthesize the gold nanorods used for this study. First CTAB coated seed particles were prepared by adding 25 μl of HAuCl_4 (0.1M) to 10ml of CTAB (0.1M). Next 60 μl of ice cold NaBH_4 (0.1M) was introduced while continuously stirring for a few minutes. The resulting solution quickly turns light brown, which indicates the formation of gold seeds. The solution was kept at 25°C for approximately one hour without stirring.

To synthesize aspect ratio (AR) 6 gold nanorods the growth solution was prepared by adding 50 μl of HAuCl_4 (0.1M) to 10ml of CTAB (0.1M). At room temperature 20 μl of AgNO_3 (0.1M) was added, followed by 70 μl of ascorbic acid (0.1M) with gentle stirring; the resulting solution becomes colorless. Next, 100 μl of HCl (1M) was introduced; the pH of the solution was maintained at approximately 3. Finally, 24 μl of the seed particle suspension was added to the growth solution. This solution was left undisturbed overnight at room temperature.

Before use, the nanorod suspensions were centrifuged at 15000 rpm for 10 minutes to remove the excess CTAB; this translates into 21130 g using the geometry of the rotor (radius 8.4 cm). Subsequently, the suspension was centrifuged again at 5600 rpm (2945 g) for 5 minutes to remove spheres from rods. The nanorod suspensions were stored in the refrigerator.

The nanorod suspension have been analyzed using UV-Vis spectroscopy; a typical spectrum is shown in Figure 7.1(A). It is evident that the suspension still contains a considerable amount of spheres. From careful analysis of the (relative) transverse and longitudinal peaks, we estimate that the nanorod and nanosphere densities amount to approximately $N_{\text{rods}} = 2.0 \times 10^{11} \text{ cm}^{-3}$ and $N_{\text{spheres}} = 2.2 \times 10^{10} \text{ cm}^{-3}$, respectively. Moreover, from the scanning electron microscopy (SEM) images length and width distributions have been determined for 1000 nanorods; the resulting histograms are shown in Fig-

Figure 7.1: (A) Typical UV-Vis spectrum of the gold nanorod suspensions used in this work. The peak near 530 nm is due to the transverse nanorod plasmon resonance and also contains contributions from spheres in the suspension. The peak centered near 980 nm reflects the longitudinal plasmon resonance of the nanorods. (B, C) Histograms of nanorod length L and width W , respectively; in total 1000 nanorods in SEM images were counted.

Figure 7.2: Atomic force microscopy (AFM) image of a PFDTs stripe (brighter region) on an SiO_2 substrate. The height of the PFDTs layer relative to the substrate amounts to approximately 1 nm; the width of the stripe is 6 μm .

ures 7.1(A,B). The resulting nanorods have an average length $L = 56 \pm 12 \text{ nm}$ and diameter $W = 10 \pm 1 \text{ nm}$; the error derives from the standard deviation in the size distributions.

7.2.3 Sample preparation and droplet deposition

The radial patterned surfaces consisting of alternating hydrophilic and hydrophobic stripes on silicon wafers were manufactured using standard clean-room facilities. The hydrophobic regions are formed by self-assembled monolayers (SAMs) of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTs, 97%, ABCR, Germany). Details of the surface preparation and the pattern designs are explained elsewhere.⁴⁸ In Figure 7.2 an atomic force microscopy image of a PFDTs stripe is shown, demonstrating the homogeneity of the PFDTs layer. The thickness amounts to approximately 1 nm; the RMS roughness is below 0.5 nm.

A schematic representation of the radial stripe-patterned gradient surface is shown in Figure 7.3(A). In our previous work,^{48,49} we demonstrated that such patterns induce controlled motion of pure liquid droplets over distances up to a few millimeters. Typically, the pattern designs consist of an isotropic hydrophobic region, coated homogeneously with PFDTs where the droplet is deposited; this corresponds to the center of the radial pattern in Figure 7.3.

Figure 7.3: (A) Schematic representation of the pattern used to create the radial wettability gradients; note that the stripe widths are not to scale. The gradient is created by the transition from the homogeneous PFDTs (gray) to the unpatterned SiO_2 (blue) via radial striped regions with decreasing macroscopic hydrophobicity. (B) SEM image depicting a general overview of the residual deposits after placement, movement (from right to left) and subsequent drying of a nanorod suspension on a radial striped wettability gradient. Bright parts represent the gold nanorods, while the deposits with a darker gray shade (on the left) are most likely CTAB layers.

The gradient is formed by subsequent striped regions (indicated as radial 1, 2 and 3 in Figure 7.3) consisting of alternating hydrophobic (PFDTs) and hydrophilic (SiO_2) stripes with increasing macroscopic surface energy, which creates a preferential spreading direction for the droplets. We use a dimensionless parameter $\alpha = w_{\text{PFDTs}}/w_{\text{SiO}_2}$ to quantify the relative hydrophobicity of the pattern,⁵³ where w_{PFDTs} and w_{SiO_2} represent the hydrophobic PFDTs and hydrophilic SiO_2 stripe widths, respectively. Areas with smaller values for α correspond to larger overall surface energy, and as such are more hydrophilic. The range of α values considered in our work amounts to 0.9 – 0.25 for all patterns.

Substrates were ultrasonically cleaned in acetone for 5 minutes at room temperature. Then the substrate was rinsed with ethanol and distilled water and dried in a nitrogen flow. A $5\mu\text{l}$ droplet of the nanorod suspension was placed on the clean radial patterned substrate and allowed to evaporate at room temperature. Within two hours the solvent was completely evaporated.

7.2.4 Characterization

High-resolution scanning electron microscopy (SEM; on a Merlin Zeiss 1550 system) was used for imaging of our samples; typical voltages in the range 0.1 – 30 kV are accessible. Images that are used in this work were taken at an accelerating voltage of 2 kV.

7.3 Results

The dynamics of liquid droplets on radial patterned surfaces and the influence of design parameters has been discussed in detail by Bliznyuk *et al.*⁴⁸ Here, we study the effect of droplet dynamics on nanorod deposition and alignment on radially patterned hydrophilic stripes. As soon as a droplet of nanorod suspension has been placed on the patterned surface with a radial wettability gradient, the droplet is forced to move away from the center of the pattern. The advancing edge of the droplet will become pinned as it reaches the hydrophilic (bare SiO_2) region, which surrounds the stripe-patterned area. The receding contact line will move over the stripe-patterned regions, but will eventually also be pinned by the prolate nanoparticles in the suspension.^{11,54} Upon further evaporation of the solvent, the receding edge of the drying droplet will exhibit stick-slip like motion. As a result, the corrugated con-

tact line on the patterned areas of alternating hydrophilic and hydrophobic stripes leaves behind a trail of small patches of nanorod suspension (see also chapter 6). After complete evaporation of the solvent, islands consisting of single, sub-monolayers of nanorods remain on the hydrophilic stripes. A typical overview of the residual deposits is shown in Figure 7.3(B).

A larger overview of deposited nanorod islands is shown in the electron microscopy image in Figure 7.4(A). The nanorod deposits show up as bright regions, which are all located on the hydrophilic set of stripes. Remarkably the hydrophobic stripes are completely depleted of nanorods. The direction of receding motion was from right to left. On the right of Figures 7.3(B) and 7.4(A) the initial pinning of the receding edge due to the nanoparticles is clearly visible; considerable accumulation of nanoparticles leads to relatively large deposits at the three-phase contact line. Upon gradual receding of the contact line, the initially deposited patches as indicated by the enclosed yellow box in Figure 7.4(A) consist of nanorod islands which are nearly continuous over a length of approximately $100\mu\text{m}$. After this initial deposition, the contact line appears to slip leaving a region depleted of nanorods over a distance of approximately $10\mu\text{m}$ (gap between yellow and red boxes). Pinning and subsequent receding of the contact line again leads to deposits over a length of $50\mu\text{m}$ (indicated by the red box in Figure 7.4(A)). More generally, the length of the deposited islands seems to decrease with receding distance, as shown in the green box and further to the left. To obtain a more quantitative description of the island size and their distribution, more work is needed in this area.

As has been shown by Thiele and co-workers,^{29,55} moving contact lines of solutions containing non-soluble components over homogeneous substrates leave behind deposits of different shapes. Concentration of the suspension and receding velocity of the three-phase contact line are key parameters in defining the shape and distribution of the deposited materials. Most likely a similar mechanism applies to our system of a nanoparticle solution of the striped surface.

Now we turn our attention to the spatial distribution and the alignment of nanorods within the deposits. We zoomed in on the individual islands; two examples are shown in Figure 7.4(B) and Figure 7.4(C), with an even further enlargement in Figure 7.4(D) showing individual nanorods. Careful observation reveals that the deposited islands all consist of only a single layer of nanorods, which all lie flat on the substrate. Moreover, the narrow

Figure 7.4: (A) SEM image of nanorods deposited on a radial stripe-patterned surface. (B, C) SEM images of typical deposited islands. The image in (B) is divided into six sections for further analysis; the green arrow represents the direction of flow during drying. (D) Enlarged view of the central section in (B) showing individual nanorod orientations. A low density of spheres is clearly observed in (D), limiting the long-range ordering of the nanorods.

deposits are depleted of nanospheres; the trace nanospheres in Figure 7.4(D) are considerably smaller in number as is to be expected on the basis of their relative concentration in suspension.

Upon examining many deposits, the orientation and the mutual alignment of the elongated particles seems to be affected by the width of the deposits. For example, in the wide regions (left and right of Figure 7.4(B)) the nanorod distribution is more isotropic and loosely packed, while for the narrower regions in the middle (see also the enlarged image in Figure 7.4(D)) the nanorods are consistently more oriented along the stripe direction, packed more closely and markedly more aligned with neighboring nanorods.

To analyze the nanorod orientation with respect to the receding direction (parallel to the stripes), we divided the images of several deposited islands into different regions, as shown by the red dotted lines in Figure 7.4(B). For each region, a histogram of the nanorod orientation was obtained. For all nanorods within the region, the angle with respect to the stripe direction was determined. The resulting distributions are shown in Figure 7.5. For the widest regions in the deposited island (top and bottom panel in Figure 7.5) there does not seem to be a preferred orientation; the histogram exhibits an isotropic distribution of the nanorod orientation. As the width of the deposited island decreases (corresponding to the middle panels in Figure 7.5) the orientational distribution becomes more focused, with only small angles showing a high probability. Most prominent is the result in panel 4, which reveals a significantly larger count at small angles as compared to all others.

To quantify the extent of ordering within assemblies of anisotropic (nano)-particles, frequently the 3D order parameter S_{3D} is used in liquid crystal literature,^{56–58} which is given by

$$S_{3D} = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle \quad (7.1)$$

where θ is the angle of each nanorod with respect to a specific direction, referred to as the director. Averaging over all nanorods yields a value $S_{3D} = 1$ for perfect alignment parallel to the director, while $S_{3D} = 0$ corresponds to an isotropic distribution.

However, as outlined above in relation to Figure 7.4(C) the nanorods in our experiments are distributed within a single layer on the substrate and are all oriented parallel to the substrates. Instead of using the 3D order parameter

Figure 7.5: Histogram of nanorod orientation angles within the different sections in Figure 7.4(B). The average order parameter (Equation 7.2; details are in the text) is indicated in each panel.

in Equation 7.1, we use the 2D order parameter^{59,60} given by

$$S_{2D} = \langle 2 \cos^2 \theta - 1 \rangle. \quad (7.2)$$

Similar to the 3D order parameter, $S_{2D} = 0$ represents a random orientation, while perfect alignment of all rods parallel to the director, i.e. the direction along the stripes and thus the flow direction, yields $S_{2D} = 1$.

For all nanorods within regions as indicted in Figure 7.4(B) the angle with respect to the stripe direction was determined, and using Equation 7.2 the order parameter was calculated for the different regions. The specific values corresponding to the different regions in Figure 7.4(B) are given in the respective histograms in Figure 7.5. The numerical values confirm our statement that the narrower regions of the deposited islands exhibit more ordered arrangements as compared to the wider regions further from the center of the neck.

To visualize the relation between orientational ordering and the width d of the deposits, the order parameter S_{2D} is plotted as a function of d for different islands, including those in Figures 7.4(B) and 7.4(C). The result is shown in Figure 7.6(A), where d is normalized to the nanorod length L ; a schematic representation of the nanorod orientation and alignment as a function of width of the deposit is included in Figure 7.6(B). The various colors represent the result of analysis of different narrow regions on the surface. Clearly, the fact that all data points in Figure 7.6(A) for different deposited islands follow the same trend (dashed line) indicates that there appears to be a universal mechanism controlling the orientation of the nanorods within the drying deposits on the hydrophilic stripes. In the next section we will qualitatively discuss this in relation to other work reported in literature. Finally, the dashed line represents an exponential fit, merely serving as a guide to the eye. For very small distances, the order parameter S_{2D} approaches 1, implying that in the limit of vanishing width d the orientation is complete; for larger widths the order parameter decreases to $S_{2D} = 0$ as is to be expected for an isotropic distribution.

Finally, we focus on the width-dependent ordering of the nanorods, as expressed by the results in Figure 7.6(A). The fact that all data obtained on different islands with varying width ranges follow the same trend suggests there is a universal mechanism controlling the collective orientation of the nanorods. As outlined above, steric interaction is the most probable candidate for dictating the order. As such our results compare nicely to a vast

Figure 7.6: (A) The 2D order parameter S_{2D} as a function of width d of the deposited nanorod islands, normalized to the nanorod length L ; the dashed line represents an exponential fit serving as a guide to the eye. Colors indicate results for different narrow regions on the surface. (B) Schematic representation of orientation and alignment under the influence of capillary confinement.

amount of work devoted to understanding the isotropic-to-nematic phase transition within suspensions of anisotropic particles (rods and plates) near a wall. Interesting and relevant work in this respect is the study by Akbulut *et al.*,⁶¹ in which they measure normal forces between mica surfaces mediated by surfactant-coated ZnS nanorods in organic solvents. Upon closing the gap between the surfaces, they observe characteristics of the isotropic-to-nematic phase transition.

Many simulations have been done,^{62–64} while the analysis of results is always performed in relation to the pioneering work by Onsager.⁶⁵ In this seminal work a rigorous statistical mechanical approach is taken to determine the Helmholtz free energy in terms of virial coefficients, with contributions both from orientational and packing entropy. Many papers consider the limit of long thin rods, for which the higher order virial coefficients vanish.^{66,67} However, this does not hold for our low-aspect ratio nanorods. Although a full quantitative treatment lies outside the scope of this work, we can qualitatively explain the relation between confinement width and orientation as observed in Figure 7.6(A). The relevant parameter is the excluded volume for hard rod, i.e. spherocylinders with length L and width W

$$V_{\text{excl}} = 2(L - W)^2 W \sin \theta + 2\pi W^2 (L - W) + \frac{4}{3}\pi W^3 \quad (7.3)$$

where the first term is dominant and the last two terms are smaller contributions describing the actual shape (end caps) of the nanorods. As the width of the deposits decreases the available volume decreases therewith effectively increasing the free energy of the system. To minimize this, orientation of the nanorods and therewith reducing the excluded volume leads to a more favorable configuration from a free energy point of view.

Although our results are in qualitative agreement with previous experimental and theoretical work, there are clear differences. Many reports of earlier work considered anisotropic colloidal particles confined between two walls, i.e. a two-dimensional system. In that case the isotropic-to-nematic transition occurs within a distance corresponding to several times the long dimension of the particles. In contrast, we find that the order parameter in Figure 7.6(A) decreases substantially over distances as large as 10-20 times the rod length, which may be related to confinement being both in the direction perpendicular to the stripes as well as perpendicular to the substrate. Clearly, more work is required to provide a theoretical benchmark for these observations.

7.4 Discussion

On smooth surfaces with isotropic wetting properties, drying of a droplet containing suspended nanoparticles will give rise to deposition of most particles within a region near the contact line, which is often referred to as the ‘coffee-stain’ ring.^{11,14,16–18,31,33} On such surfaces, the nanoparticle superstructures are generally multi-layered and exhibit different arrangements at varying distance from the contact line. Recently, we showed that in the case of nanorod deposits, various locations within this coffee-stain ring exhibit different domains in terms of particle organization.¹¹ Dugyala and Basavaraj³³ reported very similar results, including a description of the different parameters enabling further control over the nanorod orientation.

Close examination of the spatial nanoparticle distributions in the results described in the aforementioned work on evaporative assembly,^{11,33} and also images such as those in Figures 7.4 and 7.7, reveals that the thickness of the deposited islands increases with distance from where the three-phase contact line was pinned during the drying of the droplets. Very close to the edge, single layers of non-close packed nanorods are observed, while further from the edge multilayered assemblies occur. This suggests that the thickness of the liquid layer in which the nanoparticles are confined have a profound influence on the resulting nanoparticle assemblies. Although the physics of our present system is completely different, the complexity of the nanoparticle interactions and layering of nanoparticles is quite similar to what has been reported in the spreading of nanofluids^{68–71}

As outlined in relation to the results in Figure 7.4, the narrow regions primarily consist of a single layer of nanorods oriented parallel to the substrate; these areas do not contain a large number of spheres. Figures 7.7(A-E) show additional deposits with the neck region composed of close packed nanorods and the wider regions are showing similar (as observed in chapter 6) hexagonally packed spheres surrounded by thin nanorods. This suggests that the combination of nanorods and nanospheres in the suspension induces depletion interaction, which may also play a role in the orientation and mutual alignment. As we have shown in our recent work¹¹ (see also chapter 5) the magnitude of depletion interactions in our suspensions comprises only a small contribution in the overall interparticle interaction. Moreover, when zooming in on the nanoparticle deposits, as shown in Figure 7.7, the separation between regions with a high rod density and sphere-rich areas is obvious. The

Figure 7.7: (A) SEM image of nanoparticle islands with wider regions connected by small neck regions on each hydrophilic stripe. (B) Zoom in on one of the necks revealing the preferential accumulation of nanospheres in the wider sections, while the narrow deposits only contain a relatively small number of nanospheres as compared to the nanorods. (C) Zoom in of the rectangular region in B. (D, E) Close-packed nanorods in the narrow regions of the neck.

nanospheres assemble in packed regions within the wider bulges of the deposited islands; in Figure 7.7(A) these nanosphere patches appear as brighter regions in the SEM image. We assume this phase separation to originate from a similar mechanism as described earlier,¹¹ where depletion interaction has a limited contribution.

In contrast to the isotropic droplets where nanorods assemble preferentially at the droplet perimeter, our results presented in this work demonstrate that a chemically defined pattern gives rise to markedly different spatial arrangements. On the radial stripe-patterned substrates with a macroscopic wettability gradient forcing liquid outward, the three-phase contact line motion is not the same in all directions. The top-left panel of Figure 7.8 schematically depicts the behaviour of a drying droplet, which is partly on a homogeneous isotropic surface (SiO_2 , on the left side) and partly in contact with the stripe-patterned surface. Once the initial translational motion of the droplet has stopped, the portion of the droplet that resides on the SiO_2 will remain pinned during drying, much like the case of a droplet on an isotropic surface. Similarly arranged regions as described previously¹¹ are observed in this part of the droplet.

On the other hand, the edge of the droplet on the stripe-patterned region recedes in a stick-slip like motion towards the hydrophilic SiO_2 region. On the stripe-patterned areas, flow of liquid from the hydrophobic PFDTs to the hydrophilic SiO_2 stripes will drive the nanorods to the center of these wetting stripes. This hydrodynamic confinement effect is depicted in the top-right panel in Figure 7.8 by the red arrows. Subsequent drying of the liquid, preferentially in the direction defined by the gradient (right to left in this case; indicated by the blue arrows) induces capillary forces that we consider to give rise to the alignment of individual nanorods.

We can compare our results to recent work on drying of colloidal nanorod suspensions on stripe-patterned surfaces⁴⁶ without a wettability gradient. A clear similarity observed in both studies is that the nanoparticles preferentially accumulate at the hydrophilic stripes. But in contrast to our present results, in the case of Ahmed and co-workers⁴⁶ there was no gradient forcing the liquid in a specific direction. As a result, the nanorods were deposited over the entire hydrophilic stripe. A ‘neck’ in the deposited nanoparticle patches, as we observed for example in Figure 7.4(A), does not occur. On the other hand, Ahmed *et al.*⁴⁶ report that confinement of the nanorods close to the edges of the deposits leads to orientation along the direction of the

Figure 7.8: (top-left) Schematic representation of a drying droplet containing suspended nanorods. (top-right) Schematic representation of the contact line (green dotted line) on the patterned surface. Red arrows indicate the hydrodynamic force driving nanorods toward the center of the hydrophilic stripes; blue arrows indicate the macroscopic receding direction of the outer perimeter (blue dotted line) of the droplet. (middle) Schematic view of nanorods within the fluid residues, and (bottom) subsequent drying leading to the capillary alignment.

three-phase contact line.

The aforementioned argument suggests that the neck occurring in our deposited nanoparticle islands is related to the gradient in our patterned surface. We assume that after the contact line becomes pinned on the striped regions, as in the right of Figure 7.4(A), the liquid is continuously pulled toward the left during drying. Due to the surface tension, the highly asymmetric residues on the hydrophilic stripes destabilize and break up into smaller fluidic islands, some remaining connected by a thin neck. Unfortunately, the limited resolution of optical microscopy does not allow us to observe such break-up of the liquid stripes. We ascribe the fact that the neck does not completely break or disappear to the nanoparticles pinning the three-phase contact line.

The receding motion of the liquid gives rise to a clear anisotropy in the deposited islands. Both isolated islands, but also patches connected by a neck will most likely give rise to unidirectional flow of residual solvent in these patches. As a consequence, both (i) the confinement of the nanorods to the residual liquid deposits (schematically shown in the middle of Figure 7.8) and (ii) the directional receding of the solvent (bottom of Figure 7.8) giving rise to capillary alignment, will enhance the orientation of the nanorods. A similar effect has been reported for the hydrodynamic alignment and assembly of cellulose nanofibrils in a focussed flow.⁷² Limitation of rotational Brownian motion in a narrow flow channel⁷³ gives rise to orientation of the high aspect ratio fibrils to ultimately produce strong cellulose filaments.

In relation to the above, the length of the deposited islands will probably depend on the nanorod density near the contact line on each hydrophilic stripe. The presence of a large number of nanorods near the contact line will keep the fluid in contact with the surface through pinning and therefore will deposit long islands. Also, the arrival of nanorods to the contact line will probably dictate the pinning time during drying. Such a mechanism based on a fixed and partially pinned contact line introduces a novel approach of droplet drying, which has the advantage of large scale deposition.

7.5 Conclusions

We have studied the deposition of anisotropic gold nanorods from drying droplets on chemically defined radial wettability gradients on morphologically flat substrates. The gradient forces the contact line to recede in the direction

parallel to the alternating hydrophilic and hydrophobic stripes, typically having widths in the order of a few micrometers. After receding and drying of the droplet, patches of nanorods remain only on the hydrophilic stripes. The patches seem to resemble a stick-slip like receding motion. More close examination reveals that the nanorod islands exhibit a variety of self-assembled nanoparticle distributions.

In this chapter, we focused on elongated parts of the patches, where only single layers of mutually aligned nanorods are observed. We presented the systematic variation of the average order parameter as a function of the width of the deposits. In wide regions, typically exceeding 10-20 times the nanorod length, isotropically oriented nanorod arrays are found, while for much narrower assemblies a strong preferential orientation parallel to the stripe direction is found.

The results have been discussed in terms of a mechanism, which takes into account effects due to hydrodynamic confinement and capillary alignment during the drying process. Essentially, during receding of the contact line the nanorod suspension is driven towards the center of the hydrophilic stripes. Consequently, this will establish the hydrodynamic confinement effect from both sides of the hydrophilic stripes. Furthermore, the drying of the fluid residues induces capillary forces in the direction along the stripes.

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Summary

Assembly of nanoparticles is of enormous interest owing to their diverse application in numerous areas of science and technology. Anisotropic nanoparticles are in this respect particularly important due to their shape anisotropy and corresponding interesting optical properties. In fact, anisotropy in nanoparticle shape also poses specific challenges when considering their assembly into nanoparticle arrays. For instance, suspended nanoparticles with a rod-like shape moving under the influence of Brownian motion not only exhibit translational but also rotational movement. In that respect, the self-assembly of nanorods at precise locations with well-defined number of assembled layers is a real challenge as compared to spherical nanoparticles. In this thesis, the deposition of gold nanoparticles is carried out by evaporation of the suspension droplets on various surfaces, followed by characterization of the self-assembly in relation to the specific characteristics of the substrate.

The dominant nanoscale interactions that govern the self-assembly process in suspension are the well-known Van der Waals attraction and electrostatic repulsion. The magnitude and also directionality of the aforementioned interactions can be tuned accordingly by varying the precise shape and size of the nanoparticle; also the solute concentration and nature of counterions is relevant. Other interactions such as depletion and steric interaction are more important in relation with phase separation of different shapes and sizes. Essentially, one cannot ignore the effect of evaporation conditions and capillary forces in the self-assembly process and their role in deposition of assembled arrays close to the contact line. Furthermore, packing and mixing entropic effects in concentrated and diluted suspension, respectively, play an important role in ordered and disordered arrangements of deposited nanoentities.

Chapter 2 reviews experimental details of this thesis and focusses on the

syntheses of low aspect ratio gold nanorods. We provide a brief summary of the different synthesis approaches, which have been described in literature, and discuss the well-known and frequently employed seed mediated technique. The synthesis of low aspect ratio nanorods as used in this thesis is done using this seed mediated approach. To tune the specific shape we studied the effect of varying the silver nitrate and HCl concentrations during synthesis. UV-Vis spectroscopy and electron microscopy (SEM) images are used to characterize the products in relation to the reagents and other conditions employed in the nanoparticle fabrication. Furthermore, the role of each species used for the synthesis is described on the basis of previously published work.

A comparison of two state-of-the-art microscopy tools is presented in chapter 3. Using both electron microscopy (SEM) and helium ion microscopy (HIM) imaging, we show how the gold core as well as the surrounding thin cetyltrimethylammonium bromide (CTAB) stabilizing layer can be visualized. Our results clearly demonstrate that in SEM electrons interact more with the gold core than the hydrocarbon layer formed by the surfactant (CTAB) molecules. On the other hand, in HIM the helium ions interact strongly with the hydrocarbon chains of the stabilizing CTAB layer around gold nanorods, essentially rendering the gold cores invisible. However, by tuning the imaging parameters, the CTAB capping layer and the gold nanoparticles can selectively be visualized using both techniques. In HIM this is achieved by simultaneously recording the secondary electron (SE) and backscattered helium ion (BSHe) signals. A similar result in SEM is achieved by switching between ultralow voltage and considerably higher voltages. This allows for a quantitative determination of the dimensions of the CTAB shell around the gold nanorods. Both techniques yield a CTAB shell thickness of 1.0-1.5 nm.

In chapter 4 we study the deposition of CTAB stabilized gold nanorods on well-defined HOPG surfaces. Droplets of nanorod suspension were dried on freshly cleaved HOPG surfaces. Nanoparticle deposits were observed in coffee stain-like rings. SEM analysis reveals that gold nanorods are preferentially deposited along the step-edges, while terraces were found to be mostly depleted of nanoparticles. Some of the terraces are decorated with small bunches of close-packed side-by-side arrays of nanorods. Interestingly, nanorods with the step-edges are oriented in such a way that their long axis is always oriented in the direction of the step-edge. However, SEM images did not enable us to confirm the position of nanorod with respect to the

lower and upper terrace of the step-edge. For this we analyzed our samples using scanning tunneling microscopy (STM). Clusters of nanorods as well as isolated nanorods were observed, but owing to the limited scan range in STM the nanorods were not found along the step-edges. Moreover, despite the fact that we have been able to image CTAB coated gold nanorods, the stabilizing layer hinders accurate quantitative analysis of the nanorod dimensions. The aforementioned limitations are not an issue in atomic force microscopy (AFM), which we used to assess the actual positions of the gold nanorod at the step-edges. From AFM images we find that the nanorods are deposited on the lower terrace of the step-edge.

Close examination of the AFM images has revealed that not only nanorods can be imaged, but we also observed the self-assembly of access CTAB over a large portion of the HOPG surface. Striped phases of CTAB superstructures occurs in islands on the surface, with typical heights in the range of 1-3 nm. The outer shape of the islands does not seems to reflect the symmetry of the substrate. However, the stripes within the islands exhibit approximately 60° and 120° angles with each other, most likely due to the structure of the HOPG. Analysis of the stripe dimensions, i.e. width, height and spacing, indicates that, in line with previous reports in literature, the stripes consist of multiple hemicylindrical micelles separated by a distance corresponding to the length of a single CTAB molecule. The self-assembled layers of CTAB on the HOPG surface appear to lead to a modification of the wettability of the surface; as a results, we observe the hydrophilic gold nanorods preferentially deposited on top of the self-assembled surfactant molecules.

In chapter 5 we study the phase separation of rods and spheres in aqueous nanoparticle suspension during evaporation at room temperature. Typical coffee stain-like deposits are observed with different nanoparticle distributions at various positions within the ring. Depending on the position relative to the contact line of the drying droplet, spheres and rods separate into various liquid crystalline phases. We attribute the phase behavior to convective flow, which changes as the environment within the droplet become denser owing to the continuous decreasing droplet volume during evaporation. Nanorods exhibit a strong preference for side-by-side alignment, giving rise to smectic phases; spheres in solution are forced out of these regions and form close packed arrays. We discuss this self-separation into nanorod and sphere-rich phases in terms of various interactions, including electrostatic, van der Waals, and depletion interactions. The experimental results are compared to

quantitative calculations of the colloidal interaction energies. The aforementioned interactions ultimately provide a net interaction energy depending on particle shape, size and orientation. Both the experimental results, as well as the theoretical analysis confirm that the side-by-side arrangement of the nanorods is the lowest energy state for our system. Although the overall attractive interaction plays a major role in bringing the nanoparticles together in suspension, we also discuss the possibility that short-range steric interaction caused by the CTAB-coating on the nanoparticle surface could play a role in the self-separation of spheres and rods. Finally we also describe and discuss the role of the surfactant on the different crystal facets of the nanorods in relation to the phase separation.

Chapter 5 covers the deposition of nanoparticles from drying suspension droplets on smooth surfaces with isotropic wetting properties, which gives rise to predominant assembly near the pinned contact line, i.e. the coffee stain ring. In chapter 6, we investigate the deposition of anisotropic gold nanorods from drying droplets on chemically defined linear and radial wettability gradients on morphologically flat substrates. Experimentally we explore the potential of using pre-defined motion of a receding contact line to control the deposition of nanoparticles from suspension. Stripe patterned wettability gradients consist of alternating hydrophilic and hydrophobic stripes with increasing macroscopic surface energy. The gradient in the surface design forces the contact line to recede in the direction parallel to the alternating hydrophilic and hydrophobic stripes having widths typically in the order of a few micrometers. Nanoparticle suspensions containing nanorods and nanospheres are deposited onto these substrates and left to dry. After moving over the pattern and evaporation of the solvent, characteristic nanoparticle deposits are observed. The liquid dynamics has a pronounced effect on the spatial distribution. Nanoparticles do not deposit on the hydrophobic regions; there is high preference to deposit on the wetting stripes. Moreover, the fact that distributed nanoparticle islands are formed suggests that the receding of the contact line occurs in a stick-slip like fashion. Furthermore, the formation of liquid bridges covering multiple stripes during motion of the droplet over the patterns is modeled. We discuss the origin and show that the residue after drying, containing both nanoparticles and the stabilizing surfactant, also resembles such dynamics.

A number of similarities between radial and linear stripe-patterned gradients have been summarized in chapter 6 and distinct differences have been

addressed. Finally, we also zoomed in on individual islands. Surprisingly a highly selective phase separation was observed within the deposited islands. In large deposits, the outer rim primarily consists of short nanorods while more inward a pure nanosphere phase was found. Analysis of the nanosphere diameters has shown that more toward the center of the islands larger spheres are assembled. The interior of the islands consisted of randomly oriented multilayered deposits with nanorods with a substantially larger length as compared to those in the outer rim. In case of short deposits, the outer rim is also composed of nanorods while spheres were primarily found in the middle of the wide region of deposits. We suggest that the moving contact line and preferential fluidic flow towards the hydrophilic stripes facilitates the packing entropy effect and gives rise to such distinct phase separation.

Controlling the alignment and orientation of nanorods on various surfaces poses major challenges. In chapter 7 we zoom in on the individual islands which were already observed in chapter 6, and more specifically on the narrow elongated regions separating neighbouring islands on the hydrophilic stripes of radial wettability gradients. Focusing on the elongated parts of the patches, where only single layers of mutually aligned nanorods are observed, we observed a systematic variation of the average order parameter as a function of the width of the deposits. In wide regions, typically exceeding 10-20 times the nanorod length, isotropically oriented nanorod layers are found, while for narrower regions a strong preferential orientation parallel to the stripe direction was found. We presented the resulting mechanisms, which takes into account the effects of hydrodynamic confinement and capillary alignment during the drying process. Essentially, during receding of the contact line the nanorod suspension is driven towards the center of the hydrophilic stripes. Consequently, this will establish a hydrodynamic confinement from both sides of the stripes. In addition, the drying of the fluid residues induces capillary forces in the direction along the stripes. Moreover, a universal relation between the extent of order within the single layers of nanoparticles and the lateral dimension of the deposits is presented and discussed. Qualitatively we attribute the alignment of rods to the width of the deposits; with decreasing width the available volume diminishes, and consequently, free energy of the system will increase. To compensate the nanorods preferentially align, therewith reducing their orientational entropy but increasing the translational entropy.

Samenvatting

Zelf-assemblage van nanodeeltjes trekt momenteel veel aandacht dankzij de vele mogelijke toepassingen in verschillende onderzoeksdomeinen en de industrie. Anisotrope nanodeeltjes zijn extra interessant vanwege hun asymmetrische vorm en de daaraan gekoppelde optische eigenschappen. Daar komt bij dat de anisotrope vorm specifieke uitdagingen opwerpt als het gaat om de zelf-assemblage in grotere structuren. Als voorbeeld noemen we nanostaafjes in oplossing, die onder invloed van Brownse beweging niet allen verplaatsen maar ook zullen roteren. In dat opzicht zorgt de zelf-assemblage van nanostaafjes structuren op goed-gedefinieerde plaatsen voor een aanzienlijke uitdaging in vergelijking met ronde deeltjes. In dit proefschrift wordt de depositie van goudstaafjes bewerkstelligd door verdamping van de vloeistof waarin de deeltjes opgelost zijn. Zelf-assemblage en de gevormde samengestelde structuren worden gekarakteriseerd en geanalyseerd in relatie tot de specifieke eigenschappen van de substraten.

De belangrijkste interacties op nanoschaal die een rol spelen in de zelf-assemblage in oplossing zijn aantrekkende Van der Waals en afstotende elektrostatische krachten. De grootte en ook de richting van de genoemde interacties kan worden ingesteld door variatie van de vorm en grootte van de nanodeeltjes. Daarnaast is ook de concentratie en type van opgeloste moleculen en ionen in de oplossing relevant. Andere interacties zoals depletie en sterische interacties zijn belangrijk in relatie tot fasescheiding van deeltjes met verschillende vorm en grootte. De rol van verdamping van het oplosmiddel en capillaire krachten op de depositie van grotere structuren kan niet verwaarloosd worden in de nabijheid van de contactlijn. Bovendien spelen stapeling en entropie ten gevolge van menging in respectievelijk geconcentreerde en verdunde oplossingen een belangrijke rol in geordende en

wanordelijke rangschikkingen van afgezette nanodeeltjes.

Hoofdstuk 2 geeft een overzicht van de experimentele aspecten van dit proefschrift en behandelt de synthese van goud nanostaafjes met een kleine aspect ratio. We geven een korte samenvatting van de verschillende methodes om nanostaafjes te maken zoals beschreven in de literatuur. In dat kader bediscussieren we de veel gebruikte methode waarbij kiem-kristallen worden toegepast. Deze fabricage methode vormt de basis voor de nanostaafjes zoals die in dit proefschrift worden gebruikt. Om de uiteindelijke vorm te kunnen beïnvloeden hebben we het effect van zilvernitraat en zoutzuur concentratie tijdens de synthese bestudeerd. UV-Vis spectroscopie en elektronen microscopie afbeeldingen worden gebruikt bij de karakterisatie van de producten in relatie tot de gebruikte reagens en andere experimentele condities tijdens het maken van de deeltjes. Daarnaast bespreken we op basis van eerder gepubliceerd werk de rol van de verschillende stoffen die gebruikt zijn voor de synthese van de nanostaafjes.

Twee state-of-the-art afbeeldende microscopietechnieken worden met elkaar vergeleken in hoofdstuk 3. Met behulp van elektronenmicroscopie (SEM) en ook met heliumionmicroscopie (HIM) kunnen we zowel de goud kern als ook de omringende dunne laag stabiliserend cetyltrimethylammonium bromide (CTAB) zichtbaar maken. Onze resultaten laten duidelijk zien dat elektronen in de SEM sterker interacteren met de goud kern dan met de koolwaterstof laag gevormd door de CTAB moleculen. Anderzijds zijn de heliumionen veel gevoeliger voor de koolwaterstof laag, waardoor het goud effectief onzichtbaar is; de ionen dringen niet diep genoeg binnen. Echter, door de parameters waarmee de afbeelding worden gemaakt te variëren kunnen de CTAB laag of de goud kern selectief zichtbaar worden gemaakt door beide technieken. In HIM bereiken we dit door tegelijkertijd de secundaire elektronen (SE) en terugverstrooide heliumionen (BSHe) te meten. Een vergelijkbaar resultaat is mogelijk in de SEM door te schakelen tussen hele lage en aanzienlijk hogere spanningen. Dit maakt het mogelijk om kwantitatief de dimensie te bepalen van de CTAB schil, die de goud staafjes omringt; beide technieken leveren een CTAB dikte van 1-1.5 nm.

In hoofdstuk 4 bestuderen we de depositie van CTAB gestabiliseerde goud nanostaafjes op goed-gedefinieerde grafiet (HOPG) oppervlakken. Druppels van de suspensie met nanostaafjes laten we indrogen of verse, gekliefde HOPG oppervlakken. Dit leidt tot gedeponeerde nanodeeltjes in typische koffievlek ringen. Analyse van SEM afbeeldingen leert ons dat de goud nanostaafjes

bij voorkeur worden afgezet langs de stapranden, terwijl terrassen nagenoeg vrij zijn van nanodeeltjes. Op sommige terrassen treffen we kleine clusters van dichtgepakte, zij-aan-zij georiënteerde staafjes aan. De staafjes in de nabijheid van de stapranden zijn in alle gevallen gericht langs die stapranden. Helaas is het niet mogelijk om op basis van SEM afbeeldingen te bepalen of de staafje langs deze stapranden op het bovenste of onderste terras liggen. Om kwantitatieve informatie over de hoogte te krijgen hebben we onze substraten onderzocht met behulp van scanning tunneling microscopie (STM). We vonden zowel clusters met nanostaafjes als ook geïsoleerde nanodeeltjes, maar gehinderd door het beperkte scanbereik in de STM hebben we geen staafjes langs de stapranden kunnen waarnemen. Hoewel het mogelijk was om de goud staafjes zichtbaar te maken met STM, bleek de stabiliserende CTAB laag een kwantitatief accurate bepaling van de hoogte en daarmee de afmeting van de nanodeeltjes onmogelijk te maken. De genoemde nadelen doen zich niet voor in atomaire krachtmicroscopie (atomic force microscopy; AFM), waardoor deze techniek ons wel in staat stelde om de exacte positie en dimensies van de staafjes te bepalen. Uit de AFM afbeelding hebben we kunnen concluderen dat de staafjes aan de onderkant van de stapranden op het HOPG terecht komen.

Zorgvuldige analyse van de AFM afbeeldingen leert dat niet alleen de nanostaafjes kunnen worden afgebeeld. We hebben ook structuren waargenomen die toegeschreven kunnen worden aan zelf-georganiseerde lagen van overtollige CTAB op grote delen van het HOPG oppervlak. Gestreepte fases van CTAB superstructuren komen voor in eilanden op het oppervlak, met typische hoogte tussen 1-3 nm. De omtrek van de eilanden lijkt geen relatie te hebben met de symmetrie van het substraat. Echter, de gestreepte patronen binnen de eilanden vertonen wel hoeken van ongeveer 60° en 120° ten opzichte van elkaar, hoogstwaarschijnlijk door de onderliggende HOPG structuur. Analyse van de dimensies van de strepen, i.e. breedte, hoogte en onderlinge afstand, impliceert dat de strepen bestaan uit halve cilindrische micellen, in overeenstemming met eerdere beschrijvingen in de literatuur. De zelf-geassembleerde CTAB lagen op het HOPG oppervlak lijken de bevochtigende eigenschappen van het substraat te veranderen. De resultaten laten zien dat ten gevolge hiervan de hydrofiele goud staafjes bij voorkeur worden afgezet op de geordende CTAB lagen.

In hoofdstuk 5 bestuderen we de fasescheiding van staafjes en bolletjes in waterige suspensies van nanodeeltjes tijdens verdamping van de vloeistof.

Na drogen blijven karakteristieke residuen over in de vorm van de bekende koffievlek. Afhankelijk van de afstand van de rand van deze vlek treffen we verschillende verdelingen van nanodeeltjes aan. Staafjes en bolletjes rangschikken zich in diverse kristallijne fases, die we toeschrijven aan convectorie in de opdrogende druppel. De nanostaafjes vertonen een sterke voorkeur om zich parallel te ordenen in een smectische fase; bolletjes in oplossing worden weggedrukt uit deze fase en clusteren samen in dichtgepakte structuren. We bespreken deze zelf-geïnduceerde fasescheiding in termen van de verschillende interacties, zoals elektrostatisch, Van der Waals en depletie interactie. Experimentele resultaten worden vergeleken met kwantitatieve berekeningen aan bovengenoemde colloïdale interacties, waaruit een totale netto interactie volgt die sterk afhangt van de vorm, afmeting en onderlinge oriëntatie van de deeltjes. Zowel de experimenten als ook de berekeningen bevestigen dat de zij-aan-zij rangschikking de energetisch meest gunstige toestand is in ons systeem. Hoewel de gezamenlijke interacties een grote rol spelen in het bij elkaar brengen van de deeltjes, bespreken we ook de mogelijkheid dat sterische interactie op korte afstand ten gevolge van de CTAB laag op het oppervlak van de nanodeeltjes ook een bijdrage levert in de zelf-organisatie van de staafjes en bolletjes in verschillende fases.

Zoals hierboven besproken handelt hoofdstuk 5 over de depositie van nanodeeltjes vanuit opdrogende druppels op gladde oppervlakken met isotrope bevochtigseigenschappen. Dit geeft aanleiding tot karakteristieke koffievlekken waarbij de deeltjes vooral samenklonteren in de buurt van de contactlijn, die vast zit op het oppervlak. In hoofdstuk 6 onderzoeken we de depositie van anisotrope goudstaafjes in verdampende druppels op chemisch gepatroneerde lineaire en radiale gradiënten van bevochtiging; de oppervlakken zijn morfologisch vlak. Middels experimenten verkennen we de mogelijkheid om door van tevoren opgelegde verplaatsing van de terugtrekkende contactlijn de depositie van de nanodeeltjes te beïnvloeden. Gestreepte patronen bestaan uit afwisselende hydrofiele en hydrofobe strepen met breedtes in de orde van enkele nanometers, die tevens een plaatsafhankelijke variatie van de totale oppervlakte-energie bewerkstelligen. De gradiënt in het ontwerp van het patroon dwingt de druppel om in de richting parallel aan de strepen te bewegen. Suspensies van nanodeeltjes bestaande uit nanobolletjes en nanostaafjes worden op deze oppervlakken neergelegd om ze vervolgens te laten indrogen. Nadat de druppel over een deel van het patroon is verplaatst en de vloeistof is verdampt, worden karakteristieke patronen van gedeponeerde nanodeeltjes

waargenomen. De dynamica van de vloeistof heeft een duidelijk effect op de ruimtelijke verdeling; de nanodeeltjes komen niet terecht op de hydrofobe gebieden, maar er is een sterke voorkeur voor de deeltjes om te verzamelen op de bevochtigende strepen. Bovendien suggereert het feit dat eilanden van nanodeeltjes ontstaan dat de terugtrekkende contactlijn op een stick-slip manier beweegt. Verder bespreken we de vorming van vloeistoflagen die meerdere strepen overbruggen tijdens de verplaatsing over de gradiënt oppervlakken. We stellen een model voor en bediscussiëren de mogelijke oorzaak van deze vloeistofstructuren. De residuen die overblijven na drogen, zoals waargenomen in SEM, bevatten zowel nanodeeltjes als ook de stabiliserende CTAB moleculen; de microscopie beelden bevestigen wat we in ons model aannemen.

Een aantal overeenkomsten tussen radiale en lineaire gestreepte gradiënt patronen zijn samengevat in hoofdstuk 6; ook worden duidelijke verschillen benoemd. Aan het eind van hetzelfde hoofdstuk richten we onze blik op de individuele eilanden op de strepen. Het is verrassend om te zien dat er ook binnen deze eilanden een selectieve fasescheiding plaatsvindt. Met name in grote clusters bestaan de buitenste gebieden vooral uit kortere staafjes terwijl meer naar het midden een nagenoeg zuivere fase met alleen nanobolletjes wordt waargenomen. Verdere analyse van de diameter van de bolletjes laat zien dat er een verloop is van steeds grotere bolletjes richting het midden van de clusters. Helemaal in het midden van de eilanden komen driedimensionale samenklontering voor die hoofdzakelijke bestaan uit aanzienlijk langere nanostaafjes dan in de nabijheid van de rand. In de kleinere clusters zien we monolagen van nanodeeltjes, waarbij de staafjes zich aan de buitenkant en bolletjes zich in het midden verzamelen. We bediscussiëren de mogelijkheid dat de bewegende contactlijn en vloeistofstromen over de hydrofiele strepen de pakkingsdichtheid en fasescheiding bevorderen.

Tot slot richten we onze aandacht in hoofdstuk 7 nogmaals op de individuele eilanden, die ook al in hoofdstuk 6 werden waargenomen, en dan voornamelijk op de dunne langgerekte gebieden die naast elkaar gelegen eilanden op de hydrofiele strepen verbinden. Als we alleen de smalle gebieden beschouwen, waar een enkele laag van onderling georiënteerde nanostaafjes voorkomt, ontwaren we een systematische variatie van de gemiddelde ordeparameter als functie van de breedte van deze gebieden. In gebieden met een breedte die typisch 10-20 keer de lengte van de staafjes bedraagt, zien we willekeurig gerangschikte nanostaafjes die geen specifieke oriëntatie verto-

nen. In smallere gebieden vinden we een sterke voorkeursoriëntatie parallel aan de richting van de strepen. We beschrijven een mogelijk mechanisme waarin we effecten van hydrodynamische opsluiting en capillaire krachten beschouwen tijdens het drogen van de vloeistof. De essentie hiervan is dat tijdens het terugtrekken van de contactlijn de nanodeeltjes in suspensie naar het midden van de hydrofiele strepen worden gestuwd, met als gevolg een opsluiting aan beide kanten van de strepen. Vervolgens geeft opdroging van de overblijvende vloeistof aanleiding tot capillaire krachten in de richting langs de strepen. De waargenomen universele relatie tussen de mate van ordening en laterale afmetingen van de lagen bespreken we kwalitatief in termen van beschikbaar volume dat afneemt en daarmee de toename van vrije energie. Ter compensatie hiervan leidt onderlinge oriëntatie van de deeltjes weliswaar tot een verlaging van de oriëntatie-entropie, maar wordt de translatie entropie gemaximaliseerd.

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Imtiaz Ahmad

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Curriculum vitae

Imtiaz Ahmad was born in Risalpur Cantt (District Nowshera, Khyber-Pakhtunkhwa) on February 14 (1978). He did his master in physics with distinction in 2001 from University of Peshawar, Pakistan. Before his master's result, he worked as a lecturer at Army Public School and College for Girls Peshawar Cantt to teach college level physics. There he worked for nearly 8 months. In the end of 2002, he was selected as a lecturer on contract basis at department of physics, University of Peshawar. After nearly three years of university level teaching, he was selected as a permanent employee at the same department in May 2005. There he taught various courses like mathematical physics, classical mechanics, nuclear physics, and laboratories etc. for ten years. In October 2011, he received financial support from university own resource scholarship program; after which he applied for PhD position at physics of interfaces and nanomaterials (PIN) group, University of Twente, The Netherlands. In January 2012, he joined the PIN group and worked there till October 2015.

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