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Self-assembly of Silica Nanospheres into Well-Ordered Structures via Annealing

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Fachhochschule Aachen Campus
Jülich

von
RIHAB JIDAR
Matrikelnummer | 3594689

Erstbetreuerin
PROF. DR. HELGA HUMMEL

Zweitbetreuerin
DR. ASMAA QDEMAT

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Rihab Jidar

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Chapter 1

Introduction

The structural properties of nanoparticles have attracted significant interest due to their potential applications in various fields such as catalysis, drug delivery, and optics [1]. Their nanoscale dimensions and large surface area to volume ratio provide unique characteristics, including higher reactivity, selectivity, and mechanical strength compared to bulk materials. Among them, silica nanoparticles (SiO_2 NPs) are particularly interesting because of their chemical stability, biocompatibility, and ease of surface functionalization[2].

Controlled self-assembly of silica nanoparticles into well-ordered structures is essential for optimizing their functional performance in advanced applications. Self-assembled monolayers (SAMs) of silica nanoparticles offer a promising route to achieve such organization. The success of this process is strongly influenced by temperature, which affects key factors like solvent evaporation rate and particle mobility. Techniques such as spin-coating and drop-casting exploit these thermally dependent behaviors to achieve desired nanoparticle arrangements. Therefore, understanding and regulating temperature effects is critical for improving the uniformity and quality of self-assembled nanostructures [3].

Several studies have explored how thermal treatment (annealing) can be used to improve the order and stability of nanoparticle assemblies. For example, Jiang et al. (2003) demonstrated that post-deposition thermal annealing enhances particle mobility, allowing silica nanospheres to rearrange into more ordered hexagonal arrays[4]. Similarly, Zhang et al. (2010) reported that annealing promotes defect healing in monolayers formed via drop-casting, especially at temperatures near the glass transition of added organic agents [5]. Annealing has also been used in combination with surface tension gradients or capillary forces to refine large-area colloidal crystal films with fewer voids and grain boundaries [6]. These studies highlight the importance of optimizing thermal parameters to promote self-organization and reduce structural defects.

However, the key question that this study aims to address is to determine whether shorter annealing durations at elevated temperatures can yield a level of ordering that is comparable to what was previously achieved in earlier studies—such as the work by Qdemat et al.[7], where a well-ordered silica nanoparticle monolayer was obtained after annealing at 70 °C for 10 days. This comparison is important because it explores whether thermal energy at higher temperatures can accelerate the ordering process, potentially reducing the required treatment time. The rationale behind this investigation is that nanoparticle self-assembly is influenced by both temperature and time, and optimizing this balance could allow for more efficient film formation without compromising structural quality.

This study investigates the self-assembly behavior of silica nanoparticles approximately 200 nm in diameter on silicon substrates using the drop-casting method, with a particular focus on the role of annealing temperature. By systematically varying the thermal conditions and characterizing the resulting structures using Scanning Electron Microscopy (SEM), we aim to evaluate how temperature influences particle organization and contributes to the formation of highly ordered monolayers. The findings aim to clarify whether more time-efficient thermal treatments can still achieve high-quality ordering, which could inform future experimental design and practical applications in nanofabrication.

Chapter 2

Theoretical Background

This chapter provides an overview of the theoretical concepts related to nanoparticle self-assembly and the techniques used to study their structure. It starts by outlining the main approaches for creating ordered nanoparticle arrangements, with particular attention to the role of annealing in improving assembly. It then covers the fundamental principles behind the key characterization methods used in this work, helping to explain how the structure and quality of the assembled layers are analyzed and interpreted.

2.1 Silica Nanoparticles

Silica is a stable and biocompatible material that plays an important role in nanotechnology because of its useful physicochemical properties. Silica nanoparticles (SiO_2 NPs) are especially interesting due to the presence of silanol (Si–OH) groups on their surface, which makes it easy to modify them chemically. This flexibility makes it possible to create many types of functional and hybrid nanomaterials for different applications. There are several ways to synthesize silica nanoparticles, including wet chemical methods, sol-gel processes, ultrasonication, dry synthesis, and reverse microemulsion techniques [8].

SiO_2 nanoparticles are well-known for their strong chemical stability and low toxicity, which makes them good options for use in areas like nano structuring, drug delivery, and optical imaging [5]. They're usually made with sizes ranging from about 10 to 500 nm. The size of the particles during synthesis can be adjusted by changing factors like how much ammonia or sodium hydroxide is used, how fast the solution is mixed, and the rate at which tetraethyl orthosilicate (TEOS) is added [6].

Besides synthetic methods, natural sources of silica are also available in agricultural waste like corn cobs and rice husks, which provide a more sustainable and affordable way to produce silica nanoparticles [9]. However, even though synthetic production allows for better control over the properties of the particles, it can be both costly and harmful to the environment [4].

The structural features of silica nanoparticles, including size, shape, and porosity, are critical in determining their biological behavior, biodistribution, and efficiency in payload delivery. While particle size and morphology largely influence cellular uptake and biodistribution, porosity plays a central role in controlling the loading and release of therapeutic or diagnostic agents [7]. Mesoporous silica nanoparticles with pore sizes typically ranging from 2 to 50 nm can be engineered into various morphologies, such as hexagonal, wrinkled, or worm-like structures by tuning synthesis parameters. These tunable pores have garnered increasing attention for their enhanced drug-loading capacities in biomedical applications [10]

Furthermore, silica nanoparticles can be prepared with good monodispersity and possess a low Hamaker constant, which helps reduce van der Waals interactions between particles, thereby facilitating more stable self-assembly [4]. Their high colloidal stability in solution and surface rich in silanol groups make them particularly suitable for extensive chemical modification, expanding their utility across fields such as cosmetics, food processing, semiconductors, and environmental remediation—particularly in water purification to remove oil, heavy metals, and radioactive contaminants [11], [12].

2.2 Nanoparticles Self-Assembly

Nanoparticle self-assembly is the process where nanoparticles spontaneously arrange themselves into well-organized structures without the need for direct human intervention. This happens through various non-covalent interactions, including van der Waals forces, electrostatic forces, hydrogen bonding, and capillary forces. These interactions work together to guide the nanoparticles into specific patterns or formations. Because of this, self-assembly is considered a highly efficient and versatile method in nanotechnology, especially for building complex structures from the bottom up. It allows researchers to create well-ordered materials at the nanoscale in a relatively simple and cost-effective way, compared to traditional top-down fabrication techniques that often require expensive tools and more complicated procedures.

Self-assembly strategies are generally divided into two broad categories: top-down and bottom-up. Although these terms are often used in different contexts, within self-assembly, they help describe the direction and control of the process. The top-down approach typically involves using external tools or patterns—such as lithography or pre-structured templates [3]. —to guide how nanoparticles are arranged on a surface. For example, photolithographic methods can create predefined patterns that nanoparticles are then directed to fill, or nanoimprinted templates can act as molds that control exactly where particles go and how they align.

In contrast, bottom-up self-assembly relies more on the natural interactions between particles to form organized structures without external patterns. This approach mimics many biological processes where order arises spontaneously. Both methods have their advantages, and in many practical applications, a combination of top-down guidance and bottom-up interactions is used to get the best results in terms of precision, efficiency, and scalability.

In contrast, the bottom-up approach involves the autonomous organization of nanoparticles driven by intermolecular forces and environmental conditions [8]. This includes methods such as:

- **Solvent evaporation-induced assembly**, where nanoparticles suspended in a volatile solvent form ordered structures as the solvent evaporates.
- **Langmuir-Blodgett technique,** in which nanoparticles are spread on a liquid surface and transferred onto a substrate as an organized monolayer.
- **Spin coating and dip coating**, which rely on controlled deposition and solvent evaporation.
- **Electrostatic self-assembly**, where oppositely charged nanoparticles and substrates attract each other to form multilayered structures.
- **DNA- or ligand-mediated assembly,** which uses biological or chemical linkers to direct the formation of well-defined architectures.
- **Self-assembly at interfaces**, such as oil-water or air-water interfaces, which can direct the formation of two-dimensional arrays.

Among these, **evaporation-driven self-assembly** is one of the most versatile techniques for forming large-area nanoparticle films and superlattices, particularly when combined with capillary forces in confined geometries. The **sol–gel process**, though primarily a synthesis method, can also facilitate self-assembly when used in combination with templating agents that guide the formation of mesoporous structures.

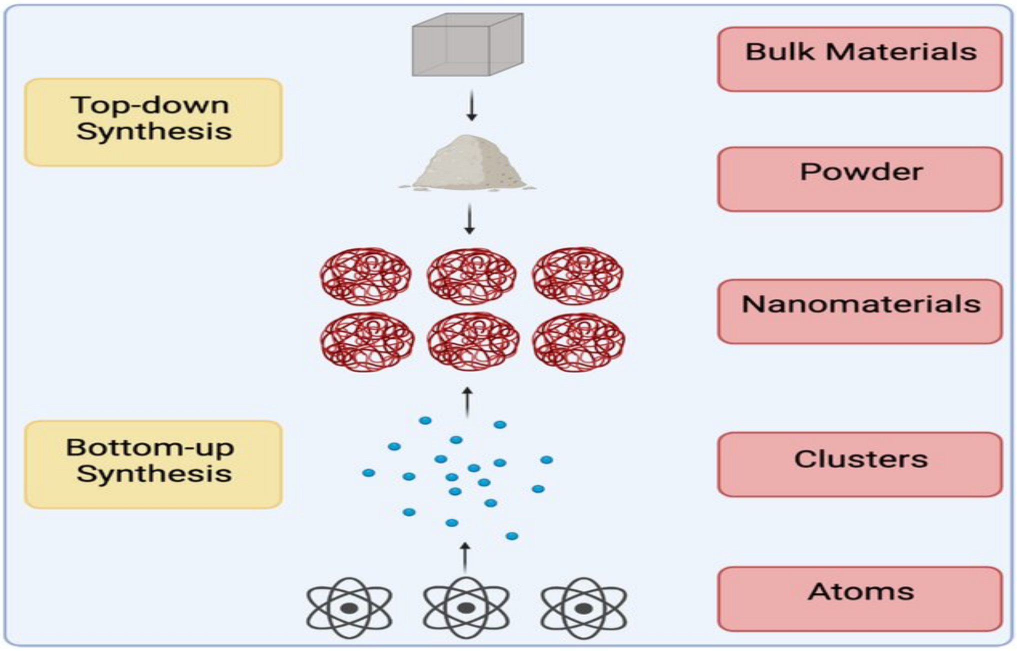


Figure 2.1: Basic illustration of physical (top-down) and chemical (bottom-up) methods for nanoparticle synthesis.[13]

2.2.1 Interparticle Interactions

Self-assembly of nanoparticles is an essential process where building blocks spontaneously arrange into ordered structures driven by thermodynamic and other constraints. However, to effectively harness nanoparticle self-assembly in technological applications and achieve efficient scale-up, a high degree of control and guidance is necessary[14]
To achieve controlled self-assembly, it is essential to understand the fundamental principles that guide the process. These principles involve various interactions such as:

Van der Waals forces

Van der Waals (vdW) forces are among the most prevalent interactions at the nanoscale, originating from electromagnetic fluctuations due to the random motion of electrons in atoms and molecules. Though relatively weak and short-ranged, they significantly influence nanoparticle behavior. In colloidal systems, vdW forces are typically attractive, often promoting aggregation of nanoparticles [11]. However, through surface modification, such as coating nanoparticles with organic ligands or polymers, these interactions can be modulated. Proper ligand functionalization enables controlled assembly, allowing nanoparticles to form stable, ordered two- and three-dimensional architectures [12].

capillary forces

Capillary forces arise when nanoparticles interact with a surrounding liquid, especially at liquid–solid interfaces. These forces are caused by both adhesive interactions (between different surfaces, like particles and substrate) and cohesive interactions (between similar surfaces, like two particles). When a thin film or liquid bridge forms between nearby particles, it creates a pressure difference called Laplace pressure, which pulls the particles together and creates an attractive force [13].

This effect becomes more pronounced in systems with surfactant-coated nanoparticles or substrates that have ionic or dipolar surface properties. In such cases, water or solvent can infiltrate and form capillary bridges that promote stronger particle aggregation. Under the right conditions, these bridges can even lead to chemical sintering, where particles fuse slightly at contact points, making the structure more stable. As a result, capillary forces play a key role in driving nanoparticles closer together during the self-assembly process and can strongly influence the final structure of the assembled film.

Electrostatic force

Electrostatic interactions are long-range forces occurring between charged nanoparticles. These interactions can be either attractive or repulsive, depending on the nature and distribution of surface charges. In colloidal dispersions, nanoparticles often acquire surface charges that create electrostatic repulsion, preventing agglomeration and maintaining a stable suspension. The strength and direction of these forces depend on factors such as ionic strength, particle geometry, and surface potential.

Control over electrostatic interactions can be achieved by modifying the pH of the medium, which alters surface charge density. Additionally, charged ligand shells can be introduced to further stabilize or direct assembly. These electrostatic manipulations are especially important for forming ordered structures in both two- and three-dimensional assemblies [14].

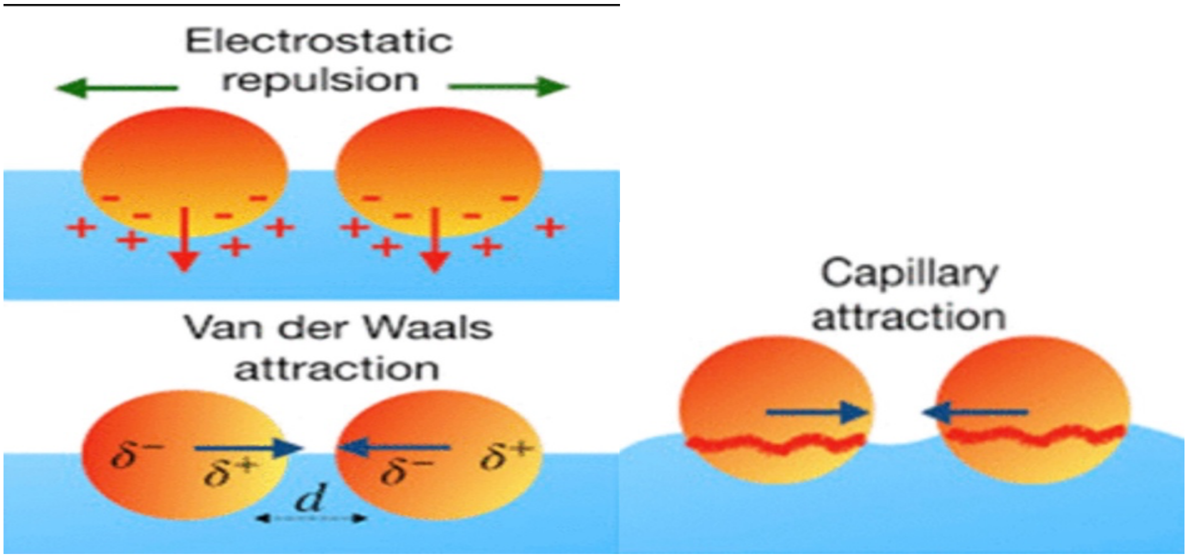


Figure 2.2: Schematic illustration of common interparticle forces involved in nanoparticle self-assembly.[15]

2.2.2 Thermodynamic and Kinetic Principles of Self-Assembly

The self-assembly of nanoparticles depends on a balance between thermodynamic forces and kinetic limitations. From a thermodynamic point of view, systems tend to organize themselves in ways that minimize their overall free energy, which usually results in more ordered structures. This tendency is influenced by several factors, including the strength and type of interparticle interactions, how the solvent interacts with the particles, and the characteristics of the surface or substrate where the assembly takes place [15]. In some systems, the process is mainly driven by entropy, such as in hard-sphere colloidal systems where particles naturally pack together to maximize disorder at the molecular level. In other systems, it is enthalpy-driven, meaning that specific attractive forces—like hydrogen bonding, electrostatic interactions, or ligand-mediated bonding—play a more significant role in determining how the particles organize [16].

However, achieving a well-ordered assembly isn't always simple or automatic, especially from a kinetic perspective. Even if an ordered structure is thermodynamically favorable, the system might struggle to reach it because of kinetic barriers. Things like a fast solvent evaporation rate, limited particle diffusion, and friction between particles can slow down or even block the self-assembly process. As a result, particles may end up trapped in disordered or imperfect arrangements, known as metastable states, which are not the most energy-efficient configurations [10].

Because of these limitations, external methods are often used to help the system reach a more ordered state. One common approach is thermal annealing. By applying heat, the particles gain more energy and mobility, which allows them to move past the kinetic obstacles that were preventing them from organizing properly. With enough time and the right conditions, thermal annealing can help the particles rearrange themselves into more stable and uniform structures that better reflect the system's thermodynamic minimum. This balance between thermodynamics and kinetics is key to controlling and optimizing the self-assembly process, especially when aiming for highly ordered nanoparticle films.

2.2.3 Role of Solvent Evaporation and Capillary Flow

Solvent evaporation plays a pivotal role in directing nanoparticle self-assembly, particularly in drop-casting method. As the solvent evaporates, capillary flow often dominates particle transport, redistributing nanoparticles within the drying droplet. A prominent manifestation of this is the "coffee-ring effect," wherein particles migrate toward and accumulate at the droplet's perimeter due to outward capillary currents driven by differential evaporation rates across the droplet surface [17].

To counteract this effect and achieve more uniform assemblies, various strategies have been developed. These include modifying the contact angle of the substrate, using surfactants such as stearyl alcohol to alter surface tension and flow behavior, or engineering solvent compositions to tune evaporation dynamics.

Controlled solvent evaporation can also facilitate gradual particle concentration and organization, enabling the formation of dense, ordered monolayers. Notably, Bigioni et al. (2006) demonstrated that slow evaporation under carefully controlled conditions can yield highly ordered nanoparticle superlattices, highlighting the importance of evaporation rate and environmental conditions in guiding self-assembly outcomes [18].

2.2.4 Surface Coating and Ligands

Surface ligands play an essential role in controlling how nanoparticles interact with each other during the self-assembly process. These ligands can influence different types of interparticle forces, including electrostatic repulsion, van der Waals attraction, depletion forces, and steric hindrance. The strength and effect of these forces depend a lot on the chemical structure and properties of the ligands, as well as the conditions of the surrounding environment.

A good example is stearyl alcohol, a long-chain organic molecule that can provide steric stabilization. When used during assembly, it forms a sort of protective layer around each nanoparticle. This helps prevent them from sticking together too randomly or clumping, which improves control over how far apart they are spaced. Important factors like the shape, thickness, and chemical activity of the ligand layer can strongly affect how the final nanoparticle film looks and how well-ordered it becomes [19]

By adjusting or "tuning" the properties of these ligands, researchers can guide the particles to form different types of structures—ranging from completely random layers to highly ordered patterns, like superlattices. In addition, more advanced techniques such as ligand exchange or targeted functionalization make it possible to program how and where particles assemble. This level of precision is especially useful when trying to create films or materials with specific structural or functional properties.

2.2.5 Influence of Particle Size and Shape on Self-Assembly

The size and shape of nanoparticles have a big impact on how well they self-assemble and what kind of structures they form. In this study, spherical silica nanoparticles were used, which naturally tend to form close-packed arrangements—usually hexagonal monolayers—because of their symmetrical, uniform shape. This kind of geometry makes it easier for the particles to organize evenly. However, the actual outcome of the assembly process can be very sensitive to particle size. When the particles are too large, their movement becomes more limited, which makes it harder for them to shift into more ordered positions. On the other hand, if the particles are too small, surface forces like van der Waals attractions become stronger and can cause them to stick together too early, leading to random clumping instead of neat layers [20].

When it comes to non-spherical particles—like rods, cubes, or prisms—the situation becomes more complex. These shapes introduce what's called anisotropy, meaning the particles have different dimensions depending on direction. As a result, they can form a much wider range of structures, including lines, layered patterns (lamellae), or more complicated lattice-like arrangements. The shape of the particles not only affects how they fit together (packing symmetry), but also changes the way they interact with each other. Even small differences in things like particle diameter or aspect ratio can have a big influence on the final structure, affecting how uniform and ordered the assembled layer turns out [21].

2.3 Temperature Influence on Self-Assembly

Temperature significantly affects nanoparticle self-assembly by modulating key processes such as particle mobility, solvent evaporation rate, and the strength and dynamics of interparticle interactions. Changes in temperature can control both the kinetic landscape and thermodynamic driving forces, influencing the structural order and uniformity of the assembled material. These temperature-dependent effects are explained in more detail in the following subsections.

2.3.1 Particle Mobility and Solvent Evaporation

Temperature is one of the most critical factors in the self-assembly of silica nanoparticles, as it influences multiple aspects of the process, particularly particle mobility and the rate of solvent evaporation. As temperature increases, the viscosity of the medium decreases, which means that nanoparticles suspended in the solvent can move more freely. This increase in mobility gives the particles a better chance to rearrange themselves into more thermodynamically stable, ordered structures. Without sufficient mobility, particles may get trapped in disordered or metastable configurations, preventing the formation of well-organized layers. In this sense, temperature acts as a driving force that helps the system overcome energy barriers that would otherwise hinder efficient self-assembly.

Alongside mobility, solvent evaporation is also strongly influenced by temperature. Higher temperatures speed up the evaporation process, which in turn affects how quickly the particles are deposited onto the substrate and how uniformly they spread out. If the solvent evaporates too quickly or unevenly, it can lead to defects like cracks, voids, or clustering. On the other hand, controlled thermal evaporation at moderate temperatures can lead to much more uniform particle layers. For example, previous research by Qdemat et al. [7] demonstrated that annealing silica nanoparticles at 70 °C for 10 days resulted in highly ordered monolayer films. This specific temperature was found to provide an ideal balance: it was warm enough to enhance particle mobility and slow enough in evaporation to allow the particles time to rearrange into a regular, hexagonal structure.

In this study, we explored whether similar or even improved levels of ordering could be achieved by using higher temperatures but shorter annealing times. We tested temperatures up to 90 °C and observed comparable or better structural ordering in the resulting nanoparticle films. This suggests that by fine-tuning the temperature, it's possible to control both the kinetics (how fast particles can move) and the dynamics of evaporation in a way that supports efficient self-assembly. It also points to the possibility of reducing the total processing time required for forming well-ordered structures, which is important for making the method more practical and scalable for future applications in materials science, photonics, and nanofabrication.

Overall, temperature serves as a key parameter that simultaneously regulates two essential components of the self-assembly process: particle diffusion and solvent removal. Managing both in a balanced way is necessary to achieve highly uniform and stable nanoparticle films. The results confirm that increasing temperature is not just about speeding up the process but also about optimizing the interplay between kinetic energy and structural organization, ultimately leading to better control over the final quality of the nanoparticle assemblies.

2.3.2 Annealing in Nanoparticle Self-Assembly

A key temperature-dependent process that further improves self-assembly quality is annealing. Annealing involves controlled thermal treatment that significantly increases nanoparticle mobility, allowing particles to reorganize into more thermodynamically stable configurations. This process is particularly effective in the presence of additives such as stearyl alcohol, which lowers local viscosity and facilitates diffusion. Through annealing, nanoparticles can rearrange into energetically favorable structures, reducing defects like cracks and voids and producing more uniform, densely packed monolayers [22].

Together with temperature-controlled evaporation and additive effects, annealing enables the system to approach a thermodynamic minimum, enhancing long-range order and the overall structural integrity of the nanoparticle films.

2.4 Role of Stearyl Alcohol in Nanoparticle Self-Assembly

Annealing, as a thermal treatment, significantly contributes to the self-assembly process by increasing the mobility of nanoparticles. Higher temperatures allow nanoparticles to overcome energy barriers and reorganize into thermodynamically stable configurations. This is especially effective when additives like stearyl alcohol are present, as they reduce local viscosity and improve nanoparticle diffusion.

The thermal process enables the particles to rearrange into more energetically favorable structures, minimizing defects such as cracks and voids. This leads to more uniform and densely packed monolayers, which is essential for creating high-quality nanoparticle films [7]. In combination with the role of stearyl alcohol, annealing helps the system reach a thermodynamic minimum, improving the long-range order and overall structural integrity of the nanoparticle assemblies.

2.5 State of the Art in Silica Nanoparticle Self-Assembly

Recent advancements in silica nanoparticle self-assembly have expanded its relevance far beyond the realm of basic scientific research, positioning it as a versatile and powerful tool across a broad spectrum of high-performance applications. Thanks to the unique properties of silica—such as chemical stability, biocompatibility, tunable surface functionality, and ease of fabrication—self-assembled layers of silica nanoparticles are now being used in fields as diverse as optics, biomedicine, electronics, surface engineering, and energy storage.

The core strength of self-assembled silica nanoparticle films lies in their ability to form uniform, highly ordered monolayers or multilayers with tunable physical and chemical characteristics. This structural control makes it possible to tailor the properties of the final material to suit very specific application needs. For example, in optics, one of the most well-established uses is in the creation of anti-reflective coatings and photonic crystals. Because silica nanoparticles can be synthesized with uniform sizes and arranged in regular patterns, they can control the behavior of light by influencing how it is reflected, transmitted, or scattered. This optical manipulation is crucial in enhancing the performance of lenses, solar cells, optical fibers, and display technologies by reducing glare, improving light absorption, or creating desired interference effects [23].

In the biomedical sector, silica nanoparticles have become popular due to their biocompatibility, low toxicity, and highly tunable surface chemistry. These properties make them excellent carriers for drug delivery, where they can be loaded with therapeutic agents and functionalized to target specific tissues or cells. Moreover, when arranged in ordered layers, they can significantly enhance the sensitivity and accuracy of biosensors. This is especially important in diagnostic applications, where detecting trace amounts of biomarkers can enable earlier and more precise detection of diseases like cancer or infections [24].

Self-assembled silica nanoparticles also play a crucial role in nano-patterning and lithography. When deposited onto substrates in ordered arrays, these nanoparticles can act as physical masks or etching templates for creating nanostructures. This bottom-up approach to nanopatterning allows for high precision at the nanoscale, making it ideal for applications in microelectronics, including the fabrication of advanced transistors, memory devices, and microchips [14], [25].

In surface engineering, the controlled nanoscale roughness achieved through self-assembly enables the fabrication of functional coatings with unique surface properties. For instance, silica nanoparticle films are used to create superhydrophobic surfaces that repel water, anti-fogging layers for optical devices, or self-cleaning coatings that mimic natural phenomena such as the lotus leaf effect. These coatings are increasingly used in consumer products, automotive windshields, and architectural glass to improve durability and performance under environmental exposure [26].

Furthermore, in the fields of catalysis and energy storage, ordered assemblies of porous silica nanoparticles provide large surface areas and customizable pore structures. These features are essential for supporting catalytic reactions or storing energy. In catalytic systems, the high surface area increases the number of active sites, improving overall reaction efficiency. In energy storage devices like batteries and fuel cells, the ordered porosity allows for better ion diffusion and enhances the performance of electrodes or membranes by facilitating more controlled transport of reactants and products [27].

Overall, the self-assembly of silica nanoparticles represents a highly scalable, cost-effective, and adaptable technique for producing next-generation materials with a wide range of functional properties. Whether it's in developing smart coatings, medical diagnostics, advanced optics, or energy devices, the ability to engineer materials from the bottom up with precision makes this approach highly attractive for both industrial applications and academic research. As new synthesis techniques and surface modification strategies continue to evolve, the potential of silica nanoparticle self-assembly is only expected to grow, opening doors to even more innovative and impactful technologies.

Chapter 3

Experimental Methods and Instruments

This chapter provides an overview of the materials used in this study, the sample preparation process; including temperature treatment steps, and the characterization technique applied to investigate the self-assembly of silica nanoparticles.

3.1 Materials

The following materials were used in the preparation and analysis of the self-assembled silica nanoparticle monolayers:

- **Silica nanoparticles:** The silica nanoparticles used in this study were monodisperse particles synthesized via the microemulsion method, as described in the literature [28][29]. The synthesis was performed in ethanol as the solvent, yielding spherical silica particles with an average diameter of approximately 200 nm.

All concentrations are expressed as volume fractions, calculated using the respective densities of silica and ethanol under the assumption of volume additivity. The silica nanoparticles were assumed to have an average density of 1.8 g/cm^3, in agreement with reported values for silica colloids of similar size. Based on the synthesis procedure, the resulting colloidal dispersion contained 5.4 vol% silica nanoparticles.

- **Silicon wafers:** Single-side polished silicon wafers with a native oxide layer (Si/SiO_2) served as substrates for nanoparticle deposition. The wafers were cut into ~1 cm × 1 cm squares.

- **Ethanol (EtOH):** Absolute ethanol (≥99.8%) was used as the solvent for both cleaning the wafers and as the dispersion medium for the nanoparticles.

- **Stearyl alcohol:** Octadecan-1-ol ($C_{18}H_{38}O$), with a melting point of ~59–60 °C, was used to control the self-assembly environment through sublimation and condensation during drying.

- **Acetone and deionized (DI) water:** These were used during the cleaning process of the silicon wafers to ensure a clean and hydrophilic surface prior to nanoparticle deposition.

3.2 Sample Preparation

3.2.1 Dispersion-Driven Formation of Ordered Silica Nanoparticle Structures

A colloidal dispersion containing 5.4 vol% silica nanoparticles in ethanol was prepared as a stock solution. Separately, a 5.4 vol% stearyl alcohol solution in ethanol was also prepared. These two stock solutions were employed to fabricate a highly ordered multilayer structure on a silicon substrate via the drop-casting technique, with the aggregation process carefully controlled.

To enhance the nanoparticle (NP) ordering across the entire sample area, stearyl alcohol was used as an additive. A working solution containing 0.1 vol% silica nanoparticles and 0.1 vol% stearyl alcohol was prepared by mixing 20 µL of the 5.4 vol% silica stock solution and 20 µL of the 5.4 vol% stearyl alcohol stock solution with 0.96 mL of ethanol.

3.2.2 Drop-Casting

The substrates used for nanoparticle (NP) deposition were N-type Si (100) wafers (thickness: 0.5 mm), obtained from Crystec GmbH. These wafers were cut into 10 × 10 mm² pieces prior to use. To remove dust particles and surface contaminants, the substrates underwent a sequential cleaning process. Initially, the wafers were sonicated in an Elmasonic P60 ultrasonic bath using ethanol, followed by distilled water (DI). After cleaning, they were stored in ethanol to maintain surface cleanliness until use.

Before deposition, the silicon wafers were further rinsed with acetone, ethanol, and DI water, then allowed to dry under ambient conditions on a clean, dust-free surface (Figure 3.1).

Silica nanoparticles were deposited onto the cleaned silicon substrates using an improved variant of the drop-casting method, which is a simple, cost-effective technique requiring no specialized equipment. In this approach, either 20 μL or 25 μL of the NP dispersion in ethanol was carefully dropped onto the center of each substrate. The deposited droplets were then left undisturbed at room temperature for 24 to 48 hours, allowing for natural solvent evaporation and promoting the self-assembly of nanoparticles into multilayer structures.

The morphology and degree of ordering of the resulting NP assemblies depend on several controllable parameters, including the evaporation rate, drop volume, and the concentrations of both silica nanoparticles and stearyl alcohol. The addition of stearyl alcohol was found to enhance NP ordering across the substrate surface. A schematic illustration of the drop-casting process is provided in Figure 3.1.

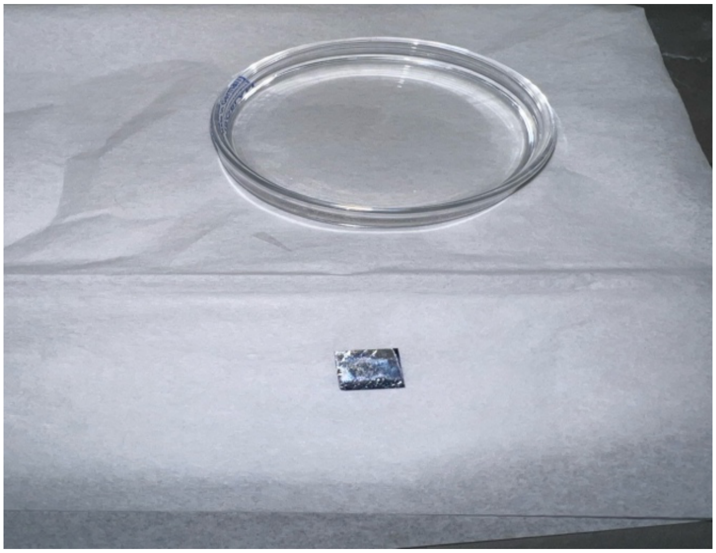


Figure 3.1: Cleaned silica wafer ready for nanoparticle deposition.

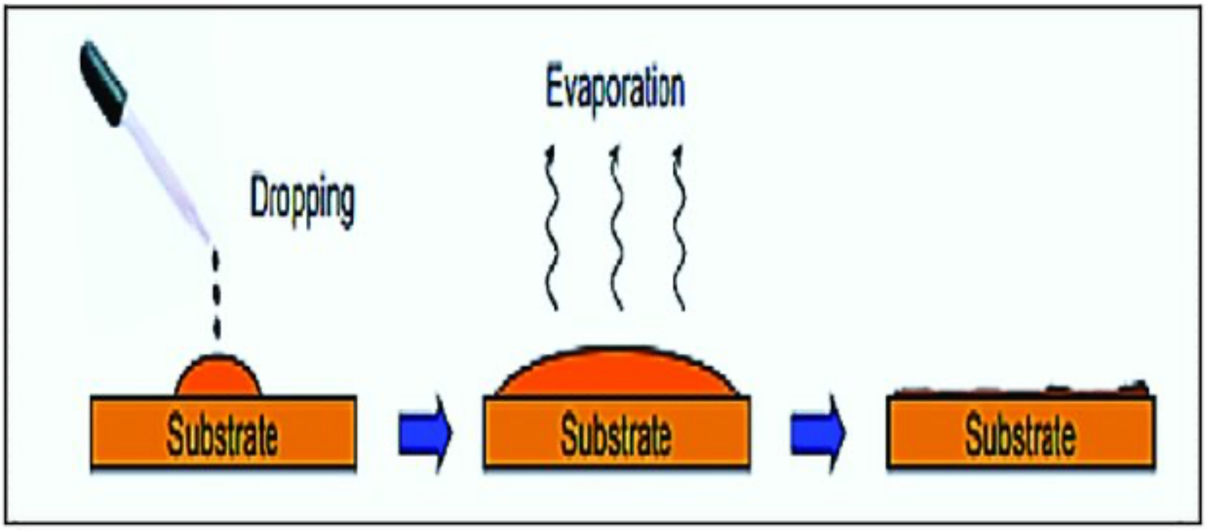


Figure 3.2: Drop-casting process showing deposition, evaporation, and film formation. (Fig taken from [30])

3.2.3 Addition of Stearyl Alcohol Grains

To improve the efficiency and quality of the nanoparticle self-assembly process and to investigate the specific role of additives in promoting structural order, two small grains of stearyl alcohol were carefully placed adjacent to the sample on the substrate prior to the annealing step. Stearyl alcohol was selected for this study due to its well-characterized thermal properties and favorable phase transition behavior. At room temperature, stearyl alcohol exists as a solid, but upon heating it undergoes a distinct phase transition and melts at approximately 60 °C [31]. This transition results in the formation of a viscous liquid that can modify the local environment around the nanoparticles.

When heated above its melting point during annealing, stearyl alcohol forms a soft, viscous layer that surrounds the sample area. This temporary, localized reduction in viscosity is crucial because it facilitates enhanced nanoparticle movement by minimizing friction and lowering resistance to diffusion. The molten stearyl alcohol effectively acts as a soft template or dynamic medium, creating conditions under which the silica nanoparticles can overcome kinetic barriers that typically hinder rearrangement and proper packing. As the particles become more mobile, they are able to reorganize into more energetically favorable, ordered configurations.

The grains of stearyl alcohol were placed strategically near the droplet of nanoparticle dispersion to ensure they were exposed to the same heating conditions and to allow for direct physical interaction during the annealing process. As the temperature increased and the alcohol melted, it partially infiltrated the surrounding nanoparticle layer, helping to prevent common issues such as particle pinning, where particles become immobilized due to strong interactions with the substrate or each other. By reducing these effects, the molten additive enabled the nanoparticles to dynamically adjust their positions and form more regular, hexagonally packed monolayers.

This environment not only improved nanoparticle mobility but also played a critical role in minimizing the formation of structural defects such as cracks, voids, or grain boundaries; defects which are often caused by uneven solvent evaporation or insufficient particle rearrangement during drying. The presence of the molten additive helped balance out the forces acting on the particles during film formation, leading to a smoother and more continuous assembly process.

Incorporating stearyl alcohol into the annealing step was therefore expected to have a noticeable impact on the final quality of the self-assembled films. It provided an additional layer of control by tuning the microenvironment in which particle assembly occurred, enabling better particle packing, more uniform spacing, and improved overall layer integrity. This method illustrates how the combination of thermal treatment with a phase-changing additive can be a simple yet powerful approach to enhancing self-assembly outcomes in nanoparticle-based materials.

3.2.4 Annealing Process

After the initial room-temperature drying stage, the samples underwent thermal annealing under controlled conditions to investigate the influence of temperature and duration on the self-assembly and structural integrity of the silica nanoparticle multilayers. The primary objective of this heat treatment was to reduce the occurrence of cracks and other defects commonly observed in the dried films.

Each sample was placed inside a clear polystyrene sample container. Small grains of stearyl alcohol were added adjacent to the nanoparticle sample to create a vapor-rich environment during heating. The stearyl alcohol vapor is known to slow final drying and enhance capillary-driven rearrangement, leading to improved long-range order and overall film uniformity.

Annealing was carried out in a laboratory oven at temperatures of 70 °C, 80 °C, and 90 °C, with corresponding treatment durations of 10 days, 6 days, and 4 days, respectively. These conditions were selected to ensure a slow, continuous sublimation of stearyl alcohol, which promotes gradual solvent removal and provides sufficient time for nanoparticles to reorganize on the substrate surface.

These annealing conditions have been selected to address a key research question: Can the annealing time required for the formation of highly ordered silica nanoparticle layers be reduced by increasing the annealing temperature? This inquiry was motivated by previous studies reporting the successful formation of highly ordered monolayers of similar nanoparticles after 10 days of annealing at 70 °C [22]. Our objective was to determine whether comparable ordering could be achieved in fewer days by using higher temperatures.

To test this hypothesis, we conducted annealing experiments at three different temperatures—70 °C, 80 °C, and 90 °C—with progressively shorter durations of 10, 6, and 4 days, respectively. These conditions were designed to maintain a balance between thermal activation for nanoparticle mobility and controlled evaporation for defect minimization.

However, the use of clear polystyrene sample containers imposed a practical limitation. These containers began to deform and melt at 90 °C, as shown in Figure 3.2, preventing us from exploring annealing temperatures above this threshold. Despite this constraint, the selected temperature range was sufficient to evaluate the temperature-time relationship and its effect on nanoparticle ordering within the accessible limits of our experimental setup.

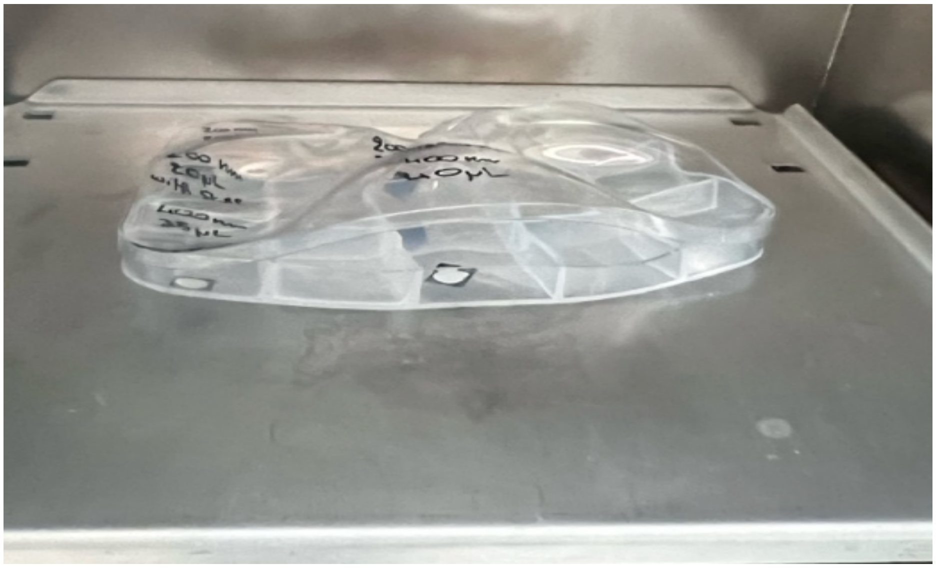


Figure 3.3: Visual result of the sample box after annealing at 90 °C for 4 days.

3.2.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a highly versatile and powerful tool used for the detailed surface characterization of materials, especially in the field of nanotechnology. It enables researchers to visualize surface morphology with nanometer-scale resolution by scanning the specimen's surface with a tightly focused beam of high-energy electrons. The resulting images provide vital information about the arrangement, packing, surface roughness, and possible defects within nanoparticle assemblies, making SEM an essential technique for analyzing the quality and structure of self-assembled films.

In the present study, SEM imaging was carried out using a Hitachi SU8000 Field Emission Scanning Electron Microscope (FE-SEM), which is housed at the PGI-7 (Peter Grünberg Institute for Electronic Materials). This advanced system is equipped with a cold field emission (CFE) source, which is known for producing a highly coherent electron beam with minimal energy spread. The electron source is based on a mono-crystalline tungsten tip, which serves as the emission point. When a strong electric field is applied to this tip, it effectively reduces the material's work function, enabling electrons to quantum mechanically tunnel through the potential barrier and be emitted into the vacuum column.

Once emitted, the electrons are accelerated by an applied voltage, typically ranging from 0.5 kV to 30 kV, depending on the desired imaging resolution and the nature of the sample. The electrons are then guided and finely focused using a three-stage electromagnetic lens system, consisting of two condenser lenses and an objective lens. These lenses shape and control the electron beam, ensuring that it is tightly focused onto the sample surface to achieve high-resolution imaging. This configuration allows researchers to precisely control both beam diameter and electron current.

A gun valve is used to regulate the electron flow, and deflection coils are employed to steer the beam across the sample in a raster scanning pattern. This systematic movement ensures that every region of the sample is exposed to the beam, and the emitted secondary or backscattered electrons from the surface are collected by detectors to form a high-contrast image.

The samples are placed on a stage located inside a high-vacuum chamber, which is crucial for maintaining beam stability and preventing unwanted scattering. The stage itself can be adjusted in multiple axes (X, Y, Z, tilt, and rotation), allowing precise alignment and focus on specific areas of interest. The instrument supports two distinct magnification modes: low magnification mode ranging from 20× to 2,000×, ideal for general overviews and locating regions of interest, and high magnification mode from 80× to as high as 800,000×, which is used for examining fine structural details at the nanoscale.

This wide range of magnification, coupled with the precision of field emission technology, makes the Hitachi SU8000 FE-SEM especially suited for studying self-assembled nanoparticle films. In this study, SEM enabled the in-depth analysis of particle distribution, domain size, structural uniformity, and the identification of defects such as voids, cracks, or grain boundaries within the assembled layers. By using this tool, we were able to visually confirm the effects of temperature and additives; such as stearyl alcohol, on the ordering quality of silica nanoparticle assemblies. The SEM results provided critical validation of the experimental outcomes and played a central role in evaluating the success of the self-assembly process.

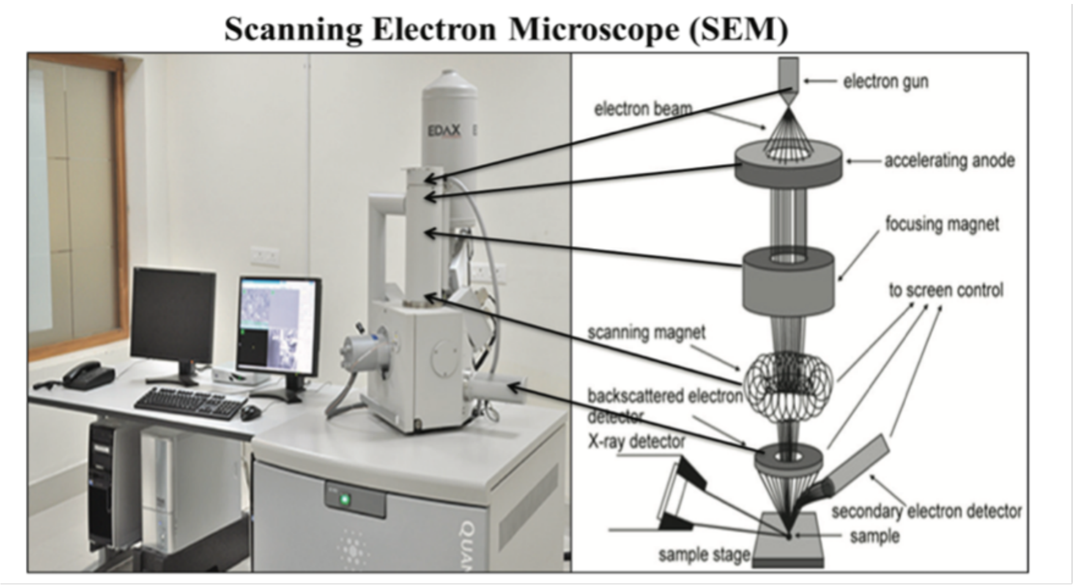


Figure 3.4: Schematic of the Scanning Electron Microscope

Chapter 4

Results and Discussion

This chapter presents and analyzes the results obtained from SEM imaging of silica nanoparticle films, focusing on structural changes before and after thermal annealing. The discussion emphasizes the effects of thermal treatment and the incorporation of stearyl alcohol on particle arrangement, surface coverage, and the degree of ordering within the films.

By comparing samples prepared with different drop-cast volumes and annealing conditions, the influence of each experimental parameter on the self-assembly behavior of the nanoparticles can be systematically assessed. The results are organized to highlight the structural differences observed between untreated and thermally treated samples, providing insight into the mechanisms responsible for enhanced ordering, reduced defects, or particle redistribution during the annealing process.

These findings contribute to a deeper understanding of the role of controlled evaporation, additive-assisted mobility, and thermal activation in guiding the formation of ordered nanoparticle assemblies.

4.1 Local characterization by SEM

4.1.1 SEM Observations Before Annealing

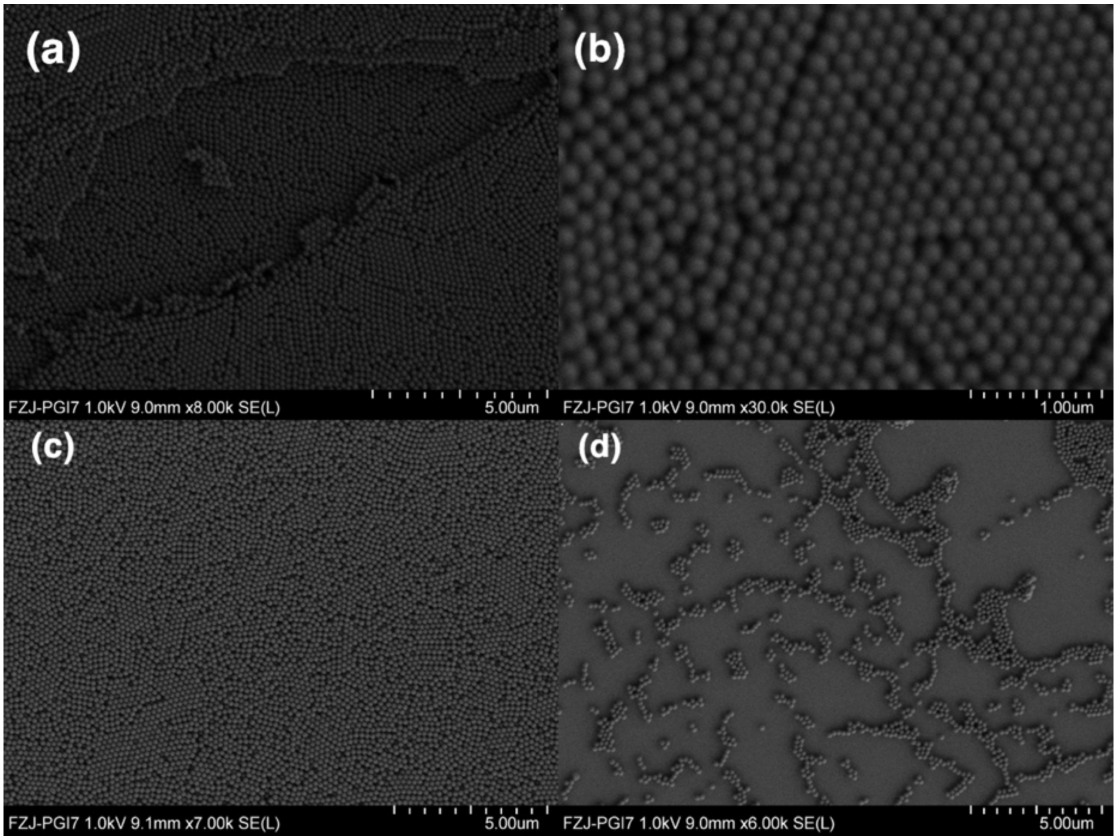


Figure 4.1: SEM images of silica nanoparticles before heat treatment.

(a) 20 µL without stearyl alcohol, (b) 20 µL with stearyl alcohol, (c) 25 µL without stearyl alcohol, (d) 25 µL with stearyl alcohol.

Figure 4.1 presents SEM images of silica nanoparticle films prepared using drop-casting, comparing samples with and without stearyl alcohol before any thermal treatment. These initial conditions are important because they show how the inclusion of stearyl alcohol affects nanoparticle organization from the earliest stages of film formation; before any annealing-induced rearrangement occurs. In image (a), where 20 µL of nanoparticle dispersion was deposited without stearyl alcohol, the resulting film appears highly disordered. The particles tend to form loosely packed clusters and irregular island-like aggregates with significant gaps between domains. This uneven surface morphology indicates that, in the absence of any additive, the nanoparticles have limited mobility during solvent evaporation, leading to poor control over assembly.

In image (b), using the same volume but incorporating stearyl alcohol, the overall structure improves noticeably. The nanoparticles form a more continuous and densely packed film, with better alignment and reduced clustering. This change can be attributed to the soft templating effect of stearyl alcohol, which begins to influence particle arrangement even before annealing. Since stearyl alcohol has a melting point of around 59.5 °C, it remains solid at room temperature but begins to interact with the nanoparticle dispersion during drying, likely acting as a lubricant that reduces interparticle friction and enables a more cohesive film to form during solvent evaporation.

Image (c), which corresponds to 25 µL without stearyl alcohol, shows a broader area of surface coverage due to the higher dispersion volume. However, despite the improved spread, the structure still lacks long-range order. The nanoparticles appear more evenly distributed than in image (a), but the film remains disorganized, and several regions display multi-layer formation or aggregation, indicating that volume alone does not guarantee uniform packing. Finally, image (d), with 25 µL and the addition of stearyl alcohol, shows a clear improvement. The surface appears more uniform and better connected, with fewer voids and smoother transitions between domains. Even though the film is still unannealed, the structural coherence is already higher, suggesting that the presence of stearyl alcohol helps direct the assembly process by promoting better wetting, spreading, and particle-particle interaction.

Taken together, these pre-annealing images show that stearyl alcohol can enhance nanoparticle organization right from the beginning of the film formation process. While it does not yet induce complete ordering, its influence is already evident in the reduced clustering, more consistent surface coverage, and smoother distribution of nanoparticles. These early improvements provide a more favorable starting point for thermal annealing, which can then build on this initial structure to achieve higher levels of ordering.

The results highlight the importance of optimizing not only the thermal conditions but also the chemical environment during deposition, as both play a critical role in the overall self-assembly process.

4.1.2 After annealing 70 degrees, 10 days

The SEM images presented in Figure 4.2 show the morphological differences in silica nanoparticle films drop-cast with 20 µL and 25 µL dispersions, both with and without the addition of stearyl alcohol. SEM Image (a), corresponding to 20 µL without stearyl alcohol, reveals partial ordering only in localized regions, with large areas showing random aggregation and uneven particle distribution. This suggests that, without any additive, the particle mobility during annealing was limited, resulting in poor self-assembly and a lack of long-range structural order. In contrast, the SEM image (b), which shows the same volume but with the addition of stearyl alcohol, exhibits a more evenly distributed layer. Although the particles are not densely packed, the improved dispersion and reduced clustering indicate that stearyl alcohol helped minimize particle pinning and enhanced lateral mobility during the drying and annealing process. This allowed for a more uniform, albeit less compact, arrangement across the substrate.

In image (c), corresponding to 25 µL without stearyl alcohol, the higher volume improved overall coverage and local particle packing compared to (a). However, the film still contains noticeable grain boundaries and irregularities, suggesting that volume alone is not sufficient to ensure uniformity and structural integrity. The most significant improvement is observed in image (d), where 25 µL of dispersion was combined with stearyl alcohol. This sample shows large, well-ordered domains with minimal voids and clear hexagonal packing over extended regions. The increased dispersion volume, combined with the soft templating effect of molten stearyl alcohol during annealing, significantly enhanced nanoparticle rearrangement and overall film quality.

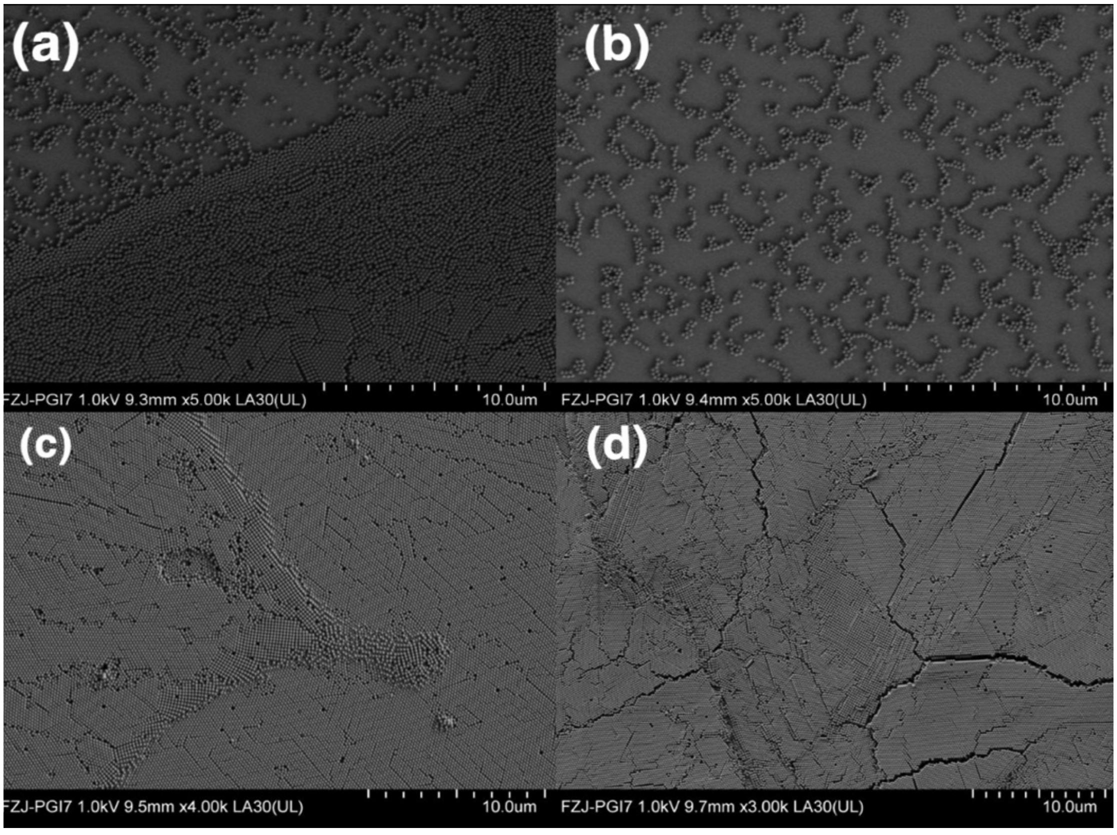


Figure 4.2: SEM images of silica nanoparticles after heat treatment at 70 °C for 10 days. (a) 20 µL without stearyl alcohol, (b) 20 µL with stearyl alcohol, (c) 25 µL without stearyl alcohol, (d) 25 µL with stearyl alcohol.

4.1.3 After annealing 80 degrees, 7 days

Figures 4.3 and 4.4 display SEM images of silica nanoparticle films annealed at 80 °C for 7 days, comparing different drop-casting volumes and the presence or absence of stearyl alcohol, observed at two magnifications: 5 µm (Figure 4.3) and 10 µm (Figure 4.4).

At the 5 µm scale, SEM image (a) shows partial local ordering, but overall poor long-range structure due to limited particle mobility. In contrast, image (b) reveals a denser and more cohesive arrangement, where the addition of stearyl alcohol clearly improved particle diffusion during annealing, promoting more uniform packing. Image (c) shows better coverage at 25 µL but remains structurally disordered, reinforcing that increased volume alone does not guarantee high-quality self-assembly. The most well-ordered structure is observed in image (d), with extended, closely packed hexagonal domains, highlighting the positive impact of both stearyl alcohol and higher volume on particle organization.

At a broader 10 µm scale (Figure 4.4), the differences become even more apparent. Image (a) reveals fragmented and poorly connected domains with large-scale irregularities, whereas image (b) shows improved large-area uniformity, with visibly reduced voids and more continuous particle layering due to the additive's role. Image (c) appears densely covered, but the particles are randomly distributed with no clear ordering. In contrast, image (d) demonstrates a highly ordered monolayer over a wide area, with minimal defects and grain boundaries. This confirms that the combination of a sufficient particle volume and a soft templating agent like stearyl alcohol significantly enhances the structural quality of self-assembled films. Together, these images provide a clear visual comparison of how both volume and additive presence influence the degree of nanoparticle ordering, and how these factors translate across scales.

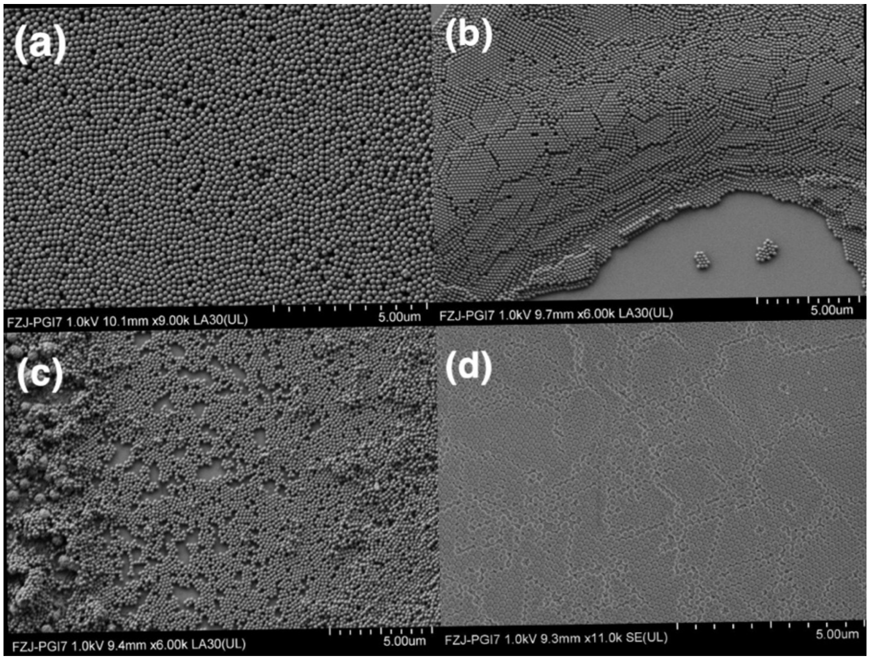
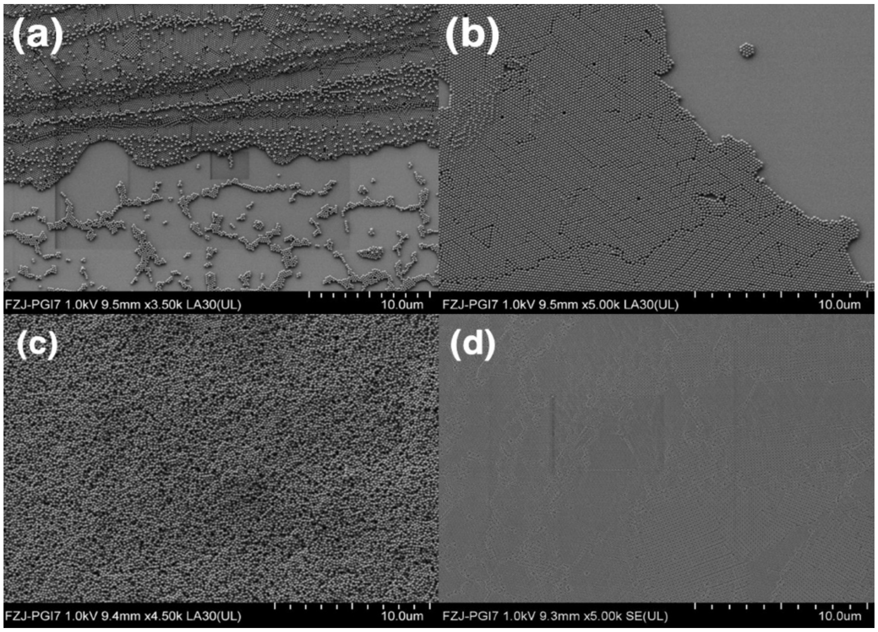


Figure 4.3: SEM images after 80 °C heat treatment (7 days) at a magnification of 5.00um

(a) 20 µL without stearyl alcohol, (b) 20 µL with stearyl alcohol, (c) 25 µL without stearyl alcohol, (d) 25 µL with stearyl alcohol.



(a)

Figure 4.4: SEM images after 80 °C heat treatment (7 days) at a magnification of 10.00um

(a) 20 µL without stearyl alcohol, (b) 20 µL with stearyl alcohol, (c) 25 µL without stearyl alcohol, (d) 25 µL with stearyl alcohol.

4.1.4 After annealing 90 degrees, 4days

Figures 4.5 and 4.6 show SEM images of silica nanoparticle self-assembly after annealing at 90 °C for 4 days, captured at two different magnifications (1 µm and 10 µm) to closely examine how particle arrangement is influenced by both dispersion volume and the presence of stearyl alcohol. This set of images directly relates to the main goal of the study, which is to determine whether shorter annealing durations at higher temperatures—such as 90 °C for 4 days—can produce nanoparticle ordering comparable to what was previously achieved at 70 °C over a much longer period of 10 days. This approach is based on the idea that ordering is controlled by a combination of time and temperature, and that higher temperatures may accelerate the self-assembly process by increasing particle mobility and reducing the time required to reach an ordered state.

The results here support that hypothesis. At 20 µL without stearyl alcohol, the film is relatively well-covered but lacks long-range structural order, with irregularities and domain boundaries clearly visible in both magnifications. Once stearyl alcohol is introduced at the same volume, ordering improves noticeably—the particles show better spacing, fewer defects, and more consistent hexagonal domains. At 25 µL without stearyl alcohol, the particle coverage is higher, but the packing is still inconsistent. However, when stearyl alcohol is added at 25 µL, the self-assembly improves significantly. Large, continuous domains form, and the hexagonal structure becomes more defined and uniform. These results confirm that higher annealing temperatures can accelerate the ordering process, especially when supported by the right combination of dispersion volume and additive. The improved structural quality observed within just four days at 90 °C demonstrates that it's possible to achieve results comparable to longer annealing times at lower temperatures, validating the main objective of this work.

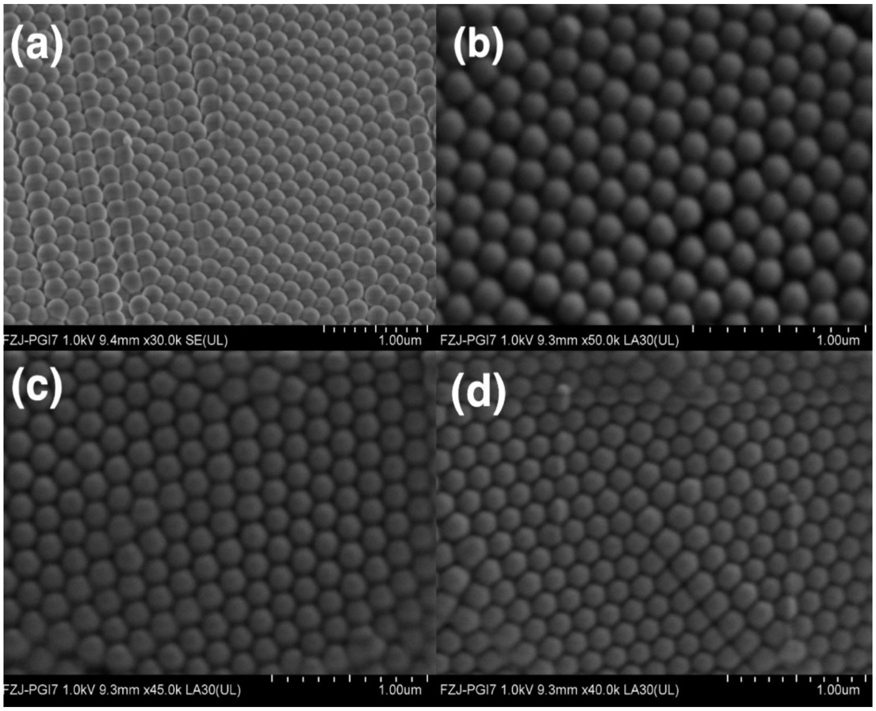


*Figure 4.5: SEM images of silica nanoparticle assemblies after 90 °C annealing for 4 days at a magnification of 1.00um***.** *(a) 20 µL without stearyl alcohol, (b) 20 µL with stearyl alcohol, (c) 25 µL without stearyl alcohol, (d) 25 µL with stearyl alcohol.*

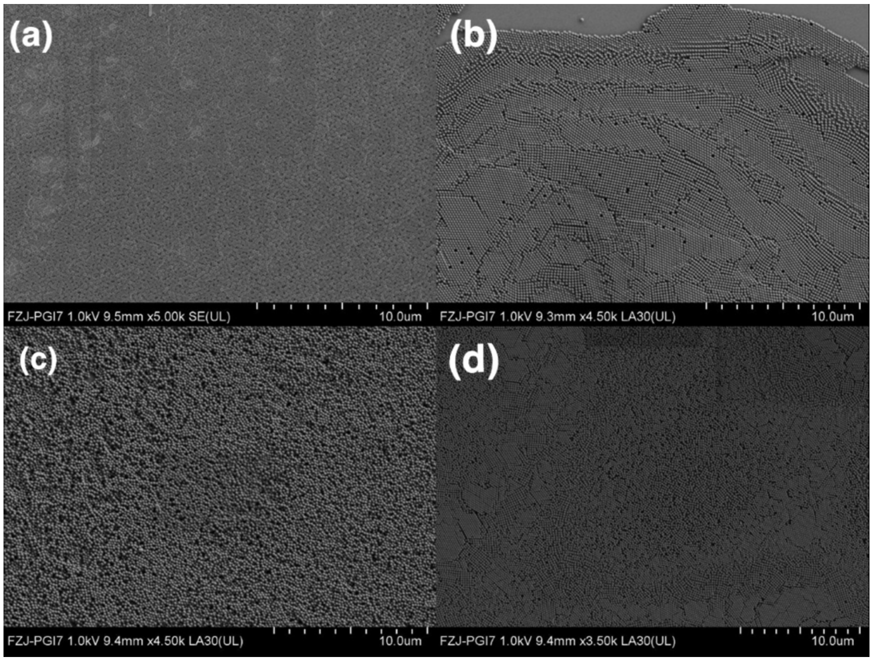


*Figure 4.6: SEM images of silica nanoparticle assemblies after 90 °C annealing for 4 days at a magnification of 10.00um***.** *(a) 20 µL without stearyl alcohol, (b) 20 µL with stearyl alcohol, (c) 25 µL without stearyl alcohol, (d) 25 µL with stearyl alcohol.*

4.2 Discussion

This study aimed to understand how annealing temperature, annealing duration, dispersion volume, and the presence of stearyl alcohol influence the self-assembly behavior of silica nanoparticles. The main goal was to test whether shorter annealing times at higher temperatures (specifically 80 °C for 7 days and 90 °C for 4 days) could produce similar or even better nanoparticle ordering compared to longer treatments at lower temperatures, like 70 °C for 10 days. The results make it clear that temperature alone plays a critical role in promoting particle mobility and ordering, but it's the combination of different parameters that ultimately determines the quality of the final structure.

One of the main findings of this work is that well-ordered silica nanoparticle monolayers can be achieved either through high thermal input or through a more balanced approach that combines moderate heating with additive assistance. At 90 °C, the thermal energy provided during the 4-day annealing step was already sufficient to promote particle diffusion and rearrangement, even in the absence of stearyl alcohol. The SEM images at both low and high magnifications showed that the particles were able to form continuous, close-packed domains with minimal defects. This means that at high enough temperatures, thermal energy can independently overcome the kinetic barriers that usually limit self-assembly.

However, when the temperature is lowered to 80 °C, thermal energy alone no longer guarantees a high level of ordering, especially for shorter annealing times. In these conditions, the presence of stearyl alcohol makes a significant difference. Stearyl alcohol, which melts at around 59.5 °C, becomes active during annealing, melting into the nanoparticle matrix and softening the environment. This softening effect increases particle mobility and allows for better rearrangement. The 25 µL sample annealed at 80 °C with stearyl alcohol showed one of the most uniform and well-ordered monolayers across all the experiments. This clearly demonstrates the synergistic effect between moderate heating and additive support. The melted stearyl alcohol acts like a temporary plasticizer, reducing interparticle friction and supporting more effective spreading and packing.

On the other hand, the influence of stearyl alcohol becomes more complex at 90 °C. At this higher temperature, where thermal energy is already high enough to drive ordering on its own, the role of stearyl alcohol seems less beneficial. In some cases, its addition even introduced mild aggregation or uneven layering. This could be due to the fact that, at elevated temperatures, the stearyl alcohol redistributes or evaporates too quickly, leading to irregularities rather than improvements. So while stearyl alcohol is very helpful under intermediate thermal conditions, its benefit becomes less predictable at very high temperatures.

The dispersion volume also played an important role. Larger volumes, like 25 µL, generally helped improve the coverage and overall film uniformity, as the higher volume facilitated better wetting and spreading across the substrate. But this was only true when stearyl alcohol was present. Without it, even higher volumes tended to form multilayered or partially aggregated structures. This again shows that while volume helps with coverage, it cannot on its own ensure a well-ordered monolayer. Instead, volume needs to be combined with effective control over temperature and interfacial forces—especially through the inclusion of additives like stearyl alcohol that can tune those interactions during the self-assembly process.

These results collectively highlight that optimal self-assembly is not the result of a single factor, but rather emerges from the interplay between different variables—mainly temperature, time, volume, and chemical environment. High temperature alone can lead to excellent ordering, but in cases where lower temperatures or shorter times are preferred or necessary (such as in temperature-sensitive materials), additives like stearyl alcohol can be used to compensate and guide the assembly process. The ability to reduce annealing time while still achieving high structural quality has important implications for the efficiency and scalability of nanoparticle-based fabrication methods.

In conclusion, this study shows that self-assembly is highly dependent on how thermal and interfacial dynamics are managed together. A careful balance between heat input, additive use, and dispersion conditions is essential to achieve reproducible, defect-minimized, and well-ordered silica nanoparticle monolayers. These findings can be especially useful for future applications that require precise nanoscale patterning under constrained processing conditions.

Chapter 5

Summary and Outlook

In summary, this thesis explored how annealing temperature, dispersion volume, and the addition of stearyl alcohol influence the self-assembly behavior of silica nanoparticles. The results clearly show that achieving well-ordered monolayers is possible through two different approaches: either by applying high thermal energy, such as 90 °C, which promotes sufficient particle mobility on its own, or by combining moderate annealing temperatures like 80 °C with stearyl alcohol and a higher dispersion volume (25 µL). Stearyl alcohol, which melts during annealing, acts as a temporary plasticizer. It reduces friction between particles, increases their mobility, and supports rearrangement into more ordered configurations—especially under conditions where thermal energy alone is not strong enough to overcome kinetic limitations.

However, the effect of stearyl alcohol is highly dependent on context. While it significantly improves ordering at intermediate temperatures, its impact becomes less consistent at higher temperatures. At 90 °C, where thermal energy already drives strong particle motion, stearyl alcohol can sometimes cause undesirable effects like aggregation or uneven layering, likely due to its redistribution and evaporation dynamics during drying. This reinforces that the benefits of additives must always be considered in relation to other experimental parameters such as temperature and drying behavior.

Outlook

Building on these results, future research could explore the use of different surfactants or plasticizing agents, especially those with tunable melting points or functional groups that allow better interaction with specific nanoparticles or substrates. Investigating how these additives influence assembly in different temperature regimes could lead to more controlled and flexible self-assembly processes. Additionally, applying the same strategies to other types of nanoparticles or substrate materials would help determine how generalizable the findings are beyond silica-based systems.

There is also a strong potential for expanding this work toward practical applications. The ability to form uniform and defect-minimized nanoparticle monolayers through controlled thermal and chemical treatment could be especially useful for technologies like optical coatings, sensors, nano-patterned surfaces, and device fabrication. Scaling up the process for larger areas or integrating it into roll-to-roll or printing methods could make it more viable for industrial settings.

Finally, implementing in situ or real-time monitoring techniques—such as environmental SEM, optical microscopy during drying, or thermal imaging—could offer deeper insight into the dynamic behavior of nanoparticle rearrangement during annealing. This would allow for more precise tuning of process parameters and enable better prediction and control of final film quality. Overall, this thesis lays the groundwork for continued development of optimized, flexible self-assembly techniques tailored to specific thermal, material, and structural requirements.

References:

[1] Y. Ji *et al.*, “Beyond the promise: Exploring the complex interactions of nanoparticles within biological systems,” *J. Hazard. Mater.*, vol. 468, p. 133800, Apr. 2024, doi: 10.1016/j.jhazmat.2024.133800.

[2] O. Hellwig, L. J. Heyderman, O. Petracic, and H. Zabel, “Competing Interactions in Patterned and Self-Assembled Magnetic Nanostructures,” in *Magnetic Nanostructures: Spin Dynamics and Spin Transport*, H. Zabel and M. Farle, Eds., Berlin, Heidelberg: Springer Berlin Heidelberg, 2013, pp. 189–234. doi: 10.1007/978-3-642-32042-2_6.

[3] K. Hamaloglu, C. Pester, A. Konradi, A. Böker, and P. Rijn, “Cross-Linking Density and Temperature Effects on the Self-Assembly of SiO2-PNIPAAm Core-Shell Particles at Interfaces,” *Chem. Weinh. Bergstr. Ger.*, vol. 19, Apr. 2013, doi: 10.1002/chem.201203900.

[4] D. Xia, A. Biswas, D. Li, and S. Brueck, “Directed Self-Assembly of Silica Nanoparticles into Nanometer-Scale Patterned Surfaces Using Spin-Coating,” *Adv. Mater.*, vol. 16, pp. 1427–1432, Sep. 2004, doi: 10.1002/adma.200400095.

[5] W. Wang and B. Gu, “Self-Assembly of Two- and Three-Dimensional Particle Arrays by Manipulating the Hydrophobicity of Silica Nanospheres,” *J. Phys. Chem. B*, vol. 109, no. 47, pp. 22175–22180, Dec. 2005, doi: 10.1021/jp053692s.

[6] A. Chabanov, Y. Jun, and D. Norris, “Elimination of cracks in self-assembled photonic band gap crystals,” *ArXiv Prepr. Cond-Mat0312403*, 2003.

[7] A. Qdemat, E. Kentzinger, J. Buitenhuis, U. Rücker, M. Ganeva, and T. Brückel, “Self assembled monolayer of silica nanoparticles with improved order by drop casting,” *RSC Adv.*, vol. 10, no. 31, pp. 18339–18347, 2020, doi: 10.1039/D0RA00936A.

[8] “H.B. Bohidar and K. Rawat. Design of nanostructures : self-assembly of nanomaterials. Wiley VCH, 2017, pp. 188 –193. isbn: 978-3-527- 81041-3.”

[9] S. Prabha, D. Durgalakshmi, S. Rajendran, and E. Lichtfouse, “Plant-derived silica nanoparticles and composites for biosensors, bioimaging, drug delivery and supercapacitors: a review,” *Environ. Chem. Lett.*, vol. 19, no. 2, pp. 1667–1691, Apr. 2021, doi: 10.1007/s10311-020-01123-5.

[10] V. Selvarajan, S. Obuobi, and P. L. R. Ee, “Silica Nanoparticles—A Versatile Tool for the Treatment of Bacterial Infections,” *Front. Chem.*, vol. Volume 8-2020, 2020, doi: 10.3389/fchem.2020.00602.

[11] J. Peerzada, P. Mulay, R. Venkat, and R. Chidambaram, “Multifaceted Application of Silica Nanoparticles. A Review,” *Silicon*, vol. 12, Jun. 2020, doi: 10.1007/s12633-019-00229-y.

[12] C. C. M. C. Carcouët *et al.*, “Nucleation and Growth of Monodisperse Silica Nanoparticles,” *Nano Lett.*, vol. 14, no. 3, pp. 1433–1438, Mar. 2014, doi: 10.1021/nl404550d.

[13] M. Huston, M. DeBella, M. Dibella, and A. Gupta, “Green Synthesis of Nanomaterials,” *Nanomaterials*, vol. 11, p. 2130, Aug. 2021, doi: 10.3390/nano11082130.

[14] M. Grzelczak, J. Vermant, E. M. Furst, and L. M. Liz-Marzán, “Directed Self-Assembly of Nanoparticles,” *ACS Nano*, vol. 4, no. 7, pp. 3591–3605, Jul. 2010, doi: 10.1021/nn100869j.

[15] E. Guzmán, F. Ortega, and R. G. Rubio, “Forces Controlling the Assembly of Particles at Fluid Interfaces,” *Langmuir*, vol. 38, no. 44, pp. 13313–13321, Nov. 2022, doi: 10.1021/acs.langmuir.2c02038.

[16] S. C. Glotzer and M. J. Solomon, “Anisotropy of building blocks and their assembly into complex structures,” *Nat. Mater.*, vol. 6, no. 8, pp. 557–562, Aug. 2007, doi: 10.1038/nmat1949.

[17] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, “Capillary flow as the cause of ring stains from dried liquid drops,” *Nature*, vol. 389, no. 6653, pp. 827–829, Oct. 1997, doi: 10.1038/39827.

[18] T. P. Bigioni, X.-M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten, and H. M. Jaeger, “Kinetically driven self assembly of highly ordered nanoparticle monolayers,” *Nat. Mater.*, vol. 5, no. 4, pp. 265–270, Apr. 2006, doi: 10.1038/nmat1611.

[19] M.-C. Daniel and D. Astruc, “Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology,” *Chem. Rev.*, vol. 104, no. 1, pp. 293–346, Jan. 2004, doi: 10.1021/cr030698+.

[20] B. Bharti, J. Meissner, U. Gasser, and G. Findenegg, “Surfactant adsorption and aggregate structure at silica nanoparticles: Effects of particle size and surface modification,” *Soft Matter*, vol. 8, pp. 6573–6581, May 2012, doi: 10.1039/C2SM25648G.

[21] W. Fang *et al.*, “Shape Matters: Impact of Mesoporous Silica Nanoparticle Morphology on Anti-Tumor Efficacy,” *Pharmaceutics*, vol. 16, no. 5, 2024, doi: 10.3390/pharmaceutics16050632.

[22] A. Qdemat, “Nanoparticle assemblies: Order by self- organization and collective magnetism.” Qdemat Asma, 2020.

[23] K. Askar *et al.*, “Scalable parallel self-assembly of nanoparticle anti-reflection coatings,” *Thin Solid Films*, vol. 621, pp. 156–164, Jan. 2017, doi: 10.1016/j.tsf.2016.11.042.

[24] B. Xu, S. Li, R. Shi, and H. Liu, “Multifunctional mesoporous silica nanoparticles for biomedical applications,” *Signal Transduct. Target. Ther.*, vol. 8, no. 1, p. 435, Nov. 2023, doi: 10.1038/s41392-023-01654-7.

[25] W. Li, G. Lalev, S. Dimov, H. Zhao, and D. T. Pham, “A study of fused silica micro/nano patterning by focused-ion-beam,” *Appl. Surf. Sci.*, vol. 253, no. 7, pp. 3608–3614, Jan. 2007, doi: 10.1016/j.apsusc.2006.07.072.

[26] M. Ghodrati, M. Mousavi-Kamazani, and Z. Bahrami, “Synthesis of superhydrophobic coatings based on silica nanostructure modified with organosilane compounds by sol–gel method for glass surfaces,” *Sci. Rep.*, vol. 13, no. 1, p. 548, Jan. 2023, doi: 10.1038/s41598-023-27811-0.

[27] A. Maity and V. Polshettiwar, “Dendritic Fibrous Nanosilica for Catalysis, Energy Harvesting, Carbon Dioxide Mitigation, Drug Delivery, and Sensing,” *ChemSusChem*, vol. 10, no. 20, pp. 3866–3913, Oct. 2017, doi: 10.1002/cssc.201701076.

[28] F. J. Arriagada and K. Osseo-Asare, “Phase and dispersion stability effects in the synthesis of silica nanoparticles in a non-ionic reverse microemulsion,” *Colloids Surf.*, vol. 69, no. 2, pp. 105–115, Dec. 1992, doi: 10.1016/0166-6622(92)80221-M.

[29] F. J. Arriagada and K. Osseo-Asare, “Synthesis of Nanosize Silica in a Nonionic Water-in-Oil Microemulsion: Effects of the Water/Surfactant Molar Ratio and Ammonia Concentration,” *J. Colloid Interface Sci.*, vol. 211, no. 2, pp. 210–220, Mar. 1999, doi: 10.1006/jcis.1998.5985.

[30] S. Madlul, N. Mahan, E. Ali, and A. Abd, “Synthesis of CdS:Cu5% thin films by chemical method based on silicon for gas sensor applications,” *Mater. Today Proc.*, vol. 45, Apr. 2021, doi: 10.1016/j.matpr.2021.03.170.

[31] C. Zhu, Y. Lin, and G. Fang, “Preparation and thermal properties of microencapsulated stearyl alcohol with silicon dioxide shell as thermal energy storage materials,” *Appl. Therm. Eng.*, vol. 169, p. 114943, Mar. 2020, doi: 10.1016/j.applthermaleng.2020.114943.

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