Fabrication and Assembly of Patchy Particles with Uniform Patches

Zhenping He

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Fabrication and Assembly of Patchy Particles with Uniform Patches

By

Zhenping He

A Dissertation Submitted to the Graduate Faculty in Chemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy, The City University of New York

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Approval Page

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Abstract

Fabrication and Assembly of Patchy Particles with Uniform Patches

by

Zhenping He

Advisor: Ilona Kretzschmar

Patchy colloidal particles have been widely studied as the self-assembly building blocks to illustrate their potential for forming complex structures. The parameters affecting the final assembly structures include (i) patch size, shape, and number per particle, (ii) their relative positions, and (iii) the surface properties of the patch material. Recent computational studies have highlighted the impact of patch shape on assembly structure; however, there are only a limited number of methods that can provide control over patch shape and size. In this thesis, a template is introduced to the Glancing Angle Vapor Deposition method (GLAD) to create surface anisotropy on colloidal particles with uniform and controlled patch size and shape. Further, a mathematical model is derived that instructs the patchy particle fabrication process and also assists in the quantitative description of patch area.

The template-assisted GLAD method is used to fabricate patchy particles, i.e., colloidal particles with a predefined patch on their surface. The patch size is controlled by varying the incident angle and rotation angle when particle size and template dimension are fixed. Due to the shadowing effect of the template and adjacent particles, a large variety of patch shapes can be achieved, including but not limited to symmetric semi-spherical caps and asymmetric crescent moon and triangular-shaped patches. A second vapor deposition enables the addition of another
patch, which partly overlaps with the first patch. The mathematical model provides instruction on selecting adequate parameters to achieve a specific patch shape. In addition, it can also be used to calculate the patch size. In the model, the patch shape is defined in a three-dimensional space thereby enabling the description of various patch shapes obtained from the different fabrication parameters. Last but not least, the model also predicts patch position and calculates the size of the overlapping region of two patches.

Overall, the template-assisted GLAD method is illustrated to be a powerful tool for the control of patch size, shape and uniformity, while providing the opportunity for scalability and reduced occurrence of defects. Such patchy particles with a specific patch shape and/or multiple patches made of different materials have great potential to provide more intricate assembly structures and potential applications.
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Chapter 1

Introduction

Patchy particles can be defined as particles that have part of their surface exhibit different properties as a result of tailoring the particle’s surface or modifying its components during fabrication. Janus particles have been widely studied owing to their two distinct hemispheres that have varying surface properties or respond differently to external stimulation. They represent a special type of patchy particles in which one patch covers exactly half of the particle. Further, recently proposed terms such as ternary particles,\(^1\) triblock particles,\(^2\) or triblock Janus particles,\(^3\) all refer to patchy particles with patches of different sizes located on opposite poles of a particle, so-called two-pole patchy particles. Spherical patchy particles with more than two patches located at specific positions and patchy particles with special particle shapes, such as cone-shaped, spheroidal, and Kayak particles, have also been proposed or tested in simulations\(^4\) and been realized experimentally.\(^5\)

Inspired by the successful design of colloidal molecules,\(^6\) the realization of colloidal particle pairs as lock and key,\(^7\) the assembly of colloidal particles in specific arrays or stacking patterns,\(^3,8-10\) such as the Kagome lattice\(^11\) and chiral chains,\(^12\) the assembly of patchy particles has drawn tremendous enthusiasm to unearth the particles’ enormous potential in fabricating complex structures because the interaction between the patches
can be tuned and thus controlled (i.e., interaction strength, interaction direction, and interaction type) much more easily compared to homogeneous particles. By studying the parameters affecting the assembly behavior of patchy particles, for example, patch size, shape, number, and relative positions on the particle surface as well as surface properties of the patches\textsuperscript{5, 13} and even the environment surrounding the patchy particles,\textsuperscript{5, 14, 15} numerous interesting structures have been predicted by theory and assembled in experiments. The distinct response to external stimulation has added more tools that allow the control of patchy particle behavior. Based on the various behaviors of different materials in an external electric\textsuperscript{16, 17} or magnetic field\textsuperscript{14} and stimulation via the environment by, for example, light,\textsuperscript{18} various assembly structures have been observed and potential applications have been reported. Besides aggregated structures in their equilibrium state, the assembly of patchy particles in dynamic or non-equilibrium state has received attention from scientists and engineers alike.\textsuperscript{19-21} Further, surface anisotropy unique to patchy particles, has stimulated investigations into the application of patchy particles in photonic crystals,\textsuperscript{22} for targeted drug delivery,\textsuperscript{23, 24} and in electronics.\textsuperscript{25} Their application as self-propelled micromotors\textsuperscript{26, 27} and flexible display screen pixels\textsuperscript{28} are also worth mentioning here. More recently, findings such as the special localized surface plasmon resonance causing a patch shape dependent chiroptical phenomenon, the weak effect of van der Waals forces on micron colloidal particles compared to nanoparticles, the stronger absorption to interfaces compared to small surfactant molecules, and specifically functionalized patches have become new research hotspots.

Using lessons learned from synthetic methods developed for uniform, plain particles with a wide range of sizes and materials, the productivity and uniformity of patchy particles
needs to be improved potentially using similar mechanisms. Beyond creating anisotropy on the particle surface, there are numerous efforts aimed at controlling the patch size, shape, number per particle, and even the relative patch position. General strategies that have been employed for controlled patchy particle fabrication utilize emulsion polymerization, Pickering emulsions, microfluidics, physical and chemical vapor deposition, electrochemistry, and post treatment/tailoring. Recent simulations show that self-assembly of block copolymers is also a possible route to achieve patchy particles with controlled patch number and positions. Further, successful synthesis of multi-patch particles has been achieved with the help of tape, template and mask techniques. Assembly studies of patchy particles carried out in simulation work point out the importance of a fine control of the patch parameters, which brings about the necessity to control patch size, shape, position, number and even surface properties along with producing patchy particles in large quantities.

This thesis strives towards the fabrication of patchy particles with uniform and controlled patch size and shape. Multi-patch particle fabrication is also achieved by a secondary metal vapor deposition. The Glancing Angle Vapor Deposition Method (GLAD) has been shown to be a powerful tool to prepare patchy particles; however, it falls short in its control of patch shape and uniformity as each batch contains particles with various patch shapes as a result of the multi-domain structure of the particle monolayers employed in the process. In order to address this important issue, a template is introduced to assist in overcoming the shortcoming of size variation and lack of shape control. Controlling the fabrication parameters (deposition angle, groove shape and size, and template orientation/angle) a wide range of patch shapes can be accessed while improving the
scalability of the method. This thesis work also resulted in a mathematical model that provides a systematic instruction for the fabrication of patchy particles with specific patch sizes and shapes. It also emerges as a tool that provides quantitative information on patch size, which provides crucial input for assembly analysis and simulation research. The model provided here cannot only be applied to the fabrication method presented in this thesis, but is also easily adjusted to other GLAD methods where the distribution of the colloidal particles is different from the one used in this thesis.

In the following, the literature is reviewed with respect to patchy particle fabrication methods in Chapter 2. The methods are compared based on (i) their ability to control patch properties, and (ii) their productivity and scalability. In addition, the assembly, properties, and potential applications of patchy particles are summarized in the reminder of Chapter 2. Chapter 3 focuses on the template-assisted GLAD method and describes achieving uniform and controlled patch sizes and shapes, including the fabrication of various templates and the experimental characterization of the fabricated patchy particles. The effect of template dimension, incident angle, and rotation angle are also discussed and supported by numerical calculations. The ability of achieving patches with both symmetric and asymmetric patch shapes that are verified by comparing experimental results with numerical predictions is discussed in Chapter 4. Detailed plots are provided that relate patch shape and size to the experimental parameters and provide instructions for fabrication. Chapter 5 highlights the numerical model that has been developed to provide the necessary quantitative analysis for Chapters 3 and 4 along with two examples of applications using this model. It is shown that the model can be generalized to study any GLAD experiment independent on the distribution of the colloidal particles. The
thesis is concluded with a discussion of the main findings and proposed future work in
Chapter 6, which is followed by preliminary data in Appendix B and Appendix C testing
the assembly of patchy particles with uniform patch sizes and shapes.
Chapter 2

Patchy Particles as Building Blocks

In this chapter, patchy particle fabrication methods are reviewed in the first section. Their ability to control patch parameters such as size and shape and produce patchy particles in bulk are discussed. New methods aiming to achieve polymeric patchy particles are also included. Following the review of fabrication methods, a summary of the state-of-the-art of self-assembly and directed assembly of patchy particles is provided focusing on the parameters affecting the assembly structures in both equilibrium and non-equilibrium states. In the last part, the properties of patchy particles, such as enhanced localized plasmons, chiroptic phenomena, and potential applications, such as flexible display screen pixels, and self-propelled micromotors, are reviewed.

2.1 Fabrication of Patchy Particles

Various techniques have been applied to generate surface anisotropy. These methods can be applied to different systems and focus on controlling one or more properties of patchy particles. To help understand the cause of the diversity in assembly structure, research efforts have focused on controlling the patch size, shape, surface roughness, and surface properties through post modification. Generally, the methods to introduce anisotropy to colloidal particles have been classified into three main approaches: phase separation,
masking protection, and self-assembly.\textsuperscript{42,43} The patch size is one parameter that has been widely demonstrated to be of significance in determining the final assembly structure, since it affects the interactions between patchy particle building blocks through the force strength and range (i.e., number of objects one patch can interact with). Patch shape, which has been shown to have a similar effect as patch size, is of more interest because of the symmetry introduced. In an external force field, such as an electric or magnetic field, the induced charge or magnetic moment is strongly affected and defined by the patch shape. Bulk fabrication methods are in high demand (i) to enable the assembly study of patchy particles in larger ensembles, (ii) to test properties of materials containing or being formed from patchy particles, and (iii) to realize potential applications of anisotropic colloidal particles. The following sections will give a general overview on how different fabrication methods attain these goals.

2.1.1 Surface Modification of Controlled Patch Size

Besides creating anisotropy, the control of patch size is one goal that all fabrication methods have in common. Utilizing emulsion polymerization has been proven to be an effective route, where the micro-sized dispersed phase distributed in the bulk phase is controlled by adjusting parameters such as surfactant concentration, stirring speed, molarities, and others.\textsuperscript{33, 44-46} Controlling the seed size also results in a control of the patch size for hybrid patchy composites (Figure 2.1.A and 2.1.B).\textsuperscript{45, 47, 48} It should be noticed that not only the exposed part contributes to the anisotropy of the patchy particles in this case, but also the embedded part can be used to affect the property of the patchy composite, when seed materials such as the magnetic seed Fe\textsubscript{3}O\textsubscript{4} are used.\textsuperscript{48} Phase separation is achieved in microfluidics device or with the help of external forces (Figure
leading to the fabrication of Janus and ternary particles. In this method, based on the specific properties of the fluids employed (which can be responsive to electric magnetic fields if mixed with the proper additives) and the flow conditions (laminar flow), these fluids will not mix but form a stable interface that ensures additives stay in their respective compartments after curing. Another widely applied method involves protecting or hiding part of the particle surface, while leaving the remaining part exposed to being modified. In this case, the patch size can be controlled by the size of the template or mask. For example, absorbing particles onto a flat substrate with or without particles in a specific stacking pattern (close-packed monolayer or multi-layer) allows modification of the exposed surfaces, whereas those areas that are in contact with the substrate or other particles in the stack stay unmodified. The patch size is controlled by the stacking pattern, the incident and rotation angle during evaporation, template geometry and others. A particle can also be partially hidden by allowing it to sink into a polymer film to a specific depth, which can be controlled by time, temperature, or solvent presence in order to control the patch size. By placing colloidal particles on or partially embed them into a larger particle or droplet, the unprotected part can be tailored and thereby the patch size can be controlled as well. The amount of surfactant used to control the contact angle also helps to control the extent of protection (Figure 2.1.D). In addition to strategies that place particles at the interface of two different fluids with different ligand additives that assemble onto the respective particle surfaces, a more direct method has been proposed to fabricate patchy particles from the self-assembly of block copolymers, which creates a new route to patchy particle fabrication. The interesting aspect of the block copolymer self-assembly method is that
patchy particles are achieved successfully using multiblock copolymers, \((A_4B_{16})_n\), while \(n\) diblock copolymers, \((A_4B_{16})\), do not form patchy particles. In addition, patch number is controlled by changing the value of \(n\) (Figure 2.1.E).

The presence of multiple patches on one particle surface enables the directional assembly of patchy particles. To build structures analogous to molecules from such colloidal particles, patch number and positions need to be controlled. Multiple seeds included in a single droplet in the emulsion polymerization method can endorse colloidal particles with more than one anisotropic surface patch.\(^{48}\) Polymerization around colloidal clusters with a specific particle pattern results also in patchy colloidal particles with a well-defined number of patches that point in specific, geometrically pre-defined directions and the properties of the exposed patch surface can be tailored through the choice of particle used in the initial colloidal cluster for further assembly studies.\(^{46}\)

The masking process can also be used to fabricate multiple patches by protecting only part of the patch. For example, ternary particles produced via this method have been reported to involve multiple surface modification steps, where different surface areas are modified at each step.\(^{56}\) The method utilizing phase separation in a microfluidic device can also generate ternary particles if parameter that affect the component ratio are finely controlled.\(^{31}\) With the help of a substrate, multiple patches can be fabricated by changing the incident metal vapor direction if the particles are not moved or by flipping the particles over using a sticky tape, which exposes the bottom half of the particle to further modification.\(^{2,35,52,53}\) Recently, methods involving chemically modified substrates that modify the part of the particle surface they touch followed by addition of a patch on the opposite pole, present a new route to both surface and shape anisotropic patchy particles.
2.1.2 Methods of Controlling Patch Shape

An important property of a patch that needs to be paid attention to is its shape. The chiroptical property of patches with asymmetric shapes\textsuperscript{56} and the packing pattern determined by patch orientation\textsuperscript{8} illustrate the importance of patch shape in self-assembly.
of colloidal particles. Considering the importance of induced charge and magnetic moment in directed assembly, patch shape is likely to also be highly relevant in field-directed assembly of patchy particles.

The review of the fabrication methods for patchy particles given above illustrates that only a few of them can achieve a variety of well-defined shapes. For example, with the help of one or two layers of particles as a mask, patches of different shapes can be fabricated uniformly depending on the packing patterns used (Figure 2.2.A).\textsuperscript{38}

Considering that the particles forming the masking layer can be of different sizes and the distribution pattern can also be controlled,\textsuperscript{61} patch shape variety is rich and achievable. Most recently, Shah et al.\textsuperscript{5} reported the preparation of spheroidal Janus and Kayak-shaped patchy particles via uniform elongational stretching under heat before or after metal vapor deposition, respectively. Obviously, the toughness or hardness of the patch cap, which is determined by the cap material, highly affects the final patch geometry along with the patch thickness. This strategy provides a powerful approach to the study of properties of non-spherical patchy particle since the aspect ratio can be controlled well.

Another approach to patch shape control involves close-packed particle monolayers and GLAD.\textsuperscript{35,36} The patch shape and size are controlled by orientation of the close-packed region with respect to the incident angle (Figure 2.2.B). For a typical run, the close-packed monolayer contains multiple small regions of approximately 3000 particles with different orientations described by the monolayer orientation angle, $\alpha$. For each small region, the patch size and shape are determined by the incident angle, i.e., the different orientations of the domains affect these two properties (Figure 2.2.B). The fact that the coexistence of multiple regions with different orientations is unavoidable eliminates the
ability of controlling patch shapes using the GLAD method itself. To improve the uniformity of the patches, a template can be introduced to assist the GLAD method by placing particles in a pre-defined orientation, which will be discussed in more detail in this thesis. The task of the template is to maintain the uniform orientation of each colloidal particle. The shadowing effect of the template and the neighboring particle determine the patch shape in cooperation with the placement of template with respect to the evaporation source.

Figure 2.2 Summary of different patch shapes reported. The control of patch properties, e.g., size and shape, may, while desired, not be achievable in one step, which means post-treatment of the particles is necessary. Potential post-treatment options that have been tested successfully are (i) etching the patch from its thin edge to reach a specific patch size, (ii) removing the exposed part of a particle to
accept a new patch,$^{56}$ and (iii) annealing the patch to change surface structure and optical properties.$^{55}$

2.1.3 Bulk Fabrication of Patchy Particles

Bulk fabrication of patchy particles represents the biggest hurdle to the realization of many potential applications of patchy particles on an industrial scale. Many methods have been reviewed recently.$^{62}$ Fabrication of patchy particles utilizing phase separation as described in the emulsion or Pickering emulsion approach has been heralded as an effective method, owing to the large amount of micro-sized dispersed phase distributed in the bulk solution resulting in a large interfacial surface area. Since patch fabrication occurs at the interface and there is no limitation for the bulk solution volume, this method is scalable; however, control of the patch size and shape is very limited in this method. The quantity of patchy particles is also high for the method of polymer bead synthesis via emulsion polymerization containing seeds or particle clusters inside or partially inside the emulsion droplets.$^{32, 46, 48, 63, 64}$ For this method, the property of the seeds and particle clusters (number, size, material and surface chemistry) is defined prior to polymerization and can be tuned to fit the requirements of the final product. A recent interesting development regarding this emulsion strategy is the achievement of non-spherical colloidal particles.$^{7, 14, 65}$ Removal of solvent is used to create the non-spherical shape, as it causes concave pits on the spherical particle surface due to polymer shrinkage. The uniformity, reproducibility, and controllability of the hollow area make this method a practical one for the study of bulk assembly of such particles. An additional improvement is the etching out of the partly embedded particles, which enables refining of the colloidal particle shape with sharp edges and benefits the assembly of these colloidal particles.
Microfluidic methods also have the potential to be scalable.\textsuperscript{1, 28, 51, 66} Although limited by the fact that only one particle is fabricated at a time, the method’s ability to continuously produce particles combined with the possibility that several units are run at the same time makes it a potential method for bulk fabrication. Recent progress is represented by the straightforward fabrication based on bulk phase reaction.\textsuperscript{67} The patches (Janus particles) are created through bipolar electrochemistry in which an induced polarization potential difference is generated on conductive objects in a direct-current (DC) electric field. By controlling the electric field strength, various metal or metal halides can be deposited on the particle surface due to the occurrence of electrochemical reactions on the particle surface. To achieve the immobilization of shape-isotropic particles in an external force field and improve the patch uniformity, a gelling agent is introduced to increase the viscosity. The gelling agent is not necessary for anisotropic particles.

It is necessary to point out that all the methods described above, work very well for the fabrication of Janus particles or patchy particles with circular patches. The bulk fabrication of patchy particles with asymmetric patches is still a subject under investigation and the basis for this thesis. Of the current methods available for the fabrication of particles with asymmetric patches, the template-assisted GLAD method has the advantage of scalability while also providing control of patch shape and uniformity.\textsuperscript{39} The template-assisted GLAD, which will be discussed in more detail in Chapter 3, benefits from the scalability of the template size, the ability of the PVD instrument to hold multiple templates in a single run, and the fact that the template can be reused.
2.2 Self- and Directed Assembly of Patchy Particles

Besides being inspired by studying the intrinsic properties of patchy particles, the interest in developing patchy particle fabrication methods is also driven by the scenario of building ‘molecules’ and crystal structures from colloidal particles. To-date, structures have been reported with (i) diamond crystal symmetry, (ii) ‘lock-and-key’ interactions, (iii) a Kagome lattice, (iv) analogues to molecules, and (v) polymer chains, which all point to the huge potential of patchy particles in forming complex structures. A deeper understanding of the effect of anisotropy has been obtained by application of electric (DC, AC) and/or magnetic fields and switchable light to direct the assembly of patchy particles. Researchers have investigated parameters affecting the behavior of patchy particles in external fields, such as patch size, shape, and composition.

2.2.1 Self-assembly of Patchy Particles

Many parameters have been studied to understand their effect on assembly. The patch size, patch number per particle, relative positions on the same particle, and anisotropic interactions are the most widely reported to affect assembly structures. Formation of micelles, lamellas, and wires caused by low coverage, reversible gels from patchy particles, crystals from triblock Janus particles and tetrahedral patchy particles and even the polymer chains from bifunctional patchy particles represent some interesting structures built from patchy particle building blocks. Generally, an assembly system at equilibrium resides in the state of lowest Gibbs free energy, which is determined by enthalpy, temperature, and entropy. This fact has encouraged researchers to focus beyond the straightforward interaction between anisotropic colloidal particles and investigate
other parameters that might play an essential role in determining assembly structures, such as pressure, temperature, and entropy. By setting the four patches at the corners of a tetrahedron and introducing ‘antibonding-like’ interactions, a promising route is provided to fabricate assemblies with the elusive diamond structure through the self-assembly of particles with small patches. Additional theoretical studies have illustrated that the stability of the diamond structure is affected by the range of the potential, the temperature, and the pressure. Only in a very narrow range of pressures and at finite temperatures is the diamond crystal the preferred structure and more stable than the bcc solid due to a higher entropy.

Another fascinating crystal structure is the Kagome lattice, which was achieved recently with triblock patchy particles with controlled patch size and position. The most interesting aspect of this assembly is the preference of an open lattice structure (Figure 2.3A) over the close-packed crystal structure that is generally observed for isotropic particles. Studying the thermodynamic stability experimentally and mathematically, researchers found that thermal fluctuation contribute to the stability of this open crystal of patchy particles, i.e., the entropy due to the rotation and vibration of patchy particles around preferred lattice positions. While the patch size and surface properties affect the arrangement in the specific lattice structure, it is the entropic contribution that contributes to the stability of the structure and is closely related to the spherical patch size.

One important characteristic of the patch surface, i.e., roughness, has not been paid too much attention to until a recent experimental report. In fact, the fabrication methods discussed above can achieve different surface roughness and the surface roughness has been shown to play a crucial role in the behavior of Janus particles at interface.
the increased overlap in volume resulting in higher entropy, the attraction (depletion force) between the smooth surfaces is larger than between two rough surfaces (Figure 2.3C). The fact that patchy particles preferentially interact with their smooth sides with other colloids provides a new pathway to control the assembly structures formed from patchy particles. The depletion force has also been employed to achieve other assembly structures, such as the ‘lock and key’ assembly that uses spherical particles with concave dimples on its surface, in which again higher entropy supports the formation of assembly. Most recently, the significance of patch shape in patchy particle assembly was revealed. Unlike the circular patches that have been widely studied, simulations show that patches of asymmetric shape such as the triangular patch enrich the assembly structures due to their directional (or orientation related) interactions. For example, two triangular patches located on opposite poles of a particle can be arranged in a staggered (tips of triangles point in opposite direction) or in an eclipsed pattern (tips of triangle point in same direction) and form fully bonded configurations in either staggered or eclipsed local arrangements, respectively, while circular patches can form both structures (Figure 2.3B). Confinement of patchy particles in a specific dimension is another approach to direct the assembly of patchy particles. Numerous structures from triblock patchy particles, including chain, double helix, triple helix, and even more complex periodic structures, have been computationally predicted by changing the size of the confining tube.75 Considering the recent progress of self-assembly of colloidal particles assisted by molecular microtubes,76 the behavior of patchy particles in confined dimensions or their assembly with the help of molecules might open a new window to utilize patchy particles.
Figure 2.3 Novel assembly structures affected by (A) patch size, (B) number, (C) shape and (D) surface roughness.

While most attention has been paid to assemblies in a static/equilibrium state, assembly in dynamic systems has been reported to have some interesting properties. For example, in a precessing magnetic field, Janus particles self-organize into tubes where the Janus particles rotate and oscillate continuously. While the particles maintain their orientation within the rotating microtube, structural transitions induced by synchronization are observed. This observation provides the potential to tune self-assembly structures
dynamically and to achieve materials that respond to external changes. In contrast to the equilibrium assembly, the behavior of patchy particles has also been studied in systems away from equilibrium. In the presence of a substrate and under non-equilibrium conditions, two- or three-patch particles self-organized into various patterns due to the irreversible nature of their binding, which might require a long time or a higher temperature to achieve the most stable state. This observation introduces and inspires the consideration of a stable state associated with the environment, the existence of metastable states, and the possibility of overcoming the barriers to a state of lower energy.

2.2.2 Directed Assembly of Patchy Particles

Manipulating patchy particles with electric or magnetic fields has been a successful tool to achieve unique structures. Dielectrophoresis induced in particles by an electric field can help to control the assembly structures through tuning the forces exerted on the colloidal particles. The induced dipole has been shown to lead to the formation of chains, crystals, and nanoparticles wires. In external electric or magnetic fields, chains from colloidal particles have been observed to form parallel to the direction of the applied external field. In a few cases it was also observed that particles assembled perpendicular to the external field direction or move across the field lines. Amoeboid cells have been observed to elongate both parallel and perpendicular to the external electric field directions at specific frequencies of the AC field, which illustrates the importance of frequencies of the AC field and stimulates the interest of studying the anisotropic particle assembly in different AC field. The anisotropy introduced to Janus particles by their caps, especially the difference in the
properties of the base particle and the cap in an external force field, endows the anisotropic colloidal particle with a distinct behavior. At low frequency in an AC electric field, Janus particles have been observed to move perpendicular to the field lines because of the unbalanced flow around the two sides of the particle, while they form staggered chains parallel to the electric field at higher frequency. The dependence of the assembly structure on the frequency of the external force field has also been confirmed by the formation of diagonal chains from protoplast cells, which occurs due to the rotation and switching frequency of 25 kHz. Besides the frequency, the degree of anisotropy, i.e., the patch size and patch number per particle, also played a role in achieving various pre-programmed structures. The patch size (anisotropic part area over the whole particle surface) is designed to be ~11% such that the particles carrying two patches have a total anisotropic area of 25%. Both perpendicular and diagonal chains relative to the field direction were observed, which were rationalized by multipolar interactions caused by the frequency dependent polarization of the two materials (patch and base particle) in the high-frequency fields.

The magnetic field is another tool that is widely used to control the assembly structures of patchy particles. Different response to an external magnetic field (ferromagnetic, ferrimagnetic, and antiferromagnetic) endows the patchy particles with the ability to form various structures, especially in presence of an additional electric field. Staggered chains from magnetic Janus particles, chain-like or meshlike structures from superparamagnetic Janus particles, and reconfigurable responsive structures that are controlled by external magnetic and electric fields are some representative experimental results. The effect of different materials on the assembly structure has also been studied
by comparing the behavior of Janus particles carrying various patch materials. The structures observed, staggered chains for Fe$_{1-x}$O, double chains for Fe$_3$O$_4$ and no assembly for α-Fe$_2$O$_3$, provide a new approach to achieving specific structures by changing the compositions of the patch material. The information revealed by the process of assembly or the movement of the chains endows patchy particles with potential application as sensors.

2.3 Properties and Potential Applications of Patchy Particles

Based on the various materials forming the patchy particles and the huge variety in assembly structures observed, patchy particles have shown interesting properties and potential for applications. Studies of patchy particle assembly dynamics and their motion in fluids announce patchy particles as ideal sensors for measuring many physical and physicochemical properties.

Patchy particles with gold, silver, or copper patches have been shown to exhibit plasmonic properties that are related to the absorption and scattering of light in metallic nanostructures. The localized surface plasmon resonance (LSPR), a phenomenon that occurs when the collective oscillation of conduction electrons resonates with the electromagnetic radiation, is related to the shape and size of metal nanoparticles. The LSPRs is strongly affected by the particle size, metal shell thickness, degree of coverage (patch size) and even the surface roughness. Calculating the spectrum for patchy

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particles with patches of different size and thickness, researchers have concluded that for a certain particle size, an increasing patch thickness or patch size will lead to a blue shift, i.e., as patch thickness is increased, the plasmon band broadens. Methods that try to modify the patch structure and thereby change the optical properties have been reported recently. For example, by adding a thin layer of Au and Cr followed by annealing for different times, the absorption peak for an Au-nanoparticle/silica composite is shifted to a smaller wavelength and narrows as a function of annealing time. Another interesting optical property is related to the patch shape. Using the GLAD method, metal (silver) patches of specific shapes are manufactured at specific fabrication parameters (incident angle 75°, rotation angle 15°) and subsequently transferred to a PDMS film with the help of a tapping technique and solvent etching of the base PS particles. The chiroptical effect observed for these metal patches with chiral structures is characterized by circular dichroism. The observed Cotton effect indicates the potential application of such patchy particles with asymmetric patch shapes as chiral materials.

The materials introduced as a result of the patching process make the patches respond differently from the particle surface. In an electric field, the induced-charge electrophoresis flow near the anisotropic patchy particle surface directs the Janus particles with an Au patch to move perpendicular to the external electric field. When the patch material is chosen such that it catalyzes reactions with the surrounding environment, particles, which are characterized as self-motile, move forming so-called self-propelled motors. The uneven concentration gradient around or the burst of bubbles from the patch help move the colloidal particles. In a few cases, this motion can even be tuned by the presence of light. When the particle size is chosen such that it
is suitable for characterization by optical microscopy, the movement or rotation of a Janus particle correspond to its surrounding flow or external force field. Thus, an instrument can be envisioned, that would record the motion of the patchy particle and thereby probe the rheological properties of its environment. Viscosity dependent assembly dynamics\textsuperscript{21} provide one way to visualize the properties of fluids in small regions and thereby enable quantitative analysis. By studying the Brownian motion of shape-anisotropic particles, hydrodynamic friction tensors can be assessed, and the non-trivial couplings between translational and rotational degrees of freedom has been discovered.\textsuperscript{101} For example, studying the image and orientation of a Janus particle (i.e., patch faces in different directions and particle changes position in 3D environment), the two rotational degrees of freedom and the center-of-mass diffusion can be tracked and solved for, respectively.\textsuperscript{102, 103}

Patchy particles of suitable size that fit the requirement of easy manipulation and that are small enough to serve as pixels are ideal to fabricate modern flexible display screens of high resolution. Recently, bifunctional Janus supraballs with fluorescent and magnetic parts have been successfully fabricated in a microfluidic device.\textsuperscript{28} If magnetically responsive Fe\textsubscript{3}O\textsubscript{4} is located only in one hemisphere of a Janus particle, the orientation of the Janus particles can be controlled by an external magnetic field such that they face in a specific direction, which means pixels can be turned on or off in a controllable fashion.

When the concept of ‘Janus particle’ was proposed initially by de Gennes, Janus particles were envisioned to act as surfactant-like species that absorb to a liquid-liquid or liquid-air interface as a monolayer. With the advantage that Janus particles absorb at an interface much stronger than surfactant molecules and still leave some space between particles as
holes for ‘breathing’, particles with proper anisotropic surface chemistry have been proclaimed to be unique solid surfactant. Experiments have shown that anisotropic particles absorb at liquid-liquid interfaces and stabilize emulsion drops. They even form micelles and/or vessels similar to surfactant molecules.\textsuperscript{104} Recently, more direct evidence has been provided to show that Janus particles have the ability to stabilize emulsions.\textsuperscript{30} In the experiment, the emulsions were stabilized by Janus particles (1.0 wt%). Through comparing the photographs tracking the phase separation of the emulsions containing Janus particles and plain particle, the researchers determined that the Janus particles’ ability to stabilize emulsion is superior compared to plain particles based on that fact that phase separation was not observed after 3 weeks.
Chapter 3

Uniform Patchy Particles with Controlled Size

In this chapter the fabrication of uniform patchy particles by template-assisted glancing angle deposition (GLAD) is reported. In the first section, different methods are reported to fabricate templates that are designed to localize and order the particles. In one case, a close-packed monolayer is used as a template to create holes in a PDMS surface through the solvent etching method. In the other, photolithography is coupled with a wet etching method to fabricate a template on a Si wafer, which has the advantage of reusability. The ability of fabricating patchy particles with uniform size is illustrated in the subsequent subchapters. The nearly linear increase of patch size with the increase of incident angle makes the prediction of patch size very easy. Scaling analysis shows that the patchy particle production is increased by 3100 times in the template-assisted GLAD method compared to the more general GLAD method. Different kinds of template geometry are studied theoretically, to study how the patch is affected by template shape and size, incident angle, and colloidal particle size.
3.1 Fabrication of Template

A careful study of the assembly simulation results (reviewed in Chapter 2) shows, that many of the proposed structures are based on the essential premise that the patchy particles used have uniform patches with a very specific patch shape and area. Despite the large number of synthetic routes proposed, an effective method with accurate control over both patch shape and size for low-symmetry patches is still missing. Physical vapor deposition (PVD) has been widely studied to generate anisotropic colloidal particles. The vertical vapor deposition onto a monolayer generates Janus particles (50% of the particle surface is modified).\(^{69, 105}\) Patches of sizes smaller than 50% and specific shapes have also been achieved through modification of multilayer.\(^{38}\) In this improved method, layers of colloidal particles are utilized as masks to control the modification on the lower layer. The uniformity of the mask layer and structure and size of the mask layer highly affect the patch size and shapes. To develop a method that can achieve patchy particles of specific size of any arbitrary value, the GLAD method was developed wherein the close-packed monolayer is tilted to specific angles in order to control the patch size.\(^{35, 36}\) However, the coexistence of multiple domains of different orientations in the as produced close-packed monolayers introduces variation to the patch size and shape, especially at small incident angles of \(\theta < 25^\circ\).

To conquer the problem of coexistence of different patch shapes and variation of patch size, aligning all colloidal particles in one orientation is a straightforward method. Through the tailoring or patterning of a substrate template, colloidal particles can be directed to bulk crystallization in pre-designed lattice structures through slow
sedimentation in solutions. The template-guided Langmuir-Blodgett deposition method provides a versatile route to fabricate a near perfect 2D colloidal lattice of the order of a hundred micrometers. The template-assisted self-assembly (TASA) has validated its capability in controlling the homo-aggregate structures from colloidal particles. The uniformity and abundant patterns, which are affected by the template dimensions, suggest the potential of combining a template with GLAD.

### 3.1.1 PDMS Template

Our original approach involved the fabrication of uniform holes in a polydimethylsiloxane (PDMS) film, where the colloidal particles are loaded into the holes in the PDMS template. Close-packed monolayers of polystyrene (PS) colloidal particles are used as a sacrificial template to create holes in the PDMS film after being etched using an organic solvent. Considering the possible occurrence of shrinkage after the removal of PS particles, the PS particles size is chosen slightly larger than that of the studied particles.

**Convective assembly of PS particles into close-packed monolayer**

The convective assembly method is used to produce close-packed monolayers of 5.0 μm sulfate latex PS particles (Invitrogen Inc.). Following the procedure and details of the process, close-packed monolayers are fabricated using the coating apparatus as shown in Figure 3.1. The glass slides used in the experiments are cleaned with concentrated sulfuric acid and Nochromix solution. PS particle latex (12% w/v, about 15 μl) is injected into the space between two glass slides. The coatings are deposited at an ambient temperature (about 25 °C) and a relative humidity of 40 – 70%. The dragging speed is
adjusted according to the ambient temperature and humidity in order to obtain close-packed monolayers. To improve the quality of the close-packed monolayer, Tween20 (1%) is added to the PS latex particle solution.

Figure 3.1 Schematic of the film coating apparatus for convective assembly method.\textsuperscript{110}

**Fabrication of PDMS Template**

The PDMS films used to cover the close-packed monolayers are produced by curing the elastomer and curing agent (10:1 w/w) (from Dow Corning) at 70 °C in an oven for a specific amount of time. To prevent the PDMS from encapsulating the entire particle layer, the PDMS film is laid on a clean glass slide and pre-cured for about 15 mins. Without the pre-curing procedure or if a too short time is used, the flexibility of the PDMS will not be reduced enough and PDMS will flow to the bottom of the particle
layer and embed the entire particle, while a too long time will harden the PDMS surface too much preventing the partial embedding needed. The pre-cured PDMS film is then put onto the close-packed monolayer followed by additional curing in the oven for 1 more hour. When the PDMS film becomes completely cured, it is removed from the oven. After being removed from the glass slide, the PDMS film with the partially embedded PS particles is immersed in tetrahydrofuran (THF) for 1 hour, followed by 15 min sonication. The aforementioned procedure is repeated as many times as needed.

Figure 3.2 Microscope image of PDMS film with holes and embedded PS particles.

Figure 3.2 shows a typical PDMS film with holes and PS particles that were not etched out of the PDMS film indicating that they are fully embedded in the PDMS. The grey
circles show the holes that are left behind after a PS particle was removed. The bright circles indicate the PS particles that were not removed.

**Filling PDMS Template with PS Particles**

PS particles with a smaller size can be assembled into the holes in the PDMS film by the same convective assembly method introduced above. The particles studied here are PS particles (2.4 μm). The concentration of the PS latex suspension is between 4 - 16% w/v. The volume fraction is adjusted by dilution with deionized water or concentration by centrifugation. For a typical experiment, a small drop (about 15 μl) is placed on the PDMS near the edge of the template area where the tip of a clean top glass slide is also touching. During the process of evaporation along with the movement of the glass slide over the template, PS particles are drawn into the holes in the PDMS film.

Figure 3.3 shows one representative PDMS film template with holes (5 μm) loaded with PS particles. From this image, we can conclude that particles are drawn into the holes. However, the results are not satisfying. The problems with using a PDMS template are: (i) the number of particles per hole is not uniform, apparently many holes are able to hold two or three PS particles; (ii) PS particles are not located in the same position within the holes, i.e., particles are distributed randomly; and (iii) the shapes of the holes are not uniform. The latter is likely a result of the shrinking of the PDMS after removal of the 5 μm template PS particles or the stress occurring in the film leading to a hexagonal cross section of the holes. In addition, seriously stretched and even connecting adjacent holes are also observed. As a result of these various problems, the use of a PDMS film template with holes was abandoned as a template for use in GLAD to fabricate uniform patchy particles.
3.1.2 Si Wafer Template

Photolithography is a very accurate technique that can be employed to achieve various patterns on Si wafers. The patterns can be designed such that the requirement from practice are met, including the shape and size of the patterns. The methods to etch a Si wafer can be classified into two types: wet etching and dry etching. Generally, anisotropic wet etching of Si wafers is widely used to exercise control. The etching rate is

Figure 3.3 PDMS film template with 5 μm PS particles filled with PS particles of 2.4 μm.
dependent on the Si wafer orientation, i.e., the crystal face that is exposed to the etchant. In our experiment, a Si wafer with a $<100>$ orientation is used to create a groove template, based on the consideration that V-shaped grooves (which conveniently puts particles at the center of the grooves) are ideally suited for this template.

Imprinting a pre-designed pattern on a Si wafer, a photomask is necessary that transfers the pattern onto the Si wafer. The dimensions of the pre-designed pattern on the photomask are: 1 cm in length and 3.5 $\mu$m in width with 3.0 $\mu$m spacing. Figure 3.4 shows an enlarged area of the mask taken with the optical microscope.

Figure 3.4 Schematic of the photomask pattern obtained via photolithography on a Si wafer.
Fabrication of Template on Si Wafers

Si wafers and Si wafers with SiO$_2$ layer are cleaned first before use. The cleaning procedure is as follows. The Si wafer is put into acetone in a glass container for 15 min at about 45 °C (sonicate for short time if necessary) to remove the organic residues. Then the wafer is taken out of the acetone solution and moved into methanol for 5 mins to remove the acetone residue, deionized water is used last to wash the Si wafer before it is dried by blowing nitrogen over the wafer.

A thin layer of SiO$_2$ is added to Si wafer surface by heating the Si wafer at 970 °C in a furnace for about 30 min. The thickness of SiO$_2$ layer is controlled by temperature and heating time. The purpose of SiO$_2$ is to protect the Si wafer underneath during wet etching. Generally, a layer of 10 nm of SiO$_2$ is needed to protect the Si wafer from until the template is created successfully.

The typical structure of the Si wafer with photoresist contains an AZ5214 layer, a HDMS layer, a SiO$_2$ layer and a Si wafer from top to bottom. A thin layer of HDMS is spin coated onto a dry, clean Si wafer in order to increase the affinity of AZ5214 (photoresist) to the Si wafer. Onto the HDMS layer, a layer of AZ5214 is spin coated (about 4 μm). The thickness of the polymer layer is controlled by the spin speed and also related to temperature and processing time.

Before spin coating the photoresist onto the Si wafer (with or without SiO$_2$), the wafer is placed on a hot plate (70 °C) for at least 10 min to remove the residual water molecules physically adsorbed on the wafer surface. Generally, to develop the pattern, the Si wafer with the photoresist is first baked for 1 min at 105 °C before being exposed to UV light.
The exposure time is usually between 3 to 10 s, depending on the thickness of the photoresist layer. A too short exposure time does not transfer the pattern to the photoresist successfully, while a too long time leads to a broadening of the pattern. After exposure, the Si wafer is emerged into a development solution (AZ 400K/DI water, ¼ v/v) for 1 to 6 min, which again depends on the thickness of the photoresist. Then the Si wafer with photoresist pattern is post-baked for about 1 min at 115 °C. For a successfully developed pattern, the SiO₂ layer should be exposed to further etching. The Si wafer is transferred to a buffered oxide etch (BOE) solution to remove the exposed SiO₂ for further wet etching of the Si wafer. The etching of SiO₂ in BOE lasts for about 1 to 4 min depending on the thickness of the SiO₂ layer.

The final etching of the Si wafer to fabricate the template is carried out in a basic solution. The etching solution contains 25% KOH (w/v), isopropanal (10%, v/v), and deionized water. The etching takes about 2 min at 60 °C. The last step of the whole experiment is to wash out the left over photoresist with acetone.
Figure 3.5 SEM image showing detail of Si wafer template.

Figure 3.5 shows an SEM image of a detailed view of a Si wafer template. It is very clear that the template on the Si wafer has mostly sharp edges and very uniform V-shaped grooves. Some edges exhibit a little bit of roughness, which is a result of the placement of the Si wafer during the exposure to the UV light. Note the slight variation does not affect the uniformity of the whole template.

**Filling Si Wafer Template with PS Particles**
The PS particles are drawn into the grooves through convective assembly. The procedure and apparatus used here are the same as stated previously. Particles of different sizes can be loaded into the template. In order to achieve uniform patches, the particles are all required to go to the center of the grooves. A few defects are observed that include particles staying out of grooves or near other particles in the groove. They can be reduced or eliminated through controlling the concentration, dragging speed, and tape technique. The tape technique utilizes a clean PDMS (fabricated using the same method as stated above) to remove particles not in grooves by lightly touching the template with the
PDMS tape/film. Figure 3.6 shows the template filled with 2.4 μm PS particles after removing of defects. Clearly, all PS particles are found within the grooves.

3.2 Fabrication of Patchy Particles

Based on the comparison between the PDMS template and Si wafer template performance, the fabrication of uniform patches is expected to produce better results using the Si wafer template. Just as stated above, most assembly simulations consider circular patches, which may be due to the fact that only very few methods have the ability to achieve less symmetric or asymmetric patches. Here, we report a template-assisted patchy particle fabrication method that combines a template that controls the particle position with the glancing angle deposition (GLAD) method and allows for the repeated use of the template. In our method, a silicon wafer template is used to help control patch shape and size by tilting it based on the angular requirement. We show that with the help of the silicon wafer template the patches created on the particle surface are uniform in shape and size. Further, we study the effect of incident angle and dimensions of the template on the patch geometry and support our observations with mathematical calculations that verify the patch shape and size. For validation of our methodology, we also perform a scaling analysis, which shows that the patchy particle production in each run is increased by 3100 times in the template-assisted GLAD method compared to the more general GLAD method.
3.2.1 Experimental Details

Figure 3.7 Schematic of template-assisted patchy particle fabrication using glancing angle deposition method and parameters affecting patch shape and area.

The PS particles studied here are of a size smaller than the width of the grooves (Molecular Probes, 1.500 ± 0.026 μm, 0.8% w/v), so that the particle top is lower than the Si wafer surface. Figure 3.7 represents a schematic view of the template assisted patchy particle fabrication using the GLAD method for both (A) V- and (B) square-shaped grooves. The angle θ corresponds to the incident angle of the Au vapor flow measured.
from the substrate side (the incident metal vapor flow is perpendicular to the grooves). \( w \) indicates the width of the groove, \( d \) is the depth of square grooves (the depth of the V-shaped grooves changes with their width), and \( r \) is the radius of PS particles. For V-shaped grooves, the particles are always located at the center of the groove (Figure 3.7 A), whereas an off-center distance \( v \) (defined as the distance from the center of the particle to the center of the groove) needs to be considered for the square-shaped groove (Figure 3.7 B). Note the shape of the resulting patch is always a half-spherical cap due to the perpendicular evaporation geometry. The height of the spherical cap is denoted as \( h \). The coated area percentage, \( A\% \), is calculated according to Equ. 3.1:

\[
A\% = \frac{\pi h}{4\pi r^2} = \frac{h}{4r}
\]

in which \( h \) is related to \( \theta \), \( w \), and the slope of the sidewall (54.74°, a constant value here) for a V-shaped groove and \( \theta \), \( w \), \( d \), and \( r \) for a square-shaped groove.

The dashed circle in Figure 3.7 B shows the case in which a particle is not located at the center of the square groove. For this case, the coated area percentage is calculated by moving the particle along the direction of the metal vapor flow until its center reaches the center of the groove, which results in replacing \( d \) with \( (d + vtan\theta) \) while all other parameters in the calculation remain unchanged.

In a typical experiment,\(^{36} \) the 35 nm gold patch is placed onto the surface of the PS particles using a bench top vacuum metal evaporation system (Cressington 308R, Ted Pella, Inc.) at a pressure of 10\(^{-6} \) mbar. Similar to the patchy-particle fabrication method using a close-packed monolayer, the incident angle of the gold vapor flow, \( \theta \), which is defined as the angle between the metal vapor flow and the substrate, is used to control the
coated area by tilting the template with respect to the vapor source in the vacuum chamber. Additionally, the template is placed such that the direction of metal vapor flow is perpendicular to the groove direction, in order to avoid any shadowing effects from the particles themselves.

3.2.2 Calculation Results

The advantage of the method described here is the achievement of uniform patch shape and size, the reusability of the template, and the increase in particle production volume. In the following, the dependence of patch size on parameters such as the width and depth of the groove, the incident angle, the size of the particles, and also the type of the template are discussed.

Generally, templates will be reused, since they are fabricated on a Si wafer and can endure long-term, multiple-time usage. Thus, for one template we can simply consider the influence of the incident angle and size of particle while all other template-related parameters are kept constant.
Figure 3.8 Coated-area percentage, $A\%$, plotted as a function of incident angle, $\theta$, for (A) V-shaped groove and (B) square-shaped groove with particles located at groove center.

Equation 3.2 shows the relation of patch height, $h$, with particle radius, $r$, and incident angle, $\theta$:

$$h = r - \left( L^2 + r^2 \right)^{\frac{1}{2}} \sin \left( 54.74^\circ - \tan \left( \frac{r}{L} \right) - \theta \right)$$

Equ. 3.2a
in which $L$ is defined as shown in Equ. 3.2b:

$$L = \frac{w}{2 \cos(54.74^\circ)} - r \tan 54.74^\circ$$

Equ.3.2b

Figure 3.8 shows the coated area percentage, $A\%$, calculated as shown in Equ. 3.1 as a function of incident angle, $\theta$, for varying particle sizes in V-shaped (A) and square-shaped grooves (B). In Figure 3.8 A, the width of the V-shaped groove is 4.0 $\mu$m. When the incident angle is equal or larger than the angle of the sidewall (54.74°) Janus particles with 50% gold coating are obtained. As this is true for any particle size, all lines in Figure 3.8 A join at the same point (54.74°, 50%). As the radius of the particles increases, the effective range of incident angles creating patches on the particles consequently increases as well. The linear appearance enables straightforward choosing of the correct incident angle required for a specific coated-area percentage. Note the relationship between $A\%$ and $\theta$ is not straightforwardly linear, but rather complex as shown by combination of Equs. 3.1 and 3.2 leading to a noticeable deviation from linearity at $\theta$ values near the 1/4 and 3/4 point of the entire range, which is more easily observed for larger particle radii.

Figure 3.8 B shows the same relationship for square-shaped grooves with dimensions of 4.0 $\mu$m width and 3.2 $\mu$m depth assuming that the particle is located at the center of the groove. The changing radius of the particle is denoted by different colors. The patch height, $h$, is calculated using Equ. 3.3 and converted to coated area percentage, $A\%$, using Equ. 3.1:
Note that in contrast to Figure 3.8 A, there is no \( \theta \) limitation. The point at which 50% coating, i.e., Janus particle, is reached depends on the ratio of groove dimension to particle radius. If the width and depth of the groove are equal to the diameter of the particle, the values of incident angles creating patchy particles ranges from \( \theta = 0^\circ \) to \( 90^\circ \). Interestingly, all lines in Figure 3.8 B join in the point Z at \( A\% = 38.3\% \) and \( \theta = 58.0^\circ \). The point Z is of interest as it enables evaporation of patches with identical surface areas onto particles of varying radii using the same template and incident angle \( \theta \). Note that the specific \( A\% \) and \( \theta \) values for point Z depend strongly on the dimensions of the groove.

The inset in Figure 3.8 B schematically shows the particle-template geometry for point Z where \( \theta = \tan^{-1}(2d/w) \), which leads to \( h = r + r\cos(\tan^{-1}(2d/w)) \) and consequently a particle-size independent coated-area percentage as shown in Equ. 3.4:

\[
A\% = \frac{(1 + \cos(\tan^{-1}(2d/w)))/4}{4} \quad \text{Equ. 3.4}
\]

Equ. 3.4 can be corrected for particles not located at the center of the groove by setting \( d = d + vtan\theta \). 

\[
h = r - \frac{w}{2\sin(\tan^{-1}(\frac{w}{2(d-r^2)}))}\sin(90^\circ - \theta - \tan^{-1}(\frac{w}{2(d-r^2)})) \quad \text{Equ. 3.3}
\]
If the template with square grooves is used, the change of patch size will be a bit more complex, since the depth of the groove is not associated with the groove width. Figure 3.9 illustrates the trend of the coated-area percentage as a function of incident angle with the change of the two dimensionless parameters $w/r$ and $d/r$. The diameter of the particle is set to 2.4 μm, whereas the width of the square groove is varied from 2.4 to 4.8 μm and the depth of the square groove is adjusted from 2.4 to 4.8 μm. When the width of the groove, $w$, is fixed, i.e., constant $w/r$ ratio, the incident angles at which patchy particle fabrication (smallest patch) begins and where Janus particle fabrication (50 % patch) occurs increase with increasing groove depth, while the effective range of incident angles resulting in patchy particles narrows. When the groove depth, $d$, is fixed, i.e., constant $w/r$ ratio, the beginning and ending points of the $\theta$-range in which patchy particles are fabricated decreases with increasing groove width with a similar narrowing of the range. From a practical point of view, a groove with a width and a depth similar to the diameter of the particle is preferred, since it provides the largest effective range of incident angles and a more precise control of the patch size with respect to $\theta$. Another advantage is that the patches will have identical shapes if they cover the same area independent of the template used, because the patch is created by the shadow of the groove walls. The slightly curved nature of the lines discussed in the context of Figure 3.8 can also be observed in Figure 3.9.
3.2.3 Experimental Results

After evaporation, the patch shape and area are characterized using a scanning electron microscope (EVO40 Zeiss). Patchy particles can be removed from the template by sonicating the templates in deionized (DI) water. SEM images are taken to check the validity of calculated results, and to prove the ability of fabricating patchy particles with patches of uniform, asymmetric shapes (semispherical cap).
Figure 3.10 SEM images of patchy particles fabricated in V-shaped grooves at different incident angles.

Figure 3.10 shows scanning electron microscopy images for 1.500 ± 0.026 µm polystyrene particles with patches created with a V-shaped template. The V-shaped template is chosen as it enables easy centering of the particles in the groove due to its V-shaped geometry. Figure 3.10 A shows a large area view of the distribution of particles in a template with V-shaped grooves (w = 3.7 ± 0.1 µm, groove pitch = 2.8 ± 0.1 µm). Most of the particles are found to form linear close-packed aggregates within the grooves. Averaging over several regions on the template yields a maximum particle packing average of 14 ± 5 %. There are some defects such as particles not staying in grooves or
not forming a perfect linear arrangement as highlighted in Figure 3.10 A by the solid and dashed arrows, respectively, which results in about $6 \pm 2\%$ of the particles having defective patches based on the statistical analysis of the experimental results. The few stray particles that are outside the grooves can be removed by stamping with a pre-cured PDMS film as described above.

In our previous work using close-packed monolayer, we reported an average domain size of 3000 particles within which all patches have a uniform shape and size. However, the particles at the edge of such a domain within a close-packed monolayer do not benefit from the same shadowing effect as particles within the domain leading to an additional patch size and shape variation of approximately $7 \pm 1\%$. The template-assisted GLAD method introduced here has the additional benefit that only the template size limits the number of patchy particles that can be produced in one fabrication cycle. For example, a template on a one square inch Si wafer with one-inch-long grooves at a density of 3845 (groove width = 3.7 μm, groove pitch = 2.8 μm) that is filled to 15% with particles (1.500 ± 0.026 μm diameter) leads to 9,300,000 patchy particles with uniform patch size and shape compared to the ca. 3000 particles in one ordered domain reported for the template-free GLAD technique.\textsuperscript{26} Note, functionalization of particles for a 1 ml particle latex solution with 4% solids would require 4600 experiments using the 1x1 inch\textsuperscript{2} template described above. This number can be dramatically decreased to 28 times if an 18-inch Si wafer (currently used by Intel) would be used for template preparation.

Figures 3.10 B-D show zoomed-in images of particles and their uniform 35 nm gold patches obtained at $\theta = 26^\circ$, $22^\circ$, and $19^\circ$. The SEM images confirm that the patch shape (bright area on particle) is a half-spherical cap, which is caused by the shadowing of the
metal vapor flow by the wall of the groove located closer to the source. Besides having
the same shape and size, all patches are symmetric around the axis parallel to the metal
evapor flow and normal to the groove surface. As $\theta$ increases from $19^\circ$ to $26^\circ$ the patch
size increases from $A\%_{19^\circ} = 3.9 \%$ to $A\%_{26^\circ} = 9.9 \%$ in good agreement with the
prediction shown in Figure 3.9 B. To verify the coated area percentage at the three
incident angles, the distance between the two corner points on the flat side of the patches
(denoted as $2l$ in Figure 3.10 B) is measured for each patch. The patch height, $h$, is then
calculated using Equ. 3.5 (note, Equ. 3.5a is used when the coated area is less than one
fourth of the entire particle surface, whereas Equ. 3.5b is used when it is larger than one
fourth):

$$h = r - (r^2 - l^2)^{\frac{1}{2}} \quad A_{\text{cap}} < \frac{1}{4} A_{\text{sphere}} \quad \text{Equ. 3.5a}$$

$$h = r + (r^2 - l^2)^{\frac{1}{2}} \quad A_{\text{cap}} > \frac{1}{4} A_{\text{sphere}} \quad \text{Equ. 3.5b}$$

The $2l$ for the patches shown in Figure 3.10 B, C, and D is measured to be $2l_{26^\circ} = 1.18 \pm
0.05$, $2l_{22^\circ} = 1.04 \pm 0.04$, and $2l_{19^\circ} = 0.79 \pm 0.09 \mu$m, respectively. These $2l$
values result in $h$ values of $h_{26^\circ} = 0.29 \pm 0.05$, $h_{22^\circ} = 0.21 \pm 0.03$, and $h_{19^\circ} = 0.11 \pm 0.05 \mu$m. Using the
$h$-values measured from SEM images, coated percent areas of $A\%_{26^\circ} = 9.9 \pm 0.8$, $A\%_{22^\circ} =
7.1 \pm 0.5$, and $A\%_{19^\circ} = 3.9 \pm 1.0 \%$ are calculated and are in good agreement with the
computationally predicted values of 10.5, 7.1, and 3.6 %, respectively. The increased
variation of patch size at the smallest incidence angle (Figure 3.10 D) is a result of non-
uniform etching of the template and/or the variation in particle size. Both sources of
patch variation can be addressed by further optimization of the template or choosing of particles with a narrower particle size distribution.

From Equs. 3.1 and 3.2, we see that for V-shaped grooves besides the incident angle, $\theta$, two other parameters, $r$ and $w$, play an important role with respect to the patch shape. The $r$ and $w$ values can be combined into one dimensionless parameter, $w/r$, which generalizes the graph (Figure 3.9 A) for V-shaped grooves and particles with $w/r$-ratios ranging from 4 to 10. The dimensionless $w/r$-ratio allows us to choose or draw a plotted line for the purpose of finding the right angle of incident for a specific coated area percentage to be obtained. Similarly, for the square grooves, the three parameters $r$, $w$, and $d$ can be combined into two dimensionless parameters $w/r$ and $d/r$. Figure 3.9 B is based on the practical consideration that particles of different sizes can be loaded into the same template. To understand the influences of the groove dimensions, a more systematic study is necessary. In addition, it may prove difficult to locate particles at the center of the square groove as capillary forces are likely to pull particles towards one or the other groove wall. This tendency may be suppressed by re-shaping the flat bottom of the groove into a concave-shaped bottom warranting further study of the evaporation geometry with the square-shaped groove.

### 3.2.4 Conclusions

The experimental results and calculations show that we are able to use a Si wafer template to assist with the fabrication of patchy particles with uniform patches through the glancing angle deposition technique. If the vapor flux is kept perpendicular to the
groove direction, the patch shape produced is always symmetric and takes the shape of one half of a spherical cap. The patch shape and size are controlled by the incident angle, \( \theta \), particle size, \( r \), and the dimensions of the template. Note a change of the vapor flux direction with respect to the groove direction enables access to a large variety of asymmetric patch shapes that are the topic of Chapter 4. The ability of fabricating uniform and controlled patches, the ease of use in carrying out the experiments, the reusability of the template, and the 3100 fold increase in particle volume make this template-assisted method interesting, versatile, and scalable. In addition, the use of industrially employed substrates and lithography techniques may allow for easier implementation in an industrial-scale process. Simple geometric models illustrate the relationship between coated-area percentage and the incident angle of vapor flux, the template dimensions, and the particle size.
Chapter 4

Patchy Particles with Controlled Shapes

As stated in Chapter 2, most reports about patchy particle assembly (experiment or simulation) are based on patchy colloidal particles with symmetric patches (in most cases circular patches). Recent interest in asymmetric patches has been caused by prediction and observation of the chiroptical effect for such patches,\textsuperscript{60} which provides new applications for particles with patches of asymmetric shapes. Simulation results by Sciortino et al.,\textsuperscript{8} reveal that the assembly of patchy particles is strongly affected by subtle changes in patch orientation and shape, which emphasizes the importance of exquisite control over patch shape and the need for asymmetric or less-symmetric patch shapes. They concluded that staggered triangular patches on opposite sides of a particle will lead to the selection of crystal structures with a staggered geometry, while patches arranged in an eclipsed geometry can only form crystal structures with eclipsed geometry.

Based on the review of patchy particle fabrication methods in Chapter 2, only a few of them allow control of patch shape or give access to a variety of patch shapes. In the method that uses particle layers with various packing patterns as masks to assist the fabrication,\textsuperscript{38} patch shapes are limited by the available mask patterns and the patch uniformity depends strongly on the quality of the mask packing pattern, which needs fine control to be obtained. In light of bulk fabrication, the throughput of this method is rather
limited. The method proposed by Shah et al.\textsuperscript{5} to prepare spheroidal Janus and ‘Kayak’-shaped patchy particles via elongational stretching under heating before or after metal deposition, respectively, enriches the capability of achieving various patch shapes through the physical vapor deposition method. As stated in Chapter 3, the application of GLAD to close-packed monolayers is suffering from the lack of patch uniformity due to the diversity of domain orientations in particle monolayers, although it can achieve a mixture of various patch shapes in each run.

In Chapter 3, we introduced a template to the GLAD method enabling (i) the fabrication of patchy particles with uniform hemispherical patches, (ii) the reuse of the template, and (iii) the scalability of the GLAD method. In this chapter, we investigate the effects of template rotation on patch size and shape leading to well-defined but asymmetric patches and the inclusion of a second evaporation leading to overlapping patches. Based on the geometric model, which will be discussed in Chapter 5, the patch shape, size, and position are predicted and validated by experiments. The patch shape is determined by the glancing angle, the shadowing from neighboring particles, and the template groove resulting in belt-like and triangular patches, whereas overlapping belt-like patches are produced by consecutive evaporations and may enable the fabrication of circular patches that span around the equator of the colloidal particle. In addition, preliminary magnetic field assembly results are included for particles with asymmetric triangular patches. These patchy particles are re-suspended after modification of the template.
4.1 Various Patch Shapes from Template-assisted GLAD

The physical vapor deposition method utilizes the shadowing effect to control the patch size and shape. A further application of the GLAD method is the fabrication of metal structures by removal of the colloidal particles. A Janus particle is produced due to the shadowing of the particle itself. For example, where close-packed monolayers are used, the fabrication benefits from the shadowing effect of the surrounding particles. In Chapter 3, to improve the uniformity of patch shapes, a template is introduced to assist the GLAD fabrication. The template causes all colloidal particles to experience the same shadowing effect. The variation of patch shape due to the coexistence of multiple orientations of close-packed domains indicates the possibility of controlling patch shapes by tuning the orientation. In Chapter 3, the incident metal vapor flow is perpendicular to the groove lines. When the template is rotated to a specific angle, the metal vapor flow will not be perpendicular to the groove lines while the incident angle is kept unchanged. This will introduce the shadowing effect of the adjacent particles, which will be the main topic of this chapter.

4.1.1 Experimental Details

A template with a V-shaped groove (width = 3.7 ± 0.1 μm, groove pitch = 2.8 ± 0.1 μm) same as in Chapter 3 is used. Sulfated polystyrene particles (Molecular Probes, 1.500 ± 0.026 μm, 8.0% w/v) are loaded into the template using a convective assembly method
that pulls an angled glass slide over the template with the grooves oriented perpendicular
to the direction of the pulling. The gold or iron patch of $50 \pm 5$ nm thickness is deposited
on the surface of the PS particles using a bench top evaporation system (Cressington
308R, Ted Pella, Inc.) at a pressure of $10^{-6}$ mbar. For the deposition of iron, the deposit
rate is 0.35 nm/s in a 3:1 Ar:O$_2$ mixture to yield Fe$_3$O$_4$ patches.$^{16}$ The direction of the
incident metal vapor is varied from the perpendicular source-groove geometry previously
used by rotation of the template within the plane of the sample stage as shown in Figure
4.1.

Figure 4.1 Schematic of metal vapor flow in template-assisted patchy particle fabrication
using glancing angle deposition method with template at various angles.
Figure 4.1 shows a schematic representation of particles in a V-shaped groove indicating the incident angle of the metal vapor flow, $\theta$, defined as the angle between the metal vapor flow and the Si wafer surface and the rotation angle, $\alpha$, measured as the angle between the orthogonal projections (white lines) of the specific evaporation direction ($I_1$) and the perpendicular direction ($I_0$) for a single evaporation (Figure 4.1). For the perpendicular direction, $I_0$, $\alpha = 0^\circ$, which corresponds to the situation in Chapter 3.

After evaporation, the patch shapes and areas are characterized using a scanning electron microscope (EVO40 Zeiss) in high-resolution mode. The patch size can be estimated using the method described in Appendix A. In brief, for the SEM images of patchy particles, the radius of the particle is first determined in pixels. Based on the value of the radius, the coordinates of each orthogonal projection point are calculated. The area of the patch is then determined by counting the number of orthogonal projection points covered by the patch.

To get the patchy particles assembled, particles need to be transferred to solution first. For particle removal, the grooved substrate with the patchy particles is placed upside down into a cleaned glass petridish. 1 ml of deionized (DI) water is added to the petridish and exposed to sonication for 30-60 s. Subsequently, the suspension is stored in a glass vial. Prior to magnetic field assembly tests, the particle solution is concentrated by centrifugation at 3500 RPM for 5 minutes followed by removal of most of the supernatant. 40 $\mu$l of the concentrated particle suspension is added to a cell, covered with a microscope glass slide, allowed to equilibrate for 5 min, and exposed to the U-shaped magnet of 0.008 T.
4.1.2 Calculation Results

Figure 4.2 Theoretically predicted patch shapes obtainable by a single evaporation as a function of rotation angle, $\alpha$, and incident angle, $\theta$.

With the help of the straightforward numerical model, the types of asymmetric shapes accessible via template-assisted GLAD method with rotation will be discussed in this section. We show that the patch shape is affected by the incident angle, the rotation angle, the particle size, and the template dimensions and explain under which conditions an asymmetric or symmetric patch is formed. For a specific incident angle, $\theta$, as we increase the rotation angle from $\alpha = 0^\circ$ (Figure 4.1, $I_0$) to $\alpha = 90^\circ$, where the projection of $I_I$ is
parallel to the grooves, three characteristic points are transitioned: (i) the point at which $\alpha$ is large enough for the metal vapor to deposit a patch on the PS particle surface (Patching Point), the point at which $\alpha$ is large enough such that the adjacent PS particle affects the patch shape (Shadowing Point), and the point at which $\alpha$ is large enough such that the patch shape is not affected by the templating groove (Groove Point).

Figure 4.2 plots the theoretical patching, shadowing and groove points for 2.0 $\mu$m diameter PS particles in a V-shaped groove of 4.0 $\mu$m width as functions of incident and rotation angles. The patching (empty red triangles), shadowing (solid red triangles) and groove point functions (solid black squares) divide the plot area into four distinct regions. Typical patch shapes predicted for the four regions are shown schematically as area defined by the blue lines on spherical particles viewing the patch from the metal vapor source. At $\theta$ and $\alpha$ in the region below the patching point function, no patch is formed on the particle surface. Between the patching point and the shadowing point functions, symmetric patches with the typical hemispherical cap caused by shadowing from the groove are formed. Larger $\theta$ and $\alpha$ angles lead to a larger patch.

In Figure 4.2, Patch 1 is obtained at $\theta_{P1} = 25^\circ$ and $\alpha_{P1} = 6^\circ$. In the region between the shadowing point and the groove point functions, the shadowing effects of both the groove and the adjacent particles cut off part of the semispherical cap resulting in asymmetric patches. Patches 2, 3, and 4 are obtained at $\theta_{P2} = 5^\circ$ and $\alpha_{P2} = 70^\circ$, $\theta_{P3} = 25^\circ$ and $\alpha_{P3} = 50^\circ$, and $\theta_{P4} = 40^\circ$ and $\alpha_{P4} = 50^\circ$, respectively. Generally, small $\theta$ and large $\alpha$ give smaller patches (Patch 2), whereas large $\theta$ and small $\alpha$ result in larger patches (Patch 4). At points beyond the groove point function, the patch shape is only affected by shadowing from the adjacent particle resulting in an asymmetric, crescent shape of the patch. Patches 5 and 6
are obtained at \( \theta_{P5} = 5^\circ \) and \( \alpha_{P5} = 88^\circ \) and \( \theta_{P6} = 40^\circ \) and \( \alpha_{P6} = 85^\circ \), respectively. At smaller \( \theta \), a thinner patch shape (Patch 5) is observed than at larger \( \theta \) (Patch 6). What should be pointed out is, at \( \theta > 54.7^\circ \), a patch is formed on the particle surface, even at \( \alpha = 0^\circ \). When \( \theta > 28.7^\circ \), the height of the hemispherical patch will be larger than the radius of the particles, which means that a very small \( \alpha \) will result in a shadow effect from the adjacent particle and affect the patch shape resulting in an overlap of the patching and shadowing point functions at \( \theta > 28.7^\circ \). This specific rotation angle, denoted as \( \theta_{C2} \), is affected by the groove width, \( w \), and particle diameter, \( d \), and can be calculated by Equation 4.1:

\[
\theta_{C2} = 54.7^\circ - \tan^{-1} \left( \frac{d}{w \cos 54.7^\circ \times \tan 54.7^\circ} \right)
\]

Equ. 4.1

Owing to the fact that the template can be reused, various particle sizes can be modified using the same template. The size of the particle affects the patching point and shadowing point functions. Figure 4.3 depicts the trends predicted for the two functions with open and solid symbols, respectively, when the particle diameter is decreased from 2.0 (red triangles) to 1.4 (green diamonds) to 0.8 \( \mu m \) (blue circles). The groove point function (solid, black squares) is not affected by particle size because it is only determined by the groove geometry.

From Figure 4.3 we can conclude that a reduced particle size requires a larger \( \alpha \) at a constant \( \theta \) for the preparation of patchy particles, whereas at a constant \( \alpha \), we need a larger \( \theta \) to obtain patchy particles with decreasing particle size. Further, the patching point and shadowing point functions nearly overlap (the rotation angle difference between these two points is less than 3\(^\circ\)) at large \( \alpha \) below a characteristic \( \theta_{C1} \), which increases with decreasing particle size. For particles with diameters of \( d = 2.0, 1.4, \) and
0.8 μm, the characteristic incident angle $\theta_{c1}$ is 1.2°, 12.6°, and 26.5°, respectively, in a V-shaped groove of 4 μm width.

Figure 4.3 Theoretically predicted patch shape diagrams for single evaporation as a function of particle diameter in a V-shaped groove of 4.0 μm width.

The overlap of these two functions implies that it is difficult to make patches with Patch 1 shape (Figure 4.2), which is only affected by the groove. Further, above a second characteristic incident angle, $\theta_{c2}$, and small $\alpha$, the patching point and shadowing point functions overlap again up to a $\theta = 54.7^\circ$ dictated by the groove geometry. $\theta_{c2}$ increases from 28.7° to 38.9° to 46.9° with decreasing radius. The range of incident angles between
$\theta_{C1}$ and $\theta_{C2}$ and the area beneath the groove point function and above the shadowing point function suggests that for a better control of the patch shape and size and a wide range of asymmetric patch shapes, a larger particle is preferred in practice. The maximum particle size for which patch shape and size is controlled entirely by the groove is given by the constraint that the particle has to be flush with the template surface. For grooves of 4.0 μm width, the maximum particle diameter is 2.06 μm (51.8% of the groove width).

Besides the patch shape, the patch size is also what the template-assisted GLAD method with rotated template aims to control. Due to the shadowing effect of the groove and adjacent particles, the patch size (i.e., the coated area percentage, $A\%$), which has the same definition as given in Chapter 3, is a function of the incident and rotation angle.

Figure 4.4 shows the calculated $A\%$ values as the function of $\alpha$ at varying $\theta$ for particles with diameters of 2.0 μm (Figure 4.4 A) and 1.6 μm (Figure 4.4 B) in V-shaped grooves of 4.0 μm width. $\theta$ is changed from 5 to 50° in 5° steps as indicated by the change in color and symbols used for plotting. All functions have in common that with increasing $\alpha$, $A\%$ first increases up to a maximum and then decreases. It is interesting that the patch maximum coincides with the groove point (dashed line in Figure 4.4). While we cannot prove that these two points are indeed the same due to the limited degree of precision attainable with our calculations, a qualitative explanation can be given for their coinciding. As $\alpha$ increases, the height of the hemispherically shaped patch increases resulting in an increased patch size. At the same time the particle portion shadowed by the adjacent particle is also increasing thereby decreasing the patch size. The rate at which the patch size increases due to the groove's shadowing effect is larger than the rate at which the patch size decreases due to shadowing from the adjacent particle. As a result,
the largest patch size occurs at the groove point since beyond this point the patch is no longer affected by the groove, which also explains the decreased rate of change in $A\%$ beyond the shadowing point.

Figure 4.4 Calculated coated-area percentage, $A\%$, plotted as a function of rotation angle, $\alpha$, at different incident angles, $\theta$, for particles of (A) 2.0 μm and (B) 1.6 μm diameter in V-shaped groove of 4.0 μm width.
Overall, the variation in $A\%$ as a function of $\alpha$ is small ranging from 5.8% for $\theta = 45^\circ$ to 12.2% for $\theta = 15^\circ$. The implication of this finding is that the incident angle, $\theta$, sets a basic $A\%$ for the patch size that can then be varied within a $9.0 \pm 3.2\%$ range by changing the rotation angle, $\alpha$. The solid line in Figure 4.4 indicates the shadowing points for various $\theta$. The patch is highly symmetric at angles below this line (Figure 4.2, Patch 1), whereas the observed change in slope is a result of the shadowing effect of the adjacent particle rendering the patch shape asymmetric for points beyond this line (Figure 4.2, Patches 2-4). Figure 4.4B presents $A\%$ at three incident angles for a 1.6 $\mu$m particle in a groove of 4.0 $\mu$m width. It is included here to show that smaller particle sizes show very similar trends, but show an increased $A\%$ range accessible (e.g., 11.8% vs. 24.2% at $\theta = 20^\circ$) in the same range of rotation angles. It also shows that patch formation at low $\theta$ occurs at higher rotation angles for smaller particles.

4.1.3 Experimental Results

Fabrication of Patchy Particles

After loading polystyrene particles into the template grooves, by changing the rotation and incident angles various patches have been fabricated on 1.500 $\pm$ 0.026 $\mu$m PS particles. The patches are characterized by SEM to validate the prediction.

Figure 4.5 shows patchy particles fabricated at different incident, $\theta$, and rotation angle, $\alpha$, combinations for a single gold evaporation (Figure 4.5A-C). The corresponding top views (row ii) for all three cases and the side views (row iii) for the single evaporation case along the vapor deposition direction obtained from the computational model are
shown. It is apparent that the patch shape and size are a strong function of both $\theta$ and $\alpha$.

The patches in Figure 4.5A (i) are fabricated at $\theta = 10^\circ$ and $\alpha = 68^\circ$, whereas the patches in Figure 4.5B (i) and 4.5C (i) are made at $\theta = 15^\circ$ and $\alpha = 68^\circ$ and $\theta = 15^\circ$ and $\alpha = 78^\circ$, respectively. The SEM images enable identification of the sharp leading and diffuse lagging boundaries,\textsuperscript{36} which result from the shadowing effect of adjacent particles and the groove and the metal vapor flow tangential to particle surface, respectively. The $A\%$ of the experimental patches shown in Figure 4.5A-C (row i) are 6.4%, 15.7%, and 16.6%, respectively. The experiments are in good agreement with the

![Figure 4.5](image)

Figure 4.5 Scanning electron microscope images of 1.500 ± 0.026 µm single-patch polystyrene patchy particles in V-shaped grooves of 3.7 µm width after single gold evaporation
conclusions drawn from Figures 4.2 and 4.3; the patch size increases at larger incident angles ($\theta = 10$ vs. $15^\circ$) when the rotation angle is fixed ($\alpha = 68^\circ$), and when $\alpha$ is increased, the patch size is affected more by the adjacent particle and less by the groove. The calculated patch sizes for the patches shown in Figure 4.5 (rows ii and iii) are 7.7, 14.7 and 21.6% in good agreement with the experimental patch areas. The somewhat larger deviation for the experimental and calculated patches shown in Figure 4.5C is the result of a portion of the patch being out of line-of-sight for the SEM as shown in the side view in Figure 4.5C (iii).

**Preliminary Assembly Results of Patchy Particles in Magnetic Field**

The assembly of patchy particles with triangular shaped patches is carried out to obtain preliminary results. The thickness of the patch is 79.2 nm indicated by the crystal microbalance in the PVD machine. The assembly is performed using a magnetic field of a U-shaped magnet with a field of 0.008 T.

Figure 4.6 summarizes first attempts at assembling patchy particles with identical iron oxide patches of the type shown in Figure 4.6A. Upon application of the magnetic field, the particles quickly assemble into chains along the magnetic field lines (Figure 4.6B). In contrast to the double chains observed for Fe$_3$O$_4$ Janus particles,$^{16}$ the patchy particle suspension yields chains that are branched and not close-packed (Figure 4.6C). Drying of the assembled chains allows imaging of the patch orientation within a chain (Figure 4.6D). The connectivity of the patches is apparent from the SEM image; however, the orientation of the patches appears to be random along the chain with a tendency to align the patch such that its longest axis is in the direction of the chain. Further experimental
and theoretical studies are underway to understand the driving forces leading to these assembly structures.

Figure 4.6 Magnetic field assembly of patchy particles with iron oxide patches

4.1.4 Conclusions

Based on the calculation and experimental results, we can conclude that the template-assisted GLAD method gives access to a large variety of asymmetric patches with controlled patch shapes when rotation of the template is enabled and $\theta$ and $\alpha$ are chosen such that the patch is produced between the shadowing and groove points. Besides the asymmetric, triangular patch shapes, hemispherical and crescent moon shaped patches are
also accessible. The abundance of shapes provides more choices for studying the effect of patch shape on patch interactions and assembly properties. Assembly tests prove that patchy particles can be easily re-suspended from the template after modification through a short exposure to sonication and can be produced in large enough quantities for assembly studies. In addition, preliminary magnetic field assembly of Fe₃O₄ patchy particles indicates that asymmetric patch shape leads to the ability to form branched chains. Promoted by the ability of fabricating patches on the surface that cannot be seen from the top, template-assisted GLAD with rotation enables modification of the lower particle surface when the particle cannot be turned easily.

4.2 Fabrication of Multiple Patches

Patchy particles with well-defined patch size and uniform asymmetric shapes have been produced successfully by changing the rotation angle and incident angle in the template-assisted GLAD method. Due to the unique properties of multi-patch particle, methods have been developed that enable the fabrication of such particles. The stamping technique has been used to assist the fabrication of multi-patch particles with patches located on the two opposite poles of the particle. The template-assisted GLAD method is extended to fabricate multi-patch particles of uniform asymmetric patches by sequential deposition. Figure 4.7 shows a schematic of multi-patch particle fabrication using the template-assisted GLAD method. The numerical model introduced in Chapter 5 is also used to predict the patch shapes and size, which are confirmed by the experiment results.
4.2.1 Experimental Details

Figure 4.7 Schematic of metal vapor flow in multi-patch particle fabrication using template-assisted GLAD.

Multi-patch particles with patches partially overlapping are fabricated by sequential evaporation. Figure 4.7 shows a schematic representation of particles in a V-shaped groove indicating the incident angle of the metal vapor flow, $\theta$, the rotation angle, $\alpha$, and the specific evaporation direction ($I_1$, $I_2$) and the perpendicular direction ($I_0$) for two subsequent evaporations. The incident angles for the two evaporations are denoted by subscripts 1 and 2 and the rotation angle is given with respect to the projection of $I_0$. The template geometry is the same as in section 4.1 (width = 3.7 ± 0.1 μm, groove pitch = 2.8
± 0.1 μm). Sulfated polystyrene particles (Molecular Probes, 1.500 ± 0.026 μm, 8.0% w/v) are loaded into the template using a convective assembly method that pulls an angled glass slide over the template with the grooves oriented perpendicular to the direction of the pulling. The two patches are of different material, Au and Fe. The gold patch of 50 ± 5 nm thickness is deposited on the surface of the PS particles using a bench top evaporation system (Cressington 308R, Ted Pella, Inc.) at a pressure of 10^{-6} mbar, while the iron oxide patch is made at a pressure of 10^{-3} mbar in 3:1 Ar:O_2 mixture.

These two metals were chosen because they have very distinct properties. Gold easily accepts ligands such as thiols and thus can provide anchor points for additional orthogonal assembly, while iron and its oxides can easily be magnetized and therefore be used to assemble the particles into chains in magnetic field. In addition, gold has a higher electron density and therefore shows a brighter contrast in SEM. After fabrication, the multi-patch particles are characterized by SEM. And the patch size is estimated using the method described in Appendix A.
4.2.2 Calculation and Experimental Results

Figure 4.8 Scanning electron microscope images of 1.500 ± 0.026 μm polystyrene particles after two evaporations of gold and iron oxide

By applying different incident angles and rotation angles for the two evaporations, these two patches can be of the same or different size or they can also appear on the same or opposing side. The fact is that these patches (if more evaporations are applied) are all partially overlapping with each other, due to fact that they all cover the top center point of the colloidal particle when observed from the top. The overlapping part can be calculated using the model described in Chapter 5.

Figure 4.8 shows patchy particles fabricated at different incident, \( \theta \), and rotation angle, \( \alpha \), combinations for two consecutive evaporations of gold and iron oxide (Figure 4.8A-C).
The corresponding top views achieved by the calculation are shown in row ii. The patches in Figure 4.8 A are fabricated at $\theta_1 = 15^\circ$, $\alpha_1 = 78^\circ$ and $\theta_2 = 10^\circ$, $\alpha_2 = 250^\circ$, while those in Figure 4.8 B and 4.8 C are prepared at $\theta_1 = 15^\circ$, $\alpha_1 = 78^\circ$, $\theta_2 = 15^\circ$, $\alpha_2 = 250^\circ$ and $\theta_1 = 20^\circ$, $\alpha_1 = 40^\circ$, $\theta_1 = 14^\circ$, $\alpha_1 = 240^\circ$, respectively. In the SEM images, the brighter patch (red line) is the first patch made of gold, and the dimmer one is the second patch (blue line) made from iron oxide. Note due to the fact that these patches are very thin (50 ± 5 nm) and the SEM probes deep enough to sample both patches in the area where they overlap, the gold patch dominates the image. We have added our predicted patch shapes to one particle in each image to help guide the eye. Row (ii) in Figure 4.8 A-C depicts the predicted patch shapes when the particle is viewed from the top of the template. The experimental $A\%$ of the patches shown in row (i) are determined to be 23.8%, 27.9% and 18.2%, respectively. The corresponding calculated $A\%$ for the predicted patches shown in row (ii) is 28.6%, 33.4% and 17.5%, respectively. The deviation between the experimental and computational patch sizes in Figure 4.8 A and 4.8 B is again due to the hidden portion of the gold patch (red line). Further, from the computed patch shapes, the overlapping part of the two patches is calculated as 4.4, 7.3, and 6.8%. From comparison of Figures 4.8 A and 4.8 B, we can determine that increasing $\theta_2$ leads to more overlap and an overall increase of $A\%$.

4.2.3 Conclusions

The sequential evaporation without flipping the particles generates overlapping patches using the template-assisted GLAD method. The experimental results confirm the
prediction from the patch shape and size. With the help of the numerical model, the size of the overlapping part can be calculated, which may not be accessible by other characterization method such as SEM. To achieve multi-patch particles with specific patch size and shapes, the numerical model, which is described in Chapter 5, can serve as an instruction. The variation of the overlapping part, which depends on the incident angle and the rotation angle and can be predicted by calculation, provides the possibility to achieve novel structures and properties, such as the motors heralded elsewhere. The particles with two long belt-like patches that partially overlap and create a patch with a partial circular shape around the waist of the particle with the two poles staying unmodified might show more intriguing properties.
Chapter 5

A Generalized Numerical Model for GLAD

From the review of the patchy particle assembly (simulation and experiments) given in Chapter 2, it is clear that quantitative information is necessary to investigate, summarize, and predict the occurrence of assembly structures. Quantitative information includes patch size, position, number of patches per particle, and even patch shape. The patch shape has drawn the interest of researchers owing to the observed chiroptical property of asymmetric patches\(^6\) and the specific stacking patterns predicted by simulations as a result of different orientations of triangular patches.\(^8\) Most simulation work, however, has focused on patchy particles with circular patches most likely because of the simplicity of modeling particles with more symmetric patch shapes. An asymmetric patch needs more parameters to define its shape accurately compared to a circular patch, for which a vertex angle is the only parameter needed.

The glancing angle deposition method\(^{35, 36, 39, 53, 59, 115}\) (GLAD) is a facile method to fabricate various patch shapes, and has the advantage of achieving asymmetric or less-symmetric patches compared with other fabrication methods. By changing the incident angle of the metal vapor flow and the orientation of the close-packed monolayer and via
the introduction of a template to assist in patch shape control and scalability of productivity (Chapter 3 and 4), various patch shapes have been accessed. The combination of GLAD with particles in specific 2D patterns\textsuperscript{106-109} is promising to achieve patches of various well-defined shapes. However, in order to apply the proposed theory to the instruction of the assembly of such patchy particles, the patch shapes need to be accurately and numerically defined, rather than just provided as scanning and transmission electron images in reported work as that represents a barrier between experimental results and comparison with theory. To avoid the need for numerous trials to obtain a specific shape, certain fabrication parameters need to be determining first illustrating the importance of a general numerical method to describe the patch shapes.

The GLAD method has been widely used to fabricate patchy particles,\textsuperscript{35, 36, 39} metal and semiconductor structures,\textsuperscript{111, 112} hollow spheres,\textsuperscript{113} and others.\textsuperscript{60} For the programmed assembly of patchy particles and the chiroptic properties of asymmetric patches, a systematic and deep study requires the numerical analysis of the patch shapes. The alignment and rotation of anisotropic particles on a non-planar interface provides a new mechanism for the assembly of patchy particles,\textsuperscript{116} which also requires the numerical analysis of patch shapes. When multiple patches are fabricated through GLAD by subsequent evaporations, the patch position needs to be defined numerically and not just visually as the first patch, for example, may be completely hidden by or may simply not be distinguishable from the second one, in order to study the properties of overlapping patches scientifically.\textsuperscript{117}

In this chapter, we introduce a generalized numerical model aiming to provide quantitative information for simulation of patches obtained with the GLAD method. This
model is shown to be applicable to not only the GLAD method that uses close-packed monolayers and V-shaped templates, but also other templates and loosely-packed colloidal particle films. The patch shape is defined by the shape boundaries. As an application of the proposed model, the template-assisted GLAD is studied in more detail in this chapter. The boundaries of patches and vertex angles are given in mathematical equations, which help predict patches fabricated at specific incident angles, monolayer orientations, and rotation angles. Due to the complexity of the resulting patch symmetry, patch positions are also defined geometrically by the boundaries, especially for the case of overlapping patches, which is different from and requires more complex numerics than circular patches. The boundary formula can also be applied to calculate or estimate the patch size and determine related parameters for specific patch shapes. At the same time, more patch shapes are discovered which supplement the work using close-packed monolayers presented in Chapter 4.

5.1 Model Setup

In this section, the model will be built by analyzing patches obtained from the GLAD method that uses close-packed monolayers and V-shaped grooves. For the GLAD method, the shadowing effect plays the key role in determining the patch shape. Part of the patch boundary is the circular edge (lagging boundary), generated due to the half of the particle surface modified by the incident metal vapor flow when there is no shadowing effect of other objects. When a template is introduced, the shadowing effect due to the template and adjacent particle contributes to the patch shape. In the case of a
close-packed monolayer, the patch shape is affected mainly by surrounding particles, which introduces more complexity.

Figure 5.1 Schematic of setup for GLAD with (A) V-shaped template and (B) close-packed monolayer.

The patch boundary is defined in three-dimensional (3D) space by describing the X, Y, Z position of each point of the boundary. First, for the template-assisted GLAD method (using the V-shape grooves, Chapters 3 and 4), the center of the studied particle is set as
the origin at (0, 0, 0). The X, Y, Z axes are defined as depicted in Figure 5.1A. The Y axis is parallel to the groove wall, the Z axis is perpendicular to the template surface, and the X axis is perpendicular to the grooves and parallel to the template surface. To be consistent with previous work, the particle radius is denoted as \( r \), the groove width is \( w \), the incident angle is \( \theta \), and the rotation angle is \( \alpha \). For the groove template prepared by etching of a Si wafer, the groove’s characteristic angle (as it may be different from 54.7\(^\circ\)) is denoted as \( \sigma \). Clearly, all points on the groove edge have the same X value of \( w/2 \), and Z values of \( H \), which can be calculated using Equation 5.1a. The direction vectors of the incident metal vapor flow \( (n_x, n_y, n_z) \) can be calculated following Equations 5.1b, 5.1c, and 5.1d.

\[
H = \frac{w}{2} \times \tan \sigma - \frac{r}{\cos \sigma} \tag{5.1a}
\]

\[
n_x = \cos \theta \cos \alpha \tag{5.1b}
\]

\[
n_y = \cos \theta \sin \alpha \tag{5.1c}
\]

\[
n_z = \sin \theta \tag{5.1d}
\]

The values of these parameters are fixed when particle size, groove dimension, rotation angle, and incident angle are constant and are used to simplify the equations. The equations for the lagging boundary can be achieved by meeting the condition that the vector from any point on the boundary is normal to the incident metal vapor flow, i.e., direct in vector \( (n_x, n_y, n_z) \). The boundary due to the shadowing effect of the groove wall meets the condition that any point on it is also on the plane defined by the groove edge and the direction vector \( (n_x, n_y, n_z) \). The boundary due to the shadowing effect of the adjacent particles meets the condition that the distance from the center of the adjacent
particle to the line of the direction vector \((n_x, n_y, n_z)\) passing through the point on the boundary equals to \(r\). The part of the lagging boundary covered by the groove and particle shadow will be cut off and replaced by the corresponding boundaries due to the groove and adjacent particle. The intersections of these boundaries determine the final points of each boundary section.

For the GLAD method with a close-packed monolayer, the center of the studied particle is also set as the origin point \((0, 0, 0)\). The XY plane is set parallel to the substrate and the directions of the X axis and Y axes are chosen as illustrated in Figure 5.1b. The Z axis is normal to the XY plane. The particle radius is \(r\). When the substrate is rotated to change the monolayer orientation, \(\alpha\), it can be equated to a rotation of the incident metal vapor flow. In Figure 5.1b, the dotted arrows show the metal vapor flow of two directions with \(\alpha = 0\) and \(\alpha = 30^\circ\). The direction vector of the incident metal vapor flow is again denoted as \((n_x, n_y, n_z)\), which can be calculated using Equations 5.1b, 5.1c, and 5.1d. Similarly, the patch also has a lagging boundary that can be calculated in the same way. Since there are more surrounding particles than in the case of the template-assisted GLAD method, more boundary sections will exist owing to the corresponding shadowing effect. These boundary sections can be determined using the same method described above. The only difference is the number of times the procedures will be repeated as the number of surrounding particles increases. Intersections will again be solved to provide the final shape for each boundary section.
GLAD Method with V-shaped Grooves

For the template with a V-shaped groove, the equations can be simplified by denoting the Z value of groove edge line as \( D \) and using the incident vapor flow direction vector \((n_x, n_y, n_z)\), instead of the parameters that they are derived from.

The lagging boundary can be calculated by solving the following set of equations (5.2) for \( y \) and \( z \) as the function of \( x \):

\[
\begin{align*}
  x^2 + y^2 + z^2 &= r^2 \\
  x \times n_x + y \times n_y + z \times n_z &= 0
\end{align*}
\]

(5.2)

The boundary due to the shadowing effect of groove is obtained from the following set of equations (5.3):

\[
\begin{align*}
  x^2 + y^2 + z^2 &= r^2 \\
  \left( x - \frac{w}{2} \right) \times n_z - (z - H) \times n_x &= 0
\end{align*}
\]

(5.3)

The boundary due to the shadowing effect of other particles is calculated from yet another set of equations (5.4):

\[
\begin{align*}
  x^2 + y^2 + z^2 &= r^2 \\
  ((y - y_1) \times n_z - (z - z_1) \times n_y)^2 + ((x - x_1) \times n_z - (z - z_1) \times n_x)^2 + ((x - x_1) \times n_y - (y - y_1) \times n_x)^2 &= r^2
\end{align*}
\]

(5.4)

By solving the last set of equations (5.4), \( Y \) and \( Z \) values will be obtained as functions of \( X \). The \( x_1, y_1 \) and \( z_1 \) values are the center coordinates of the particle that cast a shadow on the particle of interest. The exact boundaries can be calculated and a graph as that shown in Figure 5.2 will be provided. The procedure for obtaining the graph in Figure 5.2 is detail in the following.
Figure 5.2 Schematic of the three types of patch boundaries (green – Groove boundary, red – Lagging boundary, and blue – Shadowing boundary) drawn based on the equations describing the patch shape mathematically.

**GLAD Method with Close-Packed Monolayer**

For the GLAD method employing a close-packed monolayer, the lagging boundary can also be achieved by solving Equation 5.2. Since the studied particle is surrounded by many more particles, the shadowing effect from additional particles should be taken into consideration. A change of the monolayer orientation will affect different particles and result in different patch shapes. Despite this fact, the boundaries resulting from these particles are still calculated using Equation 5.4. However, different $xI$, $yI$ and $zI$ values need to be provided for each particle and a graph visualizing the boundaries similar to that in Figure 5.2 can be obtained. Note Equation 5.4 can also be used for loosely-packed layers as long as $xI$, $yI$, and $zI$ coordinates of each of the surrounding particles are known.
5.2 Quantitative Analysis

In the following, we will first present the case of the GLAD method with a template that has V-shaped grooves, followed by the case that uses close-packed monolayer where shadowing effects caused by more particles need to be taken into consideration. As an application of the mathematical expressions for these boundaries, the patch size related properties and previously unreported patch shapes are discussed for specific parameter sets.

For the template-assisted GLAD method, due to the symmetry, the range of rotation angles, $\alpha$ is set from 0° to 90°. For $\alpha$ that are larger than 90°, the patch shape boundary can be described by changing one or both of the X and Y values to the opposite number that are obtained at $180° - \alpha$ (or $\alpha - 180°$, or $360° - \alpha$) and are located in the range from 0°-90° (more details are provided in Appendix A). Based on the method described above, the lagging boundary can be determined by Equations 5.5.1 and 5.5.2, in which the Y and Z values of the points on the boundary are functions of the X value that ranges between [-r, r]. Based on the equations, each X value corresponds to a set of two Y and Z values, which is easily illustrated by the following method. The red line in Figure 5.2 shows one example of a calculated lagging boundary. We should point out that these two sets of equations [Equations 5.5.1 and 5.5.2] result in the entire red circle. However, parts of the red lines displayed are not part of the boundary as they are overwritten by the shadowing effects of the groove wall and the adjacent particles that are discussed next.
The Y and Z values of the points on the boundary that are caused by the shadowing effect of the groove are also described as functions of the X values in Equations 5.6.1 and 5.6.2. And for each X value there are two sets of Y and Z-values found. The green circle in Figure 5.2 shows an example of such a calculated boundary.
and particles radius $r$ are not given first, the expression will be complex and difficult to read. So, the method is illustrated below by solving the sets of equations in Equation 5.4, in which the Y- and Z-values are provided as functions of the X-value (solved by Matlab, Mathematica, or other mathematical software). Note as mentioned above the $xI$, $yI$, and $zI$ coordinates represent the center of the particle that casts the shadow onto the particle of interest.

The boundary of the final patch is formed by portions of the red, green, and blue lines. In order to determine which portion of these calculated boundaries are part of the final patch, three intersecting points need to be defined. Note even if the original range of X values ranges from $-r$ to $r$, the range for the different equations needs to be considered carefully to make sure that no imaginary numbers are introduced in the process. The three points of intersection are calculated by realizing that the crossed lines have to the same X, Y and Z values at the intersecting point. Figure 5.2 shows the schematic of these boundaries and provides a visual aid that should be used to check the final patch shape. The position of such asymmetric or less-symmetric patches is also defined by these equations in 3D. As we have shown, the description of such patchy particles is complicated, however necessary when a second patch is fabricated on the same particle.

For the GLAD method with a close-packed monolayer, as stated in section 5.1, the patch is defined by more boundaries cast from surrounding particles. To define each contributing boundary, the $xI$, $yI$ and $zI$ values will be assigned specific values for each particle before solving the set of equations given in 5.4. After solving all boundary equations, a similar procedure as that detailed for the GLAD method with V-shaped grooves is followed to define the patch shape numerically.
Figure 5.3 Definition of vertex angles of the patch from GLAD method (A) with V-shaped grooves and (B) with close-packed monolayers. (C) Vertex angles as a function of incident angle.

One application of these boundary equations is to find the vertex angle. The vertex angle is a key parameter to describe the size of circular patches used in many simulations and experiments. It can also be used to estimate the patch dimensions of patches that are
fabricated on a spherical surface. The vertex angle provides dimensional data to estimate the patch shape in the case of a patch with oblong shape.

In the case where the patch is formed using the template-assisted GLAD method with the vapor hitting the sample perpendicular to the groove direction, the shape is always a semi-spherical cap, as shown in Figure 5.3A (see also Chapter 3). The vertex angles, \( \nu_L \) and \( \nu_p \), are shown in Figure 5.3A, where \( \nu_L \) is defined as the angle between the two sharp points at the flat side of the hemispherical cap with respect to the particle center, and \( \nu_p \) is defined as the angle defined by the height of the hemispherical cap with respect to the particle center. It can be easily shown that the ratio of these two vertex angles is always 2:1. The value of the vertex angle \( \nu_p \) is calculated using Equation 5.7a, when the patch shape is not affected by the adjacent particle. As stated in Chapter 4, the patch shape will need more parameters to define, and the vertex angles used to define the patch can also be achieved following the same method.

\[

\nu_p = 90^\circ - \sin^{-1}\left(\frac{\sqrt{H^2 + w^2/4} \times \sin (\tan^{-1}\frac{2H}{w} - \tan^{-1}\frac{H}{2w})}{r}\right) \quad (5.7a)
\]

\[

\nu_p = 90^\circ - \sin^{-1}(1 - 2 \times \sin \theta) \quad (5.7b)
\]

\[

\nu_{L1} = 180^\circ + 2 \times \tan^{-1}\frac{\sin \theta}{\sqrt{3}} - 2 \times \cos^{-1}\frac{\sqrt{3 + \sin^2 \theta}}{2} \quad (5.7c)
\]

\[

\nu_{L2} = 2 \times \tan^{-1}\frac{\sqrt{3}}{\sin \theta} + 2 \times \cos^{-1}\frac{\sqrt{3 + \sin^2 \theta}}{2} \quad (5.7d)
\]

For the GLAD method that uses close-packed monolayers, computing the vertex angle is a more complex problem. Here, we will study the case when the monolayer orientation is 30°. The vertex angles \( \nu_{L1} \) and \( \nu_{L2} \) are defined by the intersections of boundaries as shown in Figure 5.3B, and the vertex angle \( \nu_p \) is set by the points with the highest Z value on the
two lateral boundaries. The three angles are all related to the incident angle, \( \theta \), and their values are given above in Equations 5.7b, 5.7c, and 5.7d. Figure 5.3C shows the trends in these three angles when \( \theta \) is increased from 0.1° to 30°. With increasing angle \( \theta \), the vertex angle \( \nu_{L1} \) also increases. The same trend is also found for \( \nu_p \), while \( \nu_{L2} \) decreases. Unlike \( \nu_{L1} \), the rate of increase for \( \nu_p \) is much larger when \( \theta \) is near 0, and the rate of increase slows with increasing \( \theta \). This fact can be visually confirmed by the change that the patch shape will gradually change from oblong shape to trapezoid shape, and this trend has been supported by experimental results. Of importance is here that the ratio of \( \nu_{L1} \) to \( \nu_p \) can provide estimated dimensional information for the oblong patch. The trend of the ratio is plotted as the inset of Figure 5.3C, in which \( \theta \) increases from 0.1° to 30°. The ratio decreases dramatically with the increase of \( \theta \) in the range 0.1° (about 25.08) to 5° (about 3.67), and after that decreases much more slowly. The ratio is about 1.79 at \( \theta = 30° \). From the trend plot, it is clear that at small incident angle in order to get a patch with a specific dimension, the incident angle should be handled carefully, and at a higher incident angle, the patch dimension (ratio of \( \nu_{L1} \) to \( \nu_p \)) does not change too much with the increase of patch size.

Based on the boundary equations, the patch size (i.e., covered surface area percentage) can be calculated through the integration of the particle surface or estimated through drawing the patch shape graph using the method provided in Appendix A. The patch position can also be determined, which is especially important for particles with multiple patches since patches may overlap in various ways. The size of the overlapping portion can also be calculated or estimated as described above. The calculated patch sizes and
shapes that were presented in Chapters 3 and 4 are based on the numerical model described in this chapter.

Figure 5.4 Patchy particles fabricated by GLAD method with close-packed monolayer.

These equations provide a powerful tool to predict the patch shape, which instructs the selection of proper parameters to obtain a specific patch. As an example, Figure 5.4 gives two examples of patch shapes that have not been discussed previously. Figure 5.4 shows the image when the close-packed monolayer is observed along the incident metal vapor flow. For the brown particle, which is the subject of study, the patch shape is the same as what is shown in Figure 5.4. The patch in Figure 5.4A is obtained with $\theta = 60^\circ$, $\alpha = 0^\circ$, and the patch in Figure 5.4B requires a $\theta = 55^\circ$ and an $\alpha = 30^\circ$. By comparison with previous results, it is clear that the higher $\theta$, the more complex the patch shape is and the more sections the boundary is composed of.
5.3 Extension of the Numerical Model

Modification of Rotation Angle $\alpha$

Figure 5.5 Procedure employed for the modification of $\alpha$ when $\alpha > 90^\circ$.

For the GLAD method with V-shaped grooves, the effect of the rotation angle can be treated more simply when a sequential evaporation is applied to fabricate multi-patch particles. When $\alpha$ is larger than $90^\circ$, the boundary can also be calculated by converting the changing $\alpha$ such that it falls into the range from $0^\circ$ to $90^\circ$. The procedure used for this conversion is shown schematically in the following graph. The $(x, y, z)$ coordinates are first solved using the parameters used in the evaporation including the altered $\alpha$. Then the
values of \((x, y, z)\) used for the boundaries are altered again as shown in the red rectangular in Figure 5.5.

For the GLAD method with close-packed monolayer, the patch shape will repeat every 60°. So, for those \(\alpha\) that are larger than 60°, the \(\alpha\) is first treated (denoted as \(\alpha_{\text{alter}}\)) to locate it in the range from 0° to 60° by deducting \(N \times 60°\), where \(N\) is an integer. The \((x, y, z)\) coordinates obtained based on the altered \(\alpha_{\text{alter}}\) are used to determine the final \((x, y, z)_{\text{final}}\) coordinates used for the boundary equations. The \((x, y, z)_{\text{final}}\) is solved using the following equations 5.8.

\[
\begin{align*}
    x_{\text{final}} &= \sqrt{x^2 + y^2} \times \cos \alpha \\
    y_{\text{final}} &= \sqrt{x^2 + y^2} \times \sin \alpha \\
    z_{\text{final}} &= z
\end{align*}
\]  

(5.8)

**Numerical Solution for Boundaries due to Adjacent Particles**

For the boundaries caused by the shadowing from adjacent particles, the complexity of the calculation may take too long to converge to the final boundary equation. In practice, a numerical solution (approximate solution) may be enough to provide the required solution. In the following, another method is described, which will give a relatively simple result through a complicated process. In this method, the center of the particle that affects the patch shape is denoted as \((x_0, y_0, z_0)\) (each shadowing particle has its own set of values, especially for the GLAD with close-packed monolayer). The close-packed monolayer is first rotated until the incident metal vapor flow is parallel to the X axis of the coordinate system used, which can be divided into two steps: first the system is rotated along Z axis by \(-\alpha\) degree, and the particle center is denoted as \((x_{0t}, y_{0t}, z_{0t})\), which can be calculated using Equation 5.9. Next, the system is rotated along Y axis by \(-\theta\)
degrees, and the particle center is now denoted as \((x_t, y_t, z_t)\), which is calculated using Equation 5.10.

\[
\begin{align*}
  x_{0t} &= x_0 \times \cos \alpha + y_0 \times \sin \alpha \\
  y_{0t} &= y_0 \times \cos \alpha - x_0 \times \sin \alpha \\
  z_{0t} &= z_0
\end{align*}
\] (5.9)

\[
\begin{align*}
  x_t &= x_{0t} \times \cos \theta + z_0 \times \sin \theta \\
  y_t &= y_{0t} \\
  z_t &= z_{0t} \times \cos \theta - x_{0t} \times \sin \theta
\end{align*}
\] (5.10)

Then using Equation 5.11, the boundary equation is solved for the new XYZ coordinate as shown in Equation 5.12. Similarly, any one of the X, Y, and Z-values can be taken as a variable while the remaining two are expressed as functions of the chosen one, i.e., Equation 5.12. To get the boundary equations in the original coordinate system, the system is first rotated around the Y axis by \(\theta\) degree followed by rotation along the Z axis by \(\alpha\) degree. Similarly, \((x_f, y_f, z_f)\) are then used to describe the boundary after rotation along the Y axis, and \((x, y, z)\) is used for the final equation after rotation along the Z axis (Equation 5.13 and Equation 5.14, respectively). Based on the results, similar boundaries can also be drawn as Figure 5.2.

\[
\begin{align*}
  x_{tf}^2 + y_{tf}^2 + z_{tf}^2 &= r^2 \\
  (y_{tf} - y_t)^2 + (z_{tf} - z_t)^2 &= r^2
\end{align*}
\] (5.11)

\[
\begin{align*}
  y_{tf} &= \frac{-x_{tf} \times y_t + y_{tf}^3 + y_t \times z_{tf}^2 - \sqrt{z_t^2 \times (4 \times r^2 \times (y_t^2 + z_t^2) - (x_{tf}^2 + y_{tf}^2 + z_{tf}^2))^2}}{2 \times (y_t^2 + z_t^2)} \\
  z_{tf} &= \frac{-x_{tf}^2 \times z_t^2 + y_{tf}^2 \times z_t^2 + z_t^4 + y_t \times \sqrt{z_t^2 \times (4 \times r^2 \times (y_t^2 + z_t^2) - (x_{tf}^2 + y_{tf}^2 + z_{tf}^2))^2}}{2 \times z_t \times (y_t^2 + z_t^2)}
\end{align*}
\] (5.12.1)
\[
\begin{aligned}
\begin{cases}
y_{tf} = \frac{-x_{tf}^2 + y_{tf}^3 + y_{tf}z_{tf}^2 + \sqrt{z_{tf}^2(4x^2 + y_{tf}^2 + z_{tf}^2) - (x_{tf}^2 + y_{tf}^2 + z_{tf}^2)^2}}{2(y_{tf}^2 + z_{tf}^2)} \\
z_{tf} = \frac{-x_{tf}^2 + y_{tf}^3 + z_{tf}^2 + z_{tf}^4 - y_{tf} \times \sqrt{z_{tf}^2(4x^2 + y_{tf}^2 + z_{tf}^2) - (x_{tf}^2 + y_{tf}^2 + z_{tf}^2)^2}}{2x_{tf} \times (y_{tf}^2 + z_{tf}^2)}
\end{cases}
\end{aligned}
\] (5.12.2)

\[
\begin{cases}
x_f = x_{tf} \times \cos \theta - z_{tf} \times \sin \theta \\
y_f = y_{tf} \\
z_f = z_{tf} \times \cos \theta + x_{tf} \times \sin \theta
\end{cases}
\] (5.13)

\[
\begin{cases}
x = x_f \times \cos \alpha - y_f \times \sin \alpha \\
y = y_f \times \cos \alpha + x_f \times \sin \alpha \\
z = z_f
\end{cases}
\] (5.14)

### 5.4 Conclusions

In summary, a mathematical method is proposed that numerically describes the shape and position of the patches obtained through the GLAD method and is applicable to the template-assisted method and the method that uses close-packed and even loosely-packed monolayers. The validity of this model has been proved by the calculation and predictions in Chapter 3 and Chapter 4. Y and Z values of patch boundary are calculated as a function of the X-value, which provides accurate information about patch shape and position that is needed for applying it as instructive tool to the study of the properties of patchy particles. The equations can be used to study patch position and the size of single or overlapping patches. As one application of these equations, the vertex angle is studied, showing the trends in the change of the patch shape as a function of the incident angle.

The exploration of the patch shape at a large incident angle indicates that this mathematical tool can be used as supplement to the GLAD method and provides
quantitative information. In addition if used as an instructive tool, these equations can also aid in the fabrication of patches with very specific shapes and sizes.
Chapter 6

Conclusion and Future Work

6.1 Concluding Remarks

In this thesis, we have presented a systematic study of the fabrication of patchy particles by the template-assisted glancing angle deposition method (GLAD). The experimental results illustrate the advantages of the method: patch uniformity, product scalability, various patch shapes, and template reusability. To predict the patch at specific fabrication parameters (incident angle, rotation angle, template dimension, and particle size), a numerical model is developed, which can also serve as an instructive tool for fabrication, even for general GLAD methods.

As one important tool to help design colloidal particle crystals, the template shows the advantage of arranging colloidal particles in a specific regular pattern. The comparison between the performances of the PDMS template and Si wafer template on loading and arranging PS particles demonstrates the superior performance of the Si wafer template in achieving uniform particle orientation. The combination of Si wafer template with V-shaped grooves and GLAD leads to the successful fabrication of patchy particles of uniform asymmetric patches (semispherical cap). When the incident angle is perpendicular to the groove lines, the nearly linear increase in rate vs incident angle
makes it easier to achieve patches of a specific size. The effect of incident angle and template dimensions (V-shaped and square grooves) on patch size are studied carefully to allow for a systematic conclusion.

The rotation of the template while keeping the incident angle unchanged introduces the shadowing effect because of the adjacent particles. The shadowing effect is affected by the rotation angle and in cooperation with the shadowing due to the template achieves a variety of patch shapes, such as triangular shape, belt-like shape, and crescent moon shape, which have been confirmed by SEM characterization. A study of the patch size and shape as a function of gradually increasing incident and rotation angles provides the patch shape diagram with four regions intersected by the patching point, shadowing point and groove point functions. The sequential evaporation makes the fabrication of particles of partially overlapping patches (patches can be of different materials) possible. The expectation of patch shape and size including the size of the overlapping part are also consistent with the experimental results. The preliminary assembly results obtained with patchy particles that carry triangular patches in magnetic field provides a first indication of the potential novel assembly behaviors to be expected from such patchy particles with asymmetric patches.

The numerical model aiming to provide instruction for patchy particle fabrication with GLAD using both a close-packed monolayer and a template with grooves as a substrate is also provided here. The numerical formula used for calculation of the patch boundaries are classified by the origins of the shadowing effect and can be used to define the patch shape mathematically thereby providing quantitative information. The shape analysis of the patches achieved by GLAD with close-packed monolayers and V-shaped grooves
provides a representative application of the numerical model. With the help of this model, more patch possibilities can be discovered to add to previous work.

To conclude, this research shows that the template-assisted GLAD method has the ability to achieve particles with controlled, uniform, and asymmetric patches. The numerical model helps by assisting and instructing the fabrication process using the GLAD method and providing quantitative analysis. The asymmetric patches accessed via template-assisted GLAD are promising for the discovery of novel structures and properties.

6.2 Future Work

Specific Thoughts about the Directions for Future Work

1. In the present study we developed the template-assisted GLAD method to achieve asymmetric patches. One new development of this method could be to obtain patchy particles with multiple patches in one step without the need for sequential evaporation or a stamping technique. The patches can be formed from different materials. In this design, polymer layers or metal layers of different composition are deposited on the different sides of the groove. Next, the particles are loaded into the template. After triggering the chemical reactions, the patches will form where the particles are touching the polymer or metal layers. One advantage of this method is the uniformity. If the template contains wells fabricated by wet-etching of a Si wafer with the help of a photomask of circular or square dots, patchy particles with as many as four patches can be achieved.
2. As one special result of sequential evaporation of template-assisted GLAD, patchy particles with a circular belt patch surrounding the equator are of special interest. This kind of patchy particle can be fabricated using the following procedure: first belt patches are fabricated at rotation angle of 0°; then a stamp is utilized to flip these patchy particles in order to add another belt patch at the same rotation angle. If the ring patch is made of Au, the patchy particles will not assemble in static magnetic field, but will respond to changing magnetic due to the circular current generated. And the competition of the magnetic field and electric field might result in dynamic assembly structures. This approach would open up a new approach to materials with dynamic properties.

3. Inspired by the self-propelled micromotor, patchy particles with two partially overlapping patches should be studied systematically. Since the overlapping part can be controlled and calculated by the numerical model, the effect of overlapping size on the property of the micromotor can be studied and better understood.

4. The Brownian motion of patchy particles is a hot topic of research. What we are interested in is the fabrication and study of the motion of colloidal particle polymer or oligomers. The polymer chains or oligomers are fabricated by connecting the particles with each other through the polymer brush on particle surface using the V-shaped template. The effect of the stiffness and the patch size added after chain assembly on the Brownian motion is what should be studied here. The experimental results might be of significance to the study of polymer or macromolecular molecules.
Appendix A: Method to Calculate Patch Size

In this section, a method is presented aiming to provide the patch size (coated area percentage, $A\%$) of a patchy particle. Several methods have been reported with the ability of achieving patchy particles with controlled patch size, and in all assembly simulations quantitative information about the patch, i.e., patch size, is required. Only few methods have been reported that enable the calculation or estimation of the patch size, considering the clear emergence of asymmetric patches. The method described here can be applied to estimate the size of patches achieved from any method and provide patches sizes close to their true values.

The patch size (coated area percentage, $A\%$) on the PS particles is measured using the following approach. The surface of a sphere is divided evenly by planes that pass through the center of the sphere, where the angle between each two adjacent planes is $360^\circ/m$ and $m$ is an integer, as shown in Figure A.1A. Further, the sphere surface can also be divided evenly by parallel planes that are perpendicular to the cross section of the sphere when the distance between each two adjacent planes is $r/n$ (the first plane goes through one of the poles of the sphere), where $r$ is the radius of the sphere and $n$ is an integer (Figure A.1B). Sectioning a sphere in this fashion, leads to a surface that is divided into $2 \times m \times n$ sections with an identical surface area. Now, one point is chosen from each section and
its orthogonal projection onto a plane perpendicular to the diameter is obtained such that each of these orthogonal projection points correspond to one piece of the sphere surface transferring the calculation of the sphere surface area to counting the number of points on a plane.

Figure A.1 Schematic of planes used to cut sphere surface evenly.

Figure A.2 shows the distribution of the projection points on the 2D plane. For the SEM images of patchy particles, the radius of the particle is first determined in pixels. Based on the value of the radius, the coordinates of each orthogonal projection point are calculated. The area of the patch will be determined by counting the number of these orthogonal projection points covered by the patch, which can be done with the help of a computer. Figure A.3 shows one example of a patch size calculation, in which the light green color shows the patch. The number of dots covered by this patch is counted to about 29, which means the patch size (coated area percentage) is about 7.25%
(29 ÷ (2 × 20 × 10)). The precision of the patch surface area can be improved by increasing the values of $m$ and $n$.

Figure A.2 Distribution of projection points on plane. Each point corresponds to one piece of the spherical surface having the same surface area

In reality, we first need to get the patch imaged. If part of the patch cannot be observed using an imaging tool, a tape may be needed to flip the patchy particle in order to get the hidden part exposed to the characterization tool. For the images (SEM, TEM and etc.) of patchy particles, the radius of the particle is first determined in pixels. Based on the value of the radius, the coordinates of each orthogonal projection point are calculated. The area of the patch is then determined by counting the number of orthogonal projection points covered by the patch. The precision of the patch surface area is improved by increasing $m$ and $n$. 
Figure A.3 Schematic of patch size calculated by counting the number of dots covered by the patch
Appendix B: Assembly of Patchy Particle Clusters

In this section, the preliminary results from the assembly of patchy particle clusters will be discussed. The patchy particles are fabricated using the GLAD method with a close-packed monolayer. The simplest patchy particle cluster containing two particles is assembled first to check the feasibility of the proposed idea.

One ultimate goal of colloidal particle assembly is to create structures from colloidal particles that resemble molecules. The formation of colloidal crystals or lattices shows the method of stacking colloidal particles similar to arranging atoms in a solid. Similarly, researchers strive to build colloidal molecules from colloidal particles in analogy to atoms forming molecules. Efforts reaching towards this goal are colloidal molecules\(^{6,7,29}\) and chiral chains\(^{12}\). The research of colloidal molecules focuses on the fabrication, but no reports about the aggregation of such colloidal molecules have been reported. Chiral chains reported are composed of dimmers, whose component and structures are fixed.

The intention of the research proposed in this section is the systematic study of the assembly of clusters with patchy particles of different size and material. The two patchy particles are linked together by hydrophobic force between the two modified particle surfaces.
The patchy particles are fabricated using the GLAD method with a close-packed particle monolayer.\textsuperscript{35, 36} The smaller patchy particle, here a Janus particle, contains a single Au patch, while the larger multi-patch particle has an Au and a Fe patch. The difference of the two rotation angles (orientation) for the multi-patch particles is 180°. Then the Au patch is modified with 1-decanethiol, which endows the Au patch with hydrophobic properties. A linking between these two patchy particles is achieved by adding the solution of Au-Janus particles to a close-packed monolayer of multi-patch particles dropwise. A magnetic field is then utilized to assist the assembly of such clusters. The procedure is shown schematically in Figure B.1.

![Figure B.1 Schematic of the procedure of patchy particle cluster assembly.](image)

The multi-patch particles are characterized by SEM and EDS (Figure B.2) after fabrication. From the SEM images it is clear that the two patches are located on opposite sides of the top hemisphere, which is controlled by the 180° rotation angle as stated previously. The patches are of different shapes when the orientation of the particle
domains are different. The nature of the two patches is validated by characterization using element analysis (EDS). In the EDS images, the Au patch is colored red and the Fe patch is represented by the green color.

Figure B.2 SEM and EDS images showing the patch shapes and the relative position of the patches of different metals: Au (red) and Fe (green).

Figure B.3 shows the existence of patchy particle clusters. In Figure B.3 we see linked patchy particles despite the abundance of single particles. The latter might be due to the slow movement of particles or particles being stuck to the substrate. The enlarged images show the coexistence of large-small, small-small, and large-large particle pairs. The
coexistence is due to the lack of specific interactions between the Janus particle and the multi-patch particle.

Figure B.3 Microscope images of clusters of patchy and Janus particles.

Figure B.4 Microscope images of the dried assembly structures composed of clusters of patchy particles obtained upon exposure of the patchy particle mixture to a magnetic field. The inset shows structures containing fewer cluster units.
The assembly of patchy particle clusters in magnetic field was also tested. Figure B.4 shows our preliminary data for the magnetic field assembly after drying of the assembly suspension. Within the rather unordered assembly structures or particle clusters, we can distinguish structures formed mainly by the smaller Janus particles and particle clusters. In the enlarged image (inset), structures of particle clusters can be seen. Careful analysis of these assembly structures allows us to conclude that: (i) the assembly of patchy particle is a possible, (ii) movement of the relative positions of particles in clusters during assembly causes variety in cluster structure, and (iii) clusters may change structures or components, such as three particles form a cluster and participate in the assembly (enlarged image in Figure B.4).

**Future work**

Based on the analysis above, the following solutions are proposed:

1. Create specific interactions between Janus particles and multi-patch particles. The DNA strands might be able to solve the problem of specificity when two different kinds of patchy particles carry different kinds of DNA strands that obey specific interaction.

2. Increase the interaction strength to avoid the deformation of the cluster structures. One intention of this research project is to study the effect of steric hindrance on assembly structures. Increasing the interaction can help form more uniform structures and provide systematic information on how particle size is affecting the assembly structures.
Appendix C: Chiral Patchy Particles

Discovering new particle properties and inventing new materials with special properties is the goal of patchy particle research. In this Appendix C, the research of patchy particles with three patches that are positioned in specific 3-dimentional positions to form chiral patchy particles is reported for the first time.

A detailed study of current research regarding patchy particles reveals that most of the attention has been focused on structures formed from single building blocks (no matter how many patches the particles carry). Different patches can be used to attract or direct different molecules or materials, which will allow them to be arranged in a special sequence. One intention of the research proposed here is to fabricate composite materials with the help of multiple patch particles and their ability to arrange other materials. Such composites might generate more exciting properties such as the chiroptic property of asymmetric patches. The recent research on chiral chains and colloidal molecules inspires one to think about chirality and molecular structures. In our plan, a patchy particle with three different patches of specific sequence will be fabricated to investigate the influence of the spatial (3D) patch sequence on the particle’s ability to behave like a chiral center and form chiral colloidal molecules or clusters. As shown in Figure C.1 such a patchy particle cannot be superpositioned with its mirror image due to the right and left handedness of its patch sequence making it a chiral patchy particle. We hope that such
chiral patchy particle can help to direct other materials into a specific sequence in 3D and ultimately achieve chiral materials from such colloidal building blocks. The special sequence may also endow such patchy particles or crystals formed from them with novel optical properties such as chiroptic properties.

Figure C.1 Schematic of chiral patchy particle

The chiral patchy particles are fabricated by the GLAD method with a close-packed monolayer, while the difference between rotation angles is set to be about 120°. In this manner, the three patches will be located on the same hemisphere of the particle and no stamping process is required. The three patches are made of Au, Fe, and Al. The patches are characterized by SEM and EDS to check the coexistence of the three elements.

The boundaries of the patches are shown in Figure C.2A, in which the overlapping part is also characterized clearly as a triangular section. In a more extreme example, the
overlapping and boundaries are much clearer when particle size is not uniform (Figure C.2B).

Figure C.2 SEM characterization of chiral patchy particle

The different elements in the three patches are validated by EDS characterization. The elemental analysis spectrum shows energy peaks that can be assigned to Fe, Au and Al.
Their relative positions of the patches are clearly indicated by their different colors (red for Al, green for Au, and blue for Fe).

Figure C.3 EDS characterization of chiral patchy particles (red for Al, green for Au, and blue for Fe).
**Future Work**

The next step should involve the investigation of the assembly behavior of these chiral patchy particles. The particle is expected to also be responsive to a magnetic field, an electric field, and solvent polarity when the Au patch is functionalized with a thiol molecule as was described in Appendix B.

The patchy particles will also be mixed with nanoparticles made of Au, Fe and Al or other materials to build composites based on the different affinity of these nanoparticles to the three patches. The three patches can also be used as seeds in a chemical reaction to attract different materials to react with them. The influence of the sequence of these three patches is most likely to be found in the investigation of their optical properties.
Appendix D: Patchy Colloidal Oligomers and Polymers

The motion of anisotropic colloidal particles in solution is a hot area of research currently. The patchy particles in these studies are called micromotors or swimmers. Recent research on the fabrication of mobile or rigid colloidal polymers reveals the possibility to study the properties of anisotropic colloidal polymers or oligomers.

The design of this research is to align colloidal particles that have polymer brushes on the surface in a line with the help of the template with the V-shaped grooves. Then, following the procedure to create linkage between the adjacent particles chains are formed, which are subsequently modified using the template assisted GLAD method. The intention is to observe the swimming motion of such patchy particle polymers or oligomers in solution.

The colloidal particles with polymer brushes were provided by Dr. Peter van Oostrum and stored in ethanol. The particles were loaded into the V-shaped grooves of the template by convective assembly as described in Chapters 3 and 4. To reduce the number of defects caused by the fast evaporation of ethanol (particles were not close enough), 0.1 ml deionized water is added to the surface of the template after the ethanol has evaporated. Due to the surface tension and capillary forces during the drying process, the
particles are pulled closer together. This procedure is repeated 3 or 4 times until the required contact between particles is reached. Then the template with the packed colloidal particle chains is placed in a petri dish which contains the mixture of deionized water and THF (9/1, v/v). The petri dish containing the solvent mixture is heated to 55 °C before placing the template with the colloidal particle chains in it. Then the colloidal particles are kept in the solvent for 5 min. The petri dish is taken off the heating plate and allowed to cool to ambient temperature. This annealing procedure aims to create linkage between adjacent particles. After drying, the V-shaped grooves with the particles are put into the chamber of the PVD machine to modify the particle surface with patches. The fabrication parameters are tuned such that a particular patch shape and size are obtained. The colloidal polymers/oligomers are then sonicated off the substrate.

![Figure D.1 Microscope images of colloidal polymer and oligomer chains in aqueous solution](image.png)
The colloidal polymers or oligomers were characterized by microscopy as shown in Figure D.1. From the images we see the coexistence of polymers of different repeating unit. In addition, these colloidal polymers seem to contain rigid chains. The procedure can be adjusted such that the rigidity of the chain is tuned.\textsuperscript{120}

Figure D.2 Janus colloidal polymers and oligomers.

Experiments were also carried out to create Janus colloidal polymers and oligomers with an Au patch. Under the microscope, these modified structures can be easily identified as
shown in Figure D.2. We can see that the Au patch endows these structures with a bright color, which is different from the appearance of uncoated particles as shown in Figure D.1 (dark particles).

From these images, we can see that the length of these polymers or oligomers is not uniform and some structures have branches or additional particles attached to the linear section of the chain. The length of the chain can be controlled by tuning the brush length and refining the experimental procedure, which controls how many particles are touching each other. In the future, with the help of an additional electric field, longer chains might be achievable.

**Future Work**

The experimental procedure will be refined to control the length of the colloidal polymer chain. The application of an external electric field can help achieve longer colloidal polymers. By controlling the fabrication parameters during evaporation, the patch shape and size can be controlled. The Brownian motion of such anisotropic structures will be monitored, focusing on the impact of patch size and shape on the motion in solution. Multiple patches of different materials will also be fabricated on these structures hoping to discover more interesting properties.


